SYNTHESIS AND CHARACTERIZATION OF TRINUCLEAR METAL CLUSTERS CONTAINING BENZYNECHROMIUM TRICARBONYL

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A THESIS SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE DEGREE OF DOCTOR OF PHILOSOPHY

in
THE FACULTY OF GRADUATE STUDIES
Department of Chemistry

We accept this thesis as conforming to the required standard

THE UNIVERSITY OF BRITISH COLUMBIA
SEPTEMBER 1993
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Date Sept. 21, 1993
ABSTRACT

The work described in this thesis is directed towards the synthesis of metal cluster derivatives of benzynechromium tricarbonyls. To this end a number of phosphino- and arsinobenzenechromium tricarbonyl ligands such as \( \text{ER}_2\text{C}_6\text{H}_5\text{Cr(CO)}_3 \) (\( \text{ER}_2 = \text{PEt}_2, \text{AsMe}_2, \text{PPri}_2, \text{PBut}_2 \)) and \( \text{ER}\text{C}_6\text{H}_5\text{Cr(CO)}_3\text{Cr(CO)}_3 \) (\( \text{ER} = \text{AsPh}, \text{PEt}, \text{PBut} \)) have been synthesized. The structure of \( \text{PPri}_2\text{C}_6\text{H}_5\text{Cr(CO)}_3 \) was determined by means of an X-ray crystallographic study.

The reactions of the phosphino- and arsinobenzenechromium tricarbonyl ligands with the trinuclear metal clusters \( \text{Ru}_3\text{(CO)}_{12} \) and \( \text{Os}_3\text{(CO)}_{12} \) have been investigated. Twenty mono-, di- and trisubstituted complexes were prepared and characterized by using spectroscopic and microanalytical techniques. These are the first examples of metal clusters containing the \( \text{C}_6\text{H}_5\text{Cr(CO)}_3 \) group to be synthesized. The structures of four of the substituted complexes were determined by X-ray crystallographic studies.

The thermolytic reactions of some ligand substituted triruthenium and triosmium clusters were investigated with the object of preparing the metal clusters containing benzynechromium tricarbonyl. The pyrolytic products were isolated and characterized by spectroscopic and X-ray crystallographic methods. Several novel benzynechromium tricarbonyl complexes were successfully prepared and structurally characterized. The complex \( \text{Ru}_3\text{(CO)}_9[\text{C}_6\text{H}_4\text{Cr(CO)}_3][\mu_3-\text{C}_6\text{H}_5\text{Cr(CO)}_3] \) consists of an open \( \text{Ru}_3 \) triangle capped on one face by a \( \mu_3 \)-phosphinidene moiety and on the other by an unsymmetrically bound benzynechromium tricarbonyl moiety. This is the first example of an aryne to show such unsymmetrical bonding to a \( \text{Ru}_3 \) system. The X-ray crystallographic analysis for \( \text{Ru}_3\text{(CO)}_8[\text{C}_6\text{H}_4\text{Cr(CO)}_3][\mu_3-\text{PBut}^\text{t}] \) reveals a novel type of benzyne structure, which contains a closed \( \text{Ru}_3 \) framework with a symmetrical benzynechromium tricarbonyl moiety.
and a phosphinidene ligand on opposite sides. The complex Ru₃(CO)₈[µ-H][C₆H₄Cr(CO)₃][µ-AsMe₂] consists of a closed ruthenium triangle with an arsinido group, a bridging hydride and an unsymmetrically bridging benzynechromium tricarbonyl moiety. This is the first example of an aryne to show unsymmetrical bonding to a closed metal triangle system. One unexpected feature of these three complexes is the presence of Cr-Ru bonding. The Cr-Ru bond distances range from 2.920(1) to 3.097(1) Å. These are the first examples of complexes which contain Cr-Ru bonds to be characterized by X-ray diffraction analysis. The first dinuclear metal complex of benzynechromium tricarbonyl Ru₂(CO)₆[µ-H][C₆H₄Cr(CO)₃][µ-AsMe₂] was also characterized. In addition, two new benzyne complexes, which are of known structural types, were isolated and characterized.

Some pyrolytic products other than aryne complexes were isolated and characterized. The complexes H₂Os₃(CO)₈L[PPri₂C₆H₄Cr(CO)₃] (L = CO, PPri₂C₆H₅Cr(CO)₃) were derived via ortho-metallation of a C-H bond of an η⁶-bound C₆H₅ moiety and reductive elimination of a propene molecule. It is interesting to note that the complex Os₃(CO)₈[PPPh₆H₄][PPPh₂C₆H₅Cr(CO)₃] is electron deficient. This is the first example of electron unsaturation found in a structure of this type.

The investigation of the thermal reactions of the complexes containing benzynechromium tricarbonyls during this work allows some conclusions to be drawn. Phenylchromium tricarbonyl and phenyl groups in triruthenium or triosmium clusters undergo C-H cleavage and C-P cleavage. The isopropyl group undergoes facile β C-H activation and subsequent C-P activation, while methyl and tertbutyl groups remain intact. It appears that the ease of P-C cleavage follows the order: P-C(Me, Bu) > P-C(Pr) > P-C(Ph) > P-C(C₆H₅Cr(CO)₃). Comparisons of the thermal reactions of ruthenium and osmium clusters confirm that the latter are generally more thermally stable.
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LIST OF ABBREVIATIONS

The following list of abbreviations, most of which are commonly used in the chemical literature, will be employed in this thesis:

Å                  angstrom (10^{-10} m)
Anal.             analysis
atm               atmosphere
ax                 axial
BPK               benzophenone ketyl
br                 broad
Bu^t              tertiary butyl
b.p.              boiling point
Bz                 centroid of the coordinated phenyl ring
°C                degree centigrade
CAChe             Computer Aided Chemistry
Calcd             calculated
cm^{-1}           wave number
Cp                 cyclopentadienyl
Cp*               C_5Me_5
Cy                 cyclohexyl
δ                  chemical shift
d                 doublet
dd                doublet of doublets
e                 electron
Et                ethyl
eq               equatorial
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<tr>
<td>Fc</td>
<td>ferrocenyl</td>
</tr>
<tr>
<td>g</td>
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<td>h</td>
<td>hour</td>
</tr>
<tr>
<td>Hz</td>
<td>Hertz</td>
</tr>
<tr>
<td>INDO</td>
<td>Intermediate Neglect of Differential Overlap</td>
</tr>
<tr>
<td>IR</td>
<td>infrared</td>
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<tr>
<td>m</td>
<td>meta</td>
</tr>
<tr>
<td>m</td>
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</tr>
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<td>M</td>
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<td>mL</td>
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<td>millimole</td>
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<tr>
<td>NMR</td>
<td>nuclear magnetic resonance</td>
</tr>
<tr>
<td>o</td>
<td>ortho</td>
</tr>
<tr>
<td>ORTEP</td>
<td>Oak Ridge Thermal Ellipsoid Plotting Program</td>
</tr>
<tr>
<td>p</td>
<td>quintet</td>
</tr>
<tr>
<td>p</td>
<td>para</td>
</tr>
<tr>
<td>Ph</td>
<td>phenyl</td>
</tr>
<tr>
<td>$^{31}\text{P}{^1\text{H}}$</td>
<td>observe phosphorus while decoupling proton</td>
</tr>
<tr>
<td>pot</td>
<td>p-tolyl</td>
</tr>
<tr>
<td>Pr\text{\textsuperscript{i}}</td>
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xii
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<td>sept</td>
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<td>t</td>
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<tr>
<td>THF</td>
<td>tetrahydrofuran</td>
</tr>
<tr>
<td>TMEDA</td>
<td>tetramethylethylenediamine</td>
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ACKNOWLEDGMENTS

First and foremost, I wish to express my sincere gratitude to Professor W. R. Cullen, my research supervisor, for his guidance and support during the course of this work. My thanks goes to my lab. colleagues, Anna, Basil, Chandrika, Deepthi, Hao, John, Ojo, Spiros, Tucai, Xiao-chun, Xing-fang, for the friendly atmosphere created by you.

My appreciation is extended to Professor M. D. Fryzuk for help with MO calculations. Acknowledgment is given to Dr. Roshan S. Cader., Dr. K. E. Martin, Mr. C. Simpson and Mr. D. Zhang for reading the manuscript of this thesis and suggestions.

I would also like to acknowledge the help I had from all the support staff here at UBC: the people in the glass-blowing shop, the NMR staff, Mr. P. Borda the elemental analysis expert. A special thanks is due to Dr. Steven J. Rettig who solved all the crystal structures in this thesis.

To my wife, Qixin, I express my greatest thanks for her encouragement.

Finally, I would like to thank the University of British Columbia Chemistry Department for financial assistance.
CHAPTER 1

Introduction to Benzyne and Benzyne Metal Complexes

1.1 Benzyne

Benzyne (dehydrobenzene) (1) is a short-lived and highly reactive intermediate formally derived by the removal of two adjacent hydrogen atoms from a benzene ring. Although this molecule does not contain the full triple bond shown in (1), the name is appropriate since its chemistry is in many respects similar to that of a highly reactive alkyne.

![Diagram](image)

(1)

The first conclusive proof for the existence of benzyne came with the observation that equal amounts of anilines (3) and (4) were formed in the reaction of $^{14}$C-labeled chlorobenzene with KNH$_2$ as shown in Equation 1.1.

```
\begin{equation}
\text{Cl} \quad \text{KNH}_2 \quad \text{NH}_3
\end{equation}
```

This demonstrated the involvement of an intermediate like (2) [1]. Additional support for the benzyne intermediate was found by Wittig [2]. Benzyne generated in the reaction from fluorobromobenzene and lithium amalgam could be trapped with a diene such as furan to give the endoxide (5) as shown in Equation 1.2.
Benzyne can be pictured as having a weak and easily polarizable third bond produced by the overlap of the two adjacent sp² orbitals at the dehydrocarbon atoms [3]. The infrared spectrum of the matrix-isolated benzyne gives an absorption at 2080-2090 cm⁻¹ which is attributed to a C=C stretching vibration [4, 5, 6]. This is only slightly lower than the value of ca. 2200 cm⁻¹ found in acyclic alkynes. The infrared spectrum was used as the basis for the force-field calculations of the dimensions of benzyne [7]. The result shows that the length of the formal triple bond is 1.344 Å, which is approximately 0.05 Å shorter than a normal benzene C-C bond length and is interpreted as showing that benzyne is a true cyclic acetylene. This is also indicated by a variety of theoretical calculations in which the structure has been optimized [8, 9, 10]. The geometry of benzyne predicted from the most recent ab initio calculation is more distorted than that predicted from the force-field calculations. In the latter, the formal triple bond of 1.275 Å is only slightly longer than a normal C≡C bond [9].

Much of the early work on benzyne was undertaken using the halogen-metal exchange in o-dihalogenobenzene as outlined in equation 1.2 or the aryl halide-strong base route as shown in Equation 1.3 [11, 12].
A useful synthetic route to benzyne involves the decomposition of benzene-diazonium-2-carboxylate (7), which is generated in situ by diazotization of anthranilic acid (6) with pentylnitrite (Equation 1.4) [13, 14].

\[
\begin{array}{c}
\text{NH}_2 \quad \text{CONH}_2 \\
(6)
\end{array} \xrightarrow{\text{RONO}} \begin{array}{c}
\text{NH}_2 \quad \text{CO}_2^-
\end{array} \xrightarrow{\text{N}_2, \text{CO}_2} \begin{array}{c}
\text{C}_6\text{H}_4^-
\end{array} \quad \text{Eq. 1.4}
\]

The fragmentation of a large number of ortho-fused benzene derivatives also affords the benzyne intermediate. For instance, 1-aminobenzotriazole (8) can be oxidized by lead tetraacetate to give (9) which cleanly decomposes to afford benzyne (Equation 1.5) [15]. This reaction can occur even at -78 °C.

\[
\begin{array}{c}
\text{NH}_2 \quad \text{N} \\
(8)
\end{array} \xrightarrow{\text{Pb(OAc)}_4} \begin{array}{c}
\text{N} \quad \text{N} \\
(9)
\end{array} \xrightarrow{-2\text{N}_2} \begin{array}{c}
\text{C}_6\text{H}_4^-
\end{array} \quad \text{Eq. 1.5}
\]

Benzyne is a very reactive species that reacts most readily with "soft" and polarizable nucleophiles since the formal triple bond is itself highly polarizable. In the absence of either a nucleophile or a reactive unsaturated compound, benzyne reacts with itself very easily to produce biphenylene (10) and triphenylene (11) [16]. The Diels-Alder reaction is one of the most important reactions of benzyne where benzyne itself is a dienophile. This reaction is observed with a very wide range of dienes, such as furans (Equation 1.2). A number of reviews dealing with the chemistry of benzyne have appeared in the chemical literature [17].
Benzyne has been extensively studied over the last 40 years to establish its geometric and electronic structure, its chemical reactivity, and its thermodynamic properties. However, only a few examples of benzyne stabilization by transition metals have been reported.

1.2 Mononuclear Metal Complexes of Benzyne

An important aspect of organometallic chemistry is the stabilization of highly reactive species (e.g. carbene, carbyne, cyclobutadiene, benzyne etc.) by their coordination to transition metals. In 1979, the first isolated mononuclear metal complex of benzyne \(\text{CpTaMe}_2(\text{C}_6\text{H}_4)\) (12) was structurally characterized by X-ray crystallography [18a]. To date, there are eleven reported examples of crystal structures of mononuclear transition metal complexes containing a benzyne fragment [18]. Stable mononuclear benzyne derivatives are now known for the following eleven transition metals: Ti, Zr, Nb, Ta, Mo, W, Re, Ru, Ni, U, and Th.

![Diagram](12)

1.2.1 Generation of Mononuclear Metal Complexes of Benzyne

Apart from the benzyne nickel complex, all known mononuclear metal complexes of benzyne are formed by \(\beta(\text{ortho-})\) hydrogen abstraction from an aryl group \(\sigma\)-bonded to the metal complex.
When the complexes NbCp[N(2,6-Pr$_2$C$_6$H$_3$)]Ph$_2$PMe$_3$, TiCp$_2$Ph$_2$, ZrCp$_2$Ph$_2$, or cis-Ru(PMe$_3$)$_4$Ph$_2$ are heated in an aromatic solvent, the benzyne complexes Nb(NR)-(C$_6$H$_4$)PMe$_3$ (13), TiCp$_2$(η$^2$-C$_6$H$_4$) (14), ZrCp$_2$(η$^2$-C$_6$H$_4$) (15a), or Ru(PMe$_3$)$_4$(η$^2$-C$_6$H$_4$) (16) are formed by the elimination of benzene. The complex (15a) can be trapped almost quantitatively in the form of its stable trimethylphosphine adduct (15b). The methyl phenyl complexes: ZrCp$_2$(Ph)(Me), cis-Ru(PMe)$_4$(Ph)(Me) and TaCp*(Ph)(Me)$_3$ upon heating in aromatic solvents can similarly generate the corresponding benzyne complexes by methane elimination.

Sarry et al. [19] have shown that the reaction between the transition metal halides MCl$_5$, where M = Ta, Nb, W, Mo, and an excess of an aryl lithium reagent in diethyl ether solution gives a series of unexpected benzyne complexes of the general formula [Li(Et$_2$O)]$_4$[M(C$_6$H$_4$)$_2$(C$_6$H$_5$)$_4$], based on $^1$H and $^7$Li NMR spectroscopic studies. Power used a modified route to prepare [Li(THF)]$_4$[Nb(C$_6$H$_4$)$_2$(C$_6$H$_5$)$_3$][C$_6$H$_5$Li(THF)]·0.5THF·0.5C$_6$H$_4$ (17) and [Li(THF)]$_2$[Li$_4$Cl$_2$(THF)$_2$]$_2$[Ta(C$_6$H$_4$)$_2$(C$_6$H$_5$)$_4$] (18), which were characterized by X-ray crystallography [18e].
Wilkinson et al. developed a mild synthetic route to rhenium, molybdenum and tungsten benzyne derivatives [18f, 18g]. Treatment of the o-tolyl derivative Re(2-Me-C6H4)4, Mo(2-MeC6H4)4, or W(2,5-Me2C6H3)4 with PMe2Ph results in the formation of benzyne complexes such as Re(η2-2-MeC6H3)2(2-MeC6H4)2(PMe2Ph)2 (19), Mo(η2-2-MeC6H3)2(2-MeC6H4)2(PMe2Ph)2 (20), or W(η2-2,5-Me2C6H2)(2,5-Me2C6H3)2- (PMe2Ph)2 (21) by the elimination of an aryl group together with the hydrogen atom from the ortho-position of another toluenyl group.

Bennett et al. have developed a specific synthetic route to the benzyne nickel complex Ni(Cy2PCH2CH2PCy2)(C6H4) (22) [18c]. The complex (22) can be prepared by the reduction of a (2-bromophenyl)chloronickel complex with 1% sodium amalgam without the involvement of β-hydrogen elimination, as shown in Equation 1.6.

1.2.2 Structure of Mononuclear Metal Complexes of Benzyne

There are three known representations of the benzyne coordination mode in mononuclear benzyne complexes. These are shown below as (I), (II), and (III).
Here benzyne is considered to be either a two-electron donor (I) or (II), or a four electron donor (III). Table 1.1 compares the benzyne C-C bond lengths determined by X-ray crystallography in various complexes with those in free benzyne as predicted by the most recent ab initio calculations. The “triple bond” C1-C2 in the benzyne metal complexes is lengthened upon coordination. The remaining C-C bonds in the C6H4 ring are nearly of the same length or are slightly shorter than those in free benzyne.

Table 1.1 The C-C bond lengths (Å) in free benzyne and in metal complexes of benzyne

<table>
<thead>
<tr>
<th>Compound</th>
<th>C1-C2</th>
<th>C2-C3</th>
<th>C3-C4</th>
<th>C4-C5</th>
<th>C5-C6</th>
<th>C6-C1</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>C6H4</td>
<td>1.275</td>
<td>1.398</td>
<td>1.413</td>
<td>1.417</td>
<td>1.398</td>
<td>1.413</td>
<td>[9]</td>
</tr>
<tr>
<td>Ta (12)</td>
<td>1.364(5)</td>
<td>1.410(5)</td>
<td>1.362(6)</td>
<td>1.403(6)</td>
<td>1.375(6)</td>
<td>1.408(6)</td>
<td>[18a]</td>
</tr>
<tr>
<td>Ni (22)</td>
<td>1.332(6)</td>
<td>1.386(6)</td>
<td>1.383(7)</td>
<td>1.390(8)</td>
<td>1.383(7)</td>
<td>1.406(8)</td>
<td>[18c]</td>
</tr>
<tr>
<td>Nb (13)</td>
<td>1.342(11)</td>
<td>1.394(12)</td>
<td>1.393(13)</td>
<td>1.357(15)</td>
<td>1.384(14)</td>
<td>—</td>
<td>[18j]</td>
</tr>
<tr>
<td>Zr (15b)</td>
<td>1.364(8)</td>
<td>1.389(8)</td>
<td>1.383(9)</td>
<td>1.380(9)</td>
<td>1.377(9)</td>
<td>1.406(8)</td>
<td>[18d]</td>
</tr>
<tr>
<td>Ru (16)</td>
<td>1.355(3)</td>
<td>1.372(3)</td>
<td>1.411(4)</td>
<td>1.363(4)</td>
<td>1.393</td>
<td>1.382(3)</td>
<td>[18h]</td>
</tr>
<tr>
<td>Nb (17)</td>
<td>1.419(7)</td>
<td>1.410(7)</td>
<td>from 1.388 (8) to 1.416(7)</td>
<td>[18e]</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

In the benzyne-tantalum complex (12), the four ligands take up a pseudo-tetrahedral geometry around the tantalum atom. The benzyne ligand is oriented perpendicular to the plane of the Cp* ring. Electron-counting suggests that benzyne should behave as a four electron donor in (12). The C1-C2 distance of the benzyne moiety in (12) is 1.36 Å and the other C-C distances show, to some degree, an alternating pattern of bond lengths. Thus, the bonding could be represented as in (III).
In the nickel complex (22), the coordination geometry is close to trigonal planar. In this structure benzyne is considered to behave as a two electron donor. The C1-C2 bond length of 1.332(6) Å is significantly longer than the value of 1.25-1.30 Å, which is commonly observed in nickel alkyne complexes [20]. The remaining five C-C bonds in the six-membered ring are almost identical in length (average 1.38 Å). These features suggest that the complex (22) can be described in terms of the delocalized benzometallacyclopentene structure (I). The complexes (12) and (22) are electron deficient and have only 16 valence electrons. In contrast, the other benzyne complexes in Table 1.1 are electron saturated and contain 18 valence electrons.

The structure associated with the metal benzyne moiety in (13) is similar to that in (15b). For example, the carbon-carbon distances in the benzyne moiety of both complexes are equivalent within experimental error, which is consistent with a delocalized aromatic structure. The benzyne unit may be regarded as a two electron ligand in (13) or (15b), which suggests that coordination mode (I) is a reasonable representation for both complexes. The ruthenium complex (16) has a distorted trigonal bipyramidal structure, in which the benzyne is regarded as a monodentate ligand. The length of the C-C bond coordinated to the ruthenium center is 1.355(3) Å. The other C-C distances in the C₆H₄ ring range from 1.363(4) to 1.411(4) Å with notable bond alternations. Hence the bonding can be represented as in structure (II).

The niobium metal center in (17) is surrounded in an approximately trigonal bipyramidal arrangement with two equatorial benzyne ligands, an equatorial σ-phenyl and two axial σ-phenyl groups. Furthermore, solvated lithium ions and an additional phenyl group comprise a secondary coordination sphere in the complex.
1.2.3 Chemistry of Mononuclear Metal Complexes of Benzyne

Although many mononuclear benzyne complexes are known, only the chemistry of the Zr, Ni and Ru complexes has been studied to any significant extent.

Typical reactions of \([\text{ZrCp}_2(\text{C}_6\text{H}_4)]\) (15a) are summarized in Scheme 1.1. Ethylene insertion leads to the zirconaindane (23) [21]. The substituted derivatives (24a) and (24b) are formed stereospecifically from the reaction of (15a) with \(\text{cis}\) and \(\text{trans}\)-stilbene respectively [22]. \(\text{ZrCp}_2(\text{C}_6\text{H}_4)\) also reacts with nitriles to give dimeric azazirconacyclopentenes (25) which can be hydrolyzed to ketones [23]. The marked oxophilicity of the \(\text{Cp}_2\text{Zr}\) unit is illustrated by the reaction of (15a) with \(\text{W(CO)}_6\) to give the zirconaoxycarbene complex (26) [24].

![Scheme 1.1. Reactions of \([\text{ZrCp}_2(\text{C}_6\text{H}_4)]\) (15a)](image-url)
Some reactions of the benzyne nickel complex (22) are summarized in Scheme 1.2. As expected for a low-valent d\textsuperscript{10} metal complex, (22) readily reacts with electrophiles such as iodine and methyl iodide to yield complexes (27) and (28) respectively. Like the Cp\textsubscript{2}ZrC\textsubscript{6}H\textsubscript{4} derivative, (22) also undergoes insertions with unsaturated molecules like CO\textsubscript{2}, ethylene and dimethyl acetylenedicarboxylate to form metallacycles. Although acetonitrile inserts into the benzyne-zirconocene complex, it is deprotonated by the benzyne nickel complex to yield compound (33). Again in contrast to Cp\textsubscript{2}ZrC\textsubscript{6}H\textsubscript{4} (15a), the complex (22) does not undergo insertion with diphenylacetylene; instead the benzyne is displaced to give (32) [18c].

\[\text{Scheme 1.2. Reactions of } [\text{Ni(Cy}_2\text{PC}_2\text{H}_4\text{PCy}_2)(\text{C}_6\text{H}_4)] \text{ (22)}\]
Some typical reactions of the ruthenium benzyne complex (16) are summarized in Scheme 1.3 [18h]. The high basicity of the metal center in the complex makes the compound much more reactive than the other benzyne complexes or transition-metal alkyls towards weakly acidic hydrogens. For example, (16) reacts cleanly with arylamine N-H bonds, water O-H bonds, and benzyl and aryl C-H bonds. The C-C bond of acetone is cleaved by (16) to give the O-bound cyclometallated enolate complex (37). The complex (16) also reacts with benzaldehyde to form the single insertion product (38).

Scheme 1.3 Reactions of $\text{L}_4\text{Ru(C}_6\text{H}_4)\ (L = \text{PMe}_3)$ (16)
1.3 Dinuclear Metal Complexes of Benzyne

The C₆H₄ moiety in dinuclear metal complexes is bound by two σ-bonds to the metal atoms. Some authors refer to these σ-bonded compounds as o-phenylene derivatives. Interestingly, all of these complexes are formed with the late transition elements such as Os [25], Fe [26], Ir [27], Ni [28], and Pd [29]. However, no systematic synthetic methods to dinuclear metal complexes of benzyne have been developed so far.

Pyrolysis of Os₃(CO)₁₀(AsMe₂Ph)₂ or Os₃(CO)₁₁(AsMe₂Ph) in octane results in complex (39) in low yield, together with trinuclear μ₃-C₆H₄ species. The complex (40) is apparently formed by the direct trapping of tetrafluorobenzyne, which is generated by the decomposition of C₆F₅MgBr in dioxane, with Fe₃(CO)₁₂. The complex (41) is formed in low yield upon photolysis of a solution of [IrCp(CO)₂] in benzene.

Reduction of complex Ni(C₆H₅Cl)(PET₃)₂Cl (42) with lithium metal at -40 to -78 °C affords an essentially quantitative yield of an electron-deficient complex (43) (Equation 1.7). This complex (43) is extremely air sensitive and thermally unstable. Oxidative addition of o-diiodobenzene to Pd₂(dpm)₃ (44) yields the complex (45) which is an air-stable 16e species (Equation 1.8).
1.4 Metal Cluster Complexes of Benzyne

A great deal of attention has been focused on studies of polynuclear metal complexes during the past two decades. These studies have ranged from the synthesis and characterization of high nuclearity complexes to the investigation of esoteric ligand transformations promoted by coordinative interactions at two or more metallic sites. One interesting aspect of these studies is the activation of aryl C-H bonds and ligand C-P or C-As bonds which lead to benzyne metal cluster complexes.

Evidence for the existence of metal clusters containing the C₆H₄ benzyne ligand, which is formed by activation of aryl C-H and C-P bonds, was first obtained in 1972 by Nyholm and co-workers during the course of studies of the prolonged thermal reaction of Os₃(CO)₁₂ with PPh₃ [30]. Extended observations on the thermolysis of the osmium carbonyl complexes of PMe₂Ph and AsMe₂Ph were made by Deeming and co-workers [31,
32], while parallel studies in the triruthenium benzyne complex were reported by Bruce [56, 57]. Following these pioneering works, approximately 50 benzyne complexes which are based on the polynuclear osmium and ruthenium carbonyl framework have been reported. Among these, only five are triruthenium complexes [56-60]. Most investigations on these benzyne complexes have focused on structure and on their fluxional behavior; however, not much work has been done on their chemistry.

1.4.1 Structure and Spectroscopic Properties of Metal Cluster Complexes of Benzyne

The triosmium and triruthenium benzyne complexes can be classified into five different structural types, I, II, III, IV, and V as shown in Figure 1.1. However, only type IV is found for the structurally characterized triruthenium benzyne complexes.

![Figure 1.1 Five structure types of benzyne trinuclear metal clusters](image)
The type I benzyne complexes $[\text{H}_2\text{Os}_3(\text{CO})_7\text{LL'}(\text{C}_6\text{H}_3\text{R})]$ are presented in Table 1.2. A typical example of this class is compound $\text{H}_2\text{Os}_3(\text{CO})_9(\text{C}_6\text{H}_4)$ (46) [42]. The X-ray diffraction analysis shows that three osmium atoms define a closed triangle in which the three metal-metal bond lengths show significant variations. The benzyne ligand lies over one face of the triangle such that the dihedral angle between the plane of the ring and that of the triangle is between $60^\circ$ to $70^\circ$. The benzyne ligand, acting as a four-election donor, forms $\sigma$ bonds through C1 and C2 to two of the Os atoms, bridging the Os1-Os2 edge. The C1-C2 bond interacts with the third Os atom, Os3 in an $\eta^2$-fashion. The C-C distances in the ring do not vary significantly from the mean (1.43(7) Å), but the estimated standard deviations are too high for an accurate assessment.

Table 1.2 Examples of type I benzyne complexes

<table>
<thead>
<tr>
<th>Complex</th>
<th>R</th>
<th>L</th>
<th>L'</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>(46)</td>
<td>H</td>
<td>CO</td>
<td>CO</td>
<td>[33, 35, 37, 42, 47]</td>
</tr>
<tr>
<td>(47)</td>
<td>Me</td>
<td>CO</td>
<td>CO</td>
<td>[35, 42, 46]</td>
</tr>
<tr>
<td>(48)</td>
<td>Me, Me</td>
<td>CO</td>
<td>CO</td>
<td>[42]</td>
</tr>
<tr>
<td>(49)</td>
<td>Bu$^i$</td>
<td>CO</td>
<td>CO</td>
<td>[55]</td>
</tr>
<tr>
<td>(50)</td>
<td>Pr$^i$</td>
<td>CO</td>
<td>CO</td>
<td>[42]</td>
</tr>
<tr>
<td>(51)</td>
<td>CH$_3$CO</td>
<td>CO</td>
<td>CO</td>
<td>[55]</td>
</tr>
<tr>
<td>(52)</td>
<td>CH=$\equiv$CHPh</td>
<td>CO</td>
<td>CO</td>
<td>[42]</td>
</tr>
<tr>
<td>(53)</td>
<td>Cl</td>
<td>CO</td>
<td>CO</td>
<td>[42]</td>
</tr>
<tr>
<td>(54)</td>
<td>H</td>
<td>PPh$_3$</td>
<td>CO</td>
<td>[47]</td>
</tr>
<tr>
<td>(55)</td>
<td>H</td>
<td>P(OMe)$_3$</td>
<td>CO</td>
<td>[47]</td>
</tr>
<tr>
<td>(56)</td>
<td>H</td>
<td>PPh$_3$</td>
<td>PPh$_3$</td>
<td>[47, 54]</td>
</tr>
<tr>
<td>(57)</td>
<td>H</td>
<td>P(OMe)$_3$</td>
<td>P(OMe)$_3$</td>
<td>[54]</td>
</tr>
</tbody>
</table>
The two hydride ligands in (46), which are one-electron donors, were not located directly, but the distribution of the carbonyl groups indicates that they bridge the Os1-Os2 and Os1-Os3 edges.

The $^1$H NMR spectra of benzyne complexes $\text{H}_2\text{Os}_3(\text{CO})_9(\text{C}_6\text{H}_3\text{Me})$ (47), $\text{H}_2\text{Os}_3(\text{CO})_9(\text{C}_6\text{H}_3\text{Cl})$ (53), $\text{H}_2\text{Os}_3(\text{CO})_8(\text{C}_6\text{H}_4)(\text{PPh}_3)$ (54) and $\text{H}_2\text{Os}_3(\text{CO})_8(\text{C}_6\text{H}_4)-(\text{P}(\text{OMe})_3)$ (55) in solution show the existence of position isomers which can not be separated by thin layer chromatography. The isomers for (47) and (53) are assigned as shown in Figure 1.2 [42].

![Figure 1.2](image)

**Figure 1.2** Two isomeric forms of (47) and (53). $R = \text{Me, Cl}$; CO ligands omitted for clarity

In the case of (54), the PPh$_3$ ligand of the major isomer appears to occupy an axial site, while for (55), the P(OMe)$_3$ ligand in the major isomer occupies an equatorial site as shown in Figure 1.3. This feature may reflect the difference in steric requirements of the two phosphorus donor ligands, since the steric repulsion between the C$_6$H$_4$ moiety and the bulky PPh$_3$ ligand could be minimized with the PPh$_3$ occupying the axial position [47].
Figure 1.3 Proposed structures for (54) and (55) \( L = \text{PPh}_3, \text{P(OMe)}_3; \text{CO} \) ligands omitted for clarity

The examples of types \( \text{II} \) and \( \text{III} \) complexes are listed in Table 1.3, among which three compounds \( \text{HOS}_3(\text{CO})_8(\text{C}_6\text{H}_4)\text{AsMe}_2 \) (58), \( \text{HOS}_3(\text{CO})_8(\text{C}_6\text{H}_4)(\text{PC}_4\text{H}_2\text{Me}_2) \) (59) and \( \text{HOS}_3(\text{CO})_8(\text{C}_6\text{H}_4)\text{SMe} \) (60) have been characterized by X-ray crystallography. The type \( \text{II} \) structure consists of an "open" cluster of three osmium atoms with a bridging three electron donor \( \text{EX}_2 \) group, a bridging one electron donor hydride ligand, and a triply bridging four electron donor benzyne ligand \( \text{C}_6\text{H}_4 \). The Os1-Os2-Os3 angle is wide (83 to 85°) and the Os1-Os3 distance at 3.79 to 3.93 Å is too long to allow any significant direct metal-metal bonding. The bonded Os1-Os2 and Os2-Os3 distances are 2.93 Å and 2.83 Å (mean values) respectively. The hydride ligand observed in the \( ^1\text{H} \) NMR spectrum was not located directly but structural details indicate that it lies along the Os1-Os2 edge, which is the longest of the two Os-Os bonds. The \( \text{EX}_2 \) ligand forms a symmetrical bridge through an approximately tetrahedral \( \text{P(As)} \) atom or a pyramidal \( \text{S} \) atom between the non-bonded Os1 and Os3 atom. The benzyne ligand is coordinated to one face of the cluster. The ring is planar and is inclined at an angle of 69° to 72° to the Os3 plane. Since there are only two Os-Os bonds, the \( \text{C}_6\text{H}_4 \) should serve as a four-electron donor in order for the molecule to be electron precise, and the bonding can be viewed as two σ bonds (Os1-C1 and Os3-C2) and an \( \eta^2 \)-linkage between C1-C2 and Os2. The bonding with respect to the metal atoms is essentially symmetrical.
Table 1.3 Examples of type II benzyne complexes HO\(_{3}(CO)_{8}EX_{2}(C_{6}H_{3}R)L\)

<table>
<thead>
<tr>
<th>Complex ((\text{No.}))</th>
<th>EX(_{2})</th>
<th>R</th>
<th>L</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>(58)</td>
<td>AsMe(_{7})</td>
<td>H</td>
<td>CO</td>
<td>[31, 32, 38]</td>
</tr>
<tr>
<td>(59)</td>
<td>PC(<em>{4}H</em>{2}Me_{7})</td>
<td>H</td>
<td>CO</td>
<td>[51]</td>
</tr>
<tr>
<td>(60)</td>
<td>SMe</td>
<td>H</td>
<td>CO</td>
<td>[39]</td>
</tr>
<tr>
<td>(61)</td>
<td>SPri</td>
<td>H</td>
<td>CO</td>
<td>[39]</td>
</tr>
<tr>
<td>(62)</td>
<td>PMe(_{2})</td>
<td>H</td>
<td>CO</td>
<td>[31, 32]</td>
</tr>
<tr>
<td>(63)</td>
<td>PMe(_{2})</td>
<td>H</td>
<td>PMe(_{2})Ph</td>
<td>[31, 32]</td>
</tr>
<tr>
<td>(64)</td>
<td>PEt(_{2})</td>
<td>H</td>
<td>CO</td>
<td>[34]</td>
</tr>
<tr>
<td>(65)</td>
<td>AsMe(_{2})</td>
<td>Pri</td>
<td>CO</td>
<td>[38]</td>
</tr>
<tr>
<td>(66)</td>
<td>AsMe(_{2})</td>
<td>Me</td>
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<td>[41]</td>
</tr>
<tr>
<td>(67)</td>
<td>AsMe(_{2})</td>
<td>OMe</td>
<td>CO</td>
<td>[41]</td>
</tr>
<tr>
<td>(68)</td>
<td>PPh(_{2})</td>
<td>H</td>
<td>PPh(_{3})</td>
<td>[30]</td>
</tr>
<tr>
<td>(69)</td>
<td>PPh(_{2})</td>
<td>H</td>
<td>PPh(<em>{2})C(</em>{6})H(_{4})</td>
<td>[30]</td>
</tr>
</tbody>
</table>

\(a\): Examples of type III

The temperature dependent \(^{1}\text{H}\) and \(^{13}\text{C}(CO)\) NMR spectra of complex (58) (-60 °C to +27 °C) have been interpreted in terms of a reversible hydride migration from the Os\(_{1}\)-Os\(_{2}\) edge to the Os\(_{2}\)-Os\(_{3}\) edge with some angular reorganization of the carbonyl ligands [38]. As in complexes (47) and (53), the position of a substituent on the ring of the \(\mu_{3}\)-substituted benzyne does not depend upon whether the precursor is 1,2- or 1,4-disubstituted. This suggests that the hydride also migrates reversibly between the metal atoms and \(\mu_{3}\)-benzyne by way of the phenyl intermediates. Thus, the thermolysis of Os\(_{3}(CO)_{11}[AsMe_{2}(C_{6}H_{4}Me-2)]\) (68) gives only the unexpected isomer HO\(_{3}(CO)_{9}-(AsMe_{2})(\mu_{3}-C_{6}H_{3}Me-4)\) (66) instead of the 3-substituted compound as shown in Scheme1.4. Furthermore, a similar thermolysis of either Os\(_{3}(CO)_{11}[AsMe_{2}(C_{6}H_{4}OMe-2)]\)
(69a) or Os$_3$(CO)$_{11}$AsMe$_2$(C$_6$H$_4$OMe-4) (69b) gave the same 3-methoxybenzyne complex (67) in either case (Scheme 1.4).

**Scheme 1.4** Routes to HO$_3$(CO)$_9$(AsMe$_2$)(μ$_3$-C$_6$H$_3$Me-4) (66) and HO$_3$(CO)$_9$(AsMe$_2$)(μ$_3$-C$_6$H$_3$OMe-3) (67)

The reaction of Os$_3$(CO)$_{12}$ with PPh$_3$ in refluxing xylene or the thermolysis of Os$_3$(CO)$_{10}$(PPh$_3$)$_2$ affords nine products, of which two, complexes (70) and (71), have the type III structure. Types II and III have similar structures. They contain the same kind of bridging ligands: a one-electron hydride donor, a three-electron EX$_2$ donor and a four-electron benzyne donor. However, in III there is one more Os-Os bond and one less CO ligand. Again, the hydrides in (70) and (71) were not located during the crystallographic analysis. In each molecule the hydride ligand is assumed to bridge the Os1-Os2 vector.
Surprisingly, the known examples of type II do not thermally decarbonylate in order to form the third Os-Os bond present in the type III structure [38].

Both triruthenium and triosmium clusters form complexes with structure type IV and the known examples are listed in Table 1.4. Interestingly, no benzyne triruthenium complexes of any other type were known before the present work. The structures of the two complexes (77) and (78), $M_3(\text{CO})_7(\mu_3-\text{C}_6\text{H}_4)(\mu-\text{PPh}_2)_2$ ($M = \text{Os, Ru}$), offer a rare opportunity to compare similar ruthenium and osmium complexes.

Table 1.4 Examples of type IV benzyne complexes $M_3(\text{CO})_7(\mu_3-\text{C}_6\text{H}_3R)-(\mu-EX_2)_2$ ($M = \text{Os, Ru}$)

<table>
<thead>
<tr>
<th>Complex</th>
<th>M</th>
<th>EX$_2$</th>
<th>R</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>(72)</td>
<td>Os</td>
<td>PMe$_2$</td>
<td>H</td>
<td>[31, 32]</td>
</tr>
<tr>
<td>(73)</td>
<td>Os</td>
<td>AsMe$_2$</td>
<td>Pr$^i$</td>
<td>[38]</td>
</tr>
<tr>
<td>(74)</td>
<td>Os</td>
<td>AsPh$_2$</td>
<td>H</td>
<td>[30]</td>
</tr>
<tr>
<td>(75)</td>
<td>Os</td>
<td>AsMe$_2$</td>
<td>H</td>
<td>[31, 32, 38]</td>
</tr>
<tr>
<td>(76)</td>
<td>Os</td>
<td>PhC=CHPh</td>
<td>H</td>
<td>[52]</td>
</tr>
<tr>
<td>(77)</td>
<td>Os</td>
<td>PPh$_2$</td>
<td>H</td>
<td>[30, 30]</td>
</tr>
<tr>
<td>(78)</td>
<td>Ru</td>
<td>PPh$_2$</td>
<td>H</td>
<td>[56, 57, 58]</td>
</tr>
<tr>
<td>(79)</td>
<td>Ru</td>
<td>PPhFc</td>
<td>H</td>
<td>[59]</td>
</tr>
<tr>
<td>(80)</td>
<td>Ru</td>
<td>EX$_2(1)=PPh$_2$</td>
<td>H</td>
<td>[60]</td>
</tr>
<tr>
<td>(81)</td>
<td>Ru</td>
<td>P($\text{C}_6\text{H}_4\text{Me}-m$)</td>
<td>Me</td>
<td>[56, 7, 58]</td>
</tr>
<tr>
<td>(82)</td>
<td>Ru</td>
<td>P($\text{C}_6\text{H}_4\text{Me}-p$)</td>
<td>Me</td>
<td>[56, 57, 58]</td>
</tr>
</tbody>
</table>

In type IV structure, the $M_3$ atoms define a slightly distorted isosceles triangle, where the longest bond ($M_1$-$M_3 = 2.90$ to $2.94$ Å) is ca. $0.15$ Å longer than other two
bonds (2.74 to 2.79 Å). Two edges of the M₃-triangle are bridged by the three-electron donor EX₂ groups, and the third edge by a semibridging CO group. The benzyne ligand which acts as a four-electron donor is planar and forms a dihedral angle of 64° to 66° with the M₃ plane. One side of the benzyne effectively spans an edge of the triangle which is bridged by an EX₂ group.

Benzyne forms two σ bonds to the M₁ and M₃ atoms and an η²-bond to the M₂ atom. There is a systematic variation in bond lengths within the C₆H₄ ligand, which suggests that some degree of bond localization occurs. M₃ is coordinated to three carbonyl ligands, one of which is bent towards M₂ (M₃-C-O = 165-170°). M₁ and M₂ are both coordinated by two terminal carbonyls.

The fluxional behavior of the benzyne fragment in the complexes (72), (73), (75) and (77) was studied by variable temperature ¹H and ¹³C NMR techniques. Two processes were suggested to explain the rapid rotation/flipping of the benzyne ring in the cluster. At a lower temperature, a fast process interchanges the Eₐ and Eₖ bridging groups (Scheme 1.5, path A) without interchanging the a and b ends of the benzyne fragment. This process also tilts the opposite faces of the benzyne fragment toward the plane of the osmium atoms. At a higher temperature, a slower process takes place, which leads to an exchange of Cₐ with Cₖ of the benzyne, and of Eₐ with Eₖ (Scheme 1.5, path B). Each process is associated with a CO transfer and has an intermediate or transition state of Cs symmetry as shown in Scheme 1.5. A combination of these processes leads to complete rotation of the C₆H₄ ligand with respect to the metal triangle. In the case of (79), NMR studies on the fluxionality of the C₆H₄ ring show that its motion is less facile than that found in related Os₃ analogues. This may be due to an increase in steric hindrance in the ruthenium complex because of the presence of the Fc group.
Scheme 1.5 Possible fluxional processes in $M_3(CO)_7(\mu_3-C_6H_4)(\mu-EX_2)_2$

Benzyne complexes of type V are listed in Table 1.5. Six structures of this type have been determined by X-ray crystallography. Structure V consists of an "open" triangle of Os atoms ($Os_1\ldots Os_3$ open edge 3.98 to 4.13 Å) that bears $\mu_3$-EX and $\mu_3$-C$_6$H$_4$ groups on opposite sides of the plane with both acting as four-electron donors. Each Os atom is also bound to three terminal CO ligands. The Os$_1$-Os$_2$ bond bridged by C1-C2 of the ring is longer (2.89 to 2.94 Å) than the other Os$_2$-Os$_3$ bond (2.78 to 2.81 Å). The three Os-E (E = P, As) bond lengths are also inequivalent. The bond lengths range from 2.30 Å to 2.54 Å. The benzyne ligand is bound asymmetrically with one carbon atom $\sigma$-bonded to one Os$_1$ atom and the adjacent carbon atom bonded to the other two osmium atoms (Os$_2$, Os$_3$).

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Table 1.5 Examples of type V benzyne complexes Os₃(CO)₈L₉(μ₃-C₆H₃R)(μ₃-EX)

<table>
<thead>
<tr>
<th>Complex</th>
<th>EX</th>
<th>R</th>
<th>L</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>(83)</td>
<td>PMe</td>
<td>H</td>
<td>CO</td>
<td>[36, 44, 50]</td>
</tr>
<tr>
<td>(84)</td>
<td>PMe</td>
<td>H</td>
<td>PEr₃</td>
<td>[50]</td>
</tr>
<tr>
<td>(85)</td>
<td>As(p-tolyl)</td>
<td>Me</td>
<td>CO</td>
<td>[48, 49]</td>
</tr>
<tr>
<td>(86)</td>
<td>As(p-tolyl)</td>
<td>Me</td>
<td>As(p-tolyl)₃</td>
<td>[49]</td>
</tr>
<tr>
<td>(87)</td>
<td>PEr₃</td>
<td>H</td>
<td>CO</td>
<td>[36]</td>
</tr>
<tr>
<td>(88)</td>
<td>PPh</td>
<td>H</td>
<td>CO</td>
<td>[36, 44]</td>
</tr>
<tr>
<td>(89)</td>
<td>PFc</td>
<td>H</td>
<td>CO</td>
<td>[53]</td>
</tr>
<tr>
<td>(90)</td>
<td>PEr₃</td>
<td>H</td>
<td>PCy₃</td>
<td>[50]</td>
</tr>
<tr>
<td>(91)</td>
<td>PMe</td>
<td>H</td>
<td>P(OMe)₃</td>
<td>[50]</td>
</tr>
<tr>
<td>(92)ᵃ</td>
<td>PMe</td>
<td>H</td>
<td>2P(OMe)₃</td>
<td>[50]</td>
</tr>
<tr>
<td>(93)ᵃ</td>
<td>PEr₃</td>
<td>H</td>
<td>2PEr₃</td>
<td>[50]</td>
</tr>
</tbody>
</table>

ᵃ: Os₃(CO)₇L₂(μ₃-C₆H₄)(μ₃-EX).

The benzyne coordination mode in structure V is considerably different from those found in types I to IV in which benzyne has two σ M-C bonds and an η²-attachment to the third metal atom. Four different models ((A), (B), (C), and (D)), shown in Figure 1.4, have been proposed to explain the unusual bonding of the benzyne moiety in structure V.

Figure 1.4 Four bonding modes of benzyne in structure type V
Structural model (A), which has a three-center two-electron bond linking the bridging carbon atom C2, would require the benzyne ligand to be a two-electron donor. In this model the complexes are electron deficient and three Os-Os bonds could be expected to be present. Model (B) contains a carbenoid carbon atom C1 bound to Os1 and a C2 atom bridged to Os2 and Os3 atoms. Evans et al. described the benzyne ligand of (87) as an ortho-phenylene derivative with some carbenoid character, i.e. a mixture of model (A) and (B) [36]. Johnson and Lewis regarded the benzyne bond of (85) and (86) in terms of model (C) which has two σ-interactions (Os2-C2, Os1-C1) and a π-interaction between Os3 and a molecular orbital of appropriate symmetry of the C6H4 ligand. Such a π interaction is directed towards C2 of the ring, instead of the mid-point of the C1-C2 bond [19, 20]. More recently, Deeming et al. investigated the complexes (83) and (84) and advanced an alternative view of the bonding model (D), in which Os1 and Os2 are σ-bonded to the ring and there is an interaction through the π-orbital to Os3 that involves just one carbon atom [50]. Clearly more studies using MO calculations are needed to elucidate the nature of the μ3-C6H4 bonding in these type V structures.

There is one example of a benzyne trinickel complex (94) [61]. The structure of (94) consists of an isosceles triangle of nickel atoms which is bridged by a C6H4 unit on one face and a 2,2′-biphenyl unit on the other face. The four-electron donor benzyne is σ-bonded to Ni1 and Ni3, and π-bonded to Ni2 through C1 and C2 of the six-membered ring. The bonding mode is similar to that of the type II benzyne triosmium complexes.
By far the most common benzyne complexes are those based on trinuclear metal clusters. The benzyne fragments in these trinuclear (Os₃ or Ru₃) complexes are invariably planar and form σ-bonds to two metal atoms and have some π-interaction with the third metal atom. In addition, some degree of bond localization is found in the six-membered ring as well.

There are only a few examples of benzyne Ru₄ complexes ((95) to (100)) and Ru₅ complexes ((101), (102)), as shown in Figure 1.5 [58]. No osmium analogues have been reported so far. The molecular structures of (95), (96), (97) and (101) have been determined by X-ray diffraction studies. In the Ru₄ benzyne complex, a square Ru₄ unit is capped on one side by a μ₄-phosphinidene or arsinidene ligand. On the other side, the benzyne moiety functions as a six electron donor, bridging all the ruthenium atoms. The benzyne is σ-bonded to Ru1 and Ru2, and π-bonded to the Ru3 and Ru4 atoms. In (101) and (102), there is also a π coordination to the Ru5 atom. In both complexes, the benzyne acts as an eight-electron donor and Ru-C σ-bonds are shorter than the Ru-C π-bonds.
Figure 1.5 Structures of Ru₄ and Ru₅ benzyne complexes

1.4.2 Synthesis of Metal Cluster Complexes of Benzyne

There are two major synthetic routes to benzyne metal cluster complexes: the generation of coordinated arynes directly from arenes by hydrogen transfer to a metal system and the thermal decomposition of arylphosphine or arylarsine derivatives of Ru₃(CO)₁₂ and Os₃(CO)₁₂. Other methods such as decarbonylation of benzoyl or benzyl alcohol complexes have also been used. Unfortunately, all these methods lead to a mixture of products resulting in low to moderate yields of the benzyne derivatives.

(a) The Type I Benzyne Complexes

Os₃(CO)₁₂ reacts with benzene at 194 °C to yield the complex H₂Os₃(CO)₉(μ₃-C₆H₄) (46) through activation of an aryl C-H bond followed by ortho-metallation [33]. The yield of (46) can be improved by using Os₃(CO)₁₀(MeCN)₂ in refluxing benzene [42]. In
addition, Os\textsubscript{3}(CO)\textsubscript{10}(MeCN)\textsubscript{2} reacts with substituted benzenes to yield a variety of substituted benzyne complexes H\textsubscript{2}Os\textsubscript{3}(CO)\textsubscript{9}(\mu\textsubscript{3}-C\textsubscript{6}H\textsubscript{3}R) where R = Me, CHCHPh, Pr\textsuperscript{n}, Cl. The thermal decarbonylation of the benzoyl complex HOs\textsubscript{3}(CO)\textsubscript{10}(\mu-OCPH) or the benzyl alcohol derivative HOs\textsubscript{3}(CO)\textsubscript{10}(\mu-OCH\textsubscript{2}Ph) also affords the complex (46) in modest yield [35, 37]. The benzene triosmium complex Os\textsubscript{3}(CO)\textsubscript{9}(\mu\textsubscript{3}-12:12:12AH\textsubscript{6}) undergoes photoisomerisation at 5 °C in a toluene solution to produce complex (46) in high yield [47].

(b) The Type II and III Benzyne Complexes

Generally, thermolysis of the monosubstituted complexes Os\textsubscript{3}(CO)\textsubscript{11}(ER\textsubscript{2}Ph) where ER\textsubscript{2} = PMe\textsubscript{2}, PEt\textsubscript{2}, AsMe\textsubscript{2} in nonane for short times gives a mixture of products from which HOs\textsubscript{3}(CO)\textsubscript{9}(\mu-ER\textsubscript{2})(\mu\textsubscript{3}-C\textsubscript{6}H\textsubscript{4}) can be isolated in moderate yield (30%) [31, 32]. The reaction probably involves an initial activation of an aryl C-H bond, which results in the formation of an Os-C bond, followed by C-P bond cleavage and aryne capture by the metal cluster. Refluxing the disubstituted complexes Os\textsubscript{3}(CO)\textsubscript{10}(ER\textsubscript{2}Ph)\textsubscript{2} (ER\textsubscript{2} = PMe\textsubscript{2}, PEt\textsubscript{2}, AsMe\textsubscript{2}) (103) in nonane also affords the same derivatives in much lower yields [31, 32]. Interestingly, both examples of type III complexes were obtained from the thermal decomposition of Os\textsubscript{3}(CO)\textsubscript{10}(PPh\textsubscript{3})\textsubscript{2} in xylene [30]. However, no analogous compounds have been isolated from the thermal reactions of other similar starting materials such as Os\textsubscript{3}(CO)\textsubscript{10}(ER\textsubscript{2}Ph)\textsubscript{2} where R = Me, Et.

(c) The Type IV Benzyne Complexes

Thermolysis of the simple disubstituted derivatives Os\textsubscript{3}(CO)\textsubscript{10}(ER\textsubscript{2}Ph)\textsubscript{2} where ER\textsubscript{2} = PPh\textsubscript{2}, PMe\textsubscript{2}, AsMe\textsubscript{2}, AsPh\textsubscript{2} in refluxing nonane affords low yields (< 20%) of Os\textsubscript{3}(CO)\textsubscript{7}(ER\textsubscript{2})\textsubscript{2}(C\textsubscript{6}H\textsubscript{4}), together with other compounds. Pyrolysis of Ru\textsubscript{3}(CO)\textsubscript{10}-(PR\textsubscript{2}Ph)\textsubscript{2} (104) (PR\textsubscript{2} = PPh\textsubscript{2}, PFcPh) at lower temperatures in the presence of cyclohexane or toluene gives moderate yield of Ru\textsubscript{3}(CO)\textsubscript{7}(ER\textsubscript{2})\textsubscript{2}(C\textsubscript{6}H\textsubscript{4}). Thermolysis of
Ru$_3$(CO)$_{11}$(PPh$_3$) (105) in toluene also affords Ru$_3$(CO)$_7$(ER)$_2$(C$_6$H$_4$), together with the tetraruthenium and pentaruthenium benzyne complexes.

(d) The Type V Benzyne Complexes

Os$_3$(CO)$_9$(C$_6$H$_4$)(EX) (EX = PMe, PEt, PPh, As-tolyl) can be isolated in good yield (70%) from the thermal reaction of the monosubstituted osmium clusters Os$_3$(CO)$_{11}$(PRPh$_2$) (R = Me, Et, Ph) (106) in nonane, or by the reaction of Os$_3$(CO)$_{11}$-(NCMe) with As(tolyl)$_3$ in nonane. Scheme 1.6 outlines a possible reaction pathway to Os$_3$(CO)$_9$(C$_6$H$_4$)PMe (81) based on the intermediates isolated from the thermolysis of Os$_3$(CO)$_{11}$(PMePh$_2$) (107). The initial step involves the loss of CO, followed by ortho-metallation of the C$_6$H$_5$ moiety to afford (108). Loss of a second CO and coordination of a double bond of the C$_6$H$_4$ ring affords (109). The complex (109) in turn yields (81) by P-C bond cleavage and elimination of benzene.

![Scheme 1.6 A possible reaction pathway to Os$_3$(CO)$_9$(C$_6$H$_4$)PMe (81)](image-url)
1.4.3 Chemistry of Metal Cluster Complexes of Benzyne

At present, little is known about the reactivity of benzyne cluster complexes despite the fact that a large number of them have been isolated. Those studies, which have been reported in the literature, will be described below.

The complex (46), \( \text{H}_2 \text{Os}_3(\text{CO})_9(\text{C}_6\text{H}_4) \), undergoes Friedel-Crafts acetylation and alkylation under mild conditions to yield the acetylated product (110) and the alkylated product (111) in good yields (Equation 1.9) [55].

\[
\begin{align*}
\text{H}_2\text{Os}_3(\text{CO})_9(\text{C}_6\text{H}_4) & \xrightarrow{\text{RCI/AlCl}} \text{H}_2\text{Os}_3(\text{CO})_9(\text{C}_6\text{H}_3R) \\
\text{(46)} & \text{CS}_2 \ 0^\circ \text{C to R.T.} \ & \text{R} = \text{CH}_3\text{CO} \ (110) \\
& \text{R} = \text{Bu}^+ \ (111)
\end{align*}
\]

Thus, the nucleophilicity of the aryne ligands is retained despite the loss of electron density upon coordination to the metal cluster. Heating (46) in a nonane solution saturated with CO for 18 hours results in the loss of the benzyne ligand as benzene (ca. 51%) from the osmium framework (Equation 1.10) [35].

\[
\begin{align*}
\text{H}_2\text{Os}_3(\text{CO})_9(\text{C}_6\text{H}_4) & \xrightarrow{\text{CO}} \text{C}_6\text{H}_6 + \text{Os}_3(\text{CO})_{12} \\
\text{(46)} & \text{146}^\circ \text{C sealed tube} \ & \text{Eq. 1.10}
\end{align*}
\]

The carbonylation reactions of \( \text{Os}_3(\text{CO})_7(\mu_3-\text{C}_6\text{H}_4)(\mu-\text{PPh}_2)_2 \) (78), \( \text{Ru}_4(\text{CO})_{11-} \ (\mu_4-\text{C}_6\text{H}_4)(\mu_4-\text{PPh}) \) (95) and \( \text{Ru}_5(\text{CO})_{13}(\mu_5-\text{C}_6\text{H}_4)(\mu_4-\text{PPh}) \) (101) have been investigated and are summarized in Schemes 1.7 and 1.8 below. Treatment of (78) with CO at room temperature gives \( \text{Ru}_3(\text{CO})_8(\mu-\text{PPh}_2)_2(\mu-\text{C}_6\text{H}_4\text{CO}) \) (112) quantitatively. A structural study of (112) reveals that two molecules of CO are incorporated upon carbonylation of
A Ru-Ru bond is opened and an *ortho*-metallated benzoyl ligand, which triply bridges the Ru3 unit in μ-acyl fashion, is formed. In contrast to (78), the complex (95) is stable to CO at 1 atm, but under 50 atm at 60 °C, the cluster fragments to give dinuclear (113) and trinuclear (114) products. Treatment of the complex (101) with CO at 50 atm and 100 °C also results in cluster fragmentation. This affords Ru3(CO)12 and the dinuclear complex (113).

Scheme 1.7 Reagents and conditions: a, CO(1 atm, 3 days); b, refluxing in hexane.

Scheme 1.8 Reagents and conditions: a, CO (50 atm, 60-100 °C); b, toluene reflux; c, UV-radiation.
On bubbling CO through a refluxing solution of Os$_3$(CO)$_7$(PMe$_2$)$_2$(C$_6$H$_4$) (72) in nonane, the dinuclear complex Os$_2$(μ-PMe$_2$)(PMe$_2$C$_6$H$_4$(CO)Os is formed [32]. When H$_2$ is bubbled through a refluxing solution of Os$_3$(CO)$_9$(C$_6$H$_4$)PPh (88) in octane, the benzyne ligand is displaced by hydrogenation and the complex Os$_3$H$_2$(CO)$_9$PPh (115) is formed.

This complex may also be synthesized by the direct reaction of Os$_3$(CO)$_{12}$ with H$_2$PPh [44, 62].

Carbonyl ligands in benzyne complexes undergo substitution reactions. Thus (46) is activated by Me$_3$NO/MeCN to yield H$_2$Os$_3$(CO)$_8$(MeCN)(C$_6$H$_4$) (116), or H$_2$Os$_3$(CO)$_7$-(MeCN)$_2$(C$_6$H$_4$) (117), both of which are highly reactive and air sensitive. The nitrile ligands are easily displaced by PPh$_3$ or P(OMe)$_3$ in CH$_2$Cl$_2$ at room temperature to yield (54) to (57) [55]. Treatment of (117) with an excess of Ph$_2$C$_2$ affords (76) [52]. By simply heating complex (83) with PEt$_3$, P(OMe)$_3$ or PCy$_3$ in refluxing octane, substituted derivatives (84), (90), (91) and (92) are produced [50].

1.5 Benzynechromium Tricarbonyl and the Scope of this Thesis

1.5.1 Benzenechromium tricarbonyl

Benzenechromium tricarbonyl was first discovered over three decades ago [67]. Benzenechromium tricarbonyl and its derivatives have been studied extensively in a wide variety of applications that range from their use as synthetic reagents [63, 64] to models for the electron transfer processes [65] as well as in pharmaceutical chemistry [66]. The widespread use of these complexes are in part due to their robust nature and often simple and high-yield synthesis. A large number of X-ray crystal structure determinations have been carried out on the (η$^6$-arene)Cr(CO)$_3$ complexes, revealing a variety of conformations arising from their 'piano-stool' type structure. There are two fundamental conformations, the staggered (E) and eclipsed (F) (Figure 1.6). In the case of monosubstituted arenes, there
are two possible eclipsed conformations: namely *syn* (G) and *anti* (H) (Figure 1.6). The parent \( \text{C}_6\text{H}_6\text{Cr(CO)}_3 \) complex adopts the staggered conformation in the solid state [68]. The bond lengths in the benzene ring alternate slightly. Although the ring is planar, the hydrogen atoms are bent out of the plane toward the metal by 1.6°. In this manner, the C(2p) orbitals point more toward the metal, which give better overlap. A series of related structures, with mono-substituted benzenoids, show that those derivatives containing an electron-releasing group (*e.g.* -OCH₃ or -NH₂) adopt the (G) conformation, while those containing an electron-withdrawing group (*e.g.* -CO₂CH₃) adopt the (H) conformation [69].

![Figure 1.6 Staggered and eclipsed conformations for C₆H₆Cr(CO)₃ and C₆H₅RCr(CO)₃](image)

In general terms, the attachment of a chromium tricarbonyl unit to an aromatic compound can have several effects. The Cr(CO)₃ moiety is net electron-withdrawing, and thus the complexed arene becomes activated to nucleophilic substitution and deactivated to electrophilic substitution. The "electron-deficient" complexed arene ring is better able to stabilize negative charge. Furthermore, the arene protons and the benzylic protons become more acidic and therefore more easily lithiated. Finally, the Cr(CO)₃ unit blocks one face of the arene, and hence directs incoming reagents to the opposite (uncomplexed) face.
1.5.2 Benzynechromium Tricarbonyl

Although the proof for the existence of benzyne was established forty years ago, the possibility that benzynechromium tricarbonyl might exist was not investigated until the 1980's. Semmelhack et al. [71] suggested that decomposition of $\eta^6$-2-lithiochlorobenzenechromium tricarbonyl (118) involves the benzynechromium tricarbonyl intermediate (119). Thus heating a solution of (118) with excess furan yielded a complex mixture, and after oxidation with excess iodine, the major components were identified as naphthalene, 1-hydroxynaphthalene, 1,4-oxo-1,4-dihydro-naphthalene, and 2-chloro-biphenyl, all of which could be attributed to the reaction of a benzyne intermediate. These reactions are shown in Scheme 1.9 below.

![Scheme 1.9 Generating and trapping benzynechromium tricarbonyl](image-url)
However, the inefficient and nonselective trapping does not establish the presence of complex (119) as a major intermediate. The simple first order rate of decomposition of the reasonably stable lithio-derivative (118) at 0 °C is also consistent with the formation of the benzynecromium tricarbonyl intermediate. The possibility that benzynecromium tricarbonyl could be stabilized by coordination to one or more transition metal centers was not addressed before the present work.

1.5.3 The Scope of This Thesis

The principal objective of this thesis was to synthesize the metal cluster derivatives of benzynecromium tricarbonyls.

Chapter 3 deals with the synthesis and characterization of phenylchromium tricarbonyl phosphine ligands. Chapter 4 describes the substitution reactions of triruthenium and triosmium clusters with phenylchromium tricarbonyl phosphine ligands. The main focus of Chapter 5 is the preparation and characterization triruthenium and triosmium clusters containing benzynecromium tricarbonyl. Pyrolytic reactions of a number of substituted metal clusters were made in an effort to understand the relative reactivities of alkyl, aryl, and η⁶-phenyl C-H and C-P bonds towards oxidative cleavage.

References


[59] Cullen, W. R.; Chacon, S. T.; Bruce, M. I.; Einstein, F. W. B.; Jones, R. H. Organometallics 1988, 7, 2273


CHAPTER 2

General Experimental Section

Unless otherwise stated, all reactions and subsequent manipulations involving organometallic reagents were conducted under an argon atmosphere by using standard Schlenk and vacuum line techniques [1, 2].

2.1 Solvents and Reagents

Spectral or reagent grade solvents were obtained from BDH, Fisher, Eastman and Aldrich Chemical Co. THF, hexanes, diethyl ether, methanol, n-butyl ether, octane, benzene and heptane were distilled from the appropriate drying agents under nitrogen and used within 24 hours [3]. The deuterated solvents (CDCl₃, CD₂Cl₂), used in NMR spectroscopy, were obtained from the CIL and MSD isotope Lab. These solvents were distilled and stored over a bed of activated molecular sieves (Davidson type 4A) under argon.

Column chromatography was carried out by using silica gel (230-400 mesh) or neutral alumina (80-200 mesh, Brockman Activity I) obtained from BDH Co.

Phosphorus trichloride, chlorodiethylphosphine, dichloroethylphosphine, chlorodiphenylphosphine and dichlorophenylphosphine were purchased from Strem Chemicals Inc. They were stored under argon after distillation under reduced pressure [3]. The purity of all phosphines was ascertained by $^{31}$P{¹H} NMR spectroscopy.
Ruthenium chloride (supplied on loan from Johnson Mattey Ltd.), n-butyllithium (Aldrich), hexacarbonyl chromium (Strem) and osmium carbonyl (Steck) were used as received.

2.2 Instrumentation

$^1$H NMR spectra were recorded on either a Varian XL-300 (299.94 MHz), a Bruker WH-400 or a WH-200FT (400.00 MHz, or 200.00 MHz) spectrometer and were referenced to CDCl$_3$ or CD$_2$Cl$_2$ set at 7.25 ppm and 5.32 ppm respectively at room temperature. $^{31}$P{$^1$H} NMR spectra were recorded on a Varian XL-300 (121.42 MHz) or Bruker WH-200 (80.96 MHz) spectrometer. The $^{31}$P{$^1$H} NMR spectra were referenced to the external PPh$_3$ (CDCl$_3$) set at -5.6 ppm relative to 85% H$_3$PO$_4$ (aq) unless otherwise indicated. All the chemical shifts are reported in ppm and all the coupling constants are reported in Hz.

Infrared spectra were recorded by using a Perkin-Elmer 598, 783 or 1710 FTIR spectrophotometer. The samples were prepared as KBr pellets or Nujol mulls between KBr plates or as solutions in KBr cells. The spectra were calibrated with the 1601 cm$^{-1}$ band of polystyrene.

The low resolution electron impact (EI) mass spectra were obtained by using a Kratos/AEI MS902 mass spectrometer which was operated in the direct insertion mode (70eV, 120-150 °C source temperature). Fast atom bombardment (FAB) mass spectra were measured using an updated MS-9 mass spectrometer equipped with a FAB source. The matrix was 3-nitrobenzyl alcohol. Spectra were run by the staff of the Mass Spectrometry Laboratory of this department.
Single crystal X-ray structural determinations were performed on a Rigaku AFC6S diffractometer by Dr. Steven Rettig of the Departmental Crystallographic Service. Micro-analyses were carried out by Mr. Peter Borda of this department.

2.3 Starting Materials

2.3.1 Preparation of Benzenechromium Tricarbonyl

The complex was prepared, as described elsewhere [4], by refluxing a solution of Cr(CO)6 (4.0 g, 18 mmol) in C6H6 (20 mL), THF (15 mL) and n-butyl ether (120 mL) solution for 40 hours. Prolonged refluxing gave a higher yield. The resulting solution was filtered through Celite and the solvent was removed in vacuo. The complex was recrystallized from diethyl ether and light petroleum ether. Yield: 3.9 g (80%). Anal. Calcd for C9H6CrO3: C, 50.48; H, 2.83. Found: C, 50.32; H, 2.86. 1H NMR (300 MHz, CDCl3) δ: 5.4 (s). IR (CHCl3) ν(CO): 1965, 1890 cm⁻¹.

2.3.2 Preparation of Ru3(CO)12

Ruthenium carbonyl was prepared by carbonylation of methanol solutions of RuCl3·3H2O (125°C, 55 atm of CO, 20 hours) according to the literature method [5, 6]. The high pressure apparatus used in the synthesis of Ru3(CO)12 was designed and made by Baskerville and Lindsay Ltd. of England. Anal. Calcd for C12O12Ru3: C, 22.54. Found: C, 22.52. IR (KBr) ν(CO): 2060 (s), 2028 (s), 2010 (m) cm⁻¹. MS (FAB): m/e 640 [P]⁺.

2.3.3 Preparation of Os3(CO)11(MeCN)

The title complex was synthesized, as described elsewhere [7, 8], by dropping sublimed Me3NO (40 mg, 0.53 mmol) dissolved in MeOH (10 mL) into a stirred suspension of Os3(CO)12 (450 mg, 0.5 mmol) in CH3CN (10 mL) and CH2Cl2 (100 mL) at room temperature. The resulting solution was stirred for 5 hours and then filtered through a silica
pad, supported on a medium porosity Schlenk-type fritted filter to remove unreacted Me₃NO. 

\[ ^1H \text{ NMR (200 MHz, CDCl}_3 \] \delta: 2.65 (s).

2.3.4 Preparation of Os₃(CO)₁₀(MeCN)₂

The procedure was followed as for synthesis of Os₃(CO)₁₁(MeCN), except that 2 molar equivalents of Me₃NO (80.0 mg, 1.1 mmol) were used. \[ ^1H \text{ NMR (200 MHz, CDCl}_3 \] \delta: 2.65 (s).

2.3.5 Preparation of Iododimethylarsine

Dimethylidoarsine was conveniently prepared by passing sulfur dioxide into a solution containing dimethylarsinic acid (11.5 g, 0.1 mmol), potassium iodide (23.0 g), concentrated sulfuric acid (4.0 mL), and water (90 mL) for one hour [8]. \[ ^1H \text{ NMR (300 MHz, CDCl}_3 \] \delta: 2.0 (s).

2.3.6 Preparation of Bu₂PCl

The title compound was prepared according to the literature method [9]. Phosphorus trichloride (17.1 g, 0.13 mol) in diethyl ether (50 mL) was added dropwise at room temperature to a Grignard solution of Bu₄MgCl (1.2 M, 400 mL). A white precipitate formed immediately and the reaction mixture was allowed to reflux for 2 hours. Then the ethereal solution which contained the product was separated from the precipitate by decanting under nitrogen through glass wool into a round-bottom flask. Diethyl ether was removed by distillation at atmospheric pressure to leave a yellowish oil which was further purified by vacuum distillation. The product was an air-sensitive, colorless liquid (12 g, 55%). b.p.: 62-65 °C (4.6 mmHg). \[ ^31P\{^1H\} \text{ (121.4 MHz, CDCl}_3 \] \delta: 146.7 (s). \[ ^1H \text{ NMR (300 MHz, CDCl}_3 \] \delta: 1.15 (d).
2.3.7 Preparation of Bu\textsuperscript{t}PCl\textsubscript{2}

A freshly prepared Grignard solution of Bu\textsuperscript{t}MgCl (2 M, 250 mL) was added dropwise with stirring to phosphorus trichloride (68.5 g, 44 mL, 0.5 mol) dissolved in ether (200 mL) at -20 °C. Then, the temperature of the reaction mixture was allowed to rise to room temperature. The mixture was refluxed for 1 hour and then filtered to remove the white solid. Distillation under reduced pressure gave Bu\textsuperscript{t}PCl\textsubscript{2} as a colorless liquid (35 g, 45%), which solidified on standing. b.p.: 143-148 °C (760 mmHg). \textsuperscript{31}P\{\textsuperscript{1}H\} NMR (121.4 MHz, C\textsubscript{6}D\textsubscript{6}) \delta: 199.9 (s). \textsuperscript{1}H NMR (300 MHz, C\textsubscript{6}D\textsubscript{6}) \delta: 1.0 (d).

2.3.8 Preparation of PriPCl\textsubscript{2}

A Grignard solution of PriMgCl in ether (1.25 M, 800 mL) was added dropwise to a stirred diethyl ether solution of PCl\textsubscript{3} (55.0 g, 26 mL, 0.4 mol). A white precipitate formed during the addition and the reaction mixture was refluxed for additional two hours. The solution was separated from the precipitate by filtration into a flask through a medium porosity Schlenk filter. The ether solvent was removed by distillation at atmospheric pressure. The oily residue was distilled under reduced pressure. The product was an air-sensitive, colorless liquid (30 g, 65%) [10]. b.p. 27 °C (3 mmHg). \textsuperscript{31}P\{\textsuperscript{1}H\} NMR (121.4 MHz, CDCl\textsubscript{3}) \delta: 139.2 (s). \textsuperscript{1}H NMR (300 MHz, CDCl\textsubscript{3}) \delta: 1.80-1.91 (m, 2H), 1.05 (q, 6H).

2.3.9 Preparation of (CH\textsubscript{3}CN)\textsubscript{3}Cr(CO)\textsubscript{3}

This compound was synthesized by the literature method[11]. Hexacarbonylchromium (250 mg, 1.14 mmol) in acetonitrile (20 mL) was refluxed for 24 hours. The resulting yellow-green solution was filtered to remove the green precipitate and the solvent was removed in vacuo. The solid product was then used in subsequent reactions. Since it is unstable even under inert conditions at room temperature, it was used within a few hours after its preparation. MS (El) \textit{m/e} 262 [P]+.
2.3.10 Preparation of Ru$_3$(CO)$_{11}$(MeCN)

This compound was prepared according to the literature method [12]. A solution of Me$_3$NO (15 mg, 0.16 mmol) in CH$_2$Cl$_2$ (5 mL) was added to a stirred suspension of Ru$_3$(CO)$_{12}$ (100 mg, 0.15 mmol) dissolved in CH$_2$Cl$_2$ (150 mL) and acetonitrile (10 mL) at -78 °C. After all the amine oxide had been added, the reaction mixture was allowed to slowly warm to ambient temperature during which time the color of the solution changed from light orange to dark orange. The reaction mixture was filtered through a silica pad (Merck, 70-230 mesh) supported on a medium porosity Schlenk-type fritted filter to remove unreacted Me$_3$NO. The solvent was then removed under reduced pressure, leaving an orange solid that was used immediately without further purification in subsequent reactions. $^1$H NMR (300 MHz, CDCl$_3$) δ: 2.47 (s).

2.3.11 Preparation of Sodium Diphenylketyl Solution

Benzophenone (91 mg, 0.5 mmol) was dissolved in THF (20 mL) in a Schlenk tube and finely cut sodium metal was added. The mixture was stirred for two hours [13]. The resulting deep purple solution was assumed to be ca. 0.025 M in [Ph$_2$CO]$^-$.

References


CHAPTER 3
Phosphino- and Arsinobenzenechromium Tricarbonyl Ligands

3.1 Introduction

Tertiary phosphines are the most commonly encountered ancillary ligands associated with organotransition-metal compounds. Since the chemistry of the transition metals is strongly influenced by the electronic and steric properties of the ancillary ligands, the availability of a wide range of phosphorus-based ligands allows the reactivity of a metal complex to be fine-tuned. The electronic and steric properties of a phosphine can be altered in a systematic and predictable way over a wide range by varying the substituents at phosphorus.

A phosphine ligand PR$_3$, like the CO ligand, can function both as a σ-donor through the lone pair on the phosphorus atom and as a π-acceptor. For a number of years, alkyl and arylphosphines were thought to stabilize transition metal complexes through dπ-π back-bonding from the filled metal d-orbitals to the unfilled, high energy phosphorus 3d-orbitals [1]. It is only recently that the σ* orbitals of the P-R bonds have been recognized as playing a role as an electron acceptor in phosphine ligand [2].

The second important feature of PR$_3$ as a ligand is its variable steric size, which can be adjusted by changing the R groups. The steric bulk of a phosphine is generally at least as important as its electronic effect and can dominate in many cases. Tolman has quantified the steric effects of phosphines with his cone angle concept [3, 4]. In its simplest form, the cone angle is defined as the angle ($\alpha$) of a cylindrical cone, centered 2.28 Å from the phosphorus,
which touches the outermost atoms of the substituent R groups (Figure 3.1). The angle $\alpha$ can vary from ca. 118° for PMe$_3$ to ca. 182° for PBut$_3$.

![Figure 3.1 Cone angle ($\alpha$)](image)

There are a large number of known phosphorus compounds. A seven volume series, published in 1978, devoted to organophosphorus compounds lists over 100,000 derivatives [5]. However, only five phosphines or arsines with arylchromium tricarbonyl substituents were reported in the literature before the present work (Table 3.1) [6].

**Table 3.1 Known phosphino- and arsinobenzenechromium tricarbonyls**

<table>
<thead>
<tr>
<th>Compound</th>
<th>Synthesis</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ph$_2$PC$_6$H$_5$Cr(CO)$_3$</td>
<td>(i) (Bu$_3$SnC$_6$H$_5$)TCC + n-BuLi + Ph$_2$PCl &lt;br&gt; (ii) Hg (C$_6$H$_5$TCC)$_2$ + 2n-BuLi + 2ClPPh$_2$</td>
<td>[6a]</td>
</tr>
<tr>
<td>(p-tol)$_2$P[potCr(CO)$_3$]</td>
<td>P(pot)$_3$ + Cr(CO)$_6$, 170 °C</td>
<td>[6e]</td>
</tr>
<tr>
<td>PhP[C$_6$H$_5$Cr(CO)$_3$]$_2$</td>
<td>Hg(C$_6$H$_5$TCC)$_2$ + 2n-BuLi + Cl$_2$PPh</td>
<td>[6c]</td>
</tr>
<tr>
<td>Bu$_4$P[C$_6$H$_5$Cr(CO)$_3$]$_2$</td>
<td>Hg(C$_6$H$_5$TCC)$_2$ + 2n-BuLi + PCl$_3$</td>
<td>[6c]</td>
</tr>
<tr>
<td>Ph$_2$AsC$_6$H$_5$Cr(CO)$_3$</td>
<td>AsPh$_3$ + Cr(CO)$_6$, 170 °C</td>
<td>[6b]</td>
</tr>
</tbody>
</table>
3.2 Synthesis of Phosphino- and Arsinobenzenechromium Tricarbonyl Ligands

Two different strategies have been utilized previously to prepare the phosphino- and arsinobenzenechromium tricarbonyl ligands. The first is the thermal replacement of three carbonyls from Cr(CO)₆ by an aryl group attached to the phosphine. Hence, refluxing the arylphosphine and chromium hexacarbonyl in a decalin solution gives rise to two series of complexes; monomeric R₂PC₆H₅Cr(CO)₃ and dimeric [{R₂PC₆H₅}Cr(CO)₂]₂. The dimer consists of two Cr atoms bridged by two phosphine groups where each phosphine is P-bonded to one Cr-atom, and is involved in η⁶-arene bonding to the second Cr atom (Figure 3.2) [6d]. This route gives low yields, requires considerable time, and is limited in scope. For some phosphines, such as Ph₃P and (m-tolyl)₃P, only the dimers are isolated [6f].

![Figure 3.2](image)

The second strategy employed for the formation of R₂PC₆H₅Cr(CO)₃ involves the reaction of chlorophosphine with the lithium derivative of the benzenechromium tricarbonyl intermediate, (η⁶-LiC₆H₅)Cr(CO)₃ (1), in THF or Et₂O at low temperature. Lithiated benzenechromium tricarbonyl is a suitable nucleophilic precursor for reaction with a chlorophosphine.
One route to the \((\eta^6-\text{LiC}_6\text{H}_5)\text{Cr(CO)}_3\) intermediate, which was developed by Rausch (Scheme 3.1) [6c], is via a trans-metallation reaction between the bis(\(\eta^6\)-phenyltricarbonylchromium) mercury (2) and n-butyllithium. The starting material (2) is obtained in 60% yield by a ligand exchange reaction between the benzenechromium tricarbonyl and diphenylmercury in refluxing dioxane. The ethereal suspension of (2) is treated with n-BuLi at -20 °C and a clear yellow solution of (1) is produced which is extremely air-sensitive and thermally unstable. Addition of phosphorus halides like Ph\(_2\)PCl or PhPCl\(_2\) to the solution of (1) results in phosphinobenzenechromium tricarbonyl complexes in low to moderate yields.

Scheme 3.1 Rauch's route to (1) and three phosphines

(a, Ph\(_2\)Hg, dioxane; b, n-BuLi, Et\(_2\)O; c, ClPPh\(_2\); d, PCl\(_3\); e, Cl\(_2\)PPh)
In 1992 Wright *et al.* reported a more efficient route to intermediate (1) or to dilithiobenzenechromium tricarbonyl (3). These two compounds are produced via trans-metallation of $[\eta^6-(\text{Bu}^3\text{Sn})\text{C}_6\text{H}_5]\text{Cr(}\text{CO})_3$ (4) or $[\eta^6-(\text{Bu}^3\text{Sn})_2\text{C}_6\text{H}_4]\text{Cr(}\text{CO})_3$ (5) with n-BuLi in THF at -78 °C (Scheme 3.2) [6a, 7]. When (1) or (3) is treated with diphenylchlorophosphine, phosphinobenzene chromium tricarbonyl compounds are formed in good yields. The starting materials (4) and (5) can be synthesized by the thermal reaction of (MeCN)$_3\text{Cr}$(CO)$_3$ with (tributylstannyl)benzene and bis(tributylstannyl)benzene in dioxane, respectively.

![Scheme 3.2 Wright's route to (1) and two phosphines](image)

Both the lithiation procedures described above are indirect. Rauch's route needs additional steps to mercuration and Wright's route requires tributylstannyl benzene-chromium tricarbonyl as a starting material. Semmelhack developed a direct lithiation method to the intermediate (1) by simply adding n-BuLi to C$_6$H$_6$Cr(CO)$_3$ in THF at -78 °C.
in the presence of TMEDA [8]. Subsequent electrophilic trapping gives the products in good yields as shown in Scheme 3.3. Thus (1) is formed with high efficiency.

\[
\begin{align*}
\text{Cr} & \quad \text{(CO)}_3 \\
\text{Cr} & \quad \text{(CO)}_3
\end{align*}
\]

\[
\text{n-BuLi / TMEDA} \quad \text{THF} \quad \text{electrophile (E)}
\]

**Scheme 3.3** Semmelhack’s route to (1) and some reactions

\[E = \text{CO}_2, \quad \text{I}_2, \quad (\text{CH}_3)_3\text{SiCl}. \quad R = -\text{CO}_2\text{H} (72\%), \quad -\text{I} (76\%), \quad -\text{Si}(\text{CH}_3)_3 (94\%)
\]

We became interested in employing Semmelhack's method to generate \(\text{LiC}_6\text{H}_4\text{Cr(CO)}_3\) in order to synthesize some new phosphino- and arsinobenzene chromium tricarbonyl ligands. Seven new ligands were prepared in this work (Scheme 3.4). Three known ligands \(\text{Ph}_2\text{PC}_6\text{H}_5\text{Cr(CO)}_3\) (6g), \(\text{PhP}[\text{C}_6\text{H}_5\text{Cr(CO)}_3]_2\) (6h) and \(\text{Ph}_2\text{AsC}_6\text{H}_5\text{Cr(CO)}_3\) (6j) were also prepared in higher yields than previously reported in the literature by using this new synthetic route. It was found that phosphino- and arsinobenzenechromium tricarbonyl ligands were formed in good yields without the addition of TMEDA to generate \(\text{LiC}_6\text{H}_4(\text{CO})_3\). The yields of \(\text{R}_2\text{P}[\text{C}_6\text{H}_5\text{Cr(CO)}_3]\) phosphines are higher than those of \(\text{RP}[\text{C}_6\text{H}_5\text{Cr(CO)}_3]_2\). Recrystallization is employed as a separation method due to decomposition of the ligands on silica gel or alumina. Very often the crude products are red viscous oils which contain impurities. Adding hexanes to the crude products and stirring the resulting solution vigorously with a stirring rod results in the precipitation of a yellow powder which must be washed with hexanes several times. Recrystallization then affords pure products.
3.3 Characterization of Phosphino- and Arsinobenzenechromium Tricarbonyl Ligands

The phosphino- and arsinobenzenechromium tricarbonyl ligands (6) are all yellow solids, except Et₂PC₆H₅Cr(CO)₃ which is a red oily liquid. These ligands are soluble in a range of organic solvents such as THF, CH₂Cl₂, and acetone. In the solid state, the products are stable for long periods of time under an inert atmosphere. However, in solution the ligands decompose when in contact with air to yield green residues. This is presumably a consequence of oxidation of the chromium center from Cr(0) to Cr(III) and...
the phosphine to phosphine oxide. The oily phosphine PEt₂C₆H₅Cr(CO)₃ (6e) is much more air sensitive than the solid phosphines.

3.3.1 Spectroscopic Studies of Phosphino- and Arsinobenzenechromium Tricarbonyl Ligands

(a) Infrared Spectroscopy

A characteristic feature of the solution or solid-state infrared spectra of the title ligands is the absorption associated with the Cr(CO)₃ unit. The specific v(CO) absorption values for the ligands are listed in Table 3.2.

<table>
<thead>
<tr>
<th>Complex</th>
<th>Number</th>
<th>A₁ (cm⁻¹)</th>
<th>E (cm⁻¹) (s)</th>
<th>Phase</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bu₁₂PC₆H₅Cr(CO)₃</td>
<td>(6a)</td>
<td>1960(s)</td>
<td>1900, 1880, 1870</td>
<td>KBr</td>
</tr>
<tr>
<td>Bu₁P[C₆H₅Cr(CO)₃]₂</td>
<td>(6b)</td>
<td>1970(s)</td>
<td>1890 (br)</td>
<td>KBr</td>
</tr>
<tr>
<td>Pr₁₂PC₆H₅Cr(CO)₃</td>
<td>(6c)</td>
<td>1970(s)</td>
<td>1880 (br)</td>
<td>KBr</td>
</tr>
<tr>
<td>Et₂PC₆H₅Cr(CO)₃</td>
<td>(6e)</td>
<td>1978(s)</td>
<td>1885 (s)</td>
<td>cyclohexane</td>
</tr>
<tr>
<td>EtP[C₆H₅Cr(CO)₃]₂</td>
<td>(6d)</td>
<td>1965(s)</td>
<td>1882, 1861</td>
<td>KBr</td>
</tr>
<tr>
<td>Me₂AsC₆H₅Cr(CO)₃</td>
<td>(6f)</td>
<td>1960(s)</td>
<td>1880 (br)</td>
<td>KBr</td>
</tr>
<tr>
<td>Ph₂PC₆H₅Cr(CO)₃</td>
<td>(6g)</td>
<td>1980(s)</td>
<td>1900 (br)</td>
<td>KBr</td>
</tr>
<tr>
<td>PhP[C₆H₅Cr(CO₃)]₂</td>
<td>(6h)</td>
<td>1970(s)</td>
<td>1900 (br)</td>
<td>KBr</td>
</tr>
</tbody>
</table>

In solution, the spectrum is characterized by two intense C-O stretching modes, one ca. 1960-1990 cm⁻¹ and the other ca. 1860-1920 cm⁻¹. In the solid state (KBr), there are up to three absorptions or one broad absorption in the region 1860-1920 cm⁻¹. On the basis of
the local $C_{3v}$ symmetry for the $\text{Cr(CO)}_3$ group, these bands have been assigned to a non-degenerate symmetric vibration ($A_1$) and a doubly-degenerate asymmetric vibration ($E$) [9a]. Among these phosphines the ligand $\text{Bu}^2\text{PC}_6\text{H}_5\text{Cr(CO)}_3$ (6a) exhibits the lowest CO stretching frequencies (1960, 1870 cm$^{-1}$) and the ligand $\text{Ph}_2\text{PC}_6\text{H}_5\text{Cr(CO)}_3$ (6g) exhibits the highest $\nu$(CO) stretching frequencies (1980, 1900 cm$^{-1}$).

(b) Mass Spectrometry

Mass spectrometry is a convenient method for the characterization and identification of phosphino- and arsinobenzenechromium tricarbonyl ligands. All the ligands show parent ion [$P^+]$ and [$Cr^+]$ peaks. The general fragmentation process involves the successive loss of carbonyl groups followed by loss of the organic species. Table 3.3 lists the fragmentation patterns for these ligands. For the ligands $\text{Bu}^2\text{PC}_6\text{H}_5\text{Cr(CO)}_3$ (6a), $\text{Et}_2\text{PC}_6\text{H}_5\text{Cr(CO)}_3$ (6e) and $\text{Pr}^2\text{PC}_6\text{H}_5\text{Cr(CO)}_3$ (6c), which contain the alkyl organic groups, the overall fragmentation patterns are [$P^+$], [$P^+\text{-CO}$], [$P^+\text{-2CO}$], [$P^+\text{-3CO}$], [$\text{R}_2\text{PPPh}^+$], [$\text{H}_2\text{PPPhCr}^+$], [$\text{H}_2\text{PPh}^+$], [HPRPhCr$^+$], [HPRPh$^+$], and [$Cr^+]$. The principal ions of $\text{BuP}[\text{C}_6\text{H}_5\text{Cr(CO)}_3]_2$ (6b) and $\text{EtP}[\text{C}_6\text{H}_5\text{Cr(CO)}_3]_2$ (6d) are similar and are [$P^+$], [$P^+\text{-CO}$], [$P^+\text{-2CO}$], [$P^+\text{-3CO}$], [$P^+\text{-4CO}$], [$P^+\text{-6CO}$] [$P^+\text{-6CO-Cr}$], [$\text{Ph}_2\text{CrPH}^+$], and [$Cr^+$], although the relative intensities vary significantly. Both $\text{PhP}[\text{C}_6\text{H}_5\text{Cr(CO)}_3]_2$ (6h) and $\text{PhAs}[\text{C}_6\text{H}_5\text{Cr(CO)}_3]_2$ (6i) show a similar fragmentation pattern and the common species are [$P^+$], [$P^+\text{-3CO}$], [$P^+\text{-4CO}$], [$P^+\text{-6CO}$], [$\text{Ph}_3\text{CrE}^+$], [$\text{Ph}_3\text{E}^+$], [$\text{EPh}^+$], [$\text{PH}^+$], and [$Cr^+$] where E = P, As. The ligands $\text{Ph}_2\text{PC}_6\text{H}_5\text{Cr(CO)}_3$ (6g) and $\text{Ph}_2\text{AsC}_6\text{H}_5\text{Cr(CO)}_3$ (6j) also share some common fragmentations, i.e. [$P^+$], [$P\text{-3CO}^+$], [$\text{EPh}_3^+$], [$\text{EPPh}^+$], [$\text{Ph}^+$] and [$Cr^+$] (E = P, As).
Table 3.3 Mass Spectral Data for the Phosphino- and Arsinobenzenechromium tricarbonyl ligands (6)

<table>
<thead>
<tr>
<th>Ligand</th>
<th>FW</th>
<th>Mass peak m/e</th>
</tr>
</thead>
<tbody>
<tr>
<td>(6a)</td>
<td>358.34</td>
<td>[P⁺] 358, [P⁺-2CO] 302, [P⁺-3CO] 274, [Bu₅PPhCr⁺] 218,</td>
</tr>
<tr>
<td></td>
<td></td>
<td>[H₂PC₆H₅Cr⁺] 162, [H₂PC₆H₅⁺] 110, [C₆H₄⁺] 56, [Cr⁺] 52</td>
</tr>
<tr>
<td></td>
<td></td>
<td>[Et₂PPh⁺] 166, [H₂PPhCr⁺] 162, [EtHPPh⁺] 138,</td>
</tr>
<tr>
<td></td>
<td></td>
<td>[H₂PPh⁺] 109, [Cr⁺] 52</td>
</tr>
<tr>
<td></td>
<td></td>
<td>[Pr₅PPh⁺] 194, [H₂PPhCr⁺] 162, [Pr₅HPPh⁺] 152, [H₂PPh⁺] 109,</td>
</tr>
<tr>
<td></td>
<td></td>
<td>[Cr⁺] 52, [C₆H₆⁺] 42</td>
</tr>
<tr>
<td></td>
<td></td>
<td>[Ph⁺] 77, [Cr⁺] 52</td>
</tr>
<tr>
<td>(6j)</td>
<td>442.27</td>
<td>[P⁺] 442, [P⁺-3CO] 358, [AsPh₃⁺] 306, [PhCrAsPh⁺] 281,</td>
</tr>
<tr>
<td></td>
<td></td>
<td>[AsPh⁺] 152, [Ph⁺] 77, [Cr⁺] 52</td>
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<tr>
<td>(6f)</td>
<td>318.14</td>
<td>[P⁺] 318, [P⁺-2CO] 262, [P⁺-3CO] 234, [MeAsPhCr⁺] 218, [AsPhCr⁺] 204,</td>
</tr>
<tr>
<td></td>
<td></td>
<td>[Me₂AsPh⁺] 182, [MeAsPh⁺] 167, [MePhCr⁺] 144, [Cr⁺] 52</td>
</tr>
<tr>
<td></td>
<td></td>
<td>[P⁺-6CO] 346, [PhCrPPhBu⁺] 294, [PhCrPPh⁺] 238, [Cr⁺] 52</td>
</tr>
<tr>
<td></td>
<td></td>
<td>[P⁺-6CO] 318, [PhCrPPhEt⁺] 266, [PhCrPPh⁺] 238, [Ph₂PPh⁺] 215,</td>
</tr>
<tr>
<td></td>
<td></td>
<td>[Cr⁺] 52</td>
</tr>
<tr>
<td></td>
<td></td>
<td>[PhCrPPh₂⁺] 314, [Ph₃P⁺] 262, [Ph-Ph⁺] 154, [PPh⁺] 108,</td>
</tr>
<tr>
<td></td>
<td></td>
<td>[PhH⁺] 78, [Cr⁺] 52</td>
</tr>
<tr>
<td></td>
<td></td>
<td>[Ph₁As⁺] 306, [PhAs⁺] 152, [PhH⁺] 78, [Cr⁺] 52</td>
</tr>
</tbody>
</table>
(c) NMR Spectroscopy

The \(^{31}\)P NMR spectra of phosphinobenzenechromium tricarbonyl ligands are
due. They display one sharp singlet between 43 ppm and -11 ppm. Most of the
experimental chemical shifts for these ligands are in accord with those predicted by the
Grim and McFarlane equation (Equation 3.1) for tertiary phosphines [13]

\[
\delta \text{ (ppm from 85\% H}_3\text{PO}_4) = -62 + \sum \sigma^P \]  \hspace{1cm} \text{Eq. 3.1}

where \(\sigma^P\) is a constant that is derived for the substituent on phosphine. The
literature values for common substituents are: Et, 14; Pr\(^t\), 27; Bu\(^t\), 44; Ph, 18 [14]. The \(\sigma^P\)
constants for a phenylchromium tricarbonyl group derived from the experimental chemical
shifts of the individual ligands using the Equation 3.1 are listed in Table 3.4.

\textbf{Table 3.4} Comparison of experimental and calculated \(^{31}\)P NMR chemical shifts
for the ligands

<table>
<thead>
<tr>
<th>Ligands</th>
<th>(\sigma^P) for PhCr(CO(_3))</th>
<th>(\delta_{\text{exp}}) (ppm)</th>
<th>(\delta_{\text{calc}}) (ppm)</th>
<th>difference (\delta_{\text{exp}}-\delta_{\text{calc}})</th>
<th>(\Delta)</th>
</tr>
</thead>
<tbody>
<tr>
<td>([C_6H_5Cr(CO)3]_2\text{PBut})</td>
<td>19.4</td>
<td>20.7</td>
<td>22</td>
<td>-1.3</td>
<td>-6%</td>
</tr>
<tr>
<td>([C_6H_5Cr(CO)3]\text{PBut}_2)</td>
<td>16.8</td>
<td>42.8</td>
<td>46</td>
<td>-3.2</td>
<td>-7%</td>
</tr>
<tr>
<td>([C_6H_5Cr(CO)3]_2\text{PEt})</td>
<td>21.3</td>
<td>-5.5</td>
<td>-8</td>
<td>2.5</td>
<td>+45%</td>
</tr>
<tr>
<td>([C_6H_5Cr(CO)3]\text{PEt}_2)</td>
<td>20.5</td>
<td>-13.5</td>
<td>-14</td>
<td>0.5</td>
<td>+3%</td>
</tr>
<tr>
<td>([C_6H_5Cr(CO)3]_2\text{PPr}_2)</td>
<td>21.9</td>
<td>13.9</td>
<td>12</td>
<td>1.9</td>
<td>+13%</td>
</tr>
<tr>
<td>([C_6H_5Cr(CO)3]_2\text{PPh})</td>
<td>20.0</td>
<td>-4.0</td>
<td>-4</td>
<td>0</td>
<td>0%</td>
</tr>
<tr>
<td>([C_6H_5Cr(CO)3]_2\text{PPh}_2)</td>
<td>20.8</td>
<td>-5.2</td>
<td>-6</td>
<td>0.8</td>
<td>+15%</td>
</tr>
<tr>
<td>(-C_6H_5Cr(CO)3)</td>
<td>20(mean)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
A mean value of 20 is thus obtained for the constant \((\sigma^P)\) of a phenylchromium tricarbonyl group. Using this value and equation 3.1, the predicted chemical shifts \((\delta_{\text{calc}})\) for the ligands (6) are calculated and the results are tabulated in Table 3.4. The experimental chemical shifts \((\delta_{\text{exp}})\) for (6) and their differences between \(\delta_{\text{exp}}\) and \(\delta_{\text{calc}}\) are present in Table 3.4 as well. Although the deviation \(\Delta\) for \([C_6H_5Cr(CO)_3]_2PEt\) is rather high, the other values are acceptable. However, the \(\sigma^P\) for \(C_6H_5Cr(CO)_3\) group is useful for predicting the \(^{31}\)P NMR chemical shift of new phosphinobenzenechromium tricarbonyls if the \(\sigma^P\) for the other two substituents are known.

The proton NMR data for the ligands are listed in Table 3.5. A characteristic feature of the \(^1\)H NMR spectra is that the signals of protons in a ligand containing the Cr(CO)_3 group resonate at a higher fields than those of the same protons in the Cr(CO)_3-free ligand. For instance, the protons on the uncomplexed arene ligand are generally in the 7.9 to 6.7 ppm region, whereas the protons on the complexed arene ligand are at 5.8-5.2 ppm. The difference for the chemical shifts of the aromatic protons is of the order of 2 ppm. This upfield shift of the signals can be ascribed to: (i) an overall withdrawal of \(\pi\) electrons from the arene ring by the Cr(CO)_3 unit, (ii) the magnetic anisotropy effect of the ring-metal bond, and (iii) the partial sp^2-sp^3 rehybridization of the ring carbon atoms [9a]. Hence, the cumulative effect is a reduction in the deshielding of the aromatic protons. The five protons AA′BB′X on the complexed ring appear as: (a) two multiplets of 3:2 for \([C_6H_5Cr(CO)_3]PPPr\) \(_2\) (6c), \([C_6H_5Cr(CO)_3]_2PET\) (6d), \([C_6H_5Cr(CO)_3]PET\) \(_2\) (6e) and \([C_6H_5Cr(CO)_3]AsMe\) \(_2\) (6f), or 1:4 for \([C_6H_5Cr(CO)_3]PPh\) \(_2\) (6g) and AsPh\(_2\)[C\(_6\)H\(_5\)Cr(CO)\(_3\)] (6j) (b) three multiplets of 2:1:2 for \([C_6H_5Cr(CO)_3]PBut\) \(_2\) (6a), PPh[C\(_6\)H\(_5\)Cr(CO)\(_3\)] \(_2\) (6h) and \([C_6H_5Cr(CO)_3]_2AsPh\) (6i), or 1:2:2 for \([C_6H_5Cr(CO)_3]_2PBut\) \(_2\) (6b).
### Table 3.5 \(^1\)H NMR Chemical shifts of the phosphino- and arsinobenzenechromium tricarbonyl ligands (6)

<table>
<thead>
<tr>
<th>Ligand</th>
<th>(^1)H NMR (CDCl(_3)) protons on (\eta^6)-ring</th>
<th>other protons</th>
</tr>
</thead>
<tbody>
<tr>
<td>But(_2)PC(_6)H(_5)TCC (6a)</td>
<td>5.7 (t, 2H), 5.5 (t, 1H)</td>
<td>1.2 (d, 18H)</td>
</tr>
<tr>
<td></td>
<td>5.2 (t, 2H), J(H-H) = 6Hz</td>
<td>J(P-H) = 10Hz</td>
</tr>
<tr>
<td>Bu(_4)P[C(_6)H(_5)TCC](_2) (6b)</td>
<td>5.7 (t, 2H), 5.4 (t, 4H), 5.2 (d, 4H) J(H-H) = 6Hz</td>
<td>1.2 (d, 9H)</td>
</tr>
<tr>
<td></td>
<td>J(P-H) = 10Hz</td>
<td></td>
</tr>
<tr>
<td>Pri(_2)PC(_6)H(_5)TCC (6c)</td>
<td>5.3 (t, 3H), 5.18 (t, 2H)</td>
<td>1.95 (sep, 2H)</td>
</tr>
<tr>
<td></td>
<td>J(H-H) = 5 Hz</td>
<td>1.05 (dd, 12H)</td>
</tr>
<tr>
<td>EtP[C(_6)H(_5)TCC](_2) (6d)</td>
<td>5.4 (t, 6H), 5.2 (t, 4H)</td>
<td>1.8 (q, 4H)</td>
</tr>
<tr>
<td></td>
<td>J(H-H) = 6Hz</td>
<td>1.2 (m, 6H)</td>
</tr>
<tr>
<td>Et(_2)PC(_6)H(_5)TCC (6e)</td>
<td>5.4 (t, 3H), 5.2 (t, 2H)</td>
<td>1.8 (q, 4H)</td>
</tr>
<tr>
<td></td>
<td>J(H-H) = 6Hz</td>
<td>1.2 (m, 6H)</td>
</tr>
<tr>
<td>Me(_2)AsC(_6)H(_5)TCC (6f)</td>
<td>5.5 (t, 3H), 5.3 (t, 2H)</td>
<td>1.4 (s, 6H)</td>
</tr>
<tr>
<td></td>
<td>J(H-H) = 5.5Hz</td>
<td></td>
</tr>
<tr>
<td>Ph(_2)PC(_6)H(_5)TCC (6g)</td>
<td>5.45 (t, 1H), 5.2 (m, 4H)</td>
<td>7.4 (br.s, 10H)</td>
</tr>
<tr>
<td>Ph(_2)AsC(_6)H(_5)TCC (6i)</td>
<td>5.3 (br. s, 1H), 5.2 (m, 4H)</td>
<td>7.4 (s, br.,10H)</td>
</tr>
<tr>
<td>PhP[C(_6)H(_5)TCC](_2) (6h)</td>
<td>5.6 (t, 4H), 5.3 (t, 2H)</td>
<td>7.3-7.6 (m, 5H)</td>
</tr>
<tr>
<td></td>
<td>5.2 (d, 4H)</td>
<td></td>
</tr>
<tr>
<td>PhAs[C(_6)H(_5)TCC](_2) (6i)</td>
<td>5.5 (t, 4H), 5.3 (t, 2H)</td>
<td>7.4 (br.s, 5H)</td>
</tr>
<tr>
<td></td>
<td>5.15 (br. s, 4H)</td>
<td></td>
</tr>
</tbody>
</table>

The methyl groups in C\(_6\)H\(_5\)Cr(CO)\(_3\)AsMe\(_2\) show a singlet at 1.3 ppm. The tert-butyl groups in (6a) and (6b) display a doublet at 1.2 ppm due to coupling to phosphorus (J(P-H) = 10 Hz). The isopropyl protons in (6c) resonate between 1.0 and 1.1 ppm for the CH\(_3\) protons and between 1.9 and 2.0 ppm for the CH protons. The methylidyne proton signals appear as two overlapping septets that arise from coupling to one phosphorus and six methyl protons. Two doublets of doublets for the methyl protons indicate that the
magnetic environments of the two methyl groups in each isopropyl group are different. Each doublet of doublets is interpreted as coupling to one phosphorus and one CH proton ($J(P-H) = 10.5$ Hz, $J(H-H) = 6$ Hz). The ethyl groups display signals between 1.0 and 1.4 ppm for the methyl protons and between 1.6 and 2.0 ppm for the methylene protons. The CH$_2$ protons show quartets due to coupling to three methyl protons, and the methyl protons show triplets of doublets due to coupling to one phosphorus and to the CH$_2$ protons. The phenyl protons in (6g) and (6j) display a broad singlet at 7.4 ppm by accidental degeneration.

3.3.2 Molecular Structure of Pri$_2$P(C$_6$H$_5$)Cr(CO)$_3$

The crystal structure of Pri$_2$P(C$_6$H$_5$)Cr(CO)$_3$ (6c) is shown in Figure 3.3, and selected bond lengths and bond angles appear in Table 3.6 (see p62). This molecule consists of a central chromium atom linked to an $\eta^6$-phenyl ring of the diisopropylphenylphosphine ligand and to three carbonyl groups. The geometry about chromium is of the symmetrical "three-legged piano-stool" variety that is typical of ($\eta^6$-arene)Cr(CO)$_3$ complexes. The Bz-Cr-CO angles range from 125.6(1) to 127.5(1)$^\circ$, while the CO-Cr-CO angles range from 87.6(1) to 89.0(1)$^\circ$. The Cr(CO)$_3$ moiety is partially eclipsed (i.e., midway between eclipsed and staggered relative to the $\eta^6$-phenyl ring). However, the staggered structure is rare for monosubstituted arenes [9].

One of the isopropyl groups in the Pri$_2$P unit is essentially anti to the Cr(CO)$_3$ fragment. It adopts an orientation virtually perpendicular to the $\pi$-arene moiety. This conformation forces the remaining isopropyl substituent below the plane of the $\pi$-arene ring.
Figure 3.3  Molecular structure of Pr$_2$PC$_6$H$_5$Cr(CO)$_3$ (6c)
Table 3.6 Bond parameters for Pr\textsubscript{2}PC\textsubscript{6}H\textsubscript{5}Cr(CO)\textsubscript{3}

<table>
<thead>
<tr>
<th>Bond lengths from the Cr atom (Å)</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Cr-C2 1.818(3)</td>
<td>Cr-C3 1.835(3)</td>
</tr>
<tr>
<td>Cr-C9 2.195(3)</td>
<td>Cr-C6 2.206(3)</td>
</tr>
<tr>
<td>Cr-C5 2.211(3)</td>
<td>Cr-C7 2.219(3)</td>
</tr>
<tr>
<td>Cr-Bz* 1.711(1)</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Phosphorus-Carbon bond lengths (Å)</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>P-C4 1.840(3)</td>
<td>P-C10 1.850(3)</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Carbon-Carbon bond lengths within (η\textsuperscript{6}-C\textsubscript{6}H\textsubscript{5}) (Å)</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>C4-C5 1.403(4)</td>
<td>C4-C9 1.426(4)</td>
</tr>
<tr>
<td>C6-C7 1.398(5)</td>
<td>C7-C8 1.395(5)</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Selected bond angles (°)</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>C4-C5-C6 121.1(3)</td>
<td>C7-C6-C5 120.5(3)</td>
</tr>
<tr>
<td>C9-C8-C7 120.7(3)</td>
<td>C8-C9-C4 121.6(3)</td>
</tr>
<tr>
<td>C11-C10-C12 110.3(4)</td>
<td></td>
</tr>
<tr>
<td>O1-C1-Cr 178.0(3)</td>
<td>O2-C2-Cr 178.8(3)</td>
</tr>
<tr>
<td>O3-C3-Cr 177.9(3)</td>
<td></td>
</tr>
</tbody>
</table>

* Bz refers to the centroid of the coordinated phenyl ring

Specific structural features of (6c) can be compared with structural features of Ph\textsubscript{2}AsC\textsubscript{6}H\textsubscript{5}Cr(CO)\textsubscript{3} (2), a complex previously characterized by Atwood and Churchill (Table 3.7) [6b]. The ring C-C bond distances of (6c) vary between 1.382(4) and 1.426(4) Å. Unlike (2) in which there is a slight tendency toward alternation of bond lengths, there is no evidence of systematic alternation of the C-C bond lengths in (6c). All but one of these bond distances are in agreement within experimental error (3σ). However, the bond
distance C4-C9 (1.426(4) Å) is slightly longer than bond lengths of C8-C9 and C7-C8. The C-C-C angles in the arene ring average 120.0° and range from 119.0(3)° to 121.1(3)°. The arene ring may be regarded as essentially planar, although a slight folding is observed.

Table 3.7 Bond parameters for complexes Pr\textsubscript{1}2PC\textsubscript{6}H\textsubscript{5}Cr(CO)\textsubscript{3} (6c) and Ph\textsubscript{2}AsC\textsubscript{6}H\textsubscript{5}Cr(CO)\textsubscript{3} (2)

<table>
<thead>
<tr>
<th>Bonding</th>
<th>(6c)</th>
<th>(2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>&lt;P(As)-C\textsubscript{ring}&gt;\textsuperscript{a}</td>
<td>1.84</td>
<td>1.966</td>
</tr>
<tr>
<td>Cr-Bz</td>
<td>1.711(1)</td>
<td>1.708</td>
</tr>
<tr>
<td>Cr-C\textsubscript{co}</td>
<td>1.818(3)-1.839(3)</td>
<td>1.830(4)-1.839(4)</td>
</tr>
<tr>
<td>Cr-C\textsubscript{ring}</td>
<td>2.195(3)-2.231(3)</td>
<td>2.196(3)-2.220(4)</td>
</tr>
<tr>
<td>C-C(ring)</td>
<td>1.382(4)-1.426(4)</td>
<td>1.390(5)-1.411(5)</td>
</tr>
<tr>
<td>C-O</td>
<td>1.152(4)-1.158(4)</td>
<td>1.151(5)-1.155(5)</td>
</tr>
</tbody>
</table>

\textsuperscript{a} bracket refers to the mean value

The Cr-C1(carbonyl) distance trans to the P-C\textsubscript{ring} bond is longer than the other two Cr-CO bonds, while the three Cr-CO bond distances in (2) are the same (average 1.835 Å) within experimental error. The C-O bond lengths (average 1.155 Å) in (6c) are equal within experimental error and are in good agreement with values found for (2) (average 1.153 Å). As expected, the Cr-C-O angles (average 178.2°) show small deviations from linearity. This effect has been attributed to π bonding rather than to crystal packing forces [10].

The distance from chromium to the center of the ring is 1.711(1) Å, which is similar to the value for complex (2) (1.708(1) Å) and shorter than for C\textsubscript{6}H\textsubscript{6}Cr(CO)\textsubscript{3} (1.726(1) Å) [11]. The Cr-C\textsubscript{arene} bond lengths vary from 2.206(3) Å to 2.231(3) Å, where the Cr-C\textsubscript{ring} distance to the carbon atom which bears the Pr\textsubscript{1}2P group is longer than the other Cr-C\textsubscript{ring}
bond distances. In contrast, the differences in Cr-C\textsubscript{ring} bond lengths in the complex (2) are not statistically significant.

As expected, the P-C\textsubscript{ring} bond distance (1.840(3) Å) is shorter than the As-C\textsubscript{ring} (1.966(3) Å) bond distance in (2), which is similar to the value of 1.978(4) Å found for [(η\textsuperscript{6}-C\textsubscript{6}H\textsubscript{5})PhAsCH\textsubscript{2}AsPh\textsubscript{2}]Cr(CO)\textsubscript{3} [12].

### 3.3.3 Estimated Cone Angles for Phosphinobenzenechromium Tricarbonyl Ligands

The useful concept of the cone angle, as described in section 3.1, is generally accepted as a measure of the bulk of a phosphine ligand. This concept is extended to the phosphines of the unsymmetrical type PRR'R'' by measuring the angle between the M-P axis and the tangent of the van der Waals sphere for each substituent drawn from the neutral center, thus giving a ‘half’ cone angle. Two-thirds of the sum of these half angles is the cone angle of the unsymmetrical ligand as given in equation 3.2 [4].

\[
\alpha = \frac{2}{3} \sum \theta_i / 2 \quad i = 1, 2, 3
\]  
\text{Eq. 3.2}

There is an approximate group additive relationship for the cone angle of an unsymmetrical PRR'R'' ligand. Thus equation 3.2 may be used to justify utilizing 1/3 cone angle of PR\textsubscript{3} to be the contribution of R to the cone angle of PRR'R''. Hence, if the cone angles of PR\textsubscript{3}, PR'\textsubscript{3} and PR''\textsubscript{3} are known, then that of PRR'R'' may be calculated. The substituent angles (α(R)) for Et, Pr\textsuperscript{i}, Ph, and Bu\textsuperscript{t} are 44°, 53°, 48° and 61° respectively. A substituent angle for C\textsubscript{6}H\textsubscript{5}Cr(CO)\textsubscript{3} is 62°, has been determined from the crystal structure of Ru(CO)\textsubscript{3}(PPr\textsubscript{i}\textsuperscript{2}C\textsubscript{6}H\textsubscript{5}Cr(CO)\textsubscript{3})\textsubscript{2}. The steric bulk of C\textsubscript{6}H\textsubscript{5}Cr(CO)\textsubscript{3} group is therefore comparable with that of a tert-butyl group. The estimated values of the cone angles for the
phosphinobenzenechromium tricarbonyl ligands synthesized in this work as well as the values for the corresponding Cr(CO)\textsubscript{3}-free ligands are tabulated in Table 3.8. From this table, it is clearly seen that phosphinobenzene chromium tricarbonyl ligands are very bulky compared to the Cr(CO)\textsubscript{3}-free ligands.

**Table 3.8** Estimated cone angles of the phosphinobenzenechromium tricarbonyl ligands

<table>
<thead>
<tr>
<th>Ligand</th>
<th>Cone angle</th>
<th>Ligand</th>
<th>Cone angle</th>
</tr>
</thead>
<tbody>
<tr>
<td>PEt\textsubscript{2}[C\textsubscript{6}H\textsubscript{5}Cr(CO)\textsubscript{3}]</td>
<td>150°</td>
<td>PEt\textsubscript{2}Ph</td>
<td>136°\textsuperscript{a}</td>
</tr>
<tr>
<td>PPh\textsubscript{2}[C\textsubscript{6}H\textsubscript{5}Cr(CO)\textsubscript{3}]</td>
<td>158°</td>
<td>PPh\textsubscript{3}</td>
<td>145°\textsuperscript{a}</td>
</tr>
<tr>
<td>PEt[C\textsubscript{6}H\textsubscript{5}Cr(CO)\textsubscript{3}]\textsubscript{2}</td>
<td>168°</td>
<td>PEtPh\textsubscript{2}</td>
<td>140°\textsuperscript{a}</td>
</tr>
<tr>
<td>PPri\textsubscript{2}[C\textsubscript{6}H\textsubscript{5}Cr(CO)\textsubscript{3}]</td>
<td>168°</td>
<td>PPri\textsubscript{2}Ph</td>
<td>155°</td>
</tr>
<tr>
<td>PPh[C\textsubscript{6}H\textsubscript{5}Cr(CO)\textsubscript{3}]\textsubscript{2}</td>
<td>172°</td>
<td></td>
<td></td>
</tr>
<tr>
<td>PBu\textsuperscript{t}[C\textsubscript{6}H\textsubscript{5}Cr(CO)\textsubscript{3}]\textsubscript{2}</td>
<td>184°</td>
<td>PBu\textsuperscript{t}Ph\textsubscript{2}</td>
<td>157°</td>
</tr>
<tr>
<td>PBu\textsuperscript{t}2[C\textsubscript{6}H\textsubscript{5}Cr(CO)\textsubscript{3}]</td>
<td>183°</td>
<td>PBu\textsuperscript{t}2Ph</td>
<td>170°</td>
</tr>
</tbody>
</table>

\textsuperscript{a}: See reference [15]

**3.4 Summary and Future Considerations**

The synthesis of a number of new phosphino- and arsinobenzenechromium tricarbonyl ligands ER\textsubscript{2}C\textsubscript{6}H\textsubscript{5}Cr(CO)\textsubscript{3} (ER\textsubscript{2} = PEt\textsubscript{2}, PPri\textsubscript{2}, PBu\textsuperscript{t}2, PPh\textsubscript{2}, AsPh\textsubscript{2}, AsMe\textsubscript{2}), ER[C\textsubscript{6}H\textsubscript{5}Cr(CO)\textsubscript{3}]\textsubscript{2} (ER = PEt, PBu\textsuperscript{t}, PPh, AsPh) has been achieved by reacting lithium derivatives of benzenechromium tricarbonyl with appropriate chlorophosphines or iodoarsines. The spectroscopic properties of these ligands have been described. The structure of PPri\textsubscript{2}2C\textsubscript{6}H\textsubscript{5}Cr(CO)\textsubscript{3} was determined by an X-ray crystallographic study. This is
the first solid state structure to be reported for a phosphinobenzenechromium tricarbonyl ligand.

For further considerations, a series of chiral phosphine ligands, PRPhC₆H₅Cr(CO)₃ (R = Me, Et, Pr¹, Bu¹), should be synthesized. These ligands may be of interest in the study of asymmetric synthesis and catalysis. Furthermore, these ligands have three different P-C bond types: P-C(alkyl), P-C(η⁶-C₆H₅) and P-C(C₆H₅). Pyrolysis reaction studies of trinuclear metal clusters containing these ligands should be helpful in understanding the relative ease of cleavage of P-C bonds in P-C(alkyl), P-C(η⁶-C₆H₅) and P-C(C₆H₅). Further investigations into the spectroscopic properties and solid state structures of the ligands may be of interest as well.

3.5 Experimental Procedures

3.5.1 Preparation of [C₆H₅Cr(CO)₃]PBu₄₂ (6a)

A solution of C₆H₆Cr(CO)₃ (1.0 g, 4.7 mmol) in THF (20 mL) in a Schlenk tube was cooled to -78 °C and treated dropwise with n-BuLi in hexane (3.0 mL, 1.6 M, 4.8 mmol). The resulting solution was stirred at -78 °C for 50 min. Then Bu₄²PCl (1.0 mL, 5.2 mmol) was added to the solution. After it was stirred at -78 °C for one hour, the reaction mixture was warmed to room temperature and stirred continuously for an additional hour. After evaporating the solvent in vacuo, the residual oil was dissolved in CH₂Cl₂ (20 mL) and then filtered under nitrogen over a frit packed with Celite to remove LiCl. The solvent was removed in vacuo to afford a red oil. Hexane (5 mL) was added to the red oil. Then the resultant suspension was stirred vigorously. A yellow powder was formed and isolated. It was further purified by recrystallization from hexane/CH₂Cl₂ (2/1) to yield [C₆H₅Cr(CO)₃]PBu₄₂ as a yellow crystalline solid: yield 80%. MS (El) m/e 358 [P⁺].

³¹P{¹H} NMR (121.42 MHz, CDCl₃) δ: 42.8 (s). ¹H NMR (300 MHz, CDCl₃) δ: 5.7 (t,
J(H-H) = 6 Hz, 2H), 5.6 (t, J(H-H) = 6 Hz, 1H), 5.2 (t, J(H-H) = 6 Hz, 2H); 1.2 (d, J(P-H) = 10 Hz, 18H). IR (KBr) v(CO): 1960 (vs), 1900 (vs), 1880 (s), 1870 (sh), 1865 (s) cm⁻¹. Anal. Calcd for C₁₇H₂₃CrO₃P: C, 56.97; H, 6.47. Found: C, 56.80; H, 6.52.

3.5.2 Preparation of \([\text{C₆H₅Cr(CO)}₃]₂\text{PBut}^{t} \) (6b)

Benzene chromium tricarbonyl (1.62 g, 7.55 mmol) was dissolved in THF (25 mL) at -78 °C. A solution of n-butyllithium in hexane (4.8 mL, 1.6 M, 7.7 mmol) was added slowly with a syringe to the cold, stirred solution. The solution was then stirred at -78 °C for 50 min. Cl₂PBut (0.65 g, 4 mmol) in THF (10 mL) was then added dropwise with a syringe to the solution. The reaction mixture was stirred at -78 °C for an additional hour and allowed to warm to room temperature. The solvent was evaporated in vacuo. The residual red oil was dissolved in CH₂Cl₂ (20 mL) and then filtered through a short column of silica gel under nitrogen. Dark red impurities and LiCl were left on the top of the column. Evaporation of the eluate followed by crystallization of the solid residue from CH₂Cl₂/hexanes (1:2) afforded \([\text{C₆H₅Cr(CO)}₃]₂\text{PBut}^{t} \) (70% yield) as a yellow crystalline solid (6b). MS (EI) m/e 514 [P⁺]. ³¹P{¹H} NMR (121.42 MHz, CDCl₃) δ: 20.7 (s). ¹H NMR (300 MHz, CDCl₃) δ: 5.7 (t, J(H-H) = 6 Hz, 2H), 5.4 (t, J(H-H) = 6 Hz, 4H), 5.2 (d, J(H-H) = 6 Hz, 4H). 1.2 (d, J(P-H) = 10 Hz, 9H). IR (KBr) v(CO): 1970 (s), 1890 (s, br) cm⁻¹. Anal. Calcd for C₂₂H₂₁Cr₂O₃P: C, 51.37; H, 3.72. Found: C, 51.27; H, 3.71.

3.5.3 Preparation of \([\text{C₆H₅Cr(CO)}₃]\text{PPr}^{i₂} \) (6c)

Compound (6c) was synthesized by the procedure described for the preparation of (6a), except that chloroditiisopropylphosphine (0.75 mL, 5.0 mmol) was used instead of chloroditertiarybutylphosphine. Yellow crystals of (6c) were obtained after recrystallization from hexanes/CH₂Cl₂ (2:1) at -30 °C (1.1 g, 70%). MS (EI): m/e 330 [P⁺]. ³¹P{¹H} NMR (121.42 MHz, CDCl₃) δ: 13.9 (s). ¹H NMR (300 MHz, CDCl₃) δ: 5.33 (t, J(H-H) = 5 Hz, 3H), 5.18 (t, J(H-H) = 5 Hz, 2H), 1.95 (q, 2H), 1.05 (dd, J(H-H) = 5.5 Hz, 12H). IR
(KBr) ν(CO): 1970 (s), 1880 (s, br) cm⁻¹. Anal. Calcd for C₁₅H₁₉CrO₃P: C, 54.55; H, 5.76. Found: C, 54.72; H, 5.87.

3.5.4 Preparation of [C₆H₅Cr(CO)₃]₂PEt (6d)

The same general procedure used for the synthesis of (6a) was followed for the preparation of (6d). Benzenechromium tricarbonyl (2.0 g, 9.3 mmol) was mixed with n-BuLi (1.6 M, 6.3 mL) in hexane. Then dichloroethylphosphine (0.52 mL, 5.0 mmol) was added to the solution to yield yellow crystalline solid (6d) (0.7 g, 65%). MS (El) m/e 486 [P⁺]. ³¹P{¹H} NMR (121.42 MHz, CDCl₃) δ: -5.5 (s). ¹H NMR (300 MHz, CDCl₃) δ: 5.4 (t, J(H-H) = 6 Hz, 6H), 5.2 (t, J(H-H) = 6 Hz, 4H), 1.8 (q, J(H-H) = 6 Hz, 4H), 1.2 (m, 6H). IR (KBr) ν(CO): 1962 (s), 1851 (s, br) cm⁻¹. Anal. Calcd for C₂₀H₁₅O₆Cr₂P: C, 49.39; H, 3.12. Found: C, 49.75; H, 3.34.

3.5.5 Preparation of [C₆H₅Cr(CO)₃]₂PEt₂ (6e)

Chlorodiethylphosphine (0.97 mL, 8.0 mmol) was added dropwise to a stirred solution of (η⁶-phenyllithium)chromium tricarbonyl at -78 °C, which was prepared from the reaction between the benzenechromium tricarbonyl (1.7 g, 8.0 mmol) and n-BuLi (5.0 mL, 1.6 M in hexane). The resulting solution was maintained at -78 °C for 2 hours and then warmed slowly to ambient temperature. The solution was filtered through a short column of silica gel under nitrogen. Removal of the solvent in vacuo gave the title compound (6e) as a red oil, which was 90% pure by phosphorus NMR spectra. MS (El): m/e 302 [P⁺]. ³¹P{¹H} NMR (121.42 MHz, CDCl₃) δ: -13 (s). ¹H NMR (300 MHz, CDCl₃) δ: 5.4 (t, J(H-H) = 6 Hz, 3H), 5.2 (t, J(H-H) = 6 Hz, 2H), 1.8 (q, 4H), 1.2 (m, 6H). IR (CH₂Cl₂) ν (CO): 1978 (s), 1885 (s) cm⁻¹.
3.5.6 Preparation of [C₆H₅Cr(CO)₃]AsMe₂ (6f)

A procedure similar to that used to prepare (6b) was followed for the preparation of (6f). Benzenechromium tricarbonyl (0.53 g, 2.5 mmol) was mixed with n-butyllithium (1.6 M, 1.9 mL) in hexane. Then dimethylidioarsine (0.3 mL, 3 mmol) was added to the solution to yield a yellow solid (550 mg, 70%). MS (EI): m/e 318 [P⁺]. ¹H NMR (300 MHz, CDCl₃) δ: 1.4 (s, 6H), 5.5 (t, J(H-H) = 5.5 Hz, 3H), 5.3 (t, J(H-H) = 5.5 Hz, 2H). IR (KBr) ν(CO): 1960 (s), 1880 (s, br) cm⁻¹. Anal. Calcd for C₁₁H₁₁AsCrO₃: C, 41.53; H, 3.49. Found: C, 41.63; H, 3.49.

3.5.7 Preparation of [C₆H₅Cr(CO)₃]₂PPh (6h)

The same general procedure used for the synthesis of (6b) was followed for the preparation of (6h). Reaction of benzenechromium tricarbonyl (1.3 g, 6 mmol), butyllithium (1.6 M, 3.8 mL) in hexane and dichlorophenylphosphine (0.41 mL, 3 mmol) yielded the ligand (6h) (1.1 g, 70%) as a yellow crystalline solid. MS (EI) m/e 534 [P⁺]. ³¹P{¹H} NMR (121.42 MHz, CDCl₃) δ: -4.0 (s). ¹H NMR (300 MHz, CDCl₃) δ: 7.3-7.6 (m, 5H), 5.6 (t, J(H-H) = 6 Hz, 4H), 5.3 (t, J(H-H) = 6 Hz, 2H), 5.2 (d, J(H-H) = 6 Hz, 4H). IR (Nujol) ν(CO): 1970 (s), 1900 (s, br) cm⁻¹. Anal. Calcd for C₂₄H₁₅CrO₆P: C, 53.94; H, 2.83. Found: C, 53.60; H, 2.85.

3.5.8 Preparation of [C₆H₅Cr(CO)₃]PPh₂ (6g)

A procedure similar to that used to prepare (6a) was followed for the preparation of (6g), except that chlorodiphenylphosphine (0.9 mL, 5 mmol) was used. A yellow crystalline solid was obtained following recrystallization: yield 85%. MS (EI) m/e 398 [P⁺]. ³¹P{¹H} NMR (121.42 MHz, CDCl₃) δ: -5.2 (s). ¹H NMR (300 MHz, CDCl₃) δ: 7.4 (br. s, 10H), 5.4 (t, 1H), 5.2 (m, 4H). IR (KBr) ν(CO): 1980 (s), 1900 (s, br) cm⁻¹.
3.5.9 Preparation of [C₆H₅Cr(CO)₃]₂AsPh (6i)

The same general procedure used for the synthesis of (6i) was followed for the preparation of (6h). Reaction of benzenechromium tricarbonyl (2.14 g, 10 mmol), n-butyllithium (1.6 M, 6.25 mL) in hexane and phenyldiiodoarsine (2.0 g, 5 mmol) yielded the ligand (6i) (2.0 g, 70%) as a yellow solid. MS (EI): m/e 578 [P⁺]. ¹H NMR (300 MHz, CDCl₃) δ: 7.4 (br s, 5H), 5.5 (t, 4H), 5.3 (t, 2H), 5.15 (s, 4H). Anal. Calcd for C₂₄H₁₅CrO₆As: C, 49.84; H, 2.62. Found: C, 49.50; H, 2.43.

3.5.10 Preparation of [C₆H₅Cr(CO)₃]AsPh₂ (6j)

A procedure similar to that used to synthesize (6g) was followed for the preparation of (6j), except that diphenyldiarsine (1.8 g, 5 mmol) was used. A yellow crystalline solid was obtained after recrystallization: yield 80%. MS (EI) m/e 358 [P⁺]. ¹H NMR (300 MHz, CDCl₃) δ: 7.4 (br s, 10H), 5.3 (br s, 1H), 5.2 (br s, 4H). Anal. Calcd for C₂₁H₁₅O₃AsCr: C, 57.03; H, 3.42. Found: C, 56.74; H, 3.21.

References


CHAPTER 4

Metal Clusters Containing Benzenechromium Tricarbonyls

4.1 Introduction

The study of metal cluster carbonyl chemistry, where a metal cluster compound as defined by Cotton [1] is a group of two or more metal atoms in which there are substantial and direct bonds between the metal atoms, was initiated by the discovery of dodecacobonyltriiron (1) in 1907 [2]. However, the precise nature of the triiron cluster was not unequivocally determined until the X-ray structure investigation by Dahl and Wei in 1966 [3]. The first ruthenium cluster carbonyl (2) was obtained by Mond and co-workers in 1910 as an orange crystalline solid from the reaction of ruthenium metal with carbon monoxide (400 atm, 300 °C) [4]. The product was not correctly characterized until it was formulated as Ru$_3$(CO)$_{12}$ by Corey and Dahl [5] on the basis of the X-ray determined structure of the osmium analogue (3) which was synthesized by Hieber et al. in 1943 [6].

The iron complex (1) consists of a slightly distorted isosceles triangle of iron atoms. In this structure one iron atom is coordinated to two axial and two equatorial terminal carbonyls, and the other two irons are each bonded to three terminal and to two μ-bridging carbonyls. However, the ruthenium and osmium analogues (2) and (3) have a different structure. The metal triangles in (2) and (3) are essentially equilateral, and all the carbonyls are terminal, four being bonded to each metal atom with two in axial and two in equatorial positions [7, 8].

An area of considerable current interest has been the synthesis and chemistry of derivatives of Ru$_3$ clusters and Os$_3$ clusters containing Group 15 ligands. With the advent
of mild synthetic routes, many derivatives of Ru$_3$(CO)$_{12}$ and Os$_3$(CO)$_{12}$ with tertiary phosphine or arsine ligands have been synthesized. However, substituted Ru$_3$(CO)$_{12}$ and Os$_3$(CO)$_{12}$ derivatives containing benzenechromium tricarbonyl ligands were unknown before the present work.

### 4.2 Synthesis of Metal Clusters Containing Benzenechromium Tricarbonyl Ligands

#### 4.2.1 Synthesis of Triruthenium Clusters Containing Benzenechromium Tricarbonyl Ligands

Reactions between the phosphino- or arsinobenzenechromium tricarbonyls and Ru$_3$(CO)$_{12}$ were investigated and carried out by different synthetic methods. Three major strategies have been used previously to activate Ru$_3$(CO)$_{12}$ toward substitution with tertiary phosphines or arsines: thermal process, photochemical process and chemical activation process.

Relatively high temperatures (80-100 °C) are required for Ru$_3$(CO)$_{12}$ to react directly with various tertiary phosphines. The usual products formed in such reactions are tri-substituted complexes Ru$_3$(CO)$_{9}$(PR$_3$)$_3$. In several instances it has proved possible to isolate the mono- and di-substituted complexes, particularly by use of chromatographic methods, but the tri-substituted complexes are the major products [9]. Under normal reflux conditions with bulky phosphines, such as tricyclohexylphosphine, the monosubstituted complexes are the major products. The photosubstitution of Ru$_3$(CO)$_{12}$ with PPh$_3$ produces the mono-substituted complex in low yield and also results in cluster fragmentation [10]. In general, thermal and photochemical routes lead to reactions dominated by multiproduct mixtures with low yields, which also contain products derived from cluster fragmentation.
Since the 1980's, greater selectivity to carbonyl substitution of metal clusters has been achieved under a variety of mild conditions. In 1982, the Bruce group and the Arewgoda group independently reported that sodium benzophenone ketyl (BPK) induces carbonyl substitution of metal clusters [11, 12]. The proposed mechanism which involves an electron transfer process is outlined in equations 4.1-4.3[13].

\[
\begin{align*}
\text{Ru}_3(\text{CO})_{12} + e & \rightleftharpoons [\text{Ru}_3(\text{CO})_{12}]^2^- \quad \text{Eq. 4.1} \\
[\text{Ru}_3(\text{CO})_{12}]^2^- + L & \rightleftharpoons [\text{Ru}_3(\text{CO})_{11}L]^2^- + \text{CO} \quad \text{Eq. 4.2} \\
[\text{Ru}_3(\text{CO})_{11}L]^2^- + \text{Ru}_3(\text{CO})_{12} & \rightleftharpoons [\text{Ru}_3(\text{CO})_{12}]^2^- + \text{Ru}_3(\text{CO})_{11}L \quad \text{Eq. 4.3}
\end{align*}
\]

Addition of catalytic amounts of BPK to a solution of Ru$_3$(CO)$_{12}$ results in electron transfer from the ketyl radical anion to the cluster. It is likely that Ru-Ru bond cleavage occurs to generate a labile 17e metal center (Ru$_3$(CO)$_{12}^-$), which undergoes further substitution. The substituted cluster radical anion is less stable than that formed from the parent carbonyl and rapid electron transfer to unreacted Ru$_3$(CO)$_{12}$ establishes a cycle that is followed until either the Ru$_3$(CO)$_{12}$ or the ligand is completely consumed [14, 15].

There are three requirements for this reaction to occur: (i) the cluster carbonyl has to be reduced without fragmentation, and the resulting anion has to have a long enough lifetime to allow for substitution; (ii) to facilitate the transfer of an electron from the substituted radical anion to Ru$_3$(CO)$_{12}$, the substituting ligand must be a better Lewis base than the carbonyl ligand; and (iii) the ligand must not be reduced by the diphenyl ketyl radical anion. Thus, the efficiency of BPK catalysis decreases with increasing substitution. Furthermore, weak coordinating ligands such as AsPh$_3$ give moderate or low yields of the products. For most phosphines, the mono-, di-, and tri-substitution reactions proceed readily in high conversion and specificity with no fragmentation being detected. This
method has allowed many previously unknown phosphine and arsine complexes to be prepared.

Alternative reagents to BPK have been employed to induce substitution reactions on Ru$_3$(CO)$_{12}$. These include the use of a catalytic amount of PPN$^+$OAc$^-$ or PPN$^+$CN$^-$, which promotes CO substitution by tertiary phosphines, such as PPh$_3$, but not by AsPh$_3$. Other PPN$^+$ salts show varying degrees of activity [16]. Also of interest are observations that some metal dimers, like [CpFe(CO)$_2$]$_2$ [17], [Fe(CO)$_3$(μ-SMe)]$_2$ [18] or [CpMo(CO)$_3$]$_2$ [19], may be used as catalyst precursors for substitution reactions between Ru$_3$(CO)$_{12}$ and various nucleophiles. The weakly stabilized Ru$_3$(CO)$_{12-n}$(MeCN)$_n$ ($n = 1, 2$) derivatives are also potentially useful for the preparation of substitution products of Ru$_3$(CO)$_{12}$ [20].

In the present investigation the chemical activation method was used. Typically, a mixture of the Ru$_3$(CO)$_{12}$ and the stoichiometrically required amount of phosphino- and arsinobenzenechromium tricarbonyl were dissolved in tetrahydrofuran, and the reaction mixture was treated dropwise with a solution of sodium benzophenone ketyl in THF (ca. 0.025 M) or with PPN salts. Twelve substituted ruthenium clusters containing benzenechromium tricarbonyl were thus synthesized and are listed in Table 4.1.

The efficiencies of the reactions were affected by both the steric and the electronic properties of the phosphine or arsine ligands. The 1:1 or 1:2 radical anion reaction with the ligand type R$_2$E[C$_6$H$_5$Cr(CO)$_3$] ($R_2E =$ Me$_2$As, Pr$_2$P, Et$_2$P, Ph$_2$P) affords the expected mono- or di-substituted products in high yield. However, under the same conditions, the reaction with the more bulky and less basic ligands Bu$_2$PC$_6$H$_5$Cr(CO)$_3$, Ph$_2$AsC$_6$H$_5$Cr(CO)$_3$, and PhP[C$_6$H$_5$Cr(CO)$_3$]$_2$ did not give the di-substituted products but yields only the mono-substituted products in very low amounts. It was not surprising to
find that no reaction occurs with Bu\textsubscript{4}P[C\textsubscript{6}H\textsubscript{5}Cr(CO)\textsubscript{3}]\textsubscript{2} or PhAs[C\textsubscript{6}H\textsubscript{5}Cr(CO)\textsubscript{3}]\textsubscript{2} because these two ligands are more bulky and less basic, compared with the above three ligands. In contrast, the ligand PhPFe\textsubscript{2} forms mono- and disubstituted ruthenium carbonyl complexes in high yield [21]. This is probably due to the electron-releasing property of the ferrocenyl group which makes the ligand PhPFe\textsubscript{2} much more basic than PhP[C\textsubscript{6}H\textsubscript{5}Cr(CO)\textsubscript{3}]\textsubscript{2}, as the steric bulk of the two phosphines is similar.

**Table 4.1** The triruthenium complexes prepared in this work

<table>
<thead>
<tr>
<th>Ligand (L)</th>
<th>Ratio</th>
<th>Product</th>
<th>Method</th>
<th>Yield %</th>
</tr>
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<tbody>
<tr>
<td>Me\textsubscript{2}AsC\textsubscript{6}H\textsubscript{5}Cr(CO)\textsubscript{3}</td>
<td>1:1</td>
<td>Ru\textsubscript{3}(CO)\textsubscript{11}L (4a)</td>
<td>BPK</td>
<td>85</td>
</tr>
<tr>
<td></td>
<td>1:2</td>
<td>Ru\textsubscript{3}(CO)\textsubscript{10}L\textsubscript{2} (4b)</td>
<td>BPK</td>
<td>70</td>
</tr>
<tr>
<td>Pr\textsubscript{2}PC\textsubscript{6}H\textsubscript{5}Cr(CO)\textsubscript{3}</td>
<td>1:1</td>
<td>Ru\textsubscript{3}(CO)\textsubscript{11}L (4c)</td>
<td>PPNCl</td>
<td>80</td>
</tr>
<tr>
<td></td>
<td>1:2</td>
<td>Ru\textsubscript{3}(CO)\textsubscript{10}L\textsubscript{2} (4d)</td>
<td>PPNCl</td>
<td>80</td>
</tr>
<tr>
<td>Ph\textsubscript{2}PC\textsubscript{6}H\textsubscript{5}Cr(CO)\textsubscript{3}</td>
<td>1:1</td>
<td>Ru\textsubscript{3}(CO)\textsubscript{11}L (4e)</td>
<td>BPK</td>
<td>70</td>
</tr>
<tr>
<td></td>
<td>1:2</td>
<td>Ru\textsubscript{3}(CO)\textsubscript{10}L\textsubscript{2} (4f)</td>
<td>BPK</td>
<td>60</td>
</tr>
<tr>
<td>Et\textsubscript{2}PC\textsubscript{6}H\textsubscript{5}Cr(CO)\textsubscript{3}</td>
<td>1:1</td>
<td>Ru\textsubscript{3}(CO)\textsubscript{11}L (4g)</td>
<td>BPK</td>
<td>85</td>
</tr>
<tr>
<td></td>
<td>1:2</td>
<td>Ru\textsubscript{3}(CO)\textsubscript{10}L\textsubscript{2} (4h)</td>
<td>BPK</td>
<td>80</td>
</tr>
<tr>
<td>PhP[C\textsubscript{6}H\textsubscript{5}Cr(CO)\textsubscript{3}]\textsubscript{2}</td>
<td>1:1</td>
<td>Ru\textsubscript{3}(CO)\textsubscript{11}L (4i)</td>
<td>BPK</td>
<td>X</td>
</tr>
<tr>
<td>PhAs[C\textsubscript{6}H\textsubscript{5}Cr(CO)\textsubscript{3}]\textsubscript{2}</td>
<td>1:1</td>
<td>Ru\textsubscript{3}(CO)\textsubscript{11}L (4j)\textsuperscript{a}</td>
<td>BPK</td>
<td>X</td>
</tr>
<tr>
<td>Bu\textsubscript{4}PC\textsubscript{6}H\textsubscript{5}Cr(CO)\textsubscript{3}</td>
<td>1:1</td>
<td>Ru\textsubscript{3}(CO)\textsubscript{11}L (4k)</td>
<td>BPK</td>
<td>low</td>
</tr>
<tr>
<td>Bu\textsubscript{4}P[C\textsubscript{6}H\textsubscript{5}Cr(CO)\textsubscript{3}]\textsubscript{2}</td>
<td>1:1</td>
<td>Ru\textsubscript{3}(CO)\textsubscript{11}L (4l)</td>
<td>BPK</td>
<td>low</td>
</tr>
<tr>
<td>Ph\textsubscript{2}AsC\textsubscript{6}H\textsubscript{5}Cr(CO)\textsubscript{3}</td>
<td>1:1</td>
<td>Ru\textsubscript{3}(CO)\textsubscript{11}L (4m)</td>
<td>BPK</td>
<td>10</td>
</tr>
</tbody>
</table>

X: no reaction. a: expected product
The yields of di-substituted products are less than those for the mono-substituted products, and no matter how much catalyst was added, no tri-substituted ruthenium carbonyl complexes were isolated during the course of this study. A possible reason for this observation is that \([\text{Ru}_3(\text{CO})_{11}L]^-\) slows down the electron transfer to \(\text{Ru}_3(\text{CO})_{12}\) because of the electron-withdrawing property of the ligand. In addition, steric and statistical factors are unfavorable for higher substitution.

From Table 4.1, it can be seen that reactions with phosphines are more efficiently initiated than with the corresponding arsines. For instance, the complex \((4e)\) is obtained in high yield. However, the complex \((4m)\) can be isolated only in low yield. The ligand \(\text{PhP}[\text{C}_6\text{H}_5\text{Cr}(\text{CO})_3]_2\) does afford a small amount of \(\text{Ru}_3(\text{CO})_{11}\text{PhP}[\text{C}_6\text{H}_5\text{Cr}(\text{CO})_3]_2\) while no \(\text{Ru}_3(\text{CO})_{11}[\text{PhAs}\{\text{C}_6\text{H}_5\text{Cr}(\text{CO})_3\}_2]\) can be isolated. This trend presumably reflects the decreasing nucleophilicity of \(\text{ER}_3\) as the size of \(\text{E}\) increases. In previous studies of the reaction of \(\text{Fe}_3(\text{CO})_{12}\) with some bulky phosphines, some fragmentation of the \(\text{Fe}_3\) cluster was observed \([11, 22]\). For instance, a 1:1 molar ratio of \(\text{Fe}_3(\text{CO})_{12}\) with \(\text{PPh}_2\text{Fc}\) affords the monosubstituted product, \(\text{Fe}_3(\text{CO})_{11}\text{PPh}_2\text{Fc}\) in high yield. However, under the same conditions, the reaction with the more bulky ligand \(\text{PPh}_2\text{Fc}_2\) does not give the expected product; instead, \(\text{Fe}(\text{CO})_4\text{PPh}_2\text{Fc}_2\) was obtained. No products arising from the breakdown of the ruthenium cluster were observed during the preparations. This leads to the conclusion that the ruthenium analogues appears to give more stable trinuclear species. This may be correlated with a decrease in the stability of the metal-metal bonds and the metal-carbonyl bonds in the order of \(\text{Os}_3(\text{CO})_{12} > \text{Ru}_3(\text{CO})_{12} > \text{Fe}_3(\text{CO})_{12}\) \([23]\).

In general, the BPK electron transfer catalysis is the most useful method for preparing triruthenium clusters containing the phosphinobenzene chromium tricarbonyl ligand. For systems where the reaction is favorable, the method allows a high selectivity towards carbonyl substitution, short reaction times, mild conditions, and high yields. It
seems that PPN salts are less efficient catalysts for promoting CO substitution of ruthenium carbonyl by phosphinobenzene chromium tricarbonyl ligands for the same reactions. In addition the products often give a mixture of mono- and disubstituted complexes.

4.2.2 Synthesis of Triosmium Clusters Containing Benzenechromium Tricarbonyl Ligands

Like Ru$_3$(CO)$_{12}$, the carbonyl substitution reaction of Os$_3$(CO)$_{12}$ by phosphine or arsine ligands have mainly been carried out by using thermal, photochemical or chemical activation of the Os-CO bond.

In general, the direct reaction of Os$_3$(CO)$_{12}$ with phosphines or arsines in refluxing high-boiling point solvents requires temperatures greater than 100 °C and affords a mixture of Os$_3$(CO)$_{11}$L, Os$_3$(CO)$_{10}$L$_2$ and Os$_3$(CO)$_9$L$_3$ which can be separated by chromatography. These results suggest that the rates of the stepwise mono-, di- and trisubstitution reactions may not be very different. In contrast, in the case of Ru$_3$(CO)$_{12}$, the formation of Ru$_3$(CO)$_{11}$PR$_3$ is the rate-determining step [24].

Substitution reactions of Os$_3$(CO)$_{12}$ are facilitated by the use of the activated clusters, Os$_3$(CO)$_{11}$(MeCN) and Os$_3$(CO)$_{10}$(MeCN)$_2$ [25]. Other weakly-bound ligands can also be utilized, such as cyclooctene, cyclohexadiene or ammonia [26]. The synthesis of these lightly stabilized species is generally carried out by nucleophilic attack of trimethylamine N-oxide at the electrophilic carbon of a coordinated carbonyl group to release CO$_2$. These new clusters are more reactive than the parent carbonyl clusters owing to the presence of the labile ligand(s) stabilizing a formally unsaturated ‘[Os$_3$(CO)$_{11}$/10]’ cluster. The complexes Os$_3$(CO)$_{12-n}$(MeCN)$_n$ (n = 1, 2) have been found to be important
starting materials for reactions with phosphines [25, 27]. The initial step in the reactions of these complexes involves the dissociative loss of the weakly bound ligand [28, 29].

Other reagents for activation have also been employed to induce substitution reactions on Os₃(CO)₁₂. Thus, the reaction of Os₃(CO)₁₂ with PPh₃ is catalyzed by Pt(PPh₃)₄ and substitution of Os₃(CO)₁₂ with PMe₂Ph is initiated by Cp₂Fe₂(CO)₄ [30]. Sodium benzophenone ketyl is a good catalyst for substitution on Ru₃(CO)₁₂ as mentioned above, but is less efficient in the case of Os₃(CO)₁₂ [12].

In the present work two synthetic methods were employed for the preparation of a series of derivatives of Os₃(CO)₁₂ containing phosphino- and arsinobenzene chromium tricarbonyl ligands. These new complexes are summarized in Table 4.2.

<table>
<thead>
<tr>
<th>Ligand (L)</th>
<th>Ratio</th>
<th>Product</th>
<th>Method</th>
<th>Yield %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Me₂AsC₆H₅Cr(CO)₃</td>
<td>1:1</td>
<td>Os₃(CO)₁₁L</td>
<td>A</td>
<td>90</td>
</tr>
<tr>
<td></td>
<td>1:2</td>
<td>Os₃(CO)₁₀L₂</td>
<td>A</td>
<td>70</td>
</tr>
<tr>
<td>Pr₂PC₆H₅Cr(CO)₃</td>
<td>1:1</td>
<td>Os₃(CO)₁₁L</td>
<td>A</td>
<td>80</td>
</tr>
<tr>
<td></td>
<td>1:2</td>
<td>Os₃(CO)₁₀L₂</td>
<td>A</td>
<td>80</td>
</tr>
<tr>
<td>Ph₂PC₆H₅Cr(CO)₃</td>
<td>1:1</td>
<td>Os₃(CO)₁₁L</td>
<td>A</td>
<td>80</td>
</tr>
<tr>
<td>Et₂PC₆H₅Cr(CO)₃</td>
<td>1:1</td>
<td>Os₃(CO)₁₁L</td>
<td>A</td>
<td>80</td>
</tr>
<tr>
<td></td>
<td>1:2</td>
<td>Os₃(CO)₁₀L₂</td>
<td>A</td>
<td>70</td>
</tr>
<tr>
<td></td>
<td>1:1</td>
<td>Os₃(CO)₉L₃</td>
<td>thermal</td>
<td>25</td>
</tr>
<tr>
<td>Ph[P₆H₅Cr(CO)₃]₂</td>
<td>1:1</td>
<td>Os₃(CO)₁₁L</td>
<td>A</td>
<td>50</td>
</tr>
<tr>
<td>Bu₂PC₆H₅Cr(CO)₃</td>
<td>1:1</td>
<td>Os₃(CO)₁₁L</td>
<td>A</td>
<td>X</td>
</tr>
<tr>
<td>BuP[P₆H₅Cr(CO)₃]₂</td>
<td>1:1</td>
<td>Os₃(CO)₁₁L</td>
<td>A</td>
<td>X</td>
</tr>
</tbody>
</table>

X: no reaction. A: Me₃NO + CH₃CN  a: expected product

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The reactions of \( \text{Os}_3(\text{CO})_{11}(\text{MeCN}) \) with \( \text{ER}_2[\text{C}_6\text{H}_5\text{Cr}(\text{CO})_3] \) (\( \text{ER}_2 = \text{AsMe}_2, \text{PPri}_2, \text{PET}_2, \text{PPh}_2 \)) in 1:1 molar ratio in dichloromethane give high yields of the monosubstituted product \( \text{Os}_3(\text{CO})_{11}L \). The compound \( \text{Os}_3(\text{CO})_{10}(\text{MeCN})_2 \) undergoes facile displacement of both acetonitrile ligands with \( \text{ER}_2[\text{C}_6\text{H}_5\text{Cr}(\text{CO})_3] \) (\( \text{ER}_2 = \text{AsMe}_2, \text{PET}_2, \text{PPri}_2 \)) to afford the disubstituted products \( \text{Os}_3(\text{CO})_{10}L_2 \) in good yield. However, the attempted synthesis of \( \text{Os}_3(\text{CO})_{11}L, \text{or Os}_3(\text{CO})_{10}L_2 \) \( (L = \text{But}_2\text{P}[\text{C}_6\text{H}_5\text{Cr}(\text{CO})_3], \text{BuP}[\text{C}_6\text{H}_5\text{Cr}(\text{CO})_3]_2) \) was unsuccessful even after employing extended reaction times and an excess of ligands. This can be attributed to both the steric and the electronic effects of the phosphine ligands. These two ligands are very poor electron donors due to their steric bulk and the strong electron-withdrawing properties of the \( \text{C}_6\text{H}_5\text{Cr}(\text{CO})_3 \) group.

4.3 Molecular Structures of Metal Clusters Containing Benzenechromium Tricarbonyl Ligands

4.3.1 Molecular Structures of \( \text{Ru}_3(\text{CO})_{11}(\text{Ph}_2\text{PC}_6\text{H}_5\text{Cr}(\text{CO})_3) \) (4e) and \( \text{Ru}_3(\text{CO})_{11}(\text{Pr}_2\text{PC}_6\text{H}_5\text{Cr}(\text{CO})_3) \) (4c)

Two monosubstituted ruthenium complexes (4e) and (4c) have been crystallographically characterized. Table 4.3 (see p82) summarizes important bond lengths and bond angles found for these two complexes, together with those reported elsewhere for the parent ruthenium carbonyl \( \text{Ru}_3(\text{CO})_{12} \) [7a]. The atomic numbering of the (4e) and (4c) used in this discussion are presented in Figure 4.1. The molecular structures of these complexes are shown in Figure 4.2 (see p83) and Figure 4.3 (see p84), respectively. Both compounds contain slightly distorted triangular \( \text{Ru}_3 \) moieties with the phosphine ligands occupying equatorial positions and with each Ru atom having distorted octahedral coordination geometry.
There are three different Ru-Ru bonds in (4e) and (4c), the longest of which is *cis* to the tertiary phosphine. Thus, the Ru1-Ru3 bond lengths at 2.9256(7) Å in (4c) and 2.8900(7) Å in (4e) are longer than the other two Ru-Ru bond lengths in the complexes. There is little difference between the other two Ru-Ru bond lengths (maximum 0.008 Å in these complexes). The average Ru-Ru distances in (4e) and (4c) are 2.8732 and 2.8888 Å respectively, which is greater than the average (2.854 Å) in the parent ruthenium carbonyl by more than 0.019 Å. The greater size of the Ru₃ frame compared with that found in the parent carbonyl can be related to the cone angle of the phosphine ligand. A pervious literature report [31] has demonstrated that a reasonable curve can be obtained if the average Ru-Ru distance is plotted against the Tolman cone angle $\alpha$ for the P ligand. Generally, the Ru₃ frame increases with increasing cone angle of the P-ligand. Hence, it is expected to find that the average Ru-Ru distance in (4c) is longer than that in (4e) because the ligand PPr̅₂[C₆H₅Cr(CO)₃] (cone angle 164°) in (4c) is more bulky than the ligand PPh₂[C₆H₅Cr(CO)₃] (cone angle 154°) in (4e).
Table 4.3 Summary of bond lengths and bond angles for \( \text{Ru}_3(\text{CO})_{11}(\text{Ph}_2\text{P}-\text{C}_6\text{H}_5\text{Cr}(\text{CO})_3) \) (4e), \( \text{Ru}_3(\text{CO})_{11}(\text{Pr}^{i}_2\text{PC}_6\text{H}_5\text{Cr}(\text{CO})_3) \) (4c) and \( \text{Ru}_3(\text{CO})_{12} \)

<table>
<thead>
<tr>
<th></th>
<th>( \text{Ru}<em>3(\text{CO})</em>{12} )</th>
<th>(4e)</th>
<th>(4c)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cone angle</td>
<td>~95°</td>
<td>158°</td>
<td>168°</td>
</tr>
<tr>
<td>Cone angle</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Selected bond lengths (Å)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ru-P</td>
<td></td>
<td>2.371(2)</td>
<td>2.384(1)</td>
</tr>
<tr>
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<td>2.852(1)</td>
<td>2.8688(8)</td>
<td>2.8762(7)</td>
</tr>
<tr>
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<td>2.8607(8)</td>
<td>2.8646(9)</td>
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<td>Ru1-Ru3</td>
<td>2.860(1)</td>
<td>2.8900(7)</td>
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<tr>
<td>(&lt;\text{Ru-CO}(\text{ax})&gt;^a)</td>
<td>1.942</td>
<td>1.937</td>
<td>1.934</td>
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<tr>
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<td>(&lt;\text{Cr-Bz}&gt;)</td>
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<td>1.406</td>
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<tr>
<td>Selected bond angles (°)</td>
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<td></td>
<td></td>
</tr>
<tr>
<td>Ru1-Ru2-Ru3</td>
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<td>60.58(2)</td>
<td>61.28(2)</td>
</tr>
<tr>
<td>Ru2-Ru1-Ru3</td>
<td>59.92(1)</td>
<td>59.57(2)</td>
<td>59.17(2)</td>
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<td>59.90(1)</td>
<td>59.85(2)</td>
<td>59.56(2)</td>
</tr>
</tbody>
</table>

\( ^a \): here and elsewhere in this chapter bracket \(< >\) refers to the mean value
Figure 4.2 Molecular structure of $\text{Ru}_3(\text{CO})_{11}[\text{Ph}_2\text{PC}_6\text{H}_5\text{Cr(}\text{CO})_3] (4e)$
Figure 4.3 Molecular structure of $\text{Ru}_3(\text{CO})_{11}[\text{Pr}_2\text{PC}_6\text{H}_5\text{Cr(CO)}_3](4c)$
The Ru-P distance in (4c) (2.384 Å) is longer than that in (4e) (2.371 Å) by 0.01 Å, although both fall in the range 2.24 to 2.43 Å reported by Bruce [32]. It has also been reported that the Ru-P distance increases with increasing cone angle of the P-ligand [31, 32]. The present results are consistent with this trend.

The axial Ru-CO and equatorial Ru-CO distances in (4e) vary from 1.928(7) to 1.957(7) Å and from 1.886(7) to 1.919(7) Å respectively. Those in (4c) vary from 1.914(5) to 1.952(6) Å and from 1.864(5) to 1.919(6) Å respectively. The axial Ru-CO distances in both complexes are longer than the equatorial Ru-CO distances due to the mutual trans influence of the axial carbonyls. Notably, distances of Ru-00(eq) attached to the Ru1, 1.886(7) Å in (4e) and 1.864(5) Å in (4c), are the shortest among Ru-00(eq) distances of these two complexes, presumably reflecting a degree of increased back-bonding resulting from the presence of the phosphine ligand on the same ruthenium atom. The equatorial Ru-C-O moieties are all close to linear with a mean value of 177°. In contrast to this, the axial Ru-C-O moieties are distorted from linearity by 7° (mean value 173°). These values are similar to those found in Ru₃(CO)₁₂.

4.3.2 Molecular Structure of Ru₃(CO)₁₀[Prᴵ₂P(C₆H₅Cr(CO)₃)]₂ (4d)

Many phosphine complexes of the class M₃(CO)₁₀L₂ (M = Ru, Os, L = phosphine ligand) are known and some have been characterized on the basis of X-ray analysis. Only three types of structural isomers have been found in previously characterized di-substituted complexes M₃(CO)₁₀L₂, I, as shown in Figure 4.4.
In the 1,1-isomer, Ia, two ligands coordinate at equatorial sites at the same metal atom [33]. In cis-1,2-isomer, Ib, two ligands occupy equatorial positions at adjacent Ru atoms in an unsymmetric(trans, cis) arrangement [34]. The cis-1,2-isomer was first revealed by NMR spectroscopic studies for 1,2-Os3(CO)10(PEt3)2 [34] and it was confirmed later by X-ray crystallographic studies of Os3(CO)10(PPhFc2)2 [35]. The cis-1,2-isomer was also found in heterometal cluster complexes such as (OC)5W[Os(CO)3(PMe3)]2 [36]. This phenomenon has been attributed both to the electronic and steric effects [35]. A large number of M3(CO)10L2 compounds belong to the Ic geometry in which two ligands lie in equatorial positions at opposite ends of the M-M vector so as to minimize steric interactions between the two ligands [37].

The disubstituted ruthenium cluster Ru3(CO)10[Pr(\text{C}6\text{H}5\text{Cr(CO)}3)]2 (4d) has been crystallographically characterized. Figure 4.5 shows the structure of (4d) and the atom numbering scheme, while Table 4.4 (see p88) contains selected bond length data.

Figure 4.4 Three known structural isomers for M3(CO)10L2
The complex (4d) crystallizes as a 1:1 dichloromethane solvate; however, there are no close contacts between the dichloromethane molecule and (4d), therefore,
dichloromethane is not shown in the crystal structure. The molecule consists of an equilateral triangle of Ru₃ atoms with the two phosphine ligands occupying equatorial positions at opposite ends of one of the Ru-Ru bonds. In (4d), the three Ru-Ru bond distances (mean value 2.8922 Å) are basically the same within experimental error. This is in contrast to the monosubstituted complexes (4e) and (4c), in which there are significant differences in the three Ru-Ru separations with the Ru-Ru bond cis to the phosphine ligand being the longest. Furthermore, this is different from disubstituted complexes reported in the literature [35, 37], in which the frame of M₃ is an isosceles triangle. The average Ru-Ru bond distance in (4d) is longer than that in the parent carbonyl (mean 2.854 Å) by 0.04 Å and is also slightly longer than that in the monosubstituted complex (4c) (mean 2.8888 Å). The Ru-P bond distance at 2.384(1) Å is similar to that found in (4c). The two phosphine ligands are distorted slightly towards one side of the Ru₃ plane (-0.1838 Å).

Table 4.4 Summary of bond parameters of Ru₃(CO)₁₀[Pr₂P(C₆H₅Cr(CO)₃)]₂ (4d)

<table>
<thead>
<tr>
<th>Bond</th>
<th>Length (Å)</th>
<th>Bond</th>
<th>Length (Å)</th>
</tr>
</thead>
<tbody>
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<td>Ru1-Ru1*</td>
<td>2.8914(8)</td>
<td>Ru1-Ru2</td>
<td>2.8930(6)</td>
</tr>
<tr>
<td>Ru1-C1(eq)</td>
<td>1.872(5)</td>
<td>Ru1-C2(ax)</td>
<td>1.912(5)</td>
</tr>
<tr>
<td>Ru1-C3(ax)</td>
<td>1.944(5)</td>
<td>Ru2-C4(eq)</td>
<td>1.911(5)</td>
</tr>
<tr>
<td>Ru2-C5(ax)</td>
<td>1.938(6)</td>
<td>Ru-P</td>
<td>2.384(1)</td>
</tr>
<tr>
<td>&lt;P-C&gt;</td>
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<td>&lt;C≡O&gt;</td>
<td>1.140</td>
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<tr>
<td>&lt;Cr-C₆H₅&gt;</td>
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<td>&lt;Cr-CO&gt;</td>
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<tr>
<td>&lt;C-C(η₆-Ph)&gt;</td>
<td>1.41</td>
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In (4d) the introduction of the two phosphine ligands has resulted in a considerable degree of twisting of the RuL₄ units about the Ru-Ru bonds. Unlike the monosubstituted complexes, all equatorial carbonyls significantly bend away from the Ru₃ plane; CO(1) and
CO(4) lie on opposite sides of the Ru₃ plane by 0.7324 Å and 0.6385 Å respectively. As a result, all the axial carbonyls are also distorted from their idealized positions. Therefore, there are no pronounced differences in the bond distances between axial carbonyls and equatorial carbonyls (mean 1.926 Å), except that the pseudoequatorial Ru-CO(1) bond at the substituted ruthenium atom is the shortest (1.872(5) Å) due to a degree of increased back-bonding resulting from the presence of the phosphine ligand on the same ruthenium atom.

4.3.3 Molecular Structure of Os₃(CO)₉[Et₂PC₆H₅Cr(CO)₃]₃ (5h)

The molecular structure of (5h) has been determined by the single-crystal X-ray diffraction method. The relevant bond distances and angles are tabulated in Table 4.5. An ORTEP drawing of (5h) is illustrated in Figure 4.6.

<table>
<thead>
<tr>
<th>Bond</th>
<th>Length (Å)</th>
<th>Bond</th>
<th>Length (Å)</th>
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</thead>
<tbody>
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</tr>
<tr>
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<tr>
<td>Os-P</td>
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<tr>
<td>&lt;Cr-CO&gt;</td>
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<td>Cr-Bz</td>
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</table>

Table 4.5 Summary of bond parameters of Os₃(CO)₉[Et₂PC₆H₅Cr(CO)₃]₃ (5h)

Selected bond angle (°)

- Os1-C11-O1 173.5(4)   Os1-C12-O2 175.8(4)
- Os1-C13-O3 173.9(4)   <Cr-C-O> 177.9
Figure 4.6 ORTEP drawing of $\text{Os}_3(\text{CO})_9[\text{Et}_2\text{PC}_6\text{H}_5\text{Cr}(\text{CO})_3]_3$ (5h)
As a result, the molecule exhibits an exact three-fold symmetry. The molecule has a crystallographic three fold axis. Therefore, the structure contains an equilateral triangular Os₃ core and three phosphine ligands bound one to each osmium atom in pseudo-equatorial sites, putting each phosphine ligand as far away as possible from the other two ligands.

In the parent carbonyl Os₃(CO)₁₂, the average Os-Os bond distance is 2.877 Å [7], one of the three bonds being slightly longer than the other two. However, in the trisubstituted complex (5h), the Os-Os bond distances are identical at 2.9013(3) Å and are longer than those in the parent carbonyl by 0.024 Å. This is consistent with Os₃(CO)₉(PPh₃)₃ in which the average Os-Os bond distance is 2.91 Å, but in contrast to trisubstituted ruthenium clusters in which the average Ru-Ru separation is essentially the same as that found in Ru₃(CO)₁₂ [38].

In (5h) the phosphorus atoms coordinate to Os atoms at pseudo-equatorial sites. They are bent away from the Os₃ plane by 0.523 Å. The Os-P bond at 2.344(1) Å is surprisingly shorter than those found in (4e) (2.371(2) Å) and (4c) (2.384(1) Å). Furthermore, it is of interest to note that the three phosphorus ligands are severely distorted towards one side of the Os₃ plane by 0.523Å. However, in other trisubstituted complexes reported in the literature, the phosphine ligands are arranged in such a way that one lies below the M₃ plane, while the other two lie above it [38]. Furthermore, this distortion is much larger than that in (4d).

As found in mono- and di-substituted complexes, M-CO(eq) bond distances are shorter than the M-CO(ax) bond distances. Thus, Os-C11 bond length is 1.884(5) Å, while Os₁-C12 and Os₁-C13 bond lengths are 1.954(5) and 1.918(5) Å, respectively. In (5h), both the Os-C-O(eq) and Os-C-O (ax) moieties are not linear (mean 174.4°). However, in the parent carbonyl the equatorial Os-CO bond angles are close to linear (mean 178.4°).
while the axial Os-C-O bond angles are distorted from linearity (mean 175.3°) [7]. The equatorial carbonyls in (5h) do not lie in the Os₃ plane, but bend away from the plane by 0.617 Å.

The benzenechromium tricarbonyl moiety in (5h) has some structural features in common with its parent molecule C₆H₆Cr(CO)₃. Both adopt a staggered conformation. Cr-C1 distance at 2.263(4) Å in (5h) is longer than the other five Cr-C(arene) bond distances (2.207 to 2.233 Å). However, the average Cr-C(arene) bond distance (2.224 Å) in (5h) is similar to that (2.229 Å) found in the parent molecule. In addition, the average Cr-CO (1.842 Å) distance compares well with the corresponding value (1.844 Å) of the parent molecule [39]. The cis and trans bonds of the arene in (5h) do not differ significantly (mean 1.407 Å), while in C₆H₆Cr(CO)₃, the cis bonds at 1.423 Å are slightly longer than the trans bonds (1.406 Å) [39].

Structural studies have been made on a wide range of derivatives of Ru₃(CO)₁₂ of formula Ru₃(CO)₁₂₋ₙLₙ (n = 1 to 4) where L is a monodentate ligand [38], and some general trends have emerged; those of relevance to the structures of (4c), (4e), (4d), and (5h) are as follows: (i) Phosphine ligands coordinate at equatorial sites. (ii) In di- and tri-substituted complexes, the phosphine ligands occupy the sterically least demanding sites. (iii) Introduction of the phosphine ligands results in a lengthening of the M-M bonds. For Ru₃(CO)₁₁L complexes, the Ru-Ru bond cis to the ligand L is the longest of the three separations.
4.4 Spectroscopic Properties of Ruthenium and Osmium Clusters Containing Benzenechromium Tricarbonyl Ligands

(a) Infrared Spectroscopy

The carbonyl region (2200-1700 cm\(^{-1}\)) of the infrared spectra are very useful as a quick means of identifying the degree of substitution in the clusters. It is worthwhile to note that the chromium tricarbonyl frequencies also fall in this region, between 1860-1980 cm\(^{-1}\). Figure 4.7 shows three IR spectra of the complexes Os\(_3\)(CO)\(_{12-n}\)Ln (n = 1, 2, 3) where L = Et\(_2\)PC\(_6\)H\(_5\)Cr(CO)\(_3\).

![Figure 4.7 Typical IR spectra v(CO). a. Os\(_3\)(CO)\(_{11}\)L. b. Os\(_3\)(CO)\(_{10}\)L\(_2\). c. Os\(_3\)(CO)\(_9\)L\(_3\). L = Et\(_2\)PC\(_6\)H\(_5\)Cr(CO)\(_3\).](image)
For the monosubstituted complex, the carbonyl frequencies vary from 1850 to 2100 cm\(^{-1}\). There are six strong bands between 1880 and 2060 cm\(^{-1}\), together with a medium absorption at 2100 cm\(^{-1}\) which is typical for the monosubstituted complexes. The spectrum of the disubstituted complex shows two major bands (1890 (br) and 1980 (br) cm\(^{-1}\)) and one medium band at 2075 cm\(^{-1}\) which is lower than that in the monosubstituted complex by about 25 cm\(^{-1}\). In the trisubstituted complex the higher energy band (> 2000 cm\(^{-1}\)) is absent, while two main bands lie between 1880 and 1970 cm\(^{-1}\). None of the complexes exhibited any bands in the bridging carbonyl region (1800-1860 cm\(^{-1}\)).

(b) Mass Spectroscopy

Fast atom bombardment (FAB) mass spectra of these complexes give better results than electron impact spectra in which the complexes fragment and no parent peaks can be detected. In the present work all the complexes were characterized by the FAB method. The spectra clearly show the strong parent peaks. The monosubstituted complexes lose three carbonyls first [P-3CO]\(^+\) and then subsequent stepwise loss of the rest of carbonyl groups. The di- and tri-substituted complexes first lose five carbonyls [P-5CO]\(^+\) and then lose the rest of the carbonyls in a stepwise manner.

(c) NMR spectroscopy

The \(^{31}\text{P}\) NMR spectra of substituted Ru\(_3\) clusters (4) show singlets which vary in chemical shift from 28 to 95 ppm. The chemical shift of Ru\(_3\)(CO)\(_{11}\)[Et\(_2\)PC\(_6\)H\(_5\)Cr(CO)\(_3\)] at 28.2 ppm is the lowest and Ru\(_3\)(CO)\(_{11}\)[Bu\(_2\)PC\(_6\)H\(_5\)Cr(CO)\(_3\)] at 94.3 ppm is the highest. The change in the \(^{31}\text{P}\) NMR chemical shift of the benzenechromium tricarbonyl phosphines upon coordination to the Ru\(_3\) cluster is in the range of 41 to 52 ppm downfield. Singlet resonances are also observed between -16 and 28 ppm in the \(^{31}\text{P}\) NMR spectra of substituted Os\(_3\) clusters (5). The complex Os\(_3\)(CO)\(_9\)[Et\(_2\)PC\(_6\)H\(_5\)Cr(CO)\(_3\)]\(_3\) (5h) has the lowest chemical shift at -15.9 ppm, while the complex Os\(_3\)(CO)\(_{11}\)[Pr\(_2\)PC\(_6\)H\(_5\)Cr(CO)\(_3\)]
(5e) has the highest chemical shift at 27.8 ppm. The chemical shifts of (5a) to (5k) generally change from 4 to 14 ppm downfield compared with the corresponding free ligand, except for the complex Os$_3$(CO)$_9$[Et$_2$PC$_6$H$_5$Cr(CO)$_3$]$_3$ where the chemical shift changes 2 ppm upfield.

The $^1$H NMR spectra of the triruthenium clusters (4) and triosmium clusters (5) are similar to those of the free ligands. In some cases, the resonances are shifted to downfield and the splitting patterns are different. For example, the $\eta^6$-phenyl proton resonances for (4c), (4d), (5c) and (5d) are at 5.7 and 5.2 ppm compared to 5.3 and 5.2 ppm in PPr$_i^1$C$_6$H$_5$Cr(CO)$_3$. Similar resonances for (4g), (4h), (5f) and (5g) vary between 5.6 and 5.2 ppm, compared to 5.4 and 5.2 ppm in PEt$_2$C$_6$H$_5$Cr(CO)$_3$.

### 4.5 Summary and Future Considerations

The reactions of the phosphino- and arsinobenzenechromium tricarbonyl ligands with the metal clusters, Ru$_3$(CO)$_{12}$ or Os$_3$(CO)$_{12}$, have been investigated. Twenty mono-, di- and tri-substituted complexes were prepared and characterized by spectroscopic and microanalytical techniques. Generally, the complexes of M$_3$(CO)$_{12-n}$[ER$_2$C$_6$H$_5$Cr(CO)$_3$]$_n$ (M = Ru, Os; n = 1, 2; ER = AsMe, PEt, PPr$_i$, PPh) can be prepared in high yields under mild reaction conditions. The reactions of the ligand type Pr[C$_6$H$_5$Cr(CO)$_3$]$_2$ (R = Ph, Bu$^t$) with M$_3$(CO)$_{12}$ (M = Ru, Os) only afford low yields of the desired products due to the steric bulk and electron-withdrawing properties of the ligands. The structures of four of the substitution complexes were determined by X-ray crystallographic studies. These are the first structures of the metal carbonyl clusters containing benzenechromium tricarbonyl ligands to be characterized by X-ray diffraction analysis. Some general trends of the structural features in these complexes are as follows: (i) P-ligands coordinate at equatorial sites, (ii) for Ru$_3$(CO)$_{11}$L complexes the Ru-Ru bond cis to the P-ligand is the longest of
the three separations, and (iii) bonds from axial CO groups to Ru are generally longer than those from equatorial CO groups.

In order to systematically study their spectroscopic and structural properties, more triruthenium and triosmium clusters containing phosphino- and arsinobenzenechromium tricarbonyl ligands should be synthesized and characterized by spectroscopic and X-ray crystallographic methods. Furthermore, a mechanistic study on the substitution reactions of \( M_3(CO)_{12} \) (\( M = \text{Ru, Os} \)) with phosphino- and arsinobenzene chromium tricarbonyl ligands may be of interest as well.

### 4.6 Experimental Procedures

#### 4.6.1 Preparation of \( \text{Ru}_3(CO)_{11}[\text{AsMe}_2(C_6H_5Cr(CO)_3)] \) (4a)

A freshly prepared Na(Ph\(_2\)CO) solution was added dropwise to a rapidly stirred solution of \( \text{Ru}_3(CO)_{12} \) (200 mg, 0.31 mmol) and (CH\(_3\))\(_2\)As[C\(_6\)H\(_5\)Cr(CO)\(_3\)] (100 mg, 0.31 mmol) in THF (25 mL) until the solution darkened in color (typically 5 to 10 drops). When TLC examination of the reaction mixture showed that no starting material remained, the solvent was removed in vacuo. The resulting dark red oil was dissolved in CH\(_2\)Cl\(_2\) (3 mL) and was chromatographed on a silica gel column with CH\(_2\)Cl\(_2\)/hexanes (1:1.4) as eluent to give three bands. Band 1 (yellow) was \( \text{Ru}_3(CO)_{12} \) (trace amount) identified by IR spectroscopy and TLC. Band 3 was the disubstituted ruthenium cluster \( \text{Ru}_3(CO)_{10-}[\text{AsMe}_2(C_6H_5Cr(CO)_3)]_2 \) (trace amount). Band 2 gave the red crystalline \( \text{Ru}_3(CO)_{11}\text{AsMe}_2[C_6H_5Cr(CO)_3] \) compound (245 mg, 85% yield). Mass spectrum (FAB): \( m/e \) 931 [\( \text{Ru}_3\text{CO}_{14-}\text{AsMe}_2\text{C}_6\text{H}_5\text{Cr(CO)}_3 \)]\(^+\). \(^1\)H NMR (300 MHz, CDCl\(_3\)) \( \delta \): 1.9 (s, 6H), 5.3 (t, \( J(\text{H-H}) = 6.6 \text{ Hz} \), 2H), 5.4 (d, \( J(\text{H-H}) = 6 \text{ Hz} \), 2H), 5.6 (t, \( J(\text{H-H}) = 6.6 \text{ Hz} \), 1H). IR (KBr) \( \nu(\text{CO}) \): 2100 (m), 2040 (s), 2020 (s), 1970 (s), 1890 (sh), 1900 (s) cm\(^{-1}\). Anal. Calcd for \( \text{C}_{22}\text{H}_{11}\text{AsCrO}_{14-}\text{Ru}_3 \): C, 28.43; H, 1.20. Found: C, 28.14; H, 1.23.
4.6.2 Preparation of Ru$_3$(CO)$_{10}$[AsMe$_2$(C$_6$H$_5$Cr(CO)$_3$)]$_2$ (4b)

The title compound was prepared in a way similar to that used for the monosubstituted compound (4a) except that a little over 2 equivalents of the ligand Me$_2$AsC$_6$H$_5$Cr(CO)$_3$ (210 mg, 0.62 mmol) was used. The product was purified by column chromatography with CH$_2$Cl$_2$/hexanes (1/1) and was isolated in 70% yield. Mass spectrum (FAB): m/e 1223 [P$^+$.] $^1$H NMR (300 MHz, CDCl$_3$) δ: 5.5 (t, J(H-H) = 6 Hz, 2H), 5.4 (d, J(H-H) = 6.3 Hz, 4H), 5.2 (m, 4H), 2.0 (s, 12H). Anal. Calcd for C$_{32}$H$_{22}$As$_2$Cr$_2$O$_{16}$Ru$_3$: C, 31.51; H, 1.82. Found: C, 31.29; H, 1.93.

4.6.3 Preparation of Os$_3$(CO)$_{11}$[AsMe$_2$(C$_6$H$_5$Cr(CO)$_3$)] (5a)

The compound [Os$_3$(CO)$_{11}$(MeCN)] (200 mg, 0.22 mmol) was stirred in CH$_2$Cl$_2$ (30 mL) with the ligand [Me$_2$AsC$_6$H$_5$Cr(CO)$_3$] (70 mg, 0.22 mmol) for two hours at room temperature. The solution changed from cloudy light yellow to clear yellow. Silica gel (200-400 mesh, 5 mL) was then added to the crude solution and the solvent was removed in vacuo. The dried residual silica gel was added to the top of a silica gel column. By using CH$_2$Cl$_2$/hexanes (1:1.8) as eluent, the pure yellow compound (5a) was obtained in 90% yield (235 mg) from the first band. Mass spectrum (FAB): m/e 1198 [P$^+$.] $^1$H NMR (300 MHz, CDCl$_3$) δ: 5.5 (t, 1H), 5.4 (d, 2H), 5.2 (t, 2H), 2.0 (s, 6H). Anal. Calcd for C$_{22}$H$_{11}$AsCrO$_{14}$Os$_3$: C, 22.08; H, 0.93. Found: C, 22.16, H, 0.98. The second band which was eluted gave a small amount of the disubstituted cluster derivative identified by using mass spectrometry.

4.6.4 Preparation of Os$_3$(CO)$_{10}$[AsMe$_2$C$_6$H$_5$Cr(CO)$_3$]$_2$ (5b)

The procedure used for the preparation of (5b) was identical to that used for (5a) with the exception that [Os$_3$(CO)$_{10}$(MeCN)$_2$] (100 mg, 0.1 mmol) was used. The pure compound (5b) was thus obtained in 70% yield. Mass spectrum (FAB): m/e 1487 [P$^+$.] $^1$H
NMR (300 MHz, CDCl₃) δ: 5.5 (t, 4H), 5.2 (t, 6H), 1.9 (s, 12H). Anal. Calcd for C₉₂H₄₂As₂Cr₂-O₁₆Os₃: C, 25.85; H, 1.49. Found: C, 25.71; H, 1.57.

4.6.5 Preparation of Ru₃(CO)₁₁[PPr₂C₆H₅Cr(CO)₃] (4c)

Addition of PPN⁺Cl⁻ (10 mg) to a solution of Ru₃(CO)₁₂ (200 mg, 0.31 mmol) and Pr₂PC₆H₅(CO)₃ (103 mg, 0.31 mmol) in THF (40 mL) resulted in gas evolution. After stirring for 30 min., the solvent was removed from the red solution under reduced pressure. The residue was dissolved in CH₂Cl₂ (2 mL) and applied to a silica gel column, with CH₂Cl₂/hexanes (1:1.7) as eluent. The first band was identified, by IR spectroscopy, as the starting material Ru₃(CO)₁₂ and the third band was characterized as Ru₃(CO)₁₀[PPr₂C₆H₅(CO)₃]₂. The major second band was collected, and pure (4c) was obtained as a red powder in 80% yield after solvent evaporation. Crystals of (4c) were grown from CH₂Cl₂/hexanes (1/2.5) at -30 °C. The crystals thus obtained were washed with hexanes and dried in vacuo for 1 min. Mass spectrum (FAB): m/e 942 [P⁺]. ³¹P{¹H} NMR (121.4 MHz, CDCl₃) δ: 58.9 (s). ¹H NMR (300 MHz, CDCl₃) δ: 5.7 (t, J(H-H) = 6.2 Hz, 3H), 5.2 (t, J(H-H) = 6.3 Hz, 2H), 2.5 (m, 2H), 1.2-1.4 (m, 12H). IR (CH₂Cl₂) ν (CO): 2100 (s), 2049 (vs), 2017 (vs), 1978 (vs), 1907 (vs) cm⁻¹. Anal. Calcd for C₂₆H₁₉CrO₁₄PRu₃: C, 33.16; H, 2.03. Found: C, 32.84; H, 1.90.

4.6.6 Preparation of Ru₃(CO)₁₀[PPr₂C₆H₅Cr(CO)₃]₂ (4d)

The title complex was prepared in the same manner as described for the preparation of the monosubstituted cluster (4c), except that a little over 2 molar equivalents of the ligand [Pr₂PC₆H₅Cr(CO)₃] (215 mg, 0.65 mmol) was used. Following chromatography with CH₂Cl₂/hexanes (1:1.3) as eluent, pure (4d) was obtained in 70% yield as a dark red powder. X-ray-quality crystals were grown from CH₂Cl₂/hexanes (1/2.5) at -4 °C. Mass spectrum (FAB): m/e 1244 [P⁺]. ³¹P{¹H} NMR (121.4 MHz, CDCl₃) δ: 54.6 (s). ¹H NMR (300 MHz, CDCl₃) δ: 5.75 (t, 6H), 5.2 (t, J(H-H) = 6.3 Hz, 4H), 2.5 (m, J(H-H) =
6.1 Hz, 4H), 1.2-1.4 (m, 24H). IR (KBr) ν(CO): 2022 (s), 1973 (vs), 1903 (vs) cm⁻¹. Anal.
Calcd for C₄₁H₄₀Cl₂Cr₂O₁₆P₂Ru₃: C, 37.06; H, 3.04. Found: C, 37.03; H, 2.97.

4.6.7 Preparation of Os₃(CO)₁₁[PPr²_i₂{C₆H₅Cr(CO)₃}] (5c)

A solution of [Os₃(CO)₁₁(MeCN)] (200 mg, 0.22 mmol) and PPr²_i₂[Cr(CO)₃]
(76 mg, 0.23 mmol) in dichloromethane (40 mL) was stirred at room temperature for three
hours, after which time TLC showed no starting material left. A small amount of silica gel
(5 mL) was added to the crude solution. Then the solvent was evaporated to dryness under
reduced pressure. The yellow residue was separated by column chromatography with eluent
CH₂Cl₂/hexanes (1:1.7). Removal of the eluent in vacuo afforded the yellow product (5c)
in 80% yield. Mass spectrum (FAB): m/e 1209 [P⁺]. ³¹P {¹H} NMR (121.4 MHz, CDCl₃)
δ: 27.8 (s). ¹H NMR (300 MHz, CDCl₃) δ: 5.7 (t, 3H), 5.2 (t, 2H), 2.5 (m, 2H), 1.2-1.4
(m, 12H). IR (KBr) ν(CO): 2100 (w), 2050 (s), 2030-2000 (vs, br), 1990-1960 (vs, br),
1940 (w), 1910 (s), 1890 (s) cm⁻¹. Anal. Calcd for C₂₆H₁₉CrO₁₄Os₃P: C, 25.83; H, 1.59.
Found: C, 25.89; H, 1.59.

4.6.8 Preparation of Os₃(CO)₁₀[PPr²_i₂C₆H₅Cr(CO)₃]₂ (5d)

A solution of [Os₃(CO)₁₀(MeCN)₂] (200 mg, 0.32 mmol) in dichloromethane was
slowly added to a solution of the ligand Pr²_i₂PC₆H₅Cr(CO)₃ (215 mg, 0.65 mmol). The
reaction mixture was stirred for three hours at room temperature after which time the
solvent was removed in vacuo to leave a yellow solid. This was purified by using silica gel
column chromatography with CH₂Cl₂/hexanes (1:1.2) as eluent, affording the yellow
powder (5d) (380 mg) in 80% yield after removal of solvents. Mass spectrum (FAB): m/e
1513 [P⁺]. ³¹P {¹H} NMR (121.4 MHz, CDCl₃) δ: 21.7 (s). ¹H NMR (300 MHz, CDCl₃)
δ: 5.7 (t, 6H), 5.2 (t, 4H), 2.4 (m, 4H), 1.1-1.4 (m, 24H). IR (KBr): ν(CO) 2080 (m), 2010
(sh), 2000 (vs), 1970 (vs), 1900 (s, br). Anal. Calcd for C₄₀H₃₈Cr₂O₁₆Os₃P₂: C, 31.79;
H, 2.54. Found: C, 31.63; H, 2.50.
4.6.9 Preparation of Ru$_3$(CO)$_{11}$[Ph$_2$PC$_6$H$_5$Cr(CO)$_3$] (4e)

A mixture of Ru$_3$(CO)$_{12}$ (200 mg, 0.31 mmol) and diphenyl(η$_6$-phenylchromium tricarbonyl)phosphine (125 mg, 0.31 mmol) in THF (40 mL) was treated with 10 drops of BPK solution at room temperature. The solution turned dark red instantly. The progress of the reaction was monitored by using TLC. After one hour, the solvent was removed \textit{in vacuo} and the residue was chromatographed on a silica gel column with CH$_2$Cl$_2$/hexanes (1:1.6) to afford three bands. Traces of unreacted Ru$_3$(CO)$_{12}$ were eluted first, followed by the complex (4e). The last band gave a small amount of the disubstituted cluster (4f). The complex (4e) was isolated in ca. 70% yield as a red powder. This powder was dissolved in CH$_2$Cl$_2$ (10 mL), layered with hexanes (20 mL), and stored in the freezer for a week to give red-orange prism-like crystals. Mass spectrum (FAB): $m/e$ 1011 [P$^+$]. $^{31}$P-$^1$H NMR (121.4 MHz, CDCl$_3$) $\delta$: 37.3 (s). $^1$H NMR (300 MHz, CDCl$_3$) $\delta$: 7.4-7.6 (br s, 10H), 5.6 (t, J(H-H) = 6 Hz, 3H), 5.1 (t, J(H-H) = 6 Hz, 2H). IR (Nujol) $\nu$(CO): 2100 (s), 2060 (sh), 2040 (s), 2020 (vs), 2000 (vs), 1970 (vs), 1960 (sh), 1900 (s) cm$^{-1}$. Anal. Calcd for C$_{32}$H$_{15}$CrO$_{14}$PRu$_3$: C, 38.07; H, 1.50. Found: C, 38.21; H, 1.55.

4.6.10 Ru$_3$(CO)$_{10}$[Ph$_2$PC$_6$H$_5$Cr(CO)$_3$]$_2$ (4f)

The same procedure was followed as for the above complex (4e) except that 2 molar equivalents of diphenylphenylchromium tricarbonyl phosphine (250 mg, 0.62 mmol) were used. The title compound was isolated in 60% yield. Mass spectrum (FAB): $m/e$ 1381 [P$^+$]. $^{31}$P-$^1$H NMR (121.4 MHz, CDCl$_3$) $\delta$: 36.5 (s). $^1$H NMR (300 MHz, CDCl$_3$) $\delta$: 7.4-7.6 (br s, 5H), 5.5 (t, 6H), 5.1 (t, 4H). Anal. Calcd for C$_{52}$H$_{30}$Cr$_2$O$_{16}$P$_2$Ru$_3$: C, 45.26; H, 2.20. Found: C: 45.39; H, 2.28.
4.6.11 Preparation of Os₃(CO)₁₁[Ph₂PC₆H₅Cr(CO)₃] (5e)

The ligand Ph₂PC₆H₅Cr(CO)₃ (135 mg, 0.34 mmol) in CH₂Cl₂ was added to a solution of Os₃(CO)₁₁(MeCN) (300 mg, 0.33 mmol) in CH₂Cl₂ (30 mL) at room temperature. The resulting mixture was stirred for three hours. The solvent was removed in vacuo, and the crude product was subjected to column chromatography (silica gel, CH₂Cl₂/hexanes, 1:1.6), affording the yellow product (5e) in 80% yield. Mass spectrum (FAB): m/e 1277 [P⁺]. ³¹P{¹H} NMR (121.4 MHz, CD₂Cl₂) δ: 0.3 (s). ¹H NMR (300 MHz, CD₂Cl₂) δ: 7.5 (m, 10H), 5.8 (td, J(H-H) = 5.8 Hz, 1H), 5.6 (td, J(H-H) = 5.7 Hz, 2H), 5.2 (td, J(H-H) = 5.8 Hz, 2H). IR (KBr): ν(CO) 2150 (s), 2060 (vs), 2020 (vs), 2000 (vs), 1970 (vs), 1900 (vs) cm⁻¹. Anal. Calcd for C₃₂H₁₅CrO₁₄Os₃P: C, 30.07; H, 1.19. Found: C, 30.15; H, 1.23.

4.6.12 Preparation of Ru₃(CO)₁₁[Et₂PC₆H₅Cr(CO)₃] (4g)

Addition of 5 drops of initiator (BPK) solution to a mixture of Ru₃(CO)₁₂ (100 mg, 0.16 mmol) and Et₂PC₆H₅Cr(CO)₃ (50 mg, 0.17 mmol) in THF (20 mL) was sufficient to complete the reaction at room temperature. After stirring for one hour, the solvent was removed from a dark red solution under reduced pressure. Column chromatography of the residue (silica gel, CH₂Cl₂/hexanes, 1/1.6) eluted one major band which gave a red powder (4g) in 85% yield after removal of the solvent. Mass spectrum (FAB): m/e 915 [P⁺]. ³¹P{¹H} NMR (121.4 MHz, CDCl₃) δ: 28.2 (s). ¹H NMR (300 MHz, CDCl₃) δ: 5.5 (td, J(H-H) = 7 Hz, 1H), 5.3 (td, J(H-H) = 7 Hz, 2H), 5.2 (2dd, J(H-H) = 7 Hz, 2H), 2.0-2.4 (m, 4H), 1.2-1.4 (2t, J(H-H) = 7 Hz, 6H). IR (KBr): 2100 (s), 2040 (s), 2020 (s), 1980 (vs), 1970 (vs), 1950 (s), 1900 (s), 1870 (s) cm⁻¹. Anal. Calcd for C₂₄H₁₅CrO₁₄PRu₃: C, 31.55; H, 1.66. Found: C, 31.47; H, 1.66.
4.6.13 Preparation of $\text{Ru}_3(\text{CO})_{10}\{\text{Et}_2\text{PC}_6\text{H}_5\text{Cr(} \text{CO})_3\}_2$ (4h)

The preparation of (4h) was analogous to that of the monosubstituted cluster (4g) with the exception that a little over 2 molar equivalents of the ligand $\text{Et}_2\text{PC}_6\text{H}_5\text{Cr(} \text{CO})_3$ (105 mg, 0.35 mmol) were used. The dark red product (4h) was isolated in 75% yield. Mass spectrum (FAB): $m/e$ 1189 [Pt$^+$. $^{31}$P{1H} NMR (121.4 MHz, CDCl$_3$) δ: 28.4 (s). $^1$H NMR (300 MHz, CDCl$_3$) δ: 5.6 (t, $J(\text{H-H}) = 7$ Hz, 1H), 5.4 (t, $J(\text{H-H}) = 7$ Hz, 2H), 5.2 (d, $J(\text{H-H}) = 7$ Hz, 2H), 2.0-2.4 (m, 8H), 1.2-1.5 (2t, $J(\text{H-H}) = 7$ Hz, 12H). IR (KBr) v(CO): 2070 (w), 2020 (s), 2000-1910 (s, br), 1910-1880 (s, br), cm$^{-1}$. Anal. Calcd for $\text{C}_38\text{H}_{32}\text{Cl}_2\text{Cr}_2\text{O}_{16}\text{P}_2\text{Ru}_3$: C, 34.91; H, 2.54. Found: 34.74; H, 2.59.

4.6.14 Preparation of $\text{Os}_3(\text{CO})_{11}\{\text{Et}_2\text{PC}_6\text{H}_5\text{Cr(} \text{CO})_3\}_1$ (5f)

The compound $[\text{Os}_3(\text{CO})_{11}(\text{MeCN})]$ (200 mg, 0.22 mmol) was stirred with 1 molar equivalent of $[\text{Et}_2\text{PC}_6\text{H}_5\text{Cr(} \text{CO})_3]$ (65 mg, 0.22 mmol) in CH$_2$Cl$_2$ (20 mL) at room temperature until TLC indicated the disappearance of the starting material. Evaporation of the solvent followed by separation on a silica gel column eluted with CH$_2$Cl$_2$/hexanes (1/1.7) afforded the yellow product in 80% yield. Mass spectrum (FAB): $m/e$ 1182 [Pt$^+$. $^{31}$P{1H} NMR (121.4 MHz, CDCl$_3$) δ: -9.1 (s). $^1$H NMR (300 MHz, CDCl$_3$) δ: 5.5 (t, $J(\text{H-H}) = 7$ Hz, 1H), 5.4 (t, $J(\text{H-H}) = 7$ Hz, 2H), 5.2 (d, $J(\text{H-H}) = 7$ Hz, 2H), 2.2-2.4 (m, 4H), 1.2-1.4 (t, $J(\text{H-H}) = 7$ Hz, 6H). IR (KBr) v(CO): 2100 (m), 2060 (s), 2030 (s), 2000 (vs), 1980 (sh), 1970 (vs), 1910 (s), 1900 (sh), 1880(s), 1870 (sh), cm$^{-1}$. Anal. Calcd for $\text{C}_{24}\text{H}_{15}\text{CrO}_{14}\text{Os}_3\text{P}$: C, 24.40; H, 1.28. Found: C, 24.56; H, 1.31.

4.6.15 Preparation of $\text{Os}_3(\text{CO})_{10}[\text{Et}_2\text{PC}_6\text{H}_5\text{Cr(} \text{CO})_3]_2$ (5g)

The preparation of (5g) was identical to the preparation of (5f) except that $\text{Os}_3(\text{CO})_{10}(\text{MeCN})_2$ (100 mg, 0.11 mmol) and $\text{Et}_2\text{PC}_6\text{H}_5\text{Cr(} \text{CO})_3$ (70 mg, 0.23 mmol) was used. The yellow product was obtained in 70% yield. Mass spectrum (FAB): $m/e$ 1456
4.6.16 Preparation of Os₃(CO)⁹[Et₂PC₆H₅Cr(CO)₃]₃ (5h)

A solution of Os₃(CO)₁₁[Et₂PC₆H₅Cr(CO)₃] (300 mg) was heated in refluxing n-octane under a nitrogen atmosphere for 15 hours. After this time TLC showed that no starting material was present. The solvent was then removed under reduced pressure and the resulting brown oil was transferred to a silica gel column. Elution with hexane gave one yellow band which was Os₃(CO)₁₂, identified by IR spectroscopy. Subsequent elution with hexanes/CH₂Cl₂ (1:1.7) afforded three bands. Bands 1 and 3 contained trace amounts of unidentified products. The major band 2 contained the complex (5h). Orange crystals suitable for X-ray structure analysis were grown from hexanes/CH₂Cl₂ (3/1) at -30 °C. Mass spectrum (FAB): m/e 1729 [P⁺]. ³¹P{¹H} NMR (121.4 MHz, CDCl₃) δ: -15.9 (s). ¹H NMR (300 MHz, CDCl₃) δ: 5.6 (t, J(H-H) = 7 Hz, 3H), 5.4 (t, J(H-H) = 7 Hz, 6H), 5.2 (d, J(H-H) = 7 Hz, 6H), 2.0-2.5 (m, 12H), 1.2-1.4 (m, 18H). IR(KBr) ν(CO): 1965 (vs, br), 1930 (s), 1890 (vs, br) cm⁻¹. Anal. Calcd for C₄₈H₄₅Cr₃Os₃P₃: C, 33.33; H, 2.63. Found: C, 32.93; H, 2.62.

4.6.17 Preparation of Ru₃(CO)₁₁[PhP(C₆H₅Cr(CO)₃)]₂ (4i)

The title compound was prepared by three different methods. All gave the product in low yield.

Method A: 20 drops of Na⁺[Ph₂CO]⁻ (0.025 M solution in THF) was added to a solution of Ru₃(CO)₁₂ (240 mg, 0.38 mmol) and PhP[C₆H₅Cr(CO)₃]₂ (200 mg, 0.38
mmol) in THF (30 mL). The solution went red immediately. After stirring for one hour, the solution was refluxed for 10 min. The solvent was then removed, and the residue was separated on a column (silica gel, CH$_2$Cl$_2$/hexanes 1/1.5) to give the yellow product (4i) in 25% yield.

Method B was similar to method A with the exception that PPN$^+$Ac$^-$ (40 mg) was used as an initiator. The yield of product thus obtained was also low (15%).

Method C: An excess of PhP[C$_6$H$_5$Cr(CO)$_3$]$_2$ (200 mg) was added to a cool solution of Ru$_3$(CO)$_{11}$(MeCN) (100 mg, 0.15 mmol, 20 mL of CH$_2$Cl$_2$) generated in situ. The resulting solution was stirred for one hour and the solvent was removed in vacuo. The $^{31}$P NMR spectrum of the crude product indicated the title compound in low yield.

Mass spectrum (FAB): $m/e$ 1147 [P$^+$. $^{31}$P{H} NMR (121.4 MHz, CDCl$_3$) δ: 37.6 (s). $^1$H NMR (300 MHz, CDCl$_3$) δ: 7.4-7.6 (m, 5H), 5.8 (m, 6H), 5.3 (m, 4H), IR(CH$_2$Cl$_2$) v(CO): 2100 (s), 2050 (s), 2040 (s), 1970 (s), 1900 (s) cm$^{-1}$. Anal. Calcd for C$_{35}$H$_{15}$Cr$_2$O$_{17}$PRu$_3$: C, 36.69; H, 1.32. Found: C, 36.65; H, 1.40.

4.6.18 Preparation of Os$_3$(CO)$_{11}$[PhP[C$_6$H$_5$Cr(CO)$_3$]$_2$] (5i)

The compound Os$_3$(CO)$_{11}$(MeCN) (100 mg, 0.11 mmol) was stirred with an excess of PhP[C$_6$H$_5$Cr(CO)$_3$]$_2$ (80 mg) in dichloromethane (20 mL) at room temperature for 20 hours. Evaporation of the solvent followed by separation on a silica gel column eluting with CH$_2$Cl$_2$/hexanes (1/1.6) afforded the yellow product in 50% yield. Mass spectrum (FAB): $m/e$ 1415 [P$^+$. $^{31}$P{H} NMR (121.4 MHz, CDCl$_3$) δ: 0.1 (s). $^1$H NMR (300 MHz, CDCl$_3$) δ: 7.6 (m, 2H), 7.4 (m, 3H), 5.7 (t, 6H), 5.4(q, 4H). Anal. Calcd for C$_{35}$H$_{15}$Cr$_2$O$_{17}$Os$_3$: C, 29.75; H, 1.07. Found: C, 29.50; H, 1.31.
4.6.19 Attempted Preparation of Ru₃(CO)₁₁[PhAs{C₆H₅Cr(CO)₃}₂] (4j)

A mixture of Ru₃(CO)₁₂ (100 mg, 0.15 mmol) and PhAs{C₆H₅Cr(CO)₃}₂ (100 mg, 0.17 mmol) in THF (40 mL) was treated with 20 drops of BPK solution at room temperature. The resulting solution was stirred for one hour and the solution was refluxed for an additional hour. The solvent was then removed. The ¹H NMR spectrum showed no apparent new peaks except the ligand signals.

4.6.20 Attempted Preparation of Ru₃(CO)₁₁[But₂PC₆H₅Cr(CO)₃] (4k)

Addition of Na⁺[Ph₂CO]⁻ (1 mL of a 0.025 M solution in THF) to a solution of Ru₃(CO)₁₂ (150 mg, 0.24 mmol) and excess of But₂P{C₆H₅Cr(CO)₃} (168 mg, 0.47 mmol) in THF (30 mL) resulted in the appearance of a red color. After stirring for 10 hours, the solution was refluxed for an additional hour. The ³¹P NMR spectrum of the residue indicated the compound (4k) formed in very low yield.

In another preparation, the same procedure as above was employed except that the initiator PPN⁺Ac⁻ (20 mg) was used. The ³¹P NMR spectrum of the residue also indicated the title compound in very low yield. Mass spectrum (FAB): m/e, 970 [P⁺]. ³¹P{¹H} NMR (121.4 MHz, CDCl₃) δ: 94.3 (s). ¹H NMR (300 MHz, CDCl₃) δ: 5.6 (t, 3H), 5.05 (t, 2H), 1.5 (d, 18H).

4.6.21 Attempted Preparation of Os₃(CO)₁₁[But₂PC₆H₅Cr(CO)₃] (5j)

The compound Os₃(CO)₁₁(MeCN) (100 mg, 0.11 mmol) was stirred with an excess of But₂P{C₆H₅Cr(CO)₃} (50 mg) in dichloromethane (20 mL) at room temperature for 20 hours. The ³¹P NMR spectrum showed no new peaks except the ligand peak (42.6 ppm).
4.6.22 Attempted Preparation of Ru₃(CO)₁₁[ButP{C₆H₅Cr(CO)₃}₂] (4l)

The initiator Na⁺[Ph₂CO]⁻ (1 mL of a 0.025 M solution in THF) was added to a THF solution of Ru₃(CO)₁₂ (100 mg, 0.15 mmol) and ButP{C₆H₅Cr(CO)₃}₂ (80 mg, 0.16 mmol). After stirring for one hour, there was no new spot on the TLC plate. The solvent was removed in vacuo and the residue was added to heptane (20 mL). The solution was allowed to reflux for two hours. The ⁳¹P NMR spectrum of the resulting solution indicated a very low yield of the title compound. The pure product (4l) was not isolated. ⁳¹P{¹H} NMR (121.4 MHz, CDCl₃) δ: 63 (s).

4.6.23 Attempted Preparation of Os₃(CO)₁₁[ButP{C₆H₅Cr(CO)₃}₂] (5k)

The compound Os₃(CO)₁₁(MeCN) (90 mg, 0.1 mmol) was stirred with an excess of But₂P[C₆H₅Cr(CO)₃] (50 mg) in dichloromethane (20 mL) at room temperature for one day. The solvent was removed in vacuo. The ³¹P NMR spectrum of the residue showed no new peaks; the ligand peak at 20.7 ppm was observed.

4.6.24 Preparation of Ru₃(CO)₁₁[Ph₂AsC₆H₅Cr(CO)₃] (4m)

A mixture of Ru₃(CO)₁₂ (200 mg, 0.32 mmol) and Ph₂As[C₆H₅Cr(CO)₃] (140 mg, 0.32 mmol) in THF (40 mL) was treated with 20 drops of BPK solution at room temperature. The resulting solution was stirred for one hour. Evaporation of the solvent followed by separation on a silica gel column eluting with CH₂Cl₂/hexanes (1:1.6) afforded the red product in 10% yield. Mass spectrum (FAB): m/e 1054 [P⁺]. ¹H NMR (300 MHz, CDCl₃) δ: 7.3 (m, 10H), 5.3 (t, 2H), 5.1 (3H). Anal. Calcd for C₃₂H₁₅AsCrO₁₄Ru₃: C, 36.48; H, 1.44. Found: C, 36.64; H, 1.56.

References


CHAPTER 5

Thermolysis of Trinuclear Metal Clusters Containing Benzenechromium Tricarbonyls

One purpose of the present investigation was to establish if complexes containing benzenechromium tricarbonyl could be synthesized. Two different strategies have been employed to prepare these aryne metal clusters. One method involves thermolysis of Os$_3$(CO)$_{12}$ or Ru$_3$(CO)$_{12}$ derivatives containing the ligand R$_2$P[C$_6$H$_5$Cr(CO)$_3$] which can be synthesized in high yield. The other method involves thermolysis of a mixture of Os$_3$(CO)$_{12}$ or Ru$_3$(CO)$_{12}$ and the free ligand RP[C$_6$H$_5$Cr(CO)$_3$]$_2$. Generally, thermolytic reactions for ruthenium cluster derivatives are carried out in refluxing cyclohexane or heptane solvent and the reactions for osmium cluster derivatives in refluxing octane. The thermolytic reactions however often produce intractable brown solids from which no isolable compounds can be obtained.

5.1 Thermolysis of Trinuclear Metal Clusters Containing C$_6$H$_5$Cr(CO)$_3$

5.1.1 Thermolysis of Ru$_3$(CO)$_{11}$(Ph$_2$PC$_6$H$_5$Cr(CO)$_3$) (1)

The starting material (1) is stable in refluxing 1:1 cyclohexane/heptane for two hours. The complex decomposed smoothly in refluxing heptane to afford three major compounds (2) (two doublets), (3) (237.3 ppm) and (4) (242.7 ppm), together with a small amount of Ru$_3$(CO)$_{12}$ as shown by TLC and/or the $^{31}$P NMR spectrum of the reaction mixture (Figure 5.1). Refluxing a heptane solution of PPh$_2$C$_6$H$_5$Cr(CO)$_3$ and Ru$_3$(CO)$_{12}$, in a 2:1 molar ratio, for ten hours, gave the same major products (2), (3) and (4). Complex (2) can be obtained in better yield by the thermal decomposition of
Ru$_3$(CO)$_{10}$[PPh$_2$C$_6$H$_5$Cr(CO)$_3$]$_2$ in heptane. The characterization of complexes (2) and (3) is described below. Complex (4) decomposed on column chromatography.

(a) Characterization of Complex (2)

The fast atom bombardment (FAB) mass spectrum of (2) is informative; it shows a strong parent peak at $m/e$ 1216, which fragments by stepwise loss of thirteen carbonyl groups. The solid state infrared spectrum shows vibrations in the terminal carbonyl region between 1889 and 2056 cm$^{-1}$ and there are no vibrations associated with the presence of bridging carbonyl groups.

Figure 5.1 121.4 MHz $^{31}$P NMR spectrum of reaction mixture obtained by the pyrolysis of Ru$_3$(CO)$_{11}$(Ph$_2$PC$_6$H$_5$Cr(CO)$_3$) (1)
The $^{31}$P($^1$H) NMR spectrum displays two doublets at 272.8 and 211.9 ppm with a coupling of 200 Hz suggesting the presence of two different phosphido groups (Figure 5.2a). The coupling constant is similar to that of Ru$_3$(CO)$_7$(C$_6$H$_4$)(PPhFc)$_2$ (5c), but the chemical shifts are far downfield compared with the 131.0(d) and 67.8(d) ppm values measured for (5c). The $^1$H NMR spectrum of (2) is presented in Figure 5.2b. The $\eta^6$-bound phenyl region (4.5-5.8 ppm) extends both upfield and downfield of the spectral region in which the starting material resonances appear at 5.1(2H) and 5.6(3H) ppm. Homonuclear decoupling experiments revealed that $a$, $b$, $c$, $d$, and $e$ are associated with one monosubstituted $\eta^6$-phenyl group and $f$, $g$, $h$, $i$, and $j$ with the other. Hence it can be concluded that there is probably no reaction involving the $\eta^6$-bound phenyl groups in the course of the pyrolysis. The signals $l$, $m$ and $n$ at 6.5, 6.6 and 7.1 ppm have chemical shifts similar to those of the benzyne resonances of (5c) (6.4-7.0 ppm). The intensity ratio of these resonances $l$, $m$ and $n$ is 1:1:2 which implies the presence of four protons. Decoupling resonance $m$ (6.5 ppm) results in a marked decrease in the intensity of resonances $l$ and $n$. Hence this region ($l$, $m$, $n$) is assigned to a benzyne moiety. The phenyl region ($o$, $p$, $q$, $r$) of the spectrum indicates the presence of two phenyl groups in (2).
The crystal structure of (2) has been determined using X-ray crystallography. In the crystals of (2) there are two independent molecules Ru₃(CO)₇(C₆H₄)(PPhC₆H₅Cr(CO)₃) (2a) and (2b) per asymmetric unit which are separated by normal van der Waals distances. These two molecules are structurally equivalent and an ORTEP diagram of one of them is shown in Figure 5.3 (see p115). Some selected bond parameters of (2) are tabulated in Table 5.1 (see p116). The complex is of the known type containing a μ₃-benzyne ligand described in section 1.4.2. The bonding parameters for the known benzyne complexes (5a) to (5d) of this type, reported in the literature, are summarized in Table 5.2 (see p117) [1].
The molecule consists of a closed triangle of ruthenium atoms, with two of the edges bridged by two phosphido groups each acting as a three electron donor. The phosphorus atoms of the bridging groups lie on opposite sides of the Ru₃ triangle with P₂ on the side of the benzyne moiety. The planar benzyne ligand acts as a four electron donor and is situated above the Ru₃ plane with which it makes a dihedral angle of 62.90° for (2b)). One side of the benzyne spans an edge of the triangle, which is bridged by a phosphido group. This benzyne moiety forms σ bonds to two ruthenium atoms (Ru₂-C₁₄ = 2.132(6) \{2.143(6)\} Å; Ru₃-C₁₅ = 2.117(6) \{2.127(6)\} Å) and an η²-bond to Ru₁, the ruthenium atom at the apex of the triangle (Ru₁-C₁₄=2.319(6)\{2.309(6)\}; Ru₁-C₁₅ = 2.27(6) \{2.348(6)\} Å). Ru₂ and Ru₃ are nearly coplanar with the benzyne moiety, being 0.1217 \{0.1673\} Å and 0.0328 \{0.0246\} Å away respectively, which is consistent with a σ interaction. Ru₁ is displaced 2.0058 \{2.0046\} Å away from this benzyne plane. There is no systematic variation in the bond lengths within the benzyne ligand (mean value 1.39 Å), suggesting that the bond delocalization is unaffected. This is in contrast to (5b) and (5c) in which the benzyne ligands show some double bond localization features (Figure5.4, see p118). There are large variations between the three Ru-Ru distances in (2). Ru₂-Ru₃ bond is the longest (2.9227(8) \{2.9200(8)\} Å) which is significantly longer than the Ru-Ru bonds of the parent carbonyl Ru₃(CO)₁₂ (mean 2.854 Å). However, the Ru₂-Ru₃ bond distance lies in the range found for the corresponding bond M₁-M₃ in (5). The other two metal-metal bonds are shorter than those found in Ru₃(CO)₁₂. The shortest Ru₁-Ru₃ distance,
(2.724(8) - 2.736(8) Å), is spanned by a semibridging carbonyl group and is appreciably shorter than the corresponding M2-M3 bond distance in (5).

Figure 5.3 ORTEP diagram of Ru$_3$(CO)$_7$(C$_6$H$_4$)[PPhC$_6$H$_5$Cr(CO)$_3$)$_2$ (2a)
Table 5.1 Selected bond lengths (Å) and bond angles (°) of \( \text{Ru}_3(\text{CO})_7(\text{C}_6\text{H}_4)\{\text{PPhC}_6\text{H}_5\text{Cr}(\text{CO})_3\} \text{2} (2)

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a: Here and elsewhere in this chapter brackets < > refer to the mean values

There are two CO ligands on \( \text{Ru}1 \) and \( \text{Ru}2 \) and three on \( \text{Ru}3 \), one of which, CO(5), is bent towards \( \text{Ru}1 \) (\( \text{Ru}3-\text{C}5-\text{O}5 = 165.7(7)° \{167.8(8)° \}). This carbonyl can be considered to be semibridging between \( \text{Ru}1 \) and \( \text{Ru}3 \) since the angle \( \text{Ru}1-\text{Ru}3-\text{C}5 \) [designated as \( \psi \)] is 68.5(2)° which meets the criterion suggested by Crabtree and Lavin (\( \psi < 70° \)) [2]. The other six Ru-C-O angles are nearly linear, ranging from 175.6(6)° to 177.8(6)°. Furthermore, among the Ru-C(carbonyl) bonds, the \( \text{Ru}1-\text{C}2 \) bond, which is \textit{trans} to the \( \eta^2 \)-interaction on \( \text{Ru}1 \), is the shortest (1.853(8) \{1.862(8) \} Å). However, the \( \text{Ru}2- \)
C3 and Ru3-C6 bonds, which are trans to the Ru2-C14 and Ru3-C15 σ-bonds, are the longest (mean 1.940 (1.940) Å).

Table 5.2 Selected bond lengths (Å) and bond angles (°) of Ru3(CO)7(C6H4)(PR2)2 (5a) to (5d)

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<td>164(6)°</td>
<td>165.3(7)°</td>
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<td>64.0(2)°</td>
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Figure 5.4 Bond lengths and bond angles for the benzyne moiety of Ru$_3$(CO)$_7$(C$_6$H$_4$)(PPhFc)$_2$ (5c) and Ru$_3$(CO)$_7$(C$_6$H$_4$)(PPh$_2$)$_2$ (5b) (in parentheses)

The $\mu$-PR$_2$ bridging bond lengths in (2) are asymmetric as found in (5). Thus, in (2) Ru1-P1 is shorter than Ru2-P1 by 0.075 Å on average and Ru2-P2 is shorter than Ru3-P2 by an average of 0.055 Å. The two phenylchromium tricarbonyl groups are found on opposite sides of the Ru$_3$ triangle. The bond parameters of the phenylchromium tricarbonyl moieties are similar to those reported for (1) (Section 3.3). All Cr-C(arene) distances in (2) are similar (mean 2.207 {2.209} Å), Cr-C-O angles are close to linear (mean 177.8°) and average Cr-CO bond lengths are 1.833 Å. The variation of the bond lengths within the benzene rings is not significant and the average C-C bond length is 1.40 Å.

(b) Characterization of Complex (3)

It proved to be very difficult to separate complex (3) from (2) by using column chromatography, presumably because of the similar polarities of the two compounds. However, crystallization from of mixtures of (2) and (3) affords (2) as a solid, whereas (3) remains in the mother liquor.
While the structure of (3) is difficult to establish in the absence of a single crystal X-ray crystallographic study, several key features can be deduced from the spectroscopic data. The FAB mass spectrum of the complex (3) exhibits the same parent mass m/e at 1216 as (2). In addition both spectra show the presence of thirteen carbonyl groups. The $^{31}$P NMR spectrum of (3) shows a singlet at 237 ppm indicating the presence of one phosphido group or a chemically equivalent pair of phosphido groups. The $^1$H NMR spectrum shows the presence of two equivalent phenyl groups (7.2-7.8 ppm), two equivalent $\eta^6$-bound phenyl groups (4.7-5.5 ppm) and a symmetrical benzyne moiety (6.6, 7.7 ppm). Based on these spectroscopic data, the formula Ru$_3$(CO)$_7$(C$_6$H$_4$)$[\mu$-PPhC$_6$H$_5$Cr(CO)$_3$]$\_2$ can be proposed for this complex. Thus (3) is probably a geometric isomer of (2) with two phenyl groups on one side of the Ru$_3$ triangle and two phenylchromium tricarbonyl groups on the other side of the Ru$_3$ triangle. Consideration of steric interactions suggests that the two phenylchromium tricarbonyl groups should be displaced away from the center of the molecule.

![Chemical Structure](image)

Although there have been no mechanistic studies on the cluster-assisted transformations of arylphosphines and related ligands, plausible reaction pathways can be mapped out on the basis of intermediates that have been isolated. Scheme 5.1 shows a possible reaction sequence to the formation of compound Ru$_3$(CO)$_7$(C$_6$H$_4$)PPh$_2$PPhFe'
(5d), a product formed from the thermolysis of Ru$_3$(CO)$_{10}$(dppf) where dppf = 1,1'-bis(diphenylphosphino)ferrocene [1c].

![Diagram of the reaction pathway to Ru$_3$(CO)$_7$(C$_6$H$_4$)PPh$_2$PPhFc (5d)]

**Scheme 5.1 Reaction pathway to Ru$_3$(CO)$_7$(C$_6$H$_4$)PPh$_2$PPhFc (5d)**

The first step in the reaction sequence, movement of one end of the ligand to an axial site, seems to be necessary to account for the final geometry. Thermally induced loss of CO from the starting material Ru$_3$(CO)$_{10}$(dppf) provides a vacant coordination site which is easily trapped by the activation of a C-H bond of one P-Ph ring to afford intermediate B. Subsequently, a second CO is lost and a double bond in the C$_6$H$_4$ ring is
coordinated to give intermediate C. Finally, the loss of the third CO ligand, followed by the oxidative addition of a P-Ph bond gives (5d).

Similarly, it is believed that the formation of (2) or (3) also involves several steps. Firstly, oxidative-addition of the phenyl C-H bond across an Ru-Ru bond seems to be necessary. Then the bridging phosphido groups are formed through the cleavage of the P-C bonds. The C₆H₄ moiety is retained as a cluster-bound benzyne and one phenyl group presumably is lost as benzene by combination with the cluster-bound hydrogen.

5.1.2 Thermolysis of Os₃(CO)₁₁(PPh₂C₆H₅Cr(CO)₃)

Pyrolysis of Os₃(CO)₁₁(PPh₂C₆H₅Cr(CO)₃) (6) in octane for 10 hours affords two major products: Os₃(CO)₉[C₆H₄][μ₃-PC₆H₅Cr(CO)₃] (7) and Os₃(CO)₈[PhPC₆H₄]-[PPh₂C₆H₅Cr(CO)₃] (8) and at least two more minor ones as indicated by TLC and ³¹P NMR spectroscopy. One of the minor products is Os₃(CO)₁₂ as determined by infrared spectroscopy.

(a) Characterization of Os₃(CO)₉[C₆H₄][PC₆H₅Cr(CO)₃] (7)

The ³¹P NMR spectrum of complex (7) displays a singlet at 218.2 ppm indicating the presence of a phosphinidene moiety. In the ¹H NMR spectrum of (7), the signals at 5.3 ppm and 5.45 ppm are assigned to the η⁶-bound phenyl group and the resonances at 7.6 ppm and 7.15 ppm to the benzyne moiety. The FAB mass spectrum shows a parent ion centered at m/e 1143, and ions formed by initial loss of three carbonyl ligands followed by the sequential loss of nine carbonyls. The parent ion (m/e 1143) corresponds to the loss of one benzene and two carbonyl molecules from the starting material (6). The relatively simple IR spectrum in the ν(CO) region shows six strong terminal ν(CO) bands between 1900 and 2080 cm⁻¹ without any bridging carbonyl absorptions. Based on the above data, the most likely formula for complex (7) is Os₃(CO)₉(C₆H₄)PC₆H₅Cr(CO)₃.
A preliminary X-ray crystallographic study of (7) was undertaken. Unfortunately, there were so many solvent molecules in the unit cell that final refinement of the structure was not attempted. However, the preliminary structure, shown in Figure 5.5, is consistent with the spectroscopic data.

Figure 5.5  Molecular structure of $\text{Os}_3(\text{CO})_9(\text{C}_6\text{H}_4)\text{PC}_6\text{H}_5\text{Cr}(\text{CO})_3$ (7)
As expected, the structure of (7) consists of an open Os$_3$ metal framework capped on one face by an asymmetrically bonded benzyne moiety and on the other face by a PC$_6$H$_5$Cr(CO)$_3$ phosphinidene moiety. Each osmium atom has three carbonyls. Therefore, this complex is an analogue of the class of compounds typified by Os$_3$(CO)$_9$(C$_6$H$_4$)PMe (9) [3].

(b) Characterization of Os$_3$(CO)$_8$[PhPC$_6$H$_4$][PPh$_2$C$_6$H$_5$Cr(CO)$_3$] (8)

A single crystal X-ray diffraction analysis of (8) was performed and a view of the molecular structure (8) is presented in Figure 5.6, together with the atomic numbering scheme. The relevant bond lengths and bond angles are summarized in Table 5.3 (see p125). The molecular structure of complex (8) consists of three osmium atoms, with two short Os-Os bonds (Os$_2$-Os$_3$ = 2.8628(9), Os$_1$-Os$_3$ = 2.9613(9) Å) and one much longer bond (Os$_1$-Os$_2$ = 3.094(1) Å). The Os$_1$-Os$_3$ bond is bridged by the phosphorus atom of a phosphido group (Os$_1$-P$_1$ = 2.356(4), Os$_3$-P$_1$ = 2.340(3) Å) which has been formed by the loss of one benzenechromium tricarbonyl group from the original ligand PPh$_2$C$_6$H$_5$Cr(CO)$_3$. A metallated C$_6$H$_4$ group bridges Os$_2$ and P$_1$ (Os$_2$-C$_2$ = 2.18(2) Å). The eight terminal carbonyls are all essentially linear (mean Ru-C-O = 176°); three carbonyl ligands are coordinated to Os$_2$ and to Os$_3$, and two are attached to Os$_1$. Os$_1$ is also bonded to the intact ligand PPh$_2$C$_6$H$_5$Cr(CO)$_3$, which occupies an axial position on the
opposite side of the Os₃-triangle to the C₆H₄ moiety; probably to minimize the repulsive steric interactions. The dihedral angle between the C₆H₄ moiety and the Os₃ triangle is 82.16°. Surprisingly the complex is electron deficient and has only 46 electrons if the C₆H₄PPh acts as a four electron donor to the Os₃ framework. This is the first example of electron unsaturation found in a structure of this type.

Figure 5.6 ORTEP plot of Os₃(CO)₈[PhPC₆H₄][PPh₂C₆H₅Cr(CO)₃] (8)
Table 5.3 Summary of bond parameters in Os₃(CO)₈[PhPC₆H₄][PPh₂C₆H₅Cr(CO)₃] (8)

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Selected bond angles (°)

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</table>

a: here and elsewhere brackets refer to the mean values

The structure of (8) may be compared with that of Os₃(CO)₉(μ-CO)(PMeC₆H₄) (10), a decomposition product of Os₃(CO)₁₁(PMePh₂) [4]. Both molecules contain the μ₃-C₆H₄PR ligand as a four-electron-donating bridge. However, there are significant differences between the two complexes. Complex (10) contains ten carbonyls, one of which is bridging, so that the structure is electron precise. In addition, (10) is an intermediate in the formation of the benzyne complex, Os₃(CO)₉(C₆H₄)(μ₃-PMe) (9), while (8) is rather stable and is unlikely to act as a precursor to an analogous aryne complex.
The $^{31}$P NMR spectrum of complex (8) is consistent with the structure established by X-ray diffraction analysis. Thus a signal observed at -2.5 ppm is assigned to a terminal P atom, while a low field signal at 36.4 ppm is typical for a P atom bridging an Os-Os bond. This shift is ca. 36 ppm downfield from that observed in the parent complex (6) (0.3 ppm). The $^1$H NMR spectrum is also in agreement with the structure found in the solid state. In particular, the chemical shifts characteristic of an ortho-metallated phenyl ring (AA'BB') are observed at 6.8 ppm and 6.6 ppm, and five protons are also observed in the region characteristic of an $\eta^6$-bound phenyl group. The FAB mass spectrum shows the parent ion at $m/e$ 1380, and ions formed by initial loss of three carbonyls followed by five and nine carbonyls. The infrared spectrum in the $\nu$(CO) region consists of four broad bands between 1900 and 2090 cm$^{-1}$, indicative of the presence of terminal carbonyls in accord with the crystal structure.

The complex (8) is formed from (6) through the cleavage of one phenyl C-H bond and one aryl C-P bond. The cleavage of the C$_6$H$_5$Cr(CO)$_3$ moiety from (6) seems surprising because there are two phenyl groups and only one benzenechromium tricarbonyl group attached to the phosphorus atom. Therefore, the present result appears to show that P-C(C$_6$H$_5$Cr(CO)$_3$) bond breaking is more facile than P-C(phenyl) bond cleavage in thermolysis of metal clusters containing benzenechromium tricarbonyl and phenyl ligands. In
addition the thermolytic reaction of (6) certainly occurs in several steps. It is possible that some intermediates might be isolated at lower reaction temperatures and/or at shorter reaction times. Deeming et al. used this approach to isolate two intermediates \( \text{HOS}_3(\text{CO})_9[\text{PhMePC}_6\text{H}_4] \) (11) and \( \text{OS}_3(\text{CO})_8(\mu-\text{CO})[\text{MePC}_6\text{H}_4] \) (10) from the pyrolysis of \( \text{OS}_3(\text{CO})_{11}(\text{PPh}_2\text{Me}) \) [4]. In the early stages of the thermolytic reaction the concentration of (11) builds up faster than (10) and later (11) decreases while the final product \( \text{OS}_3(\text{CO})_9(\text{C}_6\text{H}_4)\text{PMe} \) (9) increases in concentration.

![Thermolytic reaction diagram](image)

A thermolysis pathway of (6) is outlined in Scheme 5.2. This is based on the isolation of the products (7) and (8) and also on the routes to (9) proposed by Deeming et al. [4]. The first step is the movement of the phosphine ligand from an equatorial to an axial position in (6). This permits \textit{ortho}-metallation of one of the phenyl-P groups to take place, resulting in intermediate (6a). An analogue of (6a), \( \text{HOOS}_3(\text{CO})_{10}[\text{Ph}_2\text{PC}_6\text{H}_4] \), was isolated and characterized from the pyrolysis of \( \text{OS}_3(\text{CO})_{12} \) with \( \text{PPh}_3 \) in refluxing xylene solution [5], although it was not seen in the present work or in Deeming's study [4]. Intermediate (6a) can further decarbonylate to yield (6b) whose analogue (11) was observed by Deeming et al. as mentioned above [4]. Complex (6b) can undergo either reductive elimination of a phenyl group to give the final product (7), or elimination of benzenechromium tricarbonyl.
to afford (6c). Furthermore, the complex (6c) undergoes a substitution by the ligand PPh$_2$C$_6$H$_5$Cr(CO)$_3$ released during the thermolysis to form (8). In this process, it is obviously impossible to convert (6c) to (7). However, analogue (10) of (6c) could lose one more carbonyl to form (9).

Scheme 5.2 Reaction pathway leading to (7) and (8)
5.1.3 Thermolysis of Os₃(CO)₁₁(PPr^1₂C₆H₅Cr(CO)₃)

The thermal decomposition of the osmium derivative Os₃(CO)₁₁(PPr^1₂C₆H₅Cr(CO)₃) (12) has been investigated. The reaction takes place smoothly in refluxing octane. There is no starting material left after heating for 24 hours as monitored by TLC chromatography. Separation of the reaction mixture affords two major yellow products:

H₂Os₃(CO)₉[PriPC₆H₄Cr(CO)₃] (13) and H₂Os₃(CO)₈[Pr^1PC₆H₄Cr(CO)₃][Pr^1₂PC₆H₅Cr(CO)₃] (14). Pyrolysis of (12) in a higher boiling solvent, such as nonane, results in lower yields of (13) and (14), and more brown colored solid that remains on the chromatography column upon workup.

(a) Characterization of H₂Os₃(CO)₉[Pr^1PC₆H₄Cr(CO)₃] (13)

The structure of (13) was solved by an X-ray diffraction study. An ORTEP diagram of the molecule with 33% probability thermal ellipsoids is depicted in Figure 5.7 and selected bond distances and bond angles are tabulated in Table 5.4 (see p131). The structure of (13) consists of a closed cluster of three osmium atoms that is bridged by two hydride ligands which were located in the structure refinement. The Os₃ triangle is capped on one face by the phosphido moiety together with the ortho-metallated phenylchromium tricarbonyl fragment. The three Os-Os bond distances within the cluster show large variations. The Os₁-Os₃ bond bridged by hydride H₁ at 3.0327(6) Å is the longest. The Os₁-Os₂ bond bridged both by hydride H₂ and the phosphorus atom at 2.9266(7) Å is 0.1061 Å shorter than the Os₁-Os₃ bond distance and 0.0783 Å longer than the Os₂-Os₃ distance of 2.8483(6) Å, which is shorter than that observed in Os₃(CO)₁₂ (2.877(3) Å) [6]. The elongation of the two osmium-osmium bonds is significant and is a feature which is characteristic of the presence of bridging hydride ligands. Formally, both Os₂ and Os₃ are 7-coordinate and Os₁ is 8-coordinate.
Figure 5.7 ORTEP diagram of $\text{H}_2\text{Os}_3(\text{CO})_9\text{[Pr}^\text{ipC}_6\text{H}_4\text{Cr(OC)}_3]$ (13)
Table 5.4  Selected bond parameters in $\text{H}_2\text{Os}_3(\text{CO})_9[\text{Pr}^1\text{PC}_6\text{H}_4\text{Cr}(\text{CO})_3]$ (13)

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Selected bond angles (°)

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$a$: Here and elsewhere brackets <> refer to mean values

The two hydrides in (13) are in different environments, e.g. H1 is displaced 0.4411 Å from the Os$_3$ plane towards the focal point of the molecule, while H2 is 0.4292 Å away from the Os$_3$ plane on the open face of the molecule. The hydride H1 is bonded to Os1 and Os3 (Os1-H1 = 1.68, Os3-H1 = 1.86 Å) and the hydride H2 is approximately symmetrically bonded to Os1 and Os2. The Os1-H2 bond at 1.74 Å and the Os2-H2 bond at 1.71 Å are almost of equal length. This symmetry is presumably due to the presence of the phosphido group.
The phosphido bridge in (13) is symmetrical (P-Os1 = 2.365(3), P-Os2 = 2.350(3) Å). The P1-Os1-Os2 plane is nearly perpendicular to the Os3 plane and the dihedral angle between them is 94.62°. The ortho-metallated phenylchromium tricarbonyl fragment is σ-bound to the Os3 atom through the metallated C2 atom. The Os3-C2 bond distance at 2.18(1) Å is similar to that of Os2-C2 of (8), as discussed in section 5.1.2. There is no systematic variation in bond lengths within the six-membered ring and the average carbon-carbon bond distance at 1.39 Å is similar to that of the benzene ring in C₆H₆Cr(CO)₃ (1.398(8) Å). The η⁶-C₆H₄ ring is planar, and inclined to the Os3 plane by 83.54°, which is comparable with that found in (8) for the C₆H₄ moiety and the Os3 plane. Overall, the μ₃-ligand donates four-electrons to the Os3 framework. As a consequence, the cluster is electron precise if three metal-metal bonds are counted in the cluster.

Each osmium atom in (13) is coordinated to three carbonyl groups: one axial and two equatorial. The average Os-C distance of the axial carbonyls at 1.96(1) Å and the equatorial carbonyls at 1.91(1) Å are similar to the corresponding bond distances found in Os₃(CO)₁₂ (mean Os-CO(ax) = 1.946(6), Os-CO(eq) = 1.912(7) Å). Four carbonyls (C₀₁, C₀₄, C₀₅ and C₀₈) are bent (average Os-C-O = 174°), while the remaining carbonyls are nearly linear (average Os-C-O = 177.6°).

The spectroscopic data for (13) are in accord with the solid-state structure. The ³¹P NMR spectrum of (13) shows one singlet at 69 ppm which is consistent with the presence of a phosphido group. The phosphorus resonance is shifted downfield ca. 41 ppm from that of the starting material (12) (27.8 ppm). The ¹H NMR spectrum in the benzenechromium tricarbonyl region shows the presence of four protons with an intensity pattern of 2:1:1. The two inequivalent hydride resonances are observed at -16.5 and -17.5 ppm as two doublets due to coupling with phosphorus. In addition, resonances due to one isopropyl group is found in the ¹H NMR spectrum. The mass spectrum gives the highest peak at m/e
1112, corresponding to the loss of one isopropyl and two carbonyl groups from the starting material (12).

(b) Characterization of $\text{H}_2\text{Os}_3(\text{CO})_8[\text{Pr}^i\text{PC}_6\text{H}_4\text{Cr(}\text{CO})_3][\text{Pr}^i_2\text{PC}_6\text{H}_5\text{Cr(}\text{CO})_3]$ (14)

The structure of (14) was established using X-ray crystallography. An ORTEP diagram with 25% probability thermal ellipsoids is shown in Figure 5.8 and selected bond lengths and bond angles are presented in Table 5.5.

![Figure 5.8 ORTEP diagram of $\text{H}_2\text{Os}_3(\text{CO})_8[\text{Pr}^i\text{PC}_6\text{H}_4\text{Cr(}\text{CO})_3][\text{Pr}^i_2\text{PC}_6\text{H}_5\text{Cr(}\text{CO})_3]$ (14)
Table 5.5 Selected bond parameters in $\text{H}_2\text{Os}_3(\text{CO})_8[\text{Pri}_2\text{PC}_6\text{H}_4\text{Cr}(\text{CO})_3]$-$[\text{Pri}_2\text{PC}_6\text{H}_5\text{Cr}(\text{CO})_3]$ (14)

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<td>2.9786(6)</td>
</tr>
<tr>
<td>Os2-Os3</td>
<td>3.1223(6)</td>
<td>Os2-C2</td>
<td>2.153(8)</td>
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<td>2.340(2)</td>
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<td>2.353(2)</td>
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<td>Os3-P2</td>
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<td>Os3-H1</td>
<td>1.89</td>
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<tr>
<td>Cr-C_{ring}</td>
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<td>Os-CO</td>
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Selected bond angles (°)

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<td>$&lt;\text{Os-C-O}&gt;$</td>
<td>173.6(8)-178.2(9)</td>
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The molecular structure of (14) is closely related to (13), except that in (14) one axial CO group on Os3 is replaced by a PPr$_2^*$[C$_6$H$_5$Cr(CO)$_3$] ligand. The metal atom framework consists of a closed triangle of Os-atoms with two bridging hydrides, one phosphido group and one phosphine ligand. The Os-Os distances in (14) span a larger range compared to (13). Bond lengths Os2-Os3 at 3.1223(6) Å, Os1-Os3 at 2.9786(6) Å and Os1-Os2 at 2.8788(7) Å in (14) are longer than the corresponding bonds in (13) (Figure 5.9). In order
to maintain an 18-electron configuration for all of the Os atoms, the Os2-Os3 bond should be included, although this interaction must be very weak because of the long bond distance.

![Figure 5.9 Atomic numbering of (13) which is consistent with that of (14) and selected bond lengths (Å). CO groups are omitted for clarity.](image)

In (14) the two hydrides were located in the structure refinement and they asymmetrically bridge the Os1-Os3 and Os2-Os3 bonds respectively. In addition, these two hydrides lie on the same side of the Os3 plane, away from the phosphido group. This is in contrast to (13), where they are situated on the opposite sides of the Os3 plane. The dihedral angles between the Os3 plane and Os1-H1-Os3 and Os2-H2-Os3 plane in (14) are 67.29° and 53.95° respectively.

The phosphido group of (14) is unsymmetrically bonded to Os1 and Os3 (P1-Os1 = 2.340(2), P1-Os3 = 2.353(2) Å). However, the phosphido bridge in (13) is symmetrical. As found in (13), the P1-Os1-Os3 plane is approximately perpendicular to the Os3 plane and the dihedral angle between these two planes is 86.73°. The phosphine group is axially bonded to Os3. The phosphine-osmium bond distance at 2.436(2) Å is longer than that of the phosphido-osmium bond (mean 2.347 Å). The ortho-metallated phenylchromium...
tricarbonyl moiety is σ-bound to Os2 (C2-Os2 = 2.153(8) Å). The Os-CO bond lengths show little variation ranging from 1.876(9) to 1.94(1) Å.

The complex (14) was also characterized by spectroscopic and microanalytical methods. Two signals at 15.9 and 55.4 ppm in the $^{31}$P NMR spectrum indicate the presence of a phosphine and a phosphido group. The $^1$H NMR spectrum shows the presence of nine protons associated with two $\eta^6$-arene rings in the region 4.9 to 6 ppm, three isopropyl groups between 1 and 3 ppm and two hydrides at -16.5 and -17.0 ppm. The FAB mass spectrum exhibits the parent ion at $m/e$ 1414, and ions from loss of carbonyl groups. The infrared spectrum in the solid state shows absorptions in the terminal carbonyl region between 1870 and 2080 cm$^{-1}$. These spectroscopic data for (14) are therefore in agreement with the crystal structure as described above.

Scheme 5.3 outlines a pathway that could account for the formation of complexes (13) and (14) from Os$_3$(CO)$_{11}$[PPr$_2$C$_6$H$_5$Cr(CO)$_3$] (12). Movement of the phosphine ligand from an equatorial to an axial position affords (12a). The intermediate (12b) results from ortho-metallation of the benzenechromium tricarbonyl moiety of (12a). A $\beta$ C-H activation of one of the isopropyl groups in (12b) by an Os(CO)$_3$ metal center leads to (12c). Elimination of a propene molecule gives (13). Substitution of one carbonyl of (13) by the phosphine ligand, which is present in solution as a result of the thermolytic reaction, affords the complex (14).
Scheme 5.3 Possible reaction sequence for the pyrolysis of \( \text{Os}_3(\text{CO})_{11}\text{PPr}_{i2}\text{C}_6\text{H}_5\text{Cr}(\text{CO})_3 \) (12)
5.1.4 Thermolysis of Ru$_3$(CO)$_{11}$(PPr$_i^1_2$C$_6$H$_5$Cr(CO)$_3$)  

Thermal decomposition of Ru$_3$(CO)$_{11}$[PPr$_i^1_2$C$_6$H$_5$Cr(CO)$_3$] (15a) in boiling cyclohexane for 30 hours, or in boiling heptane for 5 hours, affords two major new compounds: HRu$_3$(CO)$_8$[C$_6$H$_4$Cr(CO)$_3$](PPr$_i^2$) (16) (309.6 ppm) and Ru(CO)$_3$[PPr$_i^1_2$C$_6$H$_5$Cr(CO)$_3$]$_2$ (17) (76.2 ppm), along with some starting material (58.97 ppm) as indicated by $^{31}$P NMR spectroscopy (Figure 5.10a). Heating Ru$_3$(CO)$_{10}$[PPr$_i^1_2$C$_6$H$_5$Cr(CO)$_3$]$_2$ (15b) in heptane gives (16), (17) and some monosubstituted derivatives as judged by $^{31}$P NMR spectroscopy (Figure 5.10b). In each case, the isolated products are different from those obtained by thermolysis of the osmium analogue Os$_3$(CO)$_{11}$[Pr$_i^1_2$C$_6$H$_5$Cr(CO)$_3$], as discussed in section 5.1.3.

**Figure 5.10a** 121.4 MHz $^{31}$P NMR spectrum of a reaction mixture obtained by the pyrolysis of (15a) (PPh$_3$ = 0 ppm as reference)
Figure 5.10b 121.4 MHz $^{31}$P NMR spectrum of a reaction mixture obtained by the pyrolysis of $\text{Ru}_3(\text{CO})_{10}[\text{PP}_{142}\text{C}_6\text{H}_5\text{Cr}(\text{CO})_3]_2$ (15b)

(a) Characterization of $\text{Ru}_3(\text{CO})_8[\mu-\text{H}][\text{C}_6\text{H}_4\text{Cr(OC)}_3][\mu-\text{PP}_{142}]_2$ (16)

The complex (16) is a yellow crystalline material and is easily decomposed to a green powder in air. Its $^{31}$P NMR spectrum contains one sharp singlet at 309.6 ppm suggestive of the presence of a phosphido group. The unsymmetrical benzynechromium tricarbonyl moiety resonances in the $^1$H NMR spectrum are observed as two doublets (4.6, 4.9 ppm) and two triplets (4.7, 6.0 ppm) of intensity ratio 1:1:1:1. The two chemically inequivalent isopropyl groups are also found in the appropriate region. The doublet at -17.9
ppm is a typical bridging hydride signal; its doublet character arising from coupling with a phosphorus atom. The mass spectrum shows the parent ion at $m/e$ 858 indicating that the starting material has lost three carbonyl groups. These data suggest a formula as $\text{Ru}_3(\text{CO})_8[\mu-\text{H}][\text{C}_6\text{H}_4\text{Cr}(\text{CO})_3][\mu-\text{PPri}_2]$ and a likely structure is shown in Figure 5.11. The formation of complex (16) involves $\eta^6$-phenyl C-H bond and C-P bond activation. Interestingly, two isopropyl groups remain intact in the course of the thermal reaction.

![Figure 5.11 Proposed structure of Ru$_3$(CO)$_8$[μ-H][C$_6$H$_4$Cr(CO)$_3$][μ-PPri$_2$] (16)](image)

(b) Characterization of $\text{Ru}(\text{CO})_3$ [Pr$_2$P$_2$C$_6$H$_5$Cr(CO)$_3$]$_2$ (17)

The complex (17) is the first example of a monomeric ruthenium complex containing a phosphinobenzenechromium tricarbonyl ligand. The structure was solved by an X-ray diffraction study. Selected bond distances and bond angles are presented in Table 5.6 and an ORTEP diagram of (17), together with the atomic numbering scheme, is shown in Figure 5.12 (see p142). The geometry of (17) is that of a trigonal-bipyramid with three equatorial CO groups and two trans axial PPr$_2$C$_6$H$_5$Cr(CO)$_3$ ligands bound to the central Ru atom. The PPr$_2$C$_6$H$_5$Cr(CO)$_3$ ligand and Ru(CO)$_3$ moiety minimize inter-ligand repulsion by adopting a mutually staggered conformation. The structure is analogous to that of $\text{Ru}(\text{CO})_3$($\text{PMe}_3$)$_2$ (18) [7].
Table 5.6 Bond parameters of Ru(CO)$_3$[Pr$_2$PC$_6$H$_5$Cr(CO)$_3$]$_2$ (17)

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<th>Length (Å)</th>
</tr>
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<tbody>
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<td>Ru1-P2</td>
<td>2.3464(7)</td>
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<tr>
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<td>1.913</td>
<td>$&lt;$C=O$&gt;$</td>
<td>1.151</td>
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<tr>
<td>$&lt;$Cr1-C$&gt;$</td>
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<td>$&lt;$Cr2-C$&gt;$</td>
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<td>Cr1-Bz1</td>
<td>1.720(1)</td>
</tr>
<tr>
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<td>$&lt;$C-C$&gt;$</td>
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<td>$&lt;$P-C$&gt;$</td>
<td>1.857</td>
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Selected bond angles (°)

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<td>139.3(1)</td>
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<tr>
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<td>C13-Ru1-C14</td>
<td>110.8(1)</td>
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<tr>
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<td>177.0</td>
<td>$&lt;$Cr-C-O$&gt;$</td>
<td>177.9</td>
</tr>
</tbody>
</table>

a: Here and elsewhere brackets $<>$ refer to mean values

The three metal carbonyls in (17) are essentially linear (mean Ru-C-O 177°) and lie in the equatorial plane; however, the three C-Ru-C angles are different. The angle C13-Ru1-C15 at 139.3(1)° is much larger than the other two angles (C13-Ru1-C14 = 110.8(1), C14-Ru1-C15 = 109.9 (1)°). In contrast, the three C-Ru-C angles in (18) are close to 120°. The Ru-P distances of 2.36597(7) and 2.3464(7) Å compare favorably with the values in
(18) (2.334(1) and 2.345(1) Å). It is interesting to note that the P1-Ru1-P2 linkage in (17) is bent (167.61(3)°). In contrast, the P1-Ru-P2 linkage in (18) is linear (178.1(1)°). The bond parameters of the C₆H₅Cr(CO)₃ fragment are within the range found in PPr₂C₆H₅Cr(CO)₃.

Figure 5.12 ORTEP diagram of Ru(CO)₃[Pr₂PC₆H₅Cr(CO)₃]₂ (17)
The spectroscopic data for (17) are consistent with the molecular structure as established by the X-ray crystallographic study. The $^1$H NMR spectrum of (17) shows signals due to the five arene protons of the $C_6H_5Cr(CO)_3$ moiety, intensity ratio 2:1:2, between 5 and 6 ppm and the two isopropyl groups between 1 and 2.5 ppm. A singlet resonance at 76.2 ppm in the $^{31}$P NMR spectrum reveals the presence of at least one phosphine group in (17). The mass spectrum gives the parent ion at $m/e$ 846 and other ions corresponding to successive loss of nine carbonyl groups. The infrared spectrum of (17) exhibits two intense carbonyl bands: a sharp band at 1970 and a very broad band in the range of 1910 to 1870 cm$^{-1}$.

The complex Ru(CO)$_3$(PMe$_3$)$_2$ (18) exhibits one single carbonyl band at 1885 cm$^{-1}$. An analogous complex Ru(CO)$_3$(PPh$_3$)$_2$ (19) has a similar carbonyl absorption at 1890 cm$^{-1}$[8]. Therefore, the carbonyls bound to ruthenium in (17) possibly absorb in the broad band between 1910 and 1870 cm$^{-1}$. The sharp absorption band at 1970 and part of the broad band are attributed to the carbonyl ligands bound to chromium as the infrared spectrum of the free ligand Pri$_2$PC$_6$H$_5$Cr(CO)$_3$ shows two carbonyl absorptions at 1970 and 1880 cm$^{-1}$.

The complex (19) is the first example of a phosphine derivative of a ruthenium carbonyl, reported by Collman in 1965 [8, 9]. It was obtained in high yield by reduction of the ruthenium(II) complex [RuCl$_2$(CO)$_2$(PPh$_3$)$_2$] with zinc powder in the presence of carbon monoxide as shown in Equation 5.1.

$$
\text{RuCl}_2(\text{CO})_2(\text{PPh}_3)_2 \xrightarrow{\text{Zn, DMF, 100 °C}} \text{Ru(\text{CO})}_3(\text{PPh}_3)_2 \quad \text{Eq 5.1}
$$
The complex (18) resulted from the reaction of Ru$_2$(μ-CH$_2$)$_3$(PMe)$_6$ with carbon monoxide (5 atm, 60 °C). The photolysis of Ru$_3$(CO)$_{12}$ in the presence of phosphine and CO ligands can produce Ru(CO)$_4$PR$_3$ and Ru(CO)$_3$(PR$_3$)$_2$ [10a]. The complex (17) is the first example of the class Ru(CO)$_3$(PR$_3$)$_2$ to be isolated from a thermal reaction of a substituted triruthenium cluster. It should be noted that Ru$_3$(CO)$_{11}$PΦc$_3$ decomposes to Ru(CO)$_4$PΦc$_3$ at room temperature. The reason for formation of this product has been suggested to be ligand bulk [10b].

5.1.5 Thermolysis of Ru$_3$(CO)$_{12}$ and PBut$_4$[C$_6$H$_5$Cr(CO)$_3$]$_2$

Treatment of Ru$_3$(CO)$_{12}$ with the ligand PBut$_4$[C$_6$H$_5$Cr(CO)$_3$]$_2$ in 1:1 or 1:2 molar ratio in refluxing heptane affords one major compound Ru$_3$(CO)$_8$[C$_6$H$_4$Cr(CO)$_3$]PBut$_4$ (20), together with a small amount of the monosubstituted complex Ru$_3$(CO)$_{11}$[PBut-(C$_6$H$_5$Cr(CO)$_3$)]$_2$ identified via spectroscopic methods.

Characterization of Ru$_3$(CO)$_8$[C$_6$H$_4$Cr(CO)$_3$]PBut$_4$ (20)

The $^{31}$P NMR spectrum of complex (20) exhibits a singlet signal at 480.3 ppm indicating the presence of a phosphinidene group. The $^1$H NMR spectrum as shown in Figure 5.13 contains the A and B parts of an AA′BB′ system at 5.4 and 5.1 ppm which can be assigned to the resonances of the C$_6$H$_4$Cr(CO)$_3$ moiety. A doublet at 2.0 ppm with a P-H coupling of 20 Hz is assigned to the tert-butyl group. The ion with the highest m/e in the FAB mass spectrum (centered on m/e 828) corresponds to the formulation of P$^+$ = [Ru$_3$(CO)$_8$C$_6$H$_4$Cr(CO)$_3$PBut$_4$]$^+$. Other ruthenium-containing ions are formed by initial loss of two carbonyls followed by the sequential loss of nine carbonyls. The ion [P-11CO-Cr]$^+$ at 468 was also detected. The infrared spectrum exhibits six ν(CO) absorption bands between 1880 and 2080 cm$^{-1}$ which fall in the terminal carbonyl region.
The molecular structure of complex (20), determined by X-ray crystallography, reveals a novel type of aryne complex. Two different views of the structure are illustrated in Figures 5.14 and 5.15 (see p147). The important bond lengths and bond angles are summarized in Table 5.7 (see p148). The metal atom framework consists of a closed triangle of Ru-atoms which bear on opposite sides a $\mu_3$-PBut and a $\mu_3$-C$_6$H$_4$Cr(CO)$_3$ ligand. The metal-metal bond lengths vary from 2.8401(6) Å (Ru1-Ru2) to 2.9272(5) Å (Ru2-Ru3). The phosphinidene is bound almost symmetrically (Ru1-P1 = 2.324(1), Ru2-P1 = 2.313(1), Ru3-P1 = 2.199(1) Å).

![200 MHz 1H NMR spectrum of Ru$_3$(CO)$_8$[C$_6$H$_4$Cr(CO)$_3$][PBut$^\dagger$] (20)](image_url)

*Figure 5.13 200 MHz $^1$H NMR spectrum of Ru$_3$(CO)$_8$[C$_6$H$_4$Cr(CO)$_3$][PBut$^\dagger$] (20)*
Figure 5.14 ORTEP diagram of $\text{Ru}_3(\text{CO})_8[\text{C}_6\text{H}_4\text{Cr}($CO$)_3][\text{PBU}_3]$ (20)
Figure 5.15 PLUTO plot of $\text{Ru}_3(\text{CO})_8[\text{C}_6\text{H}_4\text{Cr(}\text{CO})_3][\text{PBu}^+]$ (20)
Table 5.7 Summary of bond parameters of \( \text{Ru}_3(\text{CO})_8[\text{C}_6\text{H}_4\text{Cr(\text{CO})}_3][\text{PBut}] \) (20)

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<td>Ru2-C13</td>
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Selected bond angles (°)

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<td>84.8(2)</td>
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</table>

a: Here and elsewhere brackets < > refer to mean values

Eight carbonyl ligands in (20) are distributed as follows: three each to Ru1 and Ru2, and two to Ru3. The carbonyl C-Ru distances show significant variation from 1.852(5) Å to 1.959(5) Å. The Ru2-C6 and Ru1-C3 bonds, which are trans to the σ bonds formed by
the benzyne, are shorter than the other two Ru-C(carbonyl) bonds on the same ruthenium atoms. Two equatorial carbonyls bonded to the Ru3 are close to linear (mean 178.1°), while the others bonded to Ru1 and Ru2 are somewhat bent (mean 175.4°). Carbonyls CO1 and CO4 incline toward Ru3, as their average Ru3-Ru-CO angle is only 92.3°.

The benzyne chromium tricarbonyl moiety in (20) can be regarded as being symmetrically σ-bonded to Ru1 and Ru2 through the C12 and C13 atoms respectively (Ru1-C12 = 2.228(4), Ru2-C13 = 2.208(4) Å), and η²-bonded to the Ru3 atom (Ru3-C12 = 2.331(4), Ru3-C13 = 2.296(4) Å). The η²-C-Ru bonds are longer than the σ bonds. The least-square plane of the C₆H₄ ring (χ² = 402) is tilted 81.7° from the Ru3 plane. This angle is much larger than those found in other Os₃ and Ru₃ benzyne complexes (59-72°). A slight folding of the aryne ring along the C14-...17 axis is observed. The dihedral angle between the planes C17-C12-C13-C14 and C17-C16-C15-C14 is 8.03°, and also there is variation of the bond lengths within the C₆H₄ ring (1.385-1.430 Å). These observations suggest that some degree of bond localization does occur.

The chromium atom is located further away from C12 and C13 (Cr1-C12 = 2.350(4), Cr-C13 = 2.370(4) Å) than from the other carbon atoms of the ring (mean 2.188 Å). The chromium atom to ring centroid distance (1.748(2) Å) is longer than that in C₆H₆Cr(CO)₃ (1.726 Å), indicating the movement of the metal atom away from the hydrocarbon upon aryne formation. The opening of the C9-Cr-C10 angle to 98.4(2)° is observed, while the remaining two C-Cr-C angles are only 84.1° on average. The Cr(CO)₃ moiety of the aryne fragment of (20) opens up to accommodate the Cr-Ru interaction which is described next.

One of the important features of (20) is the Ru-Cr bond (2.920(1) Å), which is the first Ru-Cr bond to be structurally characterized. A recent literature report claimed that a
mixed-metal carbide cluster \([\text{PPN}]_2[\text{Cr}_2\text{Ru}_3\text{C(CO)}_{16}]\) contained a Cr-Ru bond [11]. However, the compound was only characterized by microanalysis, IR and \(^{13}\text{C}\) NMR spectroscopy. A complex \((\text{CO})_5\text{Cr}[(\text{CO})_3\text{PMes}_3]_2\) containing an Os-Cr bond (2.966(2) and 3.023(2) Å) was reported by Pomeroy et al. in 1992 [12].

The orientation of the Ru-Cr vector is believed to be from ruthenium to the chromium atom based on the following considerations. Firstly, the movement of the chromium atom away from the aryne plane results in a loss of electron density which is compensated by the establishment of a Ru→Cr bond. Secondly, electron donation from the ruthenium atom can release electron density donated by the \(\eta^2\)-carbon atoms of the aryne moiety. It appears that the presence of the Ru-Cr bond in (20) must play an important part in stabilizing the structure. Overall, the aryne moiety acts as a four-electron donor. Consequently the Ru\(_3\) structure in (20) is electron-precise.

The present results obtained from (20) are novel in at least two ways. The complex (20) contains a benzynechromium tricarbonyl moiety and a Ru→Cr donor-acceptor bond. The complex (20) has a novel type of aryne structure. As discussed in section 1.4.2, trinuclear benzyne complexes may be catalogued into five structural types. However, none of them contains a closed trinuclear framework with a symmetrical aryne moiety and a phosphinidene ligand on opposite sides of the M\(_3\) plane.

The formation of complex (20) involves the cleavage of two P-C bonds and an aryne C-H bond in the original PBu\(^4\)[C\(_6\)H\(_5\)Cr(CO)]\(_2\) ligand. Since benzynechromium tricarbonyl is probably the by-product, a C-H bond is also formed.
5.1.6 Pyrolysis of Ru₃(CO)₁₂ and PPh[C₆H₅Cr(CO)₃]₂

The ruthenium carbonyl Ru₃(CO)₁₂ reacts with PPh[C₆H₅Cr(CO)₃]₂ in heptane under reflux for 5 hours to give one major product, Ru₃(CO)₉[C₆H₄Cr(CO)₃]-[PC₆H₅Cr(CO)₃] (22) (406.6 ppm), in ca. 50% yield, together with a small amount of the monosubstituted derivative Ru₃(CO)₁₁[PPh(C₆H₅Cr(CO)₃)]₂ (21) (43.07 ppm) as indicated by the ³¹P NMR spectrum. The reaction is much slower in refluxing cyclohexane, but gives a higher yield of (21). Pyrolysis proceeds much faster in refluxing octane; however, (21) is not a product. Figure 5.16 shows the ³¹P NMR spectra of the product mixtures measured after carrying out the reaction in three different solvents under reflux. The compounds which show resonances at 248.3, 258.9 and 422.4 ppm in the ³¹P NMR spectra did not survive after column chromatography.

Characterization of Ru₃(CO)₉[C₆H₄Cr(CO)₃][PC₆H₅Cr(CO)₃] (22)

The ³¹P NMR spectrum of (22) reveals only a singlet at 406.6 ppm, characteristic of a multiply bridging phosphinidene ligand. The proton NMR spectrum shows an AA'BB' pattern at 5.5 (t, 2H) and 4.7 (m, 2H) ppm, indicating the presence of an ortho-substituted C₆H₄ ring bound to the Cr(CO)₃ fragment. No signal was observed in the phenyl region. The FAB Mass spectrum contains a parent ion centered on m/e 1012, and fragments corresponding to stepwise loss of fifteen CO ligands. The infrared spectrum in the carbonyl region exhibits six terminal carbonyl vibrations between 1910 and 2080 cm⁻¹. The spectroscopic properties of (22) are consistent with the formula Ru₃(CO)₉[C₆H₄(CO)₃]-[PC₆H₅Cr(CO)₃], but by themselves are not sufficient to enable a complete understanding of the molecular structure. The formation of (22) seems to involve the transformation of the ligand PPh[C₆H₅Cr(CO)₃]₂ to μ₃-C₆H₄Cr(CO)₃ and μ₃-P[C₆H₅Cr(CO)₃] moieties, with the loss of a phenyl group and an η⁶-arene hydrogen atom, presumably as benzene.
Figure 5.16 121.4 MHz $^{31}$P NMR spectrum of the reaction mixtures obtained by the pyrolysis of Ru$_3$(CO)$_{12}$ with PPh[C$_6$H$_5$Cr(CO)$_3$]$_2$ in three solvents (top: cyclohexane; middle: heptane; bottom: octane)
The complete structure of (22) was determined by means of a single crystal X-ray crystallographic study. A view of the molecule is shown in Figure 5.17 and bond parameters are presented in Table 5.8 (see p155). The structure is similar to the class of benzyne derivatives (23), Os₃(CO)₉(C₆H₄)(μ₃-L) described in section 1.4.2, where L = PMe for (23a), As-tol for (23b), PEt for (23c) and PF₆ for (23d), which was previously known only for osmium complexes. This is the first example of an aryne moiety unsymmetrically bound on a ruthenium cluster. A comparison of relevant bond distances and bond angles is tabulated in Table 5.9 (see p156).

The metal atom framework in (22) can be described as an “open” triangle of Ru₃-atoms, each Ru atom bearing three terminally bound carbonyls. A μ₃-PC₆H₅Cr(CO)₃ moiety caps one face of the Ru₃ triangle and the opposite one is capped by a μ₃-C₆H₄Cr(CO)₃ moiety. In fact three Ru atoms are part of the Ru₃P butterfly assembly. The dihedral angle between the planes of the Ru₃P-butterfly is 132.4°. The two Ru-Ru bond distances are different, with the one bridged by the C16-C17 vector significantly longer (2.9124(7) Å) than the other (Rulu-Ru₂ = 2.8123(7) Å). The Ru₂···Ru₃ open edge at 4.0956(7) Å (Ru₂-Ru₁-Ru₃ = 91.34°) is too long to show any metal-metal bonding between Ru₂-Ru₃. The three Ru-P bonds are also inequivalent, and span the range 2.317(1) to 2.416(1) Å, where the longer bond is involved in the interaction with the central Ru₁-atom. A similar bond length distribution is observed in the osmium complexes (23). Three carbonyls carried by Ru₁ have similar Ru₁-C bond distances, the average being 1.927 Å. The rest of the Ru-CO bonds show significant variation in their bond lengths ranging from 1.882(7) to 1.971(6) Å.
Figure 5.17 ORTEP diagram of Ru$_3$(CO)$_9$[C$_6$H$_4$(CO)$_3$][PC$_6$H$_5$Cr(CO)$_3$] (22)
Table 5.8 Selected bond lengths (Å) and bond angles (°) for Ru$_3$(CO)$_9$[C$_6$H$_4$Cr(CO)$_3$][PC$_6$H$_5$Cr(CO)$_3$] (22)

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<td>Ru2···C17</td>
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<td>Ru2-P</td>
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Selected bond angles (°)

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<tr>
<td>C13-Cr2-C15</td>
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$a$: here and elsewhere brackets < > refer to mean values
Table 5.9  Selected bond lengths (Å) and bond angles (°) for Os₃(CO)₉(C₆H₄)(μ₃L)

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<thead>
<tr>
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<th>(23a)</th>
<th>(23b)</th>
<th>(23c)</th>
<th>(23d)</th>
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<td>[15c]</td>
<td>[15d]</td>
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<td>4.110(1)</td>
<td>4.008(2)</td>
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<td>2.113(8)</td>
<td>2.13(3)</td>
<td>2.118(7)</td>
</tr>
<tr>
<td>Os₂-C₂</td>
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<td>2.191(8)</td>
<td>2.17(3)</td>
<td>2.160(8)</td>
</tr>
<tr>
<td>Os₃-C₂</td>
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<td>2.306(9)</td>
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<td>2.415(9)</td>
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<td>Os₃-E</td>
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<td>&lt;C-C&gt;(C₆H₄)</td>
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<td>Os-Os-Os</td>
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<td>91.4(1)</td>
<td>89.0(1)</td>
<td>88.54(3)</td>
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</table>

a. E = As in (23b); E = P in others. b. benzyne and Os₃ interplanar angle.
c. bond angle: Os(1)-Os(2)-Os(3)

The aryne moiety in (22) has some very interesting features. The plane of the aryne moiety is tilted from the planes of Ru₃-Ru₁-P₁ and Ru₂-Ru₁-P₁ by 81.9° and 67.8° respectively. The lengths of the C-C bonds in the two six-membered rings are similar (mean value 1.41 Å) within experimental error (3σ). The aryne moiety is bound unsymmetrically through two σ-bonds to Ru₁ and Ru₃ atoms involving C₁₆ and C₁₇, and through a longer-bond to Ru₂ involving only one carbon C₁₆. The distances Ru₁-C₁₆ at 2.131(5) Å and Ru₃-C₁₇ at 2.103(5) Å are normal and similar to those observed in (23) (Os₁-C₁ and Os₂-
C2), which vary from 2.113(8) to 2.191(8) Å. The C16-Ru2 interaction (2.688(6) Å) in (22) is unexpectedly much longer than any comparable Os-C bond length in (23). However, the distance is comparable with the Ru-C π-bond length in a Ru4 benzyne complex reported by Knox et al. [13], where the longest bond distance is 2.689(11) Å. The dihedral angles Ru3-C17-C16-C21 = 169.6(4)° and Ru1-C16-C17-C18 = -164.0(4)° show that the aryne moiety is not a simple o-phenylene derivative bonded to Ru1 and Ru3. However, this C16-Ru2 interaction appears to be very weak because of the distance involved.

In the aryne moiety the Cr2-C16 and Cr2-C17 bonds are lengthened to 2.297(5) Å and 2.280(5) Å respectively, compared with the other Cr2-C bonds (average length 2.227 Å). The Cr2-C(aryne ring) centroid distance at 1.751(3) Å is longer than that of the P-bound Cr1-C(arene ring) (1.694(2) Å), reflecting the shift of the chromium atom away from the bound aryne ring. This inevitably results in a general lengthening of the Cr2-C bonds (average length 2.248 Å), compared with the P-bound Cr1-C(arene ring) bonds (average length 2.201 Å). As a consequence, it appears that the bonding between Cr2 and C(aryne ring) is weaker than that between Cr1 and C(arene ring).

From a steric point of view, it is surprising to note that the Cr(CO)3 moiety is not on the other side of the aromatic ring pointing “outward” to reduce steric crowding. This implies that the orientation found serves a bonding function between the Cr2 and Ru2 atoms. Further indirect evidence for bonding is provided by the opening of the C14-Cr2-C15 angle to 100.2(3)°, while the average of the other two angles C13-Cr2-C14 and C13-Cr2-C15 is observed at 81.1°. A similar geometry is also found in the complex (20). On this basis, it is reasonable to propose that there is an interaction between the chromium and ruthenium atom in (22), although the bond distance at 3.097(1) Å is rather long, being longer than that found in complex (20) by 0.177 Å. It is known that the lengths of metal-metal bonds vary over a considerable range even for compounds with the same formal bond
order and there is no sharp borderline to distinguish between bonding and nonbonding systems by consideration of distances involved. Mingos et al. suggest that even metal-metal bond lengths which exceed the sum of the metallic radii by 15% can be formally considered as indicating a bonding interaction [14]. The related compound, HRu$_3$[µ$_3$-PPh$_2$(C$_5$H$_3$)-Fe(C$_5$H$_4$PPh$_2$)](CO)$_8$ (24) is believed to contain a Fe-Ru bond of length 3.098(3) Å [1c].

\[
\text{(24)}
\]

In order for the metal atoms to achieve a total count of 50 electrons for an electron-precise open triangle, the C$_6$H$_4$Cr(CO)$_3$ moiety of (22) is required to supply four electrons to the cluster orbitals. Therefore, an electron flow from chromium to ruthenium, in the form of a Cr→Ru bond, seems very likely in order to make the C$_6$H$_4$Cr(CO)$_3$ ligand act as a four electron donor. These four electrons could be distributed as follows: two from the Cr-Ru bond and two from the two C-Ru σ-bonds involving Ru2 and Ru3. However, this approach neglects a contribution from the C16-Ru2 weak interaction.

In an effort to gain more bonding information regarding (22), semi-empirical molecular orbital calculations (INDO/1) on the model compound [Ru$_3$(CO)$_9$\{C$_6$H$_4$Cr(CO)$_3$\}{µ$_3$-PH}] (25) were performed using the CAChe Worksystem. The model compound (25) is derived from (22) by the replacement of a C$_6$H$_5$Cr(CO)$_3$ moiety with one hydrogen. The bond parameters used in the MO calculations were taken from the X-ray
crystal structure analysis of (22). The standard bond distance of P-H (1.380 Å) was used. Some preliminary results are discussed below. Figure 5.18 shows a selection of the bond orders calculated for (25), together with the atomic number scheme.

Figure 5.18 Atomic numbering scheme and selected bond orders of Ru₃(CO)₉[C₆H₄Cr(CO)₃][μ₃-PH] (25) (brackets <> refer to mean values)

The bond order for Cr₂-Ru₂ is 0.29 which indicates the presence of a weak bonding interaction between Cr₂ and Ru₂ in (22). There is also some interaction between
C16 and Ru2. However, the bond order for C16-Ru2 (0.32) is significantly less than those for C17-Ru3 (0.81) and C16-Ru1 (0.75) which can be regarded as σ-bonds. These results are consistent with the observed bond lengths for C17-Ru3 (2.103 Å), C16-Ru1 (2.131 Å) and C16-Ru2 (2.688 Å) described above. It is interesting to note that the bond orders of C16-C17 and C16-C21 (mean 1.13) are smaller than the others (mean value 1.23) on the six-membered ring, suggesting that the π-electron density of these two bonds is lower than the other bonds of the ring. As expected, the bond orders of Cr-CO and Ru-CO are greater than 1 (1.05-1.22) due to 'back bonding" from the metal atoms to the carbonyls. The average bond order of RuC-O at 2.09 is greater than that of CrC-O of 1.89, possibly implying that 'back donation" from the C6H4Cr moiety to its three carbonyl groups is stronger than from the ruthenium atom.

Variable-temperature studies of the NMR spectra of Os3(CO)9(C6H4)(μ3-L) (23) reveal a rocking motion of the benzyne moiety [15]. Such a motion apparently occurs in (22) as well, since the 1H NMR spectrum at ambient temperature shows an AA'XX' pattern for the aryne fragment.

5.1.7 Thermolysis of Ru3(CO)11(AsMe2C6H5Cr(CO)3) (26)

The reaction of the complex (26) in refluxing octane for five hours or in refluxing heptane for a longer time period provides a mixture of six products, of which three can be separated by chromatography on a silica gel column. One of the compounds is Ru3(CO)12, and the other two, HRu3(CO)8[AsMe2][C6H4Cr(CO)3] (27) and HRu2(CO)6[C6H4Cr-(CO)3][AsMe2] (28), are novel benzyne trinuclear and dinuclear complexes respectively. Both complexes are air-sensitive yellow crystals.
(a) Characterization of HRu₃(CO)₈[AsMe₂][C₆H₄Cr(CO)₃] (27)

The complex (27) has been characterized by spectroscopic methods and by X-ray crystallographic analysis. The FAB mass spectrum contains a parent peak of m/e 846 and other peaks associated with the successive loss of eleven carbonyls. The highest mass corresponds to the loss of three carbonyls from the parent complex Ru₃(CO)₁₁(AsMe₂-C₆H₅Cr(CO)₃) (26). The microanalytical data are consistent with this formulation. The $^1$H NMR spectrum of (26) is illustrated in Figure 5.19.

Figure 5.19 400 MHz $^1$H NMR Spectrum of HRu₃(CO)₈[AsMe₂][C₆H₄Cr(CO)₃] (27)
The two doublets (4.98, 4.68 ppm) and the two triplets (6.05, 4.8 ppm) with intensity ratio 1:1:1:1 suggest the presence of an asymmetrically bound aryne moiety. Two inequivalent methyl group resonances are observed at 2.5 and 2.3 ppm respectively and the presence of a bridging hydride in structure (27) is clearly established by the singlet at -18.2 ppm. Overall the formula HRu$_3$(CO)$_8$(C$_6$H$_4$Cr(CO)$_3$)AsMe$_2$ is consistent with the spectroscopic and microanalytical data.

The X-ray structure of complex (27) depicted in Figure 5.20 reveals a novel type of benzyne complex. Selected bond lengths and bond angles are tabulated in Table 5.10 (see p164). The molecule contains a closed cluster of three ruthenium atoms capped on one face by a benzynechromium tricarbonyl moiety. The three Ru-Ru bonds have different lengths: the longest metal-metal bond (Ru1-Ru3 = 3.0082(5) Å) is symmetrically bridged by the hydride observed in the $^1$H NMR and was located in the structural refinement (mean Ru-H = 1.75 Å). Another long metal-metal bond (Ru1-Ru3 = 2.9203(6) Å) is unsymmetrically bridged by the AsMe$_2$ group (Ru1-As = 2.3689(5), Ru2-As = 2.4499(5) Å) that serves as a three electron donor. The third Ru-Ru bond is of normal length at 2.8285(2) Å and is somewhat shorter than the mean value found in Ru$_3$(CO)$_{12}$ (2.854(4) Å). The As and hydride atoms are on the same side of the Ru$_3$ plane from the aryne moiety. The As-Ru1-Ru2 and H-Ru1-Ru3 planes make angles of 79.42° and 31.58° respectively with the Ru$_3$ plane.

There are eight terminal carbonyl ligands (mean angle Ru-C-O = 177°) in (27), which are distributed as follows: two to Ru1 and three each to Ru2 and Ru3. The ruthenium-carbon(CO) distances vary significantly from 1.880(3) to 1.969(4) Å with Ru3-C$_{16}$(ax) the longest. The average Ru1-CO bonds (1.883 Å) are little shorter than the other Ru-CO bonds (mean 1.925 Å).
Figure 5.20 Molecular structure of HRu$_3$(CO)$_9$($C_6$H$_4$Cr(CO)$_3$)AsMe$_2$ (27)
Table 5.10 Summary of bond parameters of HRu₃(CO)₈\{C₆H₄Cr(CO)₃\}AsMe₂ (27)

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<th>Length (Å)</th>
<th>Bond</th>
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Selected bond angles (°)

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<td>C18-Cr1-C19</td>
<td>95.2(1)</td>
<td>C17-Cr1-C18</td>
<td>82.8(2)</td>
</tr>
<tr>
<td>C17-Cr1-C19</td>
<td>82.3(1)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

a: here and elsewhere brackets <> refer to mean values

The benzynechromium tricarbonyl moiety in (27) is bound to the closed Ru₃ cluster in an unsymmetrical manner, previously observed only for open Os₃ clusters. The C₆H₄ is bonded to two Ru atoms (Ru1 and Ru2) through one carbon atom (C1) and to only one Ru atom (Ru3) through the adjacent carbon atom (C2). The unsymmetrical bonding of the C₆-
ring in (27) is evident from the following data: the Ru2-C1-C2-Ru3 conformational angle is 33.2(2)°; Ru2 is 1.323 Å from the C6-plane and Ru3 is 0.118 Å from the C6-plane but on the opposite side; atom Cl bridges the Ru1-Ru2 bond, C1-Ru1 = 2.185(3) Å, C1-Ru2 = 2.339(3) Å, and atom C2 is bound to Ru3, C2-Ru3 = 2.084(3) Å. The C2-Ru1 distance at 2.833(3) Å is too long to be considered a bonding interaction. If the Ru1-C1-Ru2 forms a three center two electron bond and Ru3-C2 forms a normal σ bond, then the C6H4 serves as a two electron donor. However, if the 18-electron rule applies, the whole benzynechromium tricarbonyl moiety is required to contribute four electrons to the cluster. This apparently is achieved by donating two electrons from chromium to the Ru1 atom. A Cr→Ru bond (2.9704(6) Å) is present in (27), being longer by 0.050 Å than that in [Ru3(CO)8(C6H4Cr(CO)3)PBut] (20) (2.920(1) Å) and shorter by 0.027 Å than that in [Ru3(CO)9(C6H4Cr(CO)3)PC6H5Cr(CO)3] (22). However, the reverse flow of electrons Ru→Cr in (20) is indicated by a distinct folding of the aromatic ring, as discussed in section 5.15. The two carbonyls attached to Cr spread apart to accommodate the Cr-Ru bond. Thus the angle C18-Cr-C19 at 95.2° is greater than C17-Cr-C19 and C17-Cr-C18 (mean 82.5°). As in (20) and (22), the Cr-ring centroid distance (1.746(2) Å) is lengthened, compared with that in C6H6Cr(CO)3 (1.726 Å).

The aryne ring is planar and is inclined at an angle of 82.4° from the Ru3 plane, thus it is close to being perpendicular to the Ru3 plane. In benzyne complexes there is considerable variation in this angle; however, it is invariably smaller in magnitude, varying from 42° to 73°. The lengths of the ortho-metallated C1-C2 and the adjacent two bonds (C1-C6 and C2-C3) (mean 1.429 Å) are longer than the other three bonds (mean 1.400 Å) in the ring. This pattern of C-C bond lengths in (27) is similar to that observed in (22) and in Os3(CO)9(C6H4)L, where L = P-Fc, or As-tol [15b, 15d].
Other structural features of (27) can be compared with the benzyne complexes (29a-29d) (Figure 5.21) of types III and IV, discussed in Section 1.4.2. The relevant bond distances and bond angles of (29) are listed in Table 5.11. All structures consist of a metal triangle with a bridging three electron donor ligand, a bridging one electron donor hydride ligand, and a triply bridging C₆H₄ moiety. However, in the complexes (29) the C₆H₄ moiety clearly acts as a four-electron donor, allowing the cluster to obey the 18-electron rule and hence the bonding can be interpreted in terms of two σ bonds Os₁-C₁ and Os₃-C₂ and an η²-linkage involving C₁, C₂, and Os₂. The complexes (29c) and (29d) have one more carbonyl than the complexes (29a) and (29b) because the Os₃ framework in the later complexes is open and has only two Os-Os bonds, while (29c) and (29d) have three metal-metal bonds.

Table 5.11 Bond lengths (Å) and bond angles (°) of (29a) - (29d)

<table>
<thead>
<tr>
<th>Bonding</th>
<th>(29a)</th>
<th>(29b)</th>
<th>(29c)</th>
<th>(29d)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Os₁-Os₂</td>
<td>2.839(4)</td>
<td>2.833(1)</td>
<td>2.739(2)</td>
<td>2.715(2)</td>
</tr>
<tr>
<td>Os₂-Os₃</td>
<td>2.946(4)</td>
<td>2.939(1)</td>
<td>2.918(2)</td>
<td>2.960(2)</td>
</tr>
<tr>
<td>Os₃-Os₁</td>
<td>3.929(5)</td>
<td>3.791(1)</td>
<td>2.892(2)</td>
<td>2.881(2)</td>
</tr>
<tr>
<td>Os₁-Os₂-Os₃</td>
<td>85.5(1)°</td>
<td>------</td>
<td>------</td>
<td>------</td>
</tr>
<tr>
<td>Os₁-C₁</td>
<td>2.138(19)</td>
<td>2.10(2)</td>
<td>2.22(4)</td>
<td>2.20(4)</td>
</tr>
<tr>
<td>Os₃-C₂</td>
<td>2.198(13)</td>
<td>2.19(2)</td>
<td>2.09(4)</td>
<td>2.14(4)</td>
</tr>
<tr>
<td>Os₂-C₁</td>
<td>2.388(14)</td>
<td>2.37(2)</td>
<td>2.38(4)</td>
<td>2.26(4)</td>
</tr>
<tr>
<td>Os₂-C₂</td>
<td>2.296(15)</td>
<td>2.35(2)</td>
<td>2.42(4)</td>
<td>2.59(4)</td>
</tr>
<tr>
<td>C₁-C₂</td>
<td>1.436(22)</td>
<td>1.42(2)</td>
<td>1.42(4)</td>
<td>1.42(4)</td>
</tr>
<tr>
<td>Os₁-E</td>
<td>2.482(3)</td>
<td>2.433(5)</td>
<td>2.26(1)</td>
<td>2.26(8)</td>
</tr>
<tr>
<td>Os₃-E</td>
<td>2.483(4)</td>
<td>2.418(4)</td>
<td>2.42(1)</td>
<td>2.42(8)</td>
</tr>
<tr>
<td>C₆H₄-Os₃</td>
<td>------</td>
<td>71.5°</td>
<td>69(3)°</td>
<td>69(3)°</td>
</tr>
</tbody>
</table>

a: E = As. b: E = S. c: E = P
(b) Characterization of \( \text{HRu}_2(\text{CO})_6\text{AsMe}_2[\text{C}_6\text{H}_4\text{Cr}(\text{CO})_3] \) (28)

The pyrolytic reaction of \( \text{Ru}_3(\text{CO})_9(\text{PPh}_3)_3 \) in refluxing decalin yielded significant amounts of dinuclear complexes, together with a small amount of a benzyne \( \text{Ru}_3 \) cluster[1]. The dinuclear complexes were only characterized by mass spectrometry, \(^1\text{H} \) NMR and IR spectroscopic methods, and were formulated as shown in (30a), (30b) and (30c). The complexes (30a) and (30b) contain ortho-metallated phosphine ligands, but no benzyne moieties. The complex (30c) contains two bridging diarylphosphido ligands resulting from two aryl C-P cleavages. There was no evidence for the formation of any ruthenium hydride species.
The thermal reaction of Os$_3$(CO)$_{11}$(AsPhMe$_2$) in refluxing octane or nonane produced mainly benzyne Os$_3$ complexes, in addition to two dimeric complexes in very low yields. These diosmium derivatives were not well characterized, but were formulated as "benzyne" (or o-phenylene) derivatives (see Section 1.3).

The structure of the pyrolysis product (28) was determined by X-ray crystallography. In view of the early studies mentioned above it was of considerable interest to find that (28) was the first example of a dinuclear o-phenylenechromium tricarbonyl derivative. An ORTEP diagram of (28) is shown in Figure 5.22 and selected bond lengths and bond angles are given in Table 5.12.

![Figure 5.22 ORTEP plot of HRu$_2$(CO)$_6$AsMe$_2$[C$_6$H$_4$Cr(CO)$_3$] (28)](image-url)
Table 5.12 Bond parameters of HRu$_2$(CO)$_6$AsMe$_2$[C$_6$H$_4$Cr(CO)$_3$] (28)

<table>
<thead>
<tr>
<th>Bond</th>
<th>Length (Å)</th>
<th>Bond</th>
<th>Length (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ru1-Ru2</td>
<td>2.9791(5)</td>
<td>Ru1-H</td>
<td>1.79(3)</td>
</tr>
<tr>
<td>Ru1-H</td>
<td>2.113(3)</td>
<td>Ru2-H</td>
<td>1.79(3)</td>
</tr>
<tr>
<td>Ru1-C1</td>
<td>2.4453(5)</td>
<td>Ru2-As</td>
<td>2.4403(5)</td>
</tr>
<tr>
<td>&lt;RuC≡O&gt;</td>
<td>1.131</td>
<td>&lt;CrC≡O&gt;</td>
<td>1.150</td>
</tr>
<tr>
<td>&lt;Cr-CO&gt;</td>
<td>1.830</td>
<td>Cr-Bz</td>
<td>1.750</td>
</tr>
<tr>
<td>C1-C2</td>
<td>1.427(4)</td>
<td>&lt;C-C&gt;ring</td>
<td>1.408</td>
</tr>
<tr>
<td>Cr1-Cring</td>
<td>2.310(3)-2.209(3)</td>
<td>Ru-CO</td>
<td>1.890(4)-1.981(4)</td>
</tr>
<tr>
<td>Selected bond angles (°)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ru-C-O</td>
<td>175.1(4)-179.4(4)</td>
<td>Cr-C-O</td>
<td>176.6(3)-178.4(3)</td>
</tr>
</tbody>
</table>

The complex (28) consists of two ruthenium atoms bonded together and bridged by the C$_6$H$_4$Cr(CO)$_3$ moiety, hydride and AsMe$_2$ groups. The molecule appears to have mirror symmetry but minor distortions are present; thus the AsMe$_2$ group is slightly asymmetrically bonded to Ru1 and Ru2, (As1-Ru1 = 2.4453(5) Å and As1-Ru2 = 2.4403(5) Å) and the conformational angle Ru1-C1-C2-Ru2 is 1.4(2)°. The bridging hydride was located in the crystal structure determination. The Ru-H distance at 1.79(3) Å is similar to those found in (27) within experimental error (3σ). The C$_6$H$_4$Cr(CO)$_3$ moiety is required to be a two-electron donor and bonding can be viewed in terms of σ bonds to Ru1 and Ru2 atoms. The two equal Ru-C(ring) distances at 2.112 Å fall in the range of 2.084(3) Å to 2.339(3) Å as observed in (27). The Cr1-C1, Cr1-C2 and Cr1-C6 bond
lengths are lengthened to 2.279 (mean) Å, longer than the remaining three Cr1-C bonds (average 2.213 Å). This same bonding trend is also found in (27). The C6H4 least-squares plane is approximately perpendicular to the Ru1-Ru2-As1 plane. The dihedral angle between them is 86.75°. The hydride is displaced 0.502 Å out of the plane of Ru1-Ru2-As1, away from the C6H4Cr(CO)3 moiety.

There appears to be no systematic pattern of C-C bond length alternation within the C6-ring. However, the C1-C2 bond distance at 1.427(4) Å is somewhat longer than the C4-C5 bond at 1.390(5) Å. The C-C distances may be on average (1.408 Å) slightly shorter than those (average 1.415 Å) found in (27).

Structures have been determined for two dinuclear metal o-phenylene complexes Ir2(CO)2Cp2(C6H4) (31) and Fe2(CO)8(C6F4) (32), as outlined in Section 1.3, and one trinuclear metal complex Os₃(CO)₈H₃(C6H₄)(HC=NPh) (33) which is the only known trinuclear o-phenylene derivative [16].

As found in (28), the metal-metal bonded atoms in (31), (32) and (33) do not quite lie in the plane of the aromatic moiety. The C-C distances average 1.379 Å for (31), 1.375 Å for (32), and 1.37 Å for (33), and there is no significant variation around the rings. As mentioned above, the average C-C lengths in the six-membered ring of (27) and (28) are
longer than these values. However, it should be noted that the C-C bond lengths of C₆H₆Cr(CO)₃ range from 1.406 to 1.423 Å and are longer than those of free benzene 1.397 Å, so the trends noted above may be a simple extension of this fundamental observation.

There are six linear terminal carbonyls which are distributed three each to Ru1 and Ru2. The Ru-CO distances which are trans to ruthenium-aryne σ bonds (C9-Ru1 = 1.972(4) and C12-Ru2 = 1.981(4) Å) are noticeably longer than the others (mean 1.912 Å), which is probably a consequence of the trans-influence of the C₆H₄Cr(CO)₃ group. The Ru-CO(eq) distances of 1.934 Å trans to the As-Ru bonds (i.e. Ru1-C8, Ru2-C11) are longer than those cis to the As-Ru bonds (Ru1-C7, Ru2-C10) by 0.044 Å. It is interesting to note that four equatorial carbonyls are bent slightly upwards towards the C₆H₄Cr(CO)₃ moiety.

The mass spectrum of (28) exhibits a parent ion at m/e 689, in agreement with the expected formulation HRu₂(CO)₆AsMe₂[C₆H₄Cr(CO)₃], together with ions formed by the consecutive loss of the nine carbonyl groups. In addition, the ¹H NMR spectrum of (28), illustrated in Figure 5.23, is in accord with the structure as determined by X-ray crystallography. Two singlets in the methyl region at 1.35 and 1.95 ppm indicate the presence of two nonequivalent methyl groups. The signal at -12.5 ppm is assigned to the bridging hydride which shows a significant downfield shift when compared with the hydride signal at -18.2 ppm observed for (27). The two symmetrical multiplets at 5.0 and 5.15 ppm are assigned to the AA'BB' system of the o-phenylene moiety.
Figure 5.23 400 MHz $^1$H NMR spectrum of HRu$_2$(CO)$_6$AsMe$_2$[C$_6$H$_4$Cr(CO)$_3$] (28)

5.2 Summary and Future Considerations

The preparation of cluster bound derivatives of benzynechromium tricarbonyl by means of pyrolysis reactions involving phosphine or arsine derivatives of benzenecchromium
tricarbonyl has been described. Two strategies were used in these syntheses. The first
involves heating the substituted complexes such as Ru$_3$(CO)$_{11}$[ER$_2$C$_6$H$_5$Cr(CO)$_3$] (ER =
PPr$^i$, PPh, AsMe) in a hydrocarbon solvent. The second involves refluxing Ru$_3$(CO)$_{12}$ or
Os$_3$(CO)$_{12}$ together with the bulky ligand such as PBut$_2$C$_6$H$_5$Cr(CO)$_3$, PPh[C$_6$H$_5$Cr-
(CO)$_3$]$_2$ under similar conditions. The pyrolytic products were isolated, and subsequently
classified by spectroscopic and X-ray crystallographic methods.

Several novel benzynechromium tricarbonyl complexes were successfully prepared
and structurally characterized. The complex Ru$_3$(CO)$_9$[C$_6$H$_4$Cr(CO)$_3$][μ$_3$-C$_6$H$_5$Cr(CO)$_3$]
(22) consists of an open Ru$_3$ triangle capped on one face by a μ$_3$-phosphinidene moiety and
on the other face by an unsymmetrically bound benzynechromium tricarbonyl moiety. It is
the first example of an aryne to show such unsymmetric bonding to an Ru$_3$ system. The
X-ray crystallographic analysis of Ru$_3$(CO)$_8$[C$_6$H$_4$Cr(CO)$_3$][μ$_3$-PBut$^i$] (20) reveals
another novel type of benzyne structure, consisting of a closed Ru$_3$ framework with a
symmetrical benzynechromium tricarbonyl moiety and a phosphinidene ligand on opposite
sides. The complex Ru$_3$(CO)$_8$[μ-H][C$_6$H$_4$Cr(CO)$_3$][μ-AsMe$_2$] (27), derived via ortho-
metallation of one C-H and one C-As bond, consists of a closed ruthenium triangle with an
arsinido group, a bridging hydride and an unsymmetrically bridging benzynechromium
tricarbonyl moiety. It is the first example of a benzyne involved in unsymmetric bonding to
a closed metal triangle system to be characterized. The molecule(Os$_3$(CO)$_8$[μ-PPPr$^i_2$][μ-
H][C$_6$H$_4$Cr-(CO)$_3$] (16), an analogue of (27), was also isolated and characterized. One
unexpected feature common to all of the four benzynechromium tricarbonyl complexes is
the presence of Cr-Ru bonding. This bonding is unprecedented and the bond distances range
from 2.920(1) in (20) to 3.097(1) Å in (22). It is believed that the presence of the Ru-Cr
bond in these complexes must play an important part in stabilizing the structure.
The first dinuclear benzynechromium tricarbonyl complex Ru$_2$(CO)$_6$[μ-H]-
[C$_6$H$_4$Cr(CO)$_3$][μ-AsMe$_2$] (28) has also been characterized. In this complex, the Ru-Ru
bond is bridged by a μ-benzynechromium tricarbonyl moiety, an arsinido moiety and a
hydride.

Two new benzyne complexes, which are of known structural type, were isolated and
characterized. The structure of Ru$_3$(CO)$_7$[C$_6$H$_4$][μ-PPhC$_6$H$_5$Cr(CO)$_3$]$_2$ (2), which is a
product of the thermolysis of Ru$_3$(CO)$_{11}$[PPh$_2$C$_6$H$_5$Cr(CO)$_3$], consists of a closed
triangle of ruthenium atoms with two of the edges bridged by phosphido groups and with
one face capped by a μ$_3$-benzyne moiety. The compound Ru$_3$(CO)$_7$[C$_6$H$_4$][μ-
PPhC$_6$H$_5$Cr(CO)$_3$]$_2$ (3), a structural isomer of the complex (2), was also isolated and
characterized. Another compound Os$_3$(CO)$_9$[μ$_3$-PC$_6$H$_5$Cr(CO)$_3$][μ$_3$-C$_6$H$_4$] (7), which is
produced from the thermolysis of Os$_3$(CO)$_{11}$[PPr$_i$$_2$C$_6$H$_5$Cr(CO)$_3$], contains an open
cluster of osmium atoms coordinated on one side by a face bridging phosphinidene ligand
and on the opposite side by a benzyne ligand.

Furthermore, pyrolysis products other than aryne complexes were isolated and
characterized. The complexes Os$_3$(CO)$_8$L[μ-H]$_2$[PPr$_i$$_2$C$_6$H$_4$Cr(CO)$_3$] (L = CO (13) and
PPr$_i$$_2$C$_6$H$_5$Cr(CO)$_3$ (14)) were derived via ortho-metallation of a C-H bond of an η$_6$-
bound C$_6$H$_5$ moiety and reductive elimination of a propene molecule. It is interesting to
note that the complex Os$_3$(CO)$_8$[PPhC$_6$H$_4$][PPh$_2$C$_6$H$_5$Cr(CO)$_3$] (8), derived via ortho-
metallation of a C$_6$H$_5$ moiety and the elimination of a benzenecromium tricarbonyl
molecule, is electron deficient. This is the first example of electron unsaturation found in a
structure of this type.

Reaction sequences have been proposed to account for the products of the pyrolysis
of the complexes Os$_3$(CO)$_{11}$[PPh$_2$C$_6$H$_5$Cr(CO)$_3$] and Os$_3$(CO)$_{11}$[PPr$_i$$_2$C$_6$H$_5$Cr(CO)$_3$].
In general, it appears that phenylchromium tricarbonyl and phenyl groups in triruthenium or triosmium clusters readily undergo C-H cleavage and C-P cleavage. The isopropyl group undergoes facile β C-H activation and subsequent C-P activation, while methyl and tert-butyl groups remain intact. It seems that the ease of P-C cleavage follows the order: P-C(Me, Bu) > P-C(Pr) > P-C(Ph) > P-C(C₆H₅Cr(CO)₃). A comparison of the thermolytic reactions of ruthenium and osmium clusters confirms that the latter are generally more thermally stable; mononuclear and dinuclear products, derived from cluster breakdown, were found only in the thermolysis products of some ruthenium complexes. This reflects the greater strength of the metal-metal bonds in the Os₃ cluster.

Many more pyrolytic reactions should be investigated in order to verify these trends and extend the results to other systems. It would certainly be interesting to study a series of thermolytic reactions involving Ru₃(CO)₁₂ or Os₃(CO)₁₂ and the following new ligands: ERPhC₆H₅Cr(CO)₃, (E = P, As; R = Me, Et, Pr, Bu). These ligands contain three different P-C bond types: P-C(alkyl), P-C(η₆-C₆H₅) and P-C(C₆H₅). Pyrolysis reaction studies of trinuclear metal clusters containing these ligands should be helpful to understand the relative ease of cleavage of P-C(alkyl), P-C(η₆-C₆H₅) and P-C(C₆H₅) bonds. The complexes which have not been well identified during this work should be further investigated and characterized by spectroscopic and X-ray crystallographic methods. Further MO calculations on the complexes Ru₃(CO)₉[C₆H₄Cr(CO)₃][PC₆H₅Cr(CO)₃], Ru₃(CO)₈[C₆H₄Cr(CO)₃][PBu] and the model complex C₆H₄Cr(CO)₃ may also prove to be useful to understand aryne bonding in the clusters.

Preparation of complexes containing benzynechromium tricarbonyls should be extended to mononuclear metal complexes as well. The synthetic routes to the mononuclear metal complexes of benzyne, as described in section 1.4.3, may be used to prepare mononuclear metal complexes containing benzynechromium tricarbonyls. For instance,
heating Cp2ZrMe(C6H5) in the presence of trimethylphosphine leads to the benzyne-
zirconocene complex Cp2Zr(C6H4)PMe3 in high yield [17]. Therefore, treatment of the
chloro(methyl) zirconocene complex Cp2ZrClMe with a lithium derivative of benzenechro-
mium tricarbonyl may result in complex Cp2Zr[Me][C6H5Cr(CO)3]. This complex may
lose methane upon heating in the presence of trimethylphosphine to form Cp2Zr[PMe]-
[C6H4Cr(CO)3].

5.3 Experimental Procedures

5.3.1 Pyrolysis of Ru3(CO)11[PPh2C6H5Cr(CO)3] (1)

The complex Ru3(CO)11(PPh2C6H5Cr(CO)3) (200 mg) was refluxed in heptane
(30 mL) for 1.5 hours. A color change from red to red-brown took place and TLC
monitoring revealed the formation of one principal product. The solvent was removed in vacuo,
and the solid residue was chromatographed on an alumina column (neutral, activity
I, 80-200 mesh) with CH2Cl2/hexanes (1:2) as eluent to give three bands. Ru3(CO)12 of
known spectral properties was isolated in trace amounts from band 1. Band 2 proved to be
the starting material (1). Band 3 afforded a red-purple solid, which was identified as the
compound (2). X-ray quality crystals of (2) were grown from CH2Cl2/hexanes at room
temperature. The major component in the mother liquor was (3) which was further purified
by column chromatography by using CH2Cl2/hexanes (1:5) as eluent.

Compound (2): 31P{1H} NMR (121.42 MHz, CDCl3) δ: 272.8 (d, J(P-P) = 199
Hz), 211.9 (d, J(P-P) = 201 Hz). 1H NMR (300 MHz, CDCl3) δ: 4.55 (t, 1H), 4.7 (t, 1H),
4.8 (t, 1H), 5.0 (t, 1H), 5.3-5.4 (m, 2H), 5.5 (t, 1H), 5.75 (t, 1H), 6.4-6.5 (m, 2H), 6.6 (t,
1H), 7.1 (d, 1H), 7.3 (t, 2H), 7.4-7.6 (br m, 6H), 7.9 (td, 2H). MS (FAB): m/e 1216 (P)+,
1132 [P-3CO⁺], 1076 [P-5CO⁺], 1020 [P-7CO⁺], 992 [P-8CO⁺], 964 [P-9CO⁺], 936 [P-
10CO⁺], 908 [P-11CO⁺], 880 [P-12CO⁺], 852 [P-13CO⁺], 775 [P-13CO-Ph]⁺. IR (KBr):
\(v(\text{CO}): 2056 \, (s), \, 2001 \, (s), \, 1965 \, (s), \, 1889 \, (s) \, \text{cm}^{-1}\). Anal. Calcd for \(\text{C}_{43}\text{H}_{24}\text{CrO}_{13}\text{P}_{2}\text{Ru}_{3}\cdot\text{CH}_{2}\text{Cl}_{2}: \, \text{C}, \, 40.56; \, \text{H}, \, 2.02. \) Found: \(\text{C}, \, 40.52; \, \text{H}, \, 2.02. \)

Compound (3): \(^{31}\text{P}\{^1\text{H}\} \text{NMR} \,(121.42 \, \text{MHz, CDCl}_3) \delta: \, 237 \, (s). \, ^1\text{H} \text{NMR} \,(300 \, \text{MHz, CDCl}_3) \delta: \, 4.7 \, (m, \, 2\text{H}), \, 4.9 \, (m, \, 2\text{H}), \, 5.2 \, (m, \, 2\text{H}), \, 5.4 \, (m, \, 2\text{H}), \, 5.5 \, (m, \, 2\text{H}), \, 6.6 \, (m, \, 2\text{H}), \, 7.0 \, (m, \, 2\text{H}), \, 7.2-7.6 \, (m, \, 8\text{H}), \, 7.8 \, (m, \, 2\text{H}). \, \text{MS} \,(\text{FAB}): \, m/e \, 1216 \, [\text{P}]^{+}, \, 1132 \, [\text{P}-3\text{CO}]^{+}, \, 1076 \, [\text{P}-5\text{CO}]^{+}, \, 1020 \, [\text{P}-7\text{CO}]^{+}, \, 992 \, [\text{P}-8\text{CO}]^{+}, \, 964 \, [\text{P}-9\text{CO}]^{+}, \, 936 \, [\text{P}-10\text{CO}]^{+}, \, 908 \, [\text{P}-11\text{CO}]^{+}, \, 880 \, [\text{P}-12\text{CO}]^{+}, \, 852 \, [\text{P}-13\text{CO}]^{+}, \, 775 \, [\text{P}-13\text{CO-Ph}]^{+}.

5.3.2 Pyrolysis of \(\text{Os}_3(\text{CO})_{11}\text{PPh}_2\text{C}_6\text{H}_5\text{Cr}(\text{CO})_3\) (6)

A solution of (6) (200 mg) in octane (30 mL) was heated under reflux at 130°C for 18 hours during which there was a color change from yellow to brown. The solution was cooled and then the solvent was removed \textit{in vacuo}. The residue was redissolved in 5 mL of dichloromethane and chromatographed on a silica gel column using CH$_2$Cl$_2$/hexanes (1:1.7) as eluent to give four bands. Band 1 was identified as \(\text{Os}_3(\text{CO})_{12}\) by means of infrared spectroscopy. Band 4 contained a small amount of an unknown orange solid which slowly decomposed on exposure to light at room temperature.

Band 2 was found to contain (7). Yellow crystals were grown from hexanes/CH$_2$Cl$_2$ (5:1) solution at -4 °C. MS (FAB): \(m/e\) 1143 [\text{P}]^{+}, 1059 [\text{P}-3\text{CO}]^{+}, 1031 [\text{P}-4\text{CO}]^{+}, 1003 [\text{P}-5\text{CO}]^{+}, 975 [\text{P}-6\text{CO}]^{+}, 892 [\text{P}-9\text{CO}]^{+}, 807 [\text{P}-12\text{CO}]^{+}. \, ^{31}\text{P}\{^1\text{H}\} \text{NMR} \,(121.42 \, \text{MHz, CDCl}_3) \delta: \, 218.2 \, (s). \, ^1\text{H} \text{NMR} \,(400 \, \text{MHz, CDCl}_3) \delta: \, 5.3 \, (t, \, 2\text{H}), \, 5.45 \, (t, \, 3\text{H}), \, 7.1 \, (q, \, 2\text{H}), \, 7.55 \, (t, \, 2\text{H}). \, \text{IR} \,(\text{CH}_2\text{Cl}_2) \, v(\text{CO}): \, 2060 \, (s), \, 2040 \, (s), \, 2000 \, (s), \, 1990 \, (s), \, 1970 \, (s), \, 1910 \, (s) \, \text{cm}^{-1}. \, \text{Anal. Calcd for C}_{24}\text{H}_9\text{CrO}_{12}\text{Os}_3\text{P}: \, \text{C}, \, 25.22; \, \text{H}, \, 0.79. \) Found: \(\text{C}, \, 25.31; \, \text{H}, \, 0.80. \)
Band 3 was identified as (8). X-ray quality crystals were grown from CH$_2$Cl$_2$/hexane (1:2) at -4 °C. Mass spectrum (FAB): m/e 1380 [P]$^+$, 1296 [P-3CO]$^+$, 1240 [P-5CO]$^+$, 1184 [P-7CO]$^+$, 1128 [P-9CO]$^+$. $^{31}$P{1H} NMR (80.96 MHz, CDCl$_3$) $\delta$: 36.4 (d, J(P-P) = 4.85 Hz), -2.51 (d, J(P-P) = 4.87 Hz). $^1$H NMR (300 MHz, CDCl$_3$) $\delta$: 7.3-7.6 (m, 15H), 6.8 (t, 2H), 6.6 (t, 2H), 6.2 (1t, 1H), 6.0 (t, 1H), 5.4 (t, 1H), 5.2 (q, 1H), 5.0 (1, 1H). IR (KBr) v(CO): 2080 (s), 2040 (s), 1970-1990 (br, vs), 1910 (s) cm$^{-1}$. Anal. Calcd for C$_{41}$H$_{24}$CrOs$_3$P$_2$CH$_2$Cl$_2$: C, 34.50; H, 1.79. Found: C, 34.61; H, 1.82.

5.3.3 Pyrolysis of Os$_3$(CO)$_{11}$(PPri$_2$C$_6$H$_5$Cr(CO)$_3$

A sample of Os$_3$(CO)$_{11}$(PPri$_2$C$_6$H$_5$Cr(CO)$_3$) (200 mg, 0.21 mmol) was heated in refluxing octane (50 mL) for 24 hours. The solvent was removed on the vacuum line and the remaining solid was dissolved in dichloromethane (20 mL). A small amount of silica gel was added to the solution and then this crude solution was evaporated to dryness. The dry silica gel was added to the top of a silica gel column which was eluted with CH$_2$Cl$_2$/hexanes (1/1.8) to give two bands.

The first band yielded H$_2$Os$_3$(CO)$_9$PPri$_2$C$_6$H$_4$Cr(CO)$_3$ (13). Yellow crystals of (13), suitable for X-ray crystal structure determination, were grown at -30 °C from a mixture of CH$_2$Cl$_2$/hexanes. MS (FAB): m/e 1112 [P]$^+$, 1028 [P-3CO]$^+$, 1000 [P-4CO]$^+$, 972 [P-5CO]$^+$, 944 [P-6CO]$^+$, 916 [P-7CO]$^+$, 888 [P-8CO]$^+$, 860 [P-9CO]$^+$, 832 [P-10CO]$^+$, 804 [P-11CO]$^+$, 776 [P-12CO]$^+$. $^{31}$P{1H} NMR (121.42 MHz, CDCl$_3$) $\delta$: 69.0 (s). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$: 5.6 (m, 2H), 5.3 (m, 1H), 4.9 (m, 1H), 2.2 (m, 1H), 1.6 (m, 6H), -16.6 (dd, J(P-H) = 3 Hz, 1H), -17.7 (d, J(P-H) = 4 Hz, 1H). IR (KBr) v(CO): 2110 (m), 2080 (m), 2040 (vs), 2000 (s), 1990 (s), 1975 (s), 1950 (s), 1880 (s), 1870 (s) cm$^{-1}$. Anal. Calcd for C$_{21}$H$_{13}$CrO$_{12}$Os$_3$P: C, 22.70; H, 1.18. Found: C, 22.68; H, 1.29.
The second band afforded H$_2$Os$_3$(CO)$_8$[PPri$_2$C$_6$H$_4$Cr(CO)$_3$]PPri$_2$C$_6$H$_5$Cr(CO)$_3$ (14). X-ray quality yellow crystals of (14) were obtained by recrystallization at -20 °C from CH$_2$Cl$_2$ with hexanes layered on the top of the solution. MS (FAB): $m/e$ 1414 [P]$^+$, 1330 [P-3CO]$^+$, 1274 [P-5CO]$^+$, 1246 [P-6CO]$^+$, 1218 [P-7CO]$^+$, 1190 [P-8CO]$^+$, 1162 [P-9CO]$^+$, 1106 [P-11CO]$^+$, 1022 [P-14CO]$^+$. $^{31}$P{1H} NMR (121.42 MHz, CDC$_1$3) δ: 55.4 (s), 15.9 (s). 1H NMR (400 MHz, CDC$_1$3) δ: 5.9 (m, 1H), 5.7 (m, 2H), 5.6 (t, 1H) 5.4 (t, 1H), 5.3 (t, 1H), 5.2 (t, 1H), 5.1 (t, 1H), 4.9 (t, 1H), 2.8 (m, 1H), 2.5 (m, 2H), 1.7-1.2 (m, 18H), -16.5 (dd, 1H), -17.1 (dd, 1H). IR (KBr) v(CO): 2080 (m), 2040 (s), 2000-1970 (br, s), 1950 (m), 1880 (br, m) cm$^{-1}$. Anal. Calcd for C$_{35}$H$_{32}$Cr$_2$O$_{14}$Os$_3$P$_2$: C, 28.07; H, 2.30. Found: C, 28.46; H, 2.30.

5.3.4 Thermolysis of Ru$_3$(CO)$_{11}$(PPri$_2$C$_6$H$_5$Cr(CO)$_3$) (15)

A cyclohexane solution (50 mL) of (15) (330 mg, 1.0 mmol) was refluxed for 20 hours. The solvent was removed under vacuum and the residue chromatographed on a column of neutral alumina. Elution with hexanes/CH$_2$Cl$_2$ (2/1) developed 4 bands. The first band contained a trace amount of Ru$_3$(CO)$_{12}$ and the third band contained the starting material (15).

The second band gave new complex (16). $^{31}$P{1H} NMR (121.42 MHz, CDC$_1$3) δ: 309.6 (s). 1H NMR (300 MHz, CDC$_1$3) δ: 6.0 (m, 1H), 4.9 (m, 1H), 4.7 (m, 1H), 4.6 (m, 1H), 3.1 (m, 1H), 2.4 (m, 1H), 1.6-1.9 (m, 12H), -17.9 (d, J(P-H) = 8.7 Hz, 1H). MS (FAB): $m/e$ 858 [P]$^+$, 774 [P-3CO]$^+$, 550 [P-11CO]$^+$. Anal. Calcd for C$_{23}$H$_{19}$CrO$_{11}$P-Ru$_3$: C, 32.21; H, 2.23. Found: C, 32.52; H, 2.35.

The fourth band gave the complex (17) which was recrystallized from toluene/hexane (1:1.8) at -4 °C to yield yellow crystals. MS (FAB): $m/e$ 846 [P]$^+$, 706 [P-5CO]$^+$, 678 [P-6CO]$^+$, 650 [P-7CO]$^+$, 622 [P-8CO]$^+$, 594 [P-9CO]$^+$. $^{31}$P{1H} NMR

179
(121.42 MHz, CDCl₃) δ: 76.2 (s). ¹H NMR (300 MHz, CDCl₃) δ: 6 (m, 4H), 5.6 (m, 2H), 5.0 (m, 4H), 2.5 (m, 4H), 1.1-1.4 (m, 24H). IR (KBr) ν(CO): 1970 (br, vs), 1900 (br, vs) cm⁻¹. Anal. Calcd for C₃₃H₃₈Cr₂O₉P₂Ru: C, 46.86; H, 4.54. Found: C, 46.86; H, 4.70.

5.3.5 Preparation of Ru₃(CO)₈[μ₃-C₆H₄Cr(CO)₃][μ₃-PBu⁴]

A heptane solution (30 mL) of Ru₃(CO)₁₂ (150 mg, 0.23 mmol) and PBU₄[C₆H₅Cr(CO)₃]₂ (130 mg, 0.25 mmol) was refluxed for 5 hours. The solvent was removed in vacuo and the residue was chromatographed on a silica gel column with CH₂Cl₂/hexanes (1:1.7) as eluent. Elution afforded three red bands. The second band was identified as Ru₃(CO)₁₁[PBU₄(C₆H₅Cr(CO)₃)₂] by mass spectrometry. The product (20) was isolated as a dark red solid (45% yield) after removal of the solvent from the first band. The solid was recrystallized from CH₂Cl₂/hexanes (1:2) by using the layer technique at -30 °C. ³¹P{¹H} NMR (121.4 MHz, CDCl₃) δ: 480.3 (s). ¹H NMR (200 MHz, CDCl₃) δ: 5.8 (m, 2H), 5.2 (m, 2H), 2.0 (d, J(H-P) = 20 Hz, 9H). MS (FAB): m/e 828 [P]⁺, 772 [P-2CO]⁺, 744 [P-3CO]⁺, 716 [P-4CO]⁺, 688 [P-5CO]⁺, 660 [P-6CO]⁺, 632 [P-7CO]⁺, 604 [P-8CO]⁺, 576 [P-9CO]⁺, 520 [P-11CO]⁺, 468 [P-11CO-Cr]⁺. IR (KBr) ν(CO): 2080 (m), 2050 (m), 2000 (s), 1940 (s), 1900 (m), 1880 (s) cm⁻¹. Anal. Calcd for C₂₁H₁₃CrO₁₁PRu₃: C, 30.48; H, 1.59. Found: C, 30.35; H, 1.59.

5.3.6 Preparation of Ru₃(CO)₉[μ₃-C₆H₄Cr(CO)₃][μ₃-P₆H₅Cr(CO)₃]

A solution of Ru₃(CO)₁₂ (180 mg, 0.28 mmol) and PPh[C₆H₅Cr(CO)₃]₂ (150 mg, 0.28 mmol) was refluxed in heptane (80 mL) for 5 hours. The solvent was removed in vacuo and the residue was chromatographed on a silica gel column by using CH₂Cl₂/hexanes (1:1.5) as eluent. The product (22) was isolated as a red solid and was recrystallized from CH₂Cl₂/pentane (1:2) at -4 °C. ³¹P{¹H} NMR (121.4 MHz, CDCl₃) δ : 406.6 (s). ¹H NMR (300 MHz, CDCl₃) δ: 4.7 (m, 2H), 5.2 (m, 3H), 5.5 (m, 2H), 5.9 (m, 2H). MS (FAB): m/e 1012 [P]⁺, 928 [P-3CO]⁺, 900 [P-4CO]⁺, 872 [P-5CO]⁺, 844 [P-

Anal. Calcd for C₂₇H₉Cr₂O₁₅PRu₃: C, 32.06; H, 0.90. Found: C, 32.02; H, 1.00. IR (Nujol) ν(CO): 2080 (s), 2045 (vs), 2020 (s), 1980 (ms), 1970 (vs), 1910 (s) cm⁻¹.

5.3.7 Pyrolysis of Ru₃(CO)₁₁[AsMe₂(C₆H₅Cr(CO)₃)] (26)

A sample of the complex (26) (400 mg, 0.43 mmol) was heated in refluxing octane (40 mL) for 5 hours. Evaporation of the solvent followed by column chromatography of this residue (silica gel, CH₂Cl₂/hexanes 1:1.8) gave 6 bands. Bands 2, 3 and 6 contained small amounts of unidentified complexes. Band 1 contained Ru₃(CO)₁₂ judged by IR spectroscopy.

Band 4 gave HRu₃(CO)₈[C₆H₄Cr(CO)₃]AsMe₂ (27), (120 mg). Crystals suitable for X-ray diffraction analysis were grown from CH₂Cl₂/hexanes (1:3) by the layering technique. Mass spectrum (FAB): m/e 846 [P]⁺, 818 [P-CO]⁺, 790 [P-2CO]⁺, 762 [P-3CO]⁺, 734 [P-4CO]⁺, 706 [P-5CO]⁺, 678 [P-6CO]⁺, 650 [P-7CO]⁺, 622 [P-8CO]⁺, 594 [P-9CO]⁺, 566 [P-10CO]⁺, 538 [P-11CO]⁺. ¹H NMR (400 MHz, CD₂Cl₂) δ: -18.2 (s, 1H), 2.3 (s, 3H), 2.5 (s, 3H), 4.7 (d, 1H), 4.8 (t, 1H), 5.0 (d, 1H), 6.05 (t, 1H). Anal. Calcd for C₁₉H₁₁₁As CrO₁₁Ru₃: C, 26.99; H, 1.31. Found: C, 26.95; H, 1.32.

Band 5 (yellow) contained HRu₂[C₆H₄Cr(CO)₃]AsMe₂ (28) (170 mg). The product was recrystallized from CH₂Cl₂/hexanes (1:2) to afford yellow crystals suitable for X-ray analysis. MS (FAB): m/e 689 [P]⁺, 633 [P-2CO]⁺, 605 [P-3CO]⁺, 577 [P-4CO]⁺, 549 [P-5CO]⁺, 521 [P-6CO]⁺, 493 [P-7CO]⁺, 465 [P-8CO]⁺, 437 [P-9CO]⁺. ¹H NMR (400 MHz CD₂Cl₂) δ: -12 (s, 1H), 1.4 (s, 3H), 1.8 (s, 3H), 5.0 (t, 2H), 5.2 (t, 2H). Anal. Calcd for C₁₇H₁₁₁AsCrO₉Ru₂: C, 29.66; H, 1.61. Found: C, 29.72; H, 1.70.
References


APPENDIX

A-1 X-ray Crystallographic Analysis of Ru$_3$(CO)$_{11}$[PPh$_2$C$_6$H$_5$Cr(CO)$_3$]

A. Crystal Data

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Corrections:
Lorentz-polarization absorption
(trans. factors: 0.89-1.00)

C. Structure Solution and Refinement

Structure Solution: patterson Method
Refinement: Full-matrix least-squares

Function Minimized:
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Least-squares Weights:
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p-factor: 0.03

Anomalous Dispersion:
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No. Observations(I > 3.00σ(I)): 3870

No. Variables: 460

Reflection/Parameter Ratio: 8.43
Residuals: R; R_w: 0.031; 0.034

Goodness of Fit Indicator: 1.20
Max Shift/Error in Final Cycle: 0.07
Max. Peak in Final Diff. Map: 0.49 e⁺/Å³
Min. Peak in Final Diff. Map: -0.48 e⁻/Å³
A-2 X-ray Crystallographic Analysis of HRu₃(CO)₈[C₆H₄Cr(CO)₃][AsMe₂]

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B. Intensity Measurements

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Scan Rate
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(8 rescans)

Scan Width
(1.52 + 0.35 tanθ)°

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No. of Reflections Measured
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Corrections
Lorentz-polarization absorption
(trans. factors: 0.68-1.00)
Secondary Extinction
(coefficient: 0.30529E-06)

C. Structure Solution and Refinement

Structure Solution
patterson Method

Refinement
Full-matrix least-squares

Function Minimized
\[ \sum w |Fo| - |Fc|^2 \]

Least-squares Weights
\[ 4Fo^2/\sigma^2(Fo^2) \]

p-factor
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Anomalous Dispersion
All non-hydrogen atoms

No. Observations(I > 3.00σ(I))
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No. Variables
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Residuals: R; R_w
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Goodness of Fit Indicator
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Max Shift/Error in Final Cycle
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Max. Peak in Final Diff. Map
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Min. Peak in Final Diff. Map
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A-3 X-ray Crystallographic Analysis of Ru₃(CO)₉PC₆H₅Cr(CO)₃[C₆H₄Cr(CO)₃]

A. Crystal Data

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</tr>
<tr>
<td>No. Reflections Used for Unit</td>
<td>25 (29.8-33.7°)</td>
</tr>
<tr>
<td>Cell Determination (2θ range)</td>
<td></td>
</tr>
<tr>
<td>Omega Scan Peak Width at</td>
<td>0.26</td>
</tr>
<tr>
<td>Lattice Parameters:</td>
<td></td>
</tr>
<tr>
<td>a</td>
<td>16.918 (2) Å</td>
</tr>
<tr>
<td>b</td>
<td>10.612 (3) Å</td>
</tr>
<tr>
<td>c</td>
<td>19.241 (2) Å</td>
</tr>
<tr>
<td>β</td>
<td>113.64 (1)°</td>
</tr>
<tr>
<td>V</td>
<td>3164 (1) Å</td>
</tr>
<tr>
<td>Space Group</td>
<td>P2₁/n (#14)</td>
</tr>
<tr>
<td>Z value</td>
<td>4</td>
</tr>
<tr>
<td>D&lt;sub&gt;calc&lt;/sub&gt;</td>
<td>2.123 g/cm³</td>
</tr>
<tr>
<td>F₀₀₀</td>
<td>1944</td>
</tr>
<tr>
<td>μ(MoKα)</td>
<td>21.42 cm⁻¹</td>
</tr>
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</table>

B. Intensity Measurements

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Diffractometer</td>
<td>Rigaku AFC6S</td>
</tr>
<tr>
<td>Radiation</td>
<td>MoKα (λ = 0.71069 Å)</td>
</tr>
<tr>
<td>Temperature</td>
<td>21 °C</td>
</tr>
<tr>
<td>Take-off Angle</td>
<td>6.0°</td>
</tr>
<tr>
<td>Detector Aperture</td>
<td>6.0 mm horizontal</td>
</tr>
<tr>
<td></td>
<td>6.0 mm vertical</td>
</tr>
<tr>
<td>Crystal to Detector Distance</td>
<td>285 mm</td>
</tr>
<tr>
<td>Property</td>
<td>Value</td>
</tr>
<tr>
<td>--------------------------------</td>
<td>--------------------------------</td>
</tr>
<tr>
<td>Scan Type</td>
<td>$\omega-2\theta$</td>
</tr>
<tr>
<td>Scan Rate</td>
<td>32.0°/min (in omega)</td>
</tr>
<tr>
<td>(8 rescans)</td>
<td></td>
</tr>
<tr>
<td>Scan Width</td>
<td>$(0.94 + 0.35 \tan\theta)°$</td>
</tr>
<tr>
<td>$2\theta_{\text{max}}$</td>
<td>65.1°</td>
</tr>
<tr>
<td>No. of Reflections Measured</td>
<td>Total: 12322</td>
</tr>
<tr>
<td></td>
<td>Unique: 11984 ($R_{\text{int}} = 0.044$)</td>
</tr>
<tr>
<td>Corrections</td>
<td>Lorentz-polarization absorption</td>
</tr>
<tr>
<td></td>
<td>(trans. factors: 0.69-1.00)</td>
</tr>
<tr>
<td></td>
<td>Decay (-2.20% decline)</td>
</tr>
<tr>
<td></td>
<td>Secondary Extinction</td>
</tr>
<tr>
<td></td>
<td>(coefficient: $0.13107\times10^{-5}$)</td>
</tr>
</tbody>
</table>

**C. Structure Solution and Refinement**

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Structure Solution</td>
<td>patterson Method</td>
</tr>
<tr>
<td>Refinement</td>
<td>Full-matrix least-squares</td>
</tr>
<tr>
<td>Function Minimized</td>
<td>$\sum w (</td>
</tr>
<tr>
<td>Least-squares Weights</td>
<td>$4F_o^2/\sigma^2(F_o^2)$</td>
</tr>
<tr>
<td>p-factor</td>
<td>0.03</td>
</tr>
<tr>
<td>Anomalous Dispersion</td>
<td>All non-hydrogen atoms</td>
</tr>
<tr>
<td>No. Observations($I&gt;3.00\sigma(I)$)</td>
<td>6096</td>
</tr>
<tr>
<td>No. Variables</td>
<td>434</td>
</tr>
<tr>
<td>Reflection/Parameter Ratio</td>
<td>14.05</td>
</tr>
<tr>
<td>Residuals: $R$; $R_w$</td>
<td>0.043; 0.048</td>
</tr>
<tr>
<td>Goodness of Fit Indicator</td>
<td>1.57</td>
</tr>
<tr>
<td>Max Shift/Error in Final Cycle</td>
<td>0.001</td>
</tr>
<tr>
<td>Max. Peak in Final Diff. Map</td>
<td>1.16 $e^-/Å^3$</td>
</tr>
<tr>
<td>Min. Peak in Final Diff. Map</td>
<td>-2.09 $e^-/Å^3$</td>
</tr>
</tbody>
</table>
A-4 X-ray Crystallographic Analysis of Ru₃(CO)₈[μ₃-C₆H₄Cr(CO)₃][μ₃-PBu₄]

A. Crystal Data

Empirical Formula
C₂₁H₁₃CrO₁₁PRu₃

Formula Weight
827.51

Crystal Color, Habit
dark, irregular

Crystal Dimensions (mm)
0.180 x 0.300 x 0.400

Crystal System
monoclinic

No. Reflections Used for Unit
25 (43.0-49.5°)

Cell Determination (2θ range)

Omega Scan Peak Width at
Half-height
0.28

Lattice Parameters:
a= 13.616 (2) Å
b= 14.229 (1) Å
c= 13.617 (2) Å
β= 94.15 (1)°
V= 2631.2 (6) Å³

Space Group
P2₁/a (#14)

Z value
4

Dcalc
2.089 g/cm³

F₀₀₀
1592

μ(MoKα)
21.64 cm⁻¹

B. Intensity Measurements

Diffractometer
Rigaku AFC6S

Radiation
MoKα (λ = 0.71069 Å)

Temperature
21 °C

Take-off Angle
6.0°

Detector Aperture
6.0 mm horizontal
6.0 mm vertical

Crystal to Detector Distance
285 mm
Scan Type: ω-2θ
Scan Rate: 32.0°/min (in omega) (8 rescans)
Scan Width: (1.21 + 0.35 tanθ)°
2θ_{max}: 60.0°
No. of Reflections Measured: Total: 8237
Unique: 7937 (R_{int} = 0.024)
Corrections: Lorentz-polarization absorption (trans. factors: 0.83-1.00)
Secondary Extinction (coefficient: 0.27225E-06)

C. Structure Solution and Refinement

Structure Solution: patterson Method
Refinement: Full-matrix least-squares
Function Minimized: \sum w (|F_o| - |F_c|)^2
Least-squares Weights: 4F_o^2/\sigma^2(F_o^2)
p-factor: 0.005
Anomalous Dispersion: All non-hydrogen atoms
No. Observations(I > 3.00\sigma(I)): 4980
No. Variables: 335
Reflection/Parameter Ratio: 14.87
Residuals: R; R_w: 0.033; 0.036
Goodness of Fit Indicator: 2.24
Max Shift/Error in Final Cycle: 0.11
Max. Peak in Final Diff. Map: 1.04 e^-/Å³
Min. Peak in Final Diff. Map: -0.61 e^-/Å³
A-5 X-ray Crystallographic Analysis of Ru₃(CO)₇[PPhC₆H₅Cr(CO)₃]₂[μ₃-C₆H₄]

A. Crystal Data

Empirical Formula
C₄₄H₂₆Cl₂Cr₂O₁₃P₂Ru₃

Formula Weight
1319.87

Crystal Color, Habit
black, prism

Crystal Dimensions (mm)
0.150 x 0.500 x 0.500

Crystal System
monoclinic

No. Reflections Used for Unit
25 (27.2-33.4°)

Cell Determination (2θ range)

Omega Scan Peak Width at
0.35

Half-height

Lattice Parameters:
a= 22.411 (2) Å
b= 17.314 (4) Å
c= 26.191 (4) Å
β= 111.68 (1)°
V= 9444 (3) Å³

Space Group
P2₁/n (#14)

Z value
8

Dcalc
1.856 g/cm³

F₀₀₀
5240

μ(MoKα)
15.98 cm⁻¹

B. Intensity Measurements

Diffractometer
Rigaku AFC6S

Radiation
MoKα (λ = 0.71069 Å)

Temperature
21 °C

Take-off Angle
6.0°

Detector Aperture
6.0 mm horizontal
6.0 mm vertical

Crystal to Detector Distance
285 mm
Scan Type: \( \omega - 2\theta \)
Scan Rate: 32.0\(^\circ\)/min (in omega)
(8 rescans)
Scan Width: \((0.85 + 0.35 \tan \theta)\)^\circ
\(2\theta_{\text{max}}\): 55.0\(^\circ\)
No. of Reflections Measured:
Total: 22926
Unique: 22367 \((R_{\text{int}} = 0.031)\)
Corrections:
Lorentz-polarization absorption
(trans. factors: 0.68-1.00)
Decay (-7.50% decline)

C. Structure Solution and Refinement

Structure Solution: patterson Method
Refinement: Full-matrix least-squares
Function Minimized: \( \Sigma w (|F_o| - |F_c|)^2 \)
Least-squares Weights: \( 4F_o^2/\sigma^2(F_o)^2 \)
p-factor: 0.00
Anomalous Dispersion: All non-hydrogen atoms
No. Observations\((I>3.00\sigma(I))\): 10119
No. Variables: 1189
Reflection/Parameter Ratio: 8.51
Residuals: \( R; R_w \): 0.037; 0.042
Goodness of Fit Indicator: 1.32
Max Shift/Error in Final Cycle: 0.06
Max. Peak in Final Diff. Map: 0.68 e\(^{-}/\AA^3\)
Min. Peak in Final Diff. Map: -0.65 e\(^{-}/\AA^3\)
A-6 X-ray Crystallographic Analysis of Ru(CO)₃[PPr₄₂C₆H₅Cr(CO)₃]₂

A. Crystal Data

Empirical Formula  
C₃₃H₃₈Cr₂O₉P₂Ru

Formula Weight  
845.67

Crystal Color, Habit  
yellow, prism

Crystal Dimensions (mm)  
0.100 x 0.350 x 0.400

Crystal System  
monoclinic

No. Reflections Used for Unit  
25 (27.0-36.8°)

Cell Determination (2θ range)  
Omega Scan Peak Width at 0.34

Lattice Parameters:

a = 15.390 (1) Å
b = 10.241 (2) Å
c = 23.490 (1) Å
β = 96.686 (6)°
V = 3677.0 (9) Å³

Space Group  
P2₁/a (#14)

Z value  
4

Dcalc  
1.528 g/cm³

F₀₀₀  
1720

μ(MoKα)  
10.98 cm⁻¹

B. Intensity Measurements

Diffractometer  
Rigaku AFC6S

Radiation  
MoKα (λ = 0.71069 Å)

Temperature  
21 °C

Take-off Angle  
6.0°

Detector Aperture  
6.0 mm horizontal
6.0 mm vertical

Crystal to Detector Distance  
285 mm
Scan Type $\omega-2\theta$
Scan Rate $32.0^\circ$/min (in omega)
(8 rescans)
Scan Width $(1.05 + 0.35 \tan\theta)^\circ$
$2\theta_{\text{max}}$ 60.0$^\circ$
No. of Reflections Measured Total: 11644
Unique: 11264 ($R_{\text{int}} = 0.041$)
Corrections Lorentz-polarization absorption
(trans. factors: 0.73-1.00)

C. Structure Solution and Refinement

Structure Solution patterson Method
Refinement Full-matrix least-squares
Function Minimized $\sum w (|F_o| - |F_c|)^2$
Least-squares Weights $4F_o^2/\sigma^2 (F_o^2)$
p-factor 0.01
Anomalous Dispersion All non-hydrogen atoms
No. Observations ($I > 3.00\sigma(I)$) 6103
No. Variables 424
Reflection/Parameter Ratio 14.39
Residuals: $R; R_w$ 0.031; 0.030
Goodness of Fit Indicator 1.45
Max Shift/Error in Final Cycle 0.13
Max. Peak in Final Diff. Map $0.43 \, \text{e}^-/\text{Å}^3$
Min. Peak in Final Diff. Map $-0.40 \, \text{e}^-/\text{Å}^3$
A-7 X-ray Crystallographic Analysis of Os₃(CO)₈[μ-
PPhC₆H₄][PPh₂C₆H₅Cr(CO)₃]

A. Crystal Data

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Empirical Formula</td>
<td>C₄₂H₂₆Cl₂CrO₁₁P₂Os₃</td>
</tr>
<tr>
<td>Formula Weight</td>
<td>1462.11</td>
</tr>
<tr>
<td>Crystal Color, Habit</td>
<td>yellow, plate</td>
</tr>
<tr>
<td>Crystal Dimensions (mm)</td>
<td>0.030 x 0.180 x 0.200</td>
</tr>
<tr>
<td>Crystal System</td>
<td>monoclinic</td>
</tr>
<tr>
<td>No. Reflections Used for Unit</td>
<td>25 (40.8-61.7°)</td>
</tr>
<tr>
<td>Cell Determination (2θ range)</td>
<td></td>
</tr>
<tr>
<td>Omega Scan Peak Width at Half-height</td>
<td></td>
</tr>
<tr>
<td>Lattice Parameters:</td>
<td>a = 13.039 (3) Å</td>
</tr>
<tr>
<td></td>
<td>b = 18.001 (2) Å</td>
</tr>
<tr>
<td></td>
<td>c = 20.125 (2) Å</td>
</tr>
<tr>
<td></td>
<td>β = 108.42 (1)°</td>
</tr>
<tr>
<td></td>
<td>V = 4481 (1) Å³</td>
</tr>
<tr>
<td>Space Group</td>
<td>P2₁/n (#14)</td>
</tr>
<tr>
<td>Z value</td>
<td>4</td>
</tr>
<tr>
<td>Dₐcalc</td>
<td>2.167 g/cm³</td>
</tr>
<tr>
<td>F₀₀₀</td>
<td>2728</td>
</tr>
<tr>
<td>μ(MoKα)</td>
<td>199.48 cm⁻¹</td>
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</table>

B. Intensity Measurements

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Diffractometer</td>
<td>Rigaku AFC6S</td>
</tr>
<tr>
<td>Radiation</td>
<td>CuKα (λ = 1.54178 Å)</td>
</tr>
<tr>
<td>Temperature</td>
<td>21 °C</td>
</tr>
<tr>
<td>Take-off Angle</td>
<td>6.0°</td>
</tr>
<tr>
<td>Detector Aperture</td>
<td>6.0 mm horizontal</td>
</tr>
<tr>
<td></td>
<td>6.0 mm vertical</td>
</tr>
</tbody>
</table>
Crystal to Detector Distance 285 mm
Scan Type \( \omega-\theta \)
Scan Rate 16.0 °/min (in omega)
(8 rescans)
Scan Width \( (1.05 + 0.20 \tan \theta)^\circ \)
\( 2\theta_{\text{max}} \) 155.4°
No. of Reflections Measured
Total: 9738
Unique: 9304 \( (R_{\text{int}} = 0.038) \)
Corrections Lorentz-polarization absorption
(trans. factors: 0.13-1.00)
Decay (-9.00% decline)
Secondary Extinction (coefficient: 0.18681E-06)

C. Structure Solution and Refinement

Structure Solution patterson Method
Refinement Full-matrix least-squares
Function Minimized \( \Sigma w (|F_o| - |F_c|)^2 \)
Least-squares Weights \( 4F_o^2/\sigma^2(F_o^2) \)
p-factor 0.01
Anomalous Dispersion All non-hydrogen atoms
No. Observations \((I > 3.00\sigma(I)) \) 6320
No. Variables 551
Reflection/Parameter Ratio 11.47
Residuals: R; R_w 0.057; 0.065
Goodness of Fit Indicator 3.11
Max Shift/Error in Final Cycle 0.14
Max. Peak in Final Diff. Map 1.65 e⁻/Å³
Min. Peak in Final Diff. Map -2.20 e⁻/Å³
A-8 X-ray Crystallographic Analysis of Os₃(CO)₉[μ-H]₂[μ-PPriC₆H₅Cr(CO)₃]

A. Crystal Data

Empirical Formula: C₂₁H₁₃CrO₁₂Os₃P
Formula Weight: 1110.90
Crystal Color, Habit: yellow, prism
Crystal Dimensions (mm): 0.180 x 0.200 x 0.350
Crystal System: orthorhombic
No. Reflections Used for Unit Cell Determination (2θ range): 25 (30.6-40.4°)
Omega Scan Peak Width at Half-height: 0.36
Lattice Parameters:

\[ a = 14.695 (2) \text{ Å} \]
\[ b = 16.696 (2) \text{ Å} \]
\[ c = 11.186 (1) \text{ Å} \]
\[ V = 2744.5 (5) \text{ Å}^3 \]
Space Group: P2₁2₁2₁ (#19)
Z value: 4
Dcalc: 2.688 g/cm³
F₀₀₀: 2008
\( \mu(\text{MoK} \alpha) \): 143.50 cm⁻¹

B. Intensity Measurements

Diffractometer: Rigaku AFC6S
Radiation: MoKα (\( \lambda = 0.71069 \text{ Å} \))
Temperature: 21 °C
Take-off Angle: 6.0°
Detector Aperture: 6.0 mm horizontal
Crystal to Detector Distance: 285 mm
Scan Type: \( \omega-2\theta \)
Scan Rate: 16.0°/min (in omega) (8 rescans)
Scan Width: \((1.00 + 0.35 \tan \theta)°\)
\(2\theta_{\text{max}}\): 65.0°
No. of Reflections Measured: Total: 5519
Corrections: Lorentz-polarization absorption (trans. factors: 0.57-1.00)
Secondary Extinction: (coefficient: 0.24803E-06)

C. Structure Solution and Refinement

Structure Solution: patterson Method
Refinement: Full-matrix least-squares
Function Minimized: \(\sum w(|Fo| - |Fc|)^2\)
Least-squares Weights: \(4Fo^2/\sigma^2(Fo^2)\)
p-factor: 0.01
Anomalous Dispersion: All non-hydrogen atoms
No. Observations(I > 3.00\(\sigma(I)\)): 3529
No. Variables: 344
Reflection/Parameter Ratio: 10.26
Residuals: \(R; R_w\): 0.030; 0.028
Goodness of Fit Indicator: 1.50
Max Shift/Error in Final Cycle: 0.10
Max. Peak in Final Diff. Map: 0.98 e/Å³
Min. Peak in Final Diff. Map: -0.97 e/Å³
A-9 X-ray Crystallographic Analysis of
\[ H_2Os_3(CO)_{8}\mu-PPriC_6H_5Cr(CO)_3]PPri_2C_6H_5Cr(CO)_3 \]

A. Crystal Data

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Empirical Formula</td>
<td>( C_{37}H_{36}Cl_4Cr_2O_{14}Os_3P_2 )</td>
</tr>
<tr>
<td>Formula Weight</td>
<td>1583.03</td>
</tr>
<tr>
<td>Crystal Color, Habit</td>
<td>yellow, prism</td>
</tr>
<tr>
<td>Crystal Dimensions (mm)</td>
<td>0.080 x 0.200 x 0.450</td>
</tr>
<tr>
<td>Crystal System</td>
<td>monoclinic</td>
</tr>
<tr>
<td>No. Reflections Used for Unit</td>
<td>25 (35.5-39.8°)</td>
</tr>
<tr>
<td>Cell Determination (2θ range)</td>
<td></td>
</tr>
<tr>
<td>Omega Scan Peak Width at Half-height</td>
<td>0.36</td>
</tr>
<tr>
<td>Lattice Parameters:</td>
<td></td>
</tr>
<tr>
<td>( a = 11.536 ) Å</td>
<td></td>
</tr>
<tr>
<td>( b = 18.354 ) Å</td>
<td></td>
</tr>
<tr>
<td>( c = 23.176 ) Å</td>
<td></td>
</tr>
<tr>
<td>( \beta = 98.43 ) (2°)</td>
<td></td>
</tr>
<tr>
<td>( V = 4854 ) (1) Å³</td>
<td></td>
</tr>
<tr>
<td>Space Group</td>
<td>( P2_1/n ) (#14)</td>
</tr>
<tr>
<td>( Z ) value</td>
<td>4</td>
</tr>
<tr>
<td>( D_{calc} )</td>
<td>2.166 g/cm³</td>
</tr>
<tr>
<td>( F_{000} )</td>
<td>2976</td>
</tr>
<tr>
<td>( \mu(MoK\alpha) )</td>
<td>86.02 cm⁻¹</td>
</tr>
</tbody>
</table>

B. Intensity Measurements

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Diffractometer</td>
<td>Rigaku AFC6S</td>
</tr>
<tr>
<td>Radiation</td>
<td>MoK( \alpha ) (( \lambda = 0.71069 ) Å)</td>
</tr>
<tr>
<td>Temperature</td>
<td>21 °C</td>
</tr>
<tr>
<td>Take-off Angle</td>
<td>6.0°</td>
</tr>
<tr>
<td>Detector Aperture</td>
<td>6.0 mm horizontal</td>
</tr>
<tr>
<td></td>
<td>6.0 mm vertical</td>
</tr>
</tbody>
</table>
Crystal to Detector Distance: 285 mm

Scan Type: \(\omega-\theta\)

Scan Rate: 32.0°/min (in omega)
(8 rescans)

Scan Width: \((1.10 + 0.35 \tan \theta)°\)

\(2\theta_{\text{max}}\): 55.0°

No. of Reflections Measured:
Total: 12048
Unique: 11490 \((R_{\text{int}} = 0.070)\)

Corrections:
Lorentz-polarization absorption
(trans. factors: 0.36-1.00)
Decay (-12.00% decline)

C. Structure Solution and Refinement

Structure Solution: patterson Method

Refinement: Full-matrix least-squares

Function Minimized: \(\Sigma w (|F_o| - |F_c|)^2\)

Least-squares Weights: \(4F_o^2/\sigma^2(F_o^2)\)

\(p\)-factor: 0.01

Anomalous Dispersion: All non-hydrogen atoms

No. Observations \((I > 3.00\sigma(I))\): 6042

No. Variables: 559

Reflection/Parameter Ratio: 10.81

Residuals: \(R; R_w\): 0.032; 0.030

Goodness of Fit Indicator: 1.50

Max Shift/Error in Final Cycle: 0.18

Max. Peak in Final Diff. Map: 1.02 \(e^-/\text{Å}^3\)

Min. Peak in Final Diff. Map: -1.12 \(e^-/\text{Å}^3\)
A-10 X-ray Crystallographic Analysis of Os₃(CO)₉[PEt₂C₆H₅Cr(CO)₃]₃

A. Crystal Data

Empirical Formula
C₄₈H₄₅Cr₃O₁₈Os₃P₃

Formula Weight
1729.38

Crystal Color, Habit
red-brown, prism

Crystal Dimensions (mm)
0.200 x 0.250 x 0.40

Crystal System
trigonal

No. Reflections Used for Unit
25 (40.1-45.5°)

Cell Determination (2θ range)
Omega Scan Peak Width at Half-height
0.40

Lattice Parameters:
a = 15.7558 (4) Å
c = 12.662 (1) Å
V = 2722.2 (3) Å³

Space Group
P₃ (147)

Z value
2

Dcalc
2.110 g/cm³

F₀₀₀
1644

μ(MoKα)
77.00 cm⁻¹

B. Intensity Measurements

Diffractometer
Rigaku AFC6S

Radiation
MoKα (λ = 0.71069 Å)

Temperature
21 °C

Take-off Angle
6.0°

Detector Aperture
6.0 mm horizontal
6.0 mm vertical

Crystal to Detector Distance
285 mm

Scan Type
ω-2θ
Scan Rate  
32.0°/min (in omega)  
(8 rescans)

Scan Width  
(1.42 + 0.35 tanθ)°

2θ_{max}  
70.0°

No. of Reflections Measured  
Total: 8652  
Unique 8006 (R_{int} = 0.044)

Corrections  
Lorentz-polarization absorption  
(trans. factors: 0.54-1.00)  
Secondary Extinction  
(coefficient: 0.39373E-06)

C. Structure Solution and Refinement

Structure Solution  
patterson Method

Refinement  
Full-matrix least-squares

Function Minimized  
Σ w (|Fo| - |Fc|)^2

Least-squares Weights  
4Fo^2/σ^2(Fo^2)

p-factor  
0.01

Anomalous Dispersion  
All non-hydrogen atoms

No. Observations(I > 3.00σ(I))  
4093

No. Variables  
227

Reflection/Parameter Ratio  
10.26

Residuals: R; R_w  
0.029; 0.025

Goodness of Fit Indicator  
1.35

Max Shift/Error in Final Cycle  
0.001

Max. Peak in Final Diff. Map  
1.28 e^-/Å^3

Min. Peak in Final Diff. Map  
-1.36 e^-/Å^3
A-11 X-ray Crystallographic Analysis of HRu₂(CO)₆[μ-C₆H₄Cr(CO)₃]AsMe₂

A. Crystal Data

**Empirical Formula**

C₁₇H₁₁AsCrO₉Ru₂

**Formula Weight**

688.33

**Crystal Color, Habit**

yellow, prism

**Crystal Dimensions (mm)**

0.200 x 0.350 x 0.400

**Crystal System**

monoclinic

**No. Reflections Used for Unit Cell Determination (2θ range)**

25 (46.4-52.5°)

**Omega Scan Peak Width at Half-height**

0.38

**Lattice Parameters:**

a = 10.862 (1) Å

b = 14.655 (2) Å

c = 14.590 (3) Å

β = 107.57 (1)°

V = 2214.1 (5) Å³

**Space Group**

P2₁/c (#14)

**Z value**

4

**Dcalc**

2.065 g/cm³

**F₀₀₀**

1320

**μ(MoKα)**

33.16 cm⁻¹

B. Intensity Measurements

**Diffractometer**

Rigaku AFC6S

**Radiation**

MoKα (λ = 0.71069 Å)

**Temperature**

21 °C

**Take-off Angle**

6.0°

**Detector Aperture**

6.0 mm horizontal

6.0 mm vertical

**Crystal to Detector Distance**

285 mm
Scan Type \( \omega-2\theta \)
Scan Rate \( 32.0^\circ/\text{min (in omega)} \)
(8 rescans)
Scan Width \( (1.31 + 0.35 \tan \theta)^\circ \)
\( 2\theta_{\text{max}} \)
65.0\(^{\circ}\)
No. of Reflections Measured
Total: 8665
Unique: 8296 \((R_{\text{int}} = 0.039)\)
 Corrections
Lorentz-polarization absorption
(trans. factors: 0.53-1.00)
Secondary Extinction
(coefficient: 0.17916E-05)

C. Structure Solution and Refinement
Structure Solution patterson Method
Refinement Full-matrix least-squares
Function Minimized \( \sum w (|F_o| - |F_c|)^2 \)
Least-squares Weights \( 4F_o^2/\sigma^2(F_o^2) \)
p-factor 0.00
Anomalous Dispersion All non-hydrogen atoms
No. Observations \((I > 3.00\sigma(I))\) 4577
No. Variables 276
Reflection/Parameter Ratio 16.58
Residuals: R; R_w 0.027; 0.025
Goodness of Fit Indicator 1.54
Max Shift/Error in Final Cycle 0.001
Max. Peak in Final Diff. Map 0.43 e^-/Å³
Min. Peak in Final Diff. Map -0.56 e^-/Å³
A-12 X-ray Crystallographic Analysis of Ru₃(CO)₁₁[PPri₂C₆H₅Cr(CO)₃]

A. Crystal Data

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Empirical Formula</td>
<td>C₂₆H₁₉CrO₁₄PRu₃</td>
</tr>
<tr>
<td>Formula Weight</td>
<td>941.61</td>
</tr>
<tr>
<td>Crystal Color, Habit</td>
<td>red, prism</td>
</tr>
<tr>
<td>Crystal Dimensions (mm)</td>
<td>0.20 x 0.30 x 0.350</td>
</tr>
<tr>
<td>Crystal System</td>
<td>monoclinic</td>
</tr>
<tr>
<td>Lattice Parameters:</td>
<td></td>
</tr>
<tr>
<td>a</td>
<td>8.555 (2) Å</td>
</tr>
<tr>
<td>b</td>
<td>21.810 (5) Å</td>
</tr>
<tr>
<td>c</td>
<td>17.159 (4) Å</td>
</tr>
<tr>
<td>β</td>
<td>97.43 (2)°</td>
</tr>
<tr>
<td>V</td>
<td>3175 (1) Å³</td>
</tr>
<tr>
<td>Space Group</td>
<td>P2₁/n (#14)</td>
</tr>
<tr>
<td>Z value</td>
<td>4</td>
</tr>
<tr>
<td>D(calc)</td>
<td>1.970 g/cm³</td>
</tr>
<tr>
<td>F₀₀₀</td>
<td>1832</td>
</tr>
<tr>
<td>μ(MoKα)</td>
<td>16.89 cm⁻¹</td>
</tr>
</tbody>
</table>

B. Intensity Measurements

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Diffractometer</td>
<td>Rigaku AFC6S</td>
</tr>
<tr>
<td>Radiation</td>
<td>MoKα (λ = 0.71069 Å)</td>
</tr>
<tr>
<td>Temperature</td>
<td>21 °C</td>
</tr>
<tr>
<td>Take-off Angle</td>
<td>6.0°</td>
</tr>
<tr>
<td>Detector Aperture</td>
<td>6.0 mm horizontal</td>
</tr>
<tr>
<td></td>
<td>6.0 mm vertical</td>
</tr>
<tr>
<td>Crystal to Detector Distance</td>
<td>285 mm</td>
</tr>
<tr>
<td>Parameter</td>
<td>Value</td>
</tr>
<tr>
<td>------------------------</td>
<td>------------------------------</td>
</tr>
<tr>
<td>Scan Type</td>
<td>$\omega-2\theta$</td>
</tr>
<tr>
<td>Scan Rate</td>
<td>16.0°/min (in omega)</td>
</tr>
<tr>
<td></td>
<td>(8 rescans)</td>
</tr>
<tr>
<td>Scan Width</td>
<td>$(0.85 + 0.35 \tan \theta)^\circ$</td>
</tr>
<tr>
<td>$2\theta_{\text{max}}$</td>
<td>55.0°</td>
</tr>
</tbody>
</table>

C. Structure Solution and Refinement

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Structure Solution</td>
<td>Patterson method</td>
</tr>
<tr>
<td>Refinement</td>
<td>Full-matrix least-squares</td>
</tr>
<tr>
<td>Function Minimized</td>
<td>$\sum w(</td>
</tr>
<tr>
<td>Least-squares Weights</td>
<td>$4\text{Fo}^2/\sigma^2(\text{Fo}^2)$</td>
</tr>
<tr>
<td>p-factor</td>
<td>0.03</td>
</tr>
<tr>
<td>Anomalous Dispersion</td>
<td>All non-hydrogen atoms</td>
</tr>
<tr>
<td>No. Observations (I &gt; 3.00$\sigma$(I))</td>
<td>4411</td>
</tr>
<tr>
<td>No. Variables</td>
<td>407</td>
</tr>
<tr>
<td>Reflection/Parameter Ratio</td>
<td>8.43</td>
</tr>
<tr>
<td>Residuals: R; $R_w$</td>
<td>0.029; 0.037</td>
</tr>
<tr>
<td>Goodness of Fit Indicator</td>
<td>1.25</td>
</tr>
<tr>
<td>Max Shift/Error in Final Cycle</td>
<td>0.22</td>
</tr>
<tr>
<td>Max. Peak in Final Diff. Map</td>
<td>0.47 $e^-/\text{Å}^3$</td>
</tr>
</tbody>
</table>
A-13 X-ray Crystallographic Analysis of Ru₃(CO)₁₀[PPri₂C₆H₅Cr(CO)₃]₂

A. Crystal Data

Empirical Formula
C₄₁H₄₀Cl₂Cr₂O₁₆P₂Ru₃

Formula Weight
1328.81

Crystal Color, Habit
dark red, prism

Crystal Dimensions (mm)
0.15 x 0.25 x 0.350

Crystal System
orthorhombic

Lattice Parameters:

\[ a= 13.832 \text{ (3) } \text{Å} \]
\[ b= 17.558 \text{ (2) } \text{Å} \]
\[ c= 10.144 \text{ (1) } \text{Å} \]

\[ V= 2463.7 \text{ (7) } \text{Å}³ \]

Space Group
P₂₁₂₁₂₁ (#18)

Z value
2

\( D_{\text{calc}} \)
1.790 g/cm³

\( F_{000} \)
1316

\( \mu(\text{MoKα}) \)
15.36 cm⁻¹

B. Intensity Measurements

Diffractometer
Rigaku AFC6S

Radiation
MoKα (\( \lambda = 0.71069 \) Å)

Temperature
21 °C

Take-off Angle
6.0°

Detector Aperture
6.0 mm horizontal
6.0 mm vertical

Crystal to Detector Distance
285 mm
<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Scan Type</td>
<td>$\omega$-$2\theta$</td>
</tr>
<tr>
<td>Scan Rate</td>
<td>16.0°/min (in omega)</td>
</tr>
<tr>
<td></td>
<td>(8 rescans)</td>
</tr>
<tr>
<td>Scan Width</td>
<td>$(0.85 + 0.35 \tan \theta)°$</td>
</tr>
<tr>
<td>$2\theta_{\text{max}}$</td>
<td>59.9°</td>
</tr>
</tbody>
</table>

C. Structure Solution and Refinement

<table>
<thead>
<tr>
<th>Step</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Structure Solution</td>
<td>patterson Method</td>
</tr>
<tr>
<td>Refinement</td>
<td>Full-matrix least-squares</td>
</tr>
<tr>
<td>Function Minimized</td>
<td>$\sum w (</td>
</tr>
<tr>
<td>Least-squares Weights</td>
<td>$4F_0^2/\sigma^2(F_0^2)$</td>
</tr>
<tr>
<td>p-factor</td>
<td>0.03</td>
</tr>
<tr>
<td>Anomalous Dispersion</td>
<td>All non-hydrogen atoms</td>
</tr>
<tr>
<td>No. Observations($I &gt; 3.00\sigma(I)$)</td>
<td>4041</td>
</tr>
<tr>
<td>No. Variables</td>
<td>307</td>
</tr>
<tr>
<td>Residuals: $R$; $R_w$</td>
<td>0.027; 0.035</td>
</tr>
<tr>
<td>Goodness of Fit Indicator</td>
<td>1.04</td>
</tr>
<tr>
<td>Max Shift/Error in Final Cycle</td>
<td>0.32</td>
</tr>
<tr>
<td>Max. Peak in Final Diff. Map</td>
<td>$0.55 \text{ e}^{-/\AA^3}$</td>
</tr>
</tbody>
</table>
A-14 X-ray Crystallographic Analysis of PPr$_2$C$_6$H$_5$Cr(CO)$_3$

A. Crystal Data

Empirical Formula  
C$_{15}$H$_{19}$Cr$_{10}$O$_3$P

Formula Weight  
330.28

Crystal Color, Habit  
yellow, prism

Crystal Dimensions (mm)  
0.20 x 0.25 x 0.30

Crystal System  
monoclinic

Lattice Parameters:

\[ a = 8.149 \text{ (2) Å} \]
\[ b = 13.485 \text{ (2) Å} \]
\[ c = 15.120 \text{ (3) Å} \]

\[ V = 1635.3 \text{ (6) Å}^3 \]

Space Group  
P2$_1$/c (#14)

Z value  
4

D$_{\text{calc}}$  
1.34 g/cm$^3$

F$_{000}$  
688

\( \mu(\text{MoK}_\alpha) \)  
7.81 cm$^{-1}$

B. Intensity Measurements

Diffractometer  
Rigaku AFC6S

Radiation  
MoK$_\alpha$ (\( \lambda = 0.71069 \) Å)

Temperature  
21 °C

Take-off Angle  
6.0°

Detector Aperture  
6.0 mm horizontal

Crystal to Detector Distance  
285 mm
C. Structure Solution and Refinement

Structure Solution: patterson Method
Refinement: Full-matrix least-squares
Function Minimized: \[ \sum w(|F_o| - |F_c|)^2 \]
Least-squares Weights: \[ 4F_o^2/\sigma^2(F_o^2) \]
p-factor: 0.03
Anomalous Dispersion: All non-hydrogen atoms
No. Observations(I > 3.00\sigma(I)): 2324
No. Variables: 257
Residuals: R; R_w: 0.033; 0.040
Goodness of Fit Indicator: 1.45
Max Shift/Error in Final Cycle: 0.00
Max. Peak in Final Diff. Map: 0.26 e/Å^3