STUDIES CONCERNING THE CHEMISTRY OF RARE EARTH ELEMENTS IN ORGANIC ENVIRONMENTS

by

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in the Department of Chemistry

We accept this thesis as conforming to the required standard

THE UNIVERSITY OF BRITISH COLUMBIA
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Department of _CHEMISTRY_

The University of British Columbia
Vancouver 8, Canada

Date _30th November 1973_
ABSTRACT

The infrared and proton magnetic resonance spectra of a number of compounds containing sites of Lewis basicity change in the presence of selected cyclopentadienyllanthanides, R₃Ln. These spectral changes indicate that the lanthanide derivatives can act as Lewis acids towards bases such as bridging and terminal carbonyl ligands, terminal nitrosyl ligands, appropriate transition metals and a carbon-carbon triple bond. Several solid adducts can be isolated and characterized. The preparation of the new compounds R₂LnM(h⁵-C₅)(CO)₃ [Ln = Dy, Ho, Er or Yb; M = Mo or W] is described, and evidence for the existence of isocarbonyl linkages in these complexes is presented.

As a synthetic route to compounds containing apparent lanthanide–transition element bonds, the direct reaction of elemental metals with transition metal organometallics is studied. Finely divided lanthanide and other metals react with substrates such as Mn(CO)₅Br, (h³-C₃H₆)Fe(CO)₃I, [(h⁵-C₅)Mo(CO)₃]₂ and (h⁵-C₅)Cr(CO)₃HgCl in THF to yield extremely reactive, air- and moisture-sensitive solutions. Some of the chemistry of these solutions and other synthetic approaches to them are outlined. The versatility of these solutions as reactive intermediates during the preparation of organometallic compounds is described.
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### ABBREVIATIONS AND COMMON NAMES

The following list of abbreviations and common names, most of which are commonly adopted in chemical research literature, will be employed in this thesis.

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<th>Formula</th>
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<td>Cp</td>
<td>C₅H₅</td>
<td>cyclopentadienyl</td>
</tr>
<tr>
<td>MeCp</td>
<td>C₆H₇</td>
<td>methylcyclopentadienyl</td>
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<tr>
<td>COT</td>
<td>C₈H₈</td>
<td>cyclooctatetraene</td>
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<tr>
<td>Me</td>
<td>CH₃</td>
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<td>Et</td>
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<td>i-Bu</td>
<td>(CH₃)₂CHCH₂</td>
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<td>Ph</td>
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<td>Et₂O</td>
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<td>diethyl ether</td>
</tr>
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<td>THF</td>
<td>C₄H₈O</td>
<td>tetrahydrofuran</td>
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<td>C₅H₅N</td>
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<td>bipy</td>
<td>C₁₀H₈N₂</td>
<td>2,2'-bipyridyl</td>
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<tr>
<td>phen</td>
<td>C₁₂H₈N₂</td>
<td>1,10-phenanthroline</td>
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<tr>
<td>Ln</td>
<td></td>
<td>a lanthanide element</td>
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<td>R₃Al</td>
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<td>n.m.r.</td>
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<td>ppm</td>
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<td>J</td>
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<td>h</td>
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<tr>
<td>Hz</td>
<td>Herz</td>
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<tr>
<td>ν</td>
<td>stretching frequency</td>
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<tr>
<td>cm⁻¹</td>
<td>wave numbers, reciprocal centimetres</td>
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<tr>
<td>Q.S.</td>
<td>quadrupole splitting</td>
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<td>I.S.</td>
<td>isomer shift</td>
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CHAPTER I

GENERAL INTRODUCTION

The work presented in this thesis is primarily concerned with the chemistry of the lanthanides or rare earths, that is elements 57-71. Scandium and yttrium are often included for discussion with these elements, but we shall only be concerned with yttrium. The coordination chemistry of the lanthanides has been an area of intense study,\(^1,^2\) whereas only a limited amount of work has been reported in the field of organolanthanides. Indeed, at the time this project began the only organic derivatives known were those containing cyclopentadienyl,\(^3,^7,^7,^10^3\) indenyl\(^4\) or phenyl\(^5\) groups, plus some ill-defined cyclooctatetraene\(^6\) and methyl\(^5\) compounds. Since that time a new series of cyclooctatetraene compounds,\(^7,^8\) some Grignard-type ytterbium species,\(^9\) a propynide of europium,\(^10\) and some cerium(IV) derivatives,\(^11\) whose reported synthesis and properties must be seriously questioned, have been prepared and reported. Very recently, some carbonyls of ytterbium and neodymium have been detected,\(^12\) by infrared spectroscopy, in argon matrices at 10°K.

Generally speaking, organolanthanides are air- and moisture-sensitive solids; they are readily attacked by halogen-containing or acidic solvents and are only soluble in strongly donor solvents which often solvate the product. In fact, the first reported organolanthanides, \(\text{Cp}_3\text{Ln}\),\(^3\) were almost certainly prepared unwittingly as ammonia solvates.\(^13\) The species which can be most readily prepared and manipulated are those containing ligands which can stabilize a negative charge (e.g. \(\text{Cp}^-\) and \(\text{COT}^2^-\)). The attempts to prepare phenyl and methyl derivatives\(^5\) have, with one notable exception, namely \(((\text{LiC}_8\text{H}_8)_4)(\text{LuC}_8\text{H}_8)_4\), resulted in polymeric materials. This behaviour is in contrast with the recently prepared alkyl transition metal derivatives,\(^15,^16\) which are monomeric solids displaying good solubility in many organic solvents.
A variety of physical techniques have been employed to determine the nature of the bonding in the compounds, Cp₃Ln. The general consensus of opinion, based upon spectral and chemical properties, is that these compounds are almost entirely ionically bonded with little or no 4f orbital involvement in any covalent interactions.

Bearing in mind the character of organolanthanides, we made some preliminary attempts to prepare new derivatives based upon the ligands: fluorenyl, phenylacetylenyl and triphenylmethyl. Although various solvents were used, including liquid ammonia, in which ytterbium metal is soluble, we were not able to reproducibly isolate any new compounds, in spite of observing distinct colour changes in the reaction mixture and obtaining new infrared spectra of the impure products. The major difficulty, aside from extensive non-stoichiometric solvation, was the separation of the products from the starting materials, say Grignard reagents, because of similar solubility and reactivity properties. In view of these difficulties, it was decided to use the known properties of isolable organolanthanides in our studies. The greatest potential for organolanthanides appeared to be in the utilization of their ability to act as Lewis acids and so this property was examined further. Specifically, investigations were carried out using some unusual base sites, in particular the oxygen atom of a transition metal carbonyl or nitrosyl. The results of these studies led us into the field of metal-metal bonds and hence elemental metal reactions were undertaken as a possible route to compounds displaying this kind of bond. The whole approach to the work has been essentially of a survey nature, namely to determine what can be done with the rare earth elements in an organic environment.
CHAPTER II
LEWIS ACIDITY OF CYCLOPENTADIENYLLANTHANIDES

2.1 INTRODUCTION

The Lewis electron pair bonding diagram for carbon monoxide reveals both ends of the molecule to possess a lone pair of electrons. Carbon monoxide normally bonds to transition metals by attachment of its carbon atom, leaving the oxygen atom coordinatively unsaturated. There are various justifications for this orientation, differing only in their level of sophistication. For example, Ballhausen and Gray\textsuperscript{21} point out that "the two electrons with the highest energy are mainly localized on the carbon nucleus" and that this orbital is of suitable symmetry and energy for overlap with transition elements resulting in linear M-C=O arrangement. Another explanation is that the carbon end of CO is the softer Lewis base part, whereas the oxygen terminal is much harder. In accord with the general criterion for soft-soft and hard-hard interactions for acids with bases,\textsuperscript{22} it is carbon which attaches to the transition elements. The latter are regarded as soft if their oxidation state is low or zero.\textsuperscript{22} An analogous argument can be made for nitric oxide bound to transition metals. Hence, for transition element carbonyls or nitrosyls and their substituted derivatives, the oxygen atom of the carbonyl or nitrosyl group may be viewed as a potential base site.

Formally isoelectronic with CO and NO\textsuperscript{+} is the CN\textsuperscript{-} group which is known to be bidentate towards Lewis acids in various environments. (e.g. CH\textsubscript{3}CNBF\textsubscript{3}\textsuperscript{23} and K\textsubscript{4}[Fe(CNBF\textsubscript{3})\textsubscript{6}]\textsuperscript{24}). In all cases, upon complex formation, the stretching frequency of the CN group is observed to increase. Simple inductive arguments would predict a lowering of this frequency as a result of electron withdrawal from the C-N bond towards the acid. Various authors have offered explanations of this phenomenon; Purcell in a series of papers\textsuperscript{25} has made the
most detailed study and his findings are summarised here. He was able to show that kinematic coupling of the C-N and N-Lewis acid vibrations could not account for all of the increase in $\nu_{\text{CN}}$. Using an extended Hückel theory method he determined that increased strengthening of the C-N link upon coordination was primarily caused by N2s overlap with the C2s and C2p$_\sigma$ orbitals; that is the $\sigma$ system was responsible for extra stabilisation of the CN group. Whilst comparing $\sigma$ and $\pi$ bonding effects in the coordination of CO and CN$^-$ using a SCF calculation according to the CNDO/2 scheme, he investigated HCO$^+$ and COH$^+$. He found that the lone pair molecular orbitals of carbon and oxygen taken together respond similarly to protonation at either end with an increase in CO bond order. However, COH$^+$ differs from HCO$^+$ in the different response of the 3$\sigma$ orbital (mainly O2s in character) which is virtually unperturbed for carbon addition, but polarised in the case of oxygen addition to decrease the CO bond order. In terms of Valence Bond theory one may say that (I) makes an enhanced contribution.

\[
\begin{align*}
:\text{C} = \overset{\ddagger}{\text{O}}: & \quad \longleftrightarrow \quad :\text{C} = \overset{\ddagger}{\text{O}}: \\
(\text{I}) & \quad (\text{II})
\end{align*}
\]

to COH$^+$, whilst (II) is preferred by HCO$^+$. This increased polarization of electrons by oxygen when coordination occurs at that atom led Purcell to speculate:

"... the CO $\sigma$ bond order of COH$^+$ is also appreciably reduced and leads us to suspect that, should attempts to prepare Lewis acid adducts of metal carbonyl complexes in which the acid coordinates to the oxygen of carbon coordinated CO, be successful, the infrared spectra of the adduct will be characterised by a pronounced lowering, relative to the carbonyl complex, of the CO stretching frequency. Furthermore, enhanced back bonding from the metal to CO would compliment polarization of the CO $\pi$ density, particular in
view of the anticipated increase in CO distance. The decrease of CO frequency should, in any event, amount to at least a few hundred wave numbers".

Recently, it has been shown that this prediction can be realised if sufficiently hard Lewis acids are employed. These adducts, in which both ends of the CO or NO molecule are bonded, are said to contain an "isocarbonyl" or "isonitrosyl" linkage respectively.

The evidence for these types of interactions has relied heavily upon infrared data, although a few crystal structures have been determined and one ultra-violet study was made. Complex formation does result in a lowering of the infrared stretching frequency of the C-O (or N-O) group. Not all the $\nu_{\text{CO}}$ (or $\nu_{\text{NO}}$) are lowered, however, if there are other non-complexing carbonyls (or nitrosyls) in the donor molecule. The absorptions of these ligands are observed to rise slightly if they change at all. The rationale is that as electrons are removed towards the Lewis acid, the electron density on the transition metal is lowered, resulting in less $\pi$ back donation into the uncomplexed carbonyls' (or nitrosyls') $\pi^*$ orbitals and so causing a higher stretching frequency to be observed for this ligand. It is readily seen that this additional effect is secondary in terms of size of $\Delta\nu_{\text{CO/NO}}$, because of the distance from the site of adduct formation.

In early 1971, when our studies began, the literature contained only four short communications dealing with isocarbonyl behaviour. There are now twenty papers published, over half of these in the last twelve months, concerning this mode of bonding. The literature review below summarises all work in the field, other than our own, up to the end of September 1973.

The first reported example of an isocarbonyl linkage, which was recognized as such, was $[(h^5-\text{Cp})\text{Fe(CO)}_2]_2\text{A1Et}_3$. $[(h^5-\text{Cp})\text{Fe(CO)}_2]_2$ is known to exist in the solid phase with two bridging and two terminal carbonyls,
whether a cis\(^{27}\) or trans\(^{28}\) arrangement of (h\(^5\)-Cp) ligands is the case. The Et\(_3\)Al molecules were shown by an X-ray crystallographic study\(^{26}\) to be coordinated to the oxygen of the bridging carbonyls in the cis isomer of [(h\(^5\)-Cp)Fe(CO)\(_2\)]\(_2\).

The Al-0 distance was measured to be 1.98(2)\(\text{Å}\),\(^{29}\) which is close to the value of 2.02(2)\(\text{Å}\) observed for the donor-acceptor bond in the bis-(trimethylaluminium)-dioxane adduct,\(^{30}\) but is significantly longer than the Al-0 distance of 1.89\(\text{Å}\) in Al(H\(_2\)O)\(_6\)\(^{3+}\)\(^{31}\) and 1.82\(\text{Å}\) in AlCl\(_3\)\cdot C\(_6\)H\(_5\)COCl.\(^{32}\) In the last two cases, however, the ligands attached to aluminium are far more electronegative than ethyl groups and would enhance the hard character of this metal, thereby helping to shorten the Al-0 bond length. The Al-0-C bond angle\(^{29}\) is 155°, which is compatible with the location of two lone pairs on the carbonyl oxygen, if one pair is involved in bonding. The Al-C bond distances\(^{29}\) are similar to values found in the (Me\(_3\)Al)\(_2\)\cdot C\(_4\)H\(_8\)O\(_2\)\(^{30}\) adduct, whilst the [(h\(^5\)-Cp)Fe(CO)\(_2\)]\(_2\) part of the complex is almost unchanged relative to the free molecule, except for a slightly shorter (0.04\(\text{Å}\)) Fe-Fe distance. In conjunction with this crystal data, infrared evidence substantiates the same mode of bonding in solution. In heptane the infrared spectrum shows a 112 cm\(^{-1}\), lowering for the bridging carbonyl and a 40 cm\(^{-1}\) raising of the terminal carbonyl absorption, relative to the parent iron compound.\(^{33}\) Further support for the formulation of this compound as an adduct is the reaction of [(h\(^5\)-Cp)Fe(CO)\(_2\)]\(_2\)\cdot 2AlEt\(_3\) with a
slight molar excess of triethylamine causing complete regeneration of 
[(h^5-Cp)Fe(\text{CO})_2]_2. In a later paper\textsuperscript{34} Shriver studied the solution infrared 
spectrum of this system in more depth. By adding the Lewis acid incrementally and measuring the associated changes in position and intensity of the carbonyl absorptions, he was able to ascertain the following: (a) addition is stepwise \textit{via} a 1:1, then to the 1:2 adduct and no further; (b) the 1:2 adduct is probably symmetrically arranged, because the symmetric stretch of the bridging carbonyl remains weak as observed in the parent iron compound; (c) although both \textit{cis} and \textit{trans} forms of [(h^5-Cp)Fe(\text{CO})_2]_2 are present, the proportion of the \textit{cis} form increases from parent to 1:1 to 1:2 adduct.

In order to determine point (c), Shriver made use of the fact that the relative intensities of the \(v_{\text{sym}}\) and \(v_{\text{asym}}\) of the terminal \text{CO} stretch reflect the \textit{cis-trans} ratio\textsuperscript{27} in the starting iron dimer, and that this donor apparently is hardly changed structurally in the adduct.

The only comment one might make about the infrared data is the interpretation of the \(2v_{\text{CO}}\) bridging bands for the 1:1 adduct. Shriver remarked that this species lacks a centre of symmetry and thus should "display two prominent \text{CO} stretching absorptions". Whilst not questioning the number of bands or that a 1:1 adduct has formed, it would seem reasonable to expect \(2v_{\text{CO}}\) bands on the grounds that one carbonyl group is complexed whilst the other is not. Closer scrutiny of the two bridging bands shows one raised and one substantially lowered\textsuperscript{\dagger} relative to the parent [(h^5-Cp)Fe(\text{CO})_2]_2, which is to be expected if only 1 group were forming an isocarbonyl link.

Further evidence\textsuperscript{34} for both \textit{cis} and \textit{trans} isomers in solution was obtained from n.m.r. experiments which showed two resonances for the \(C_5H_5\) pro-

\textsuperscript{\dagger} In fact this absorption is lowered to the exact position of the 1:2 adduct, although it is weaker in intensity of course.
tons: a large one at 2.81 ppm and a weaker one at 2.72 ppm upfield from benzene. The former peak was assigned to the cis isomer and the latter to the trans; similar results have been observed for the uncomplexed \([(h^5\text{-Cp})\text{Fe(CO)}_2]\) molecule.\(^{36a,36b}\) Shriver\(^{34}\) was also able to show from the n.m.r. data that cis to trans interconversion was slower in the complexed system. This result is to be expected because the interconversion is thought to occur via a non-bridged intermediate,\(^{36a,37}\) which would be less favourable for isocarbonyl formation.

\([(h^5\text{-Cp})\text{Ru(CO)}_2]\) is a species which is known to exist as both bridged and non-bridged isomers in solution in almost equal amounts.\(^{33,38}\) Using a similar technique to that used for the iron dimer, Shriver\(^{34}\) showed that the equilibrium could be shifted entirely to the bridged side by addition of aluminium alkyls in heptane. The infrared data were once again readily interpreted as showing a 1:1 and then a 1:2 adduct forming. Just as in the iron case cis and trans isomers were present with the cis favoured in the adduct, which could be dissociated by addition of a stronger base, such as triethylamine. This example shows quite clearly the more basic nature of the bridging carbonyl group and that this property can be utilised to force a structural rearrangement.

Unlike the previous two examples, \([(h^5\text{-Cp})\text{Mo(CO)}_3]\) has a centrosymmetric molecular structure with a metal-metal bond and six terminal carbonyl ligands in the solid state;\(^{39}\) moreover, this configuration is believed to persist in solution.\(^{40,41}\) Recently, Cotton\(^{37}\) used \(^{13}\)C n.m.r. while investigating the possibility of carbonyl transfer in the complex via a bridging intermediate. His study did not reveal any evidence for such an occurrence. Shriver et al.\(^{34}\) reacted trialkylaluminiums with \([(h^5\text{-Cp})\text{Mo(CO)}_3]\) in hydrocarbon solvent and observed new carbonyl bands immediately. The terminal \(\nu_{\text{CO}}\) were shifted to higher frequency and increased in number (2020w, 1990ms,
1979vs, 1944m, 1936m and 1911m cm$^{-1}$), whilst two new lower bands at 1774 and 1710 cm$^{-1}$ were observed. This species was termed the "equilibrium product" because all the bands increased relative to the parent as the R$_3$Al concentration was increased and reverted to the parent spectrum upon addition of triethylamine. If the mixture was kept at -3°C for a few hours, the 1990 and 1710 cm$^{-1}$ absorptions increased and bands appeared at 1860 and 1620 cm$^{-1}$. After eight days at room temperature only the 1990, 1860, 1710 and 1620 cm$^{-1}$ absorptions remained - this species was termed the "kinetic product". They suggested that the equilibrium product is consistent with a structure involving two R$_3$Al coordinated carbonyls and four terminal carbonyls. They went on to remark that the Mo-Mo bond (3.22Å in the parent) is too long to accommodate a carbonyl bridge because it is thought that 2.8Å is the limiting intermetallic separation to permit such an occurrence. However, they mentioned that Mo-Mo bonds are known in the range 2.89 - 3.09Å and it is thus "conceivable" that bridging carbonyl formation could occur with a concomitant shortening of the Mo-Mo bond. It should be remembered at this point that the shortening of the Fe-Fe bond in [(h$_5$-Cp)Fe(CO)$_2$]$_2$ upon complexation was only 0.04Å, whereas the Mo case would require a substantial reduction in the Mo-Mo bond, by an effect which is not considered to be severe.

All of the examples cited so far have involved a carbonyl group bridging two metal atoms. If one regards the state of hybridization of oxygen in the carbonyl group to be sp, sp$^2$ and sp$^3$ for linear, doubly and triply bridging situations respectively, then a gradual increase in basicity is to be expected as the percentage s character of the lone pair orbital diminishes. An experiment to demonstrate the increasing basicity for triply as opposed to doubly bridging CO was devised by Shriver.$^{34}$ He compared the two molecules [(h$_5$-Cp)NiCO]$_2$ and (h$_5$-Cp)$_3$Ni$_3$(CO)$_2$ as potential donors. The former has only doubly bridging carbonyl groups which are not coplanar with the two nickel atoms,
hence a formally bent metal-metal bond exists in solution.\textsuperscript{43} The interaction of this molecule with either triethylaluminium or triisobutylaluminium was not strong: only a 1:1 adduct was formed, the shifts of $\nu_{\text{CO}}$ were not as great as the iron and ruthenium cases considered earlier and a much higher concentration of aluminium alkyl was necessary to bring about adduct formation. On the other hand, $(h^5\text{-Cp})_3\text{Ni}_3(\text{CO})_2$, which contains only triply bridging carbynols, exhibited both 1:1 and 1:2 complex formation; the 1:1 adduct formed at one quarter the concentration of alkylaluminium required for the corresponding complex of $[(h^5\text{-Cp})\text{NiCO}]_2$.

In the compound $[(h^5\text{-Cp})\text{FeCO}]_4$ all CO ligands are triply bridging. It was not possible to follow successive addition of aluminium alkyls;\textsuperscript{34} however, a 1:4 adduct was isolated as a solid which showed only one $\nu_{\text{CO}}$, which was 150 cm$^{-1}$ lower than the single absorption of the parent.

Kotz and Turnipseed\textsuperscript{44} reported the first example of a terminal metal carbonyl involved in isocarbonyl bonding. They found that $\text{Ph}_3\text{PC}_5\text{H}_4\text{Mo(}\text{CO})_3$ (henceforth called cpylidMo(CO)$_3$), which is not very soluble in toluene, would readily dissolve if trimethylaluminium was added to the solution. A dark brown solid could be isolated from the solution. Tensimetric titrations and reactions with ethanol indicated a 1:1 adduct had formed. That the base site was an oxygen atom was suggested by the infrared spectrum which showed a low band at 1665 cm$^{-1}$ assigned to the isocarbonyl group, whilst the two non-complexed CO groups showed slightly higher absorptions than in cpylidMo(CO)$_3$. They postulated that the increased solubility of the adduct could be described by the equilibrium:

$$2\text{cpylidMo(CO)}_3 + \text{Me}_6\text{Al}_2 \rightleftharpoons 2\text{cpylidMo(CO)}_3\text{·AlMe}_3$$

Such an equilibrium would explain why rapid exchange of bridging and terminal methyl groups of the Me$_6$Al$_2$ was found to occur (by n.m.r.) in toluene even at
\(-80^\circ\text{C},\) which is a temperature well below the coalescence of methyl resonances for \(\text{Me}_6\text{Al}_2\) alone.

The variability of the site of basicity revealed itself in the interaction of the anion \([\left(h^5\text{-Cp}\right)\text{W(CO)}_3]^-\) with the two Lewis acids \(\text{Ph}_3\text{In}\) and \(\text{Ph}_3\text{Al}\).\(^{46}\) In the case of the indium compound, the symmetry-predicted three terminal \(\nu\text{CO}\) absorptions, plus two additional weak bands from the uncomplexed anion, were observed in the region 1750 - 1950 cm\(^{-1}\). These observations are consistent with the formation of an In-W bond. The \(\text{Ph}_3\text{Al}\) species, however, showed only two terminal \(\nu\text{CO}\) bands and a third strong band at 1600 cm\(^{-1}\) indicative of isocarbonyl behaviour. To determine whether the \([\left(h^5\text{-Cp}\right)\text{W(CO)}_3]^-\) anion was still intact, a slight excess of pyridine was added to the 1:1 complex in hot toluene and a 95\% recovery was effected. Presumably the harder aluminium atom is capable of forming a stronger Al-O bond than Al-W bond, whereas the weaker Lewis acid, \(\text{Ph}_3\text{In}\), prefers the softer base site of the transition element.

Organooaluminium compounds need not be the Lewis acid for isocarbonyl links to form. An experiment to demonstrate this point was conducted by Brown and Brown.\(^{47}\) They realized that the anion \([\text{Fe(CN)}_5X]^{n-}\) in the presence of transition-metal ions in the solid state adopts the nitroprusside structure in which all cyanides are bridging and the unique ligand, \(X\), would be forced into a bridging situation. They prepared \(\text{Co}_3[\text{Fe(CN)}_5\text{CO}]_2\cdot5\cdot7\text{H}_2\text{O}\) and showed it to have a face centered cubic lattice with \(a = 10.27\) Å, which is consistent with a Prussian blue structure. In addition, they compared the infrared spectrum of the starting sodium salt to that of the cobalt complex: the sodium species which has no bridging CN groups exhibited five bands in the range 2015 - 2095 cm\(^{-1}\) [2015m, 2040s, 2055s, 2075s, sh, and 2095m, sh, cm\(^{-1}\)], whereas the cobalt compound has one absorption at 1950 cm\(^{-1}\) and four others.
in the region 2025 - 2185 cm$^{-1}$.[2025m, 2090s, 2120s, sh, and 2185w cm$^{-1}$].

It had already been established$^{48}$ that CN groups exhibit an increase of their stretching frequency when strong bridging occurs, hence the 1950 cm$^{-1}$ band was assigned to isocarbonyl behaviour and the remaining absorptions were considered to be bridging cyanides. Further, comparison of the infrared spectra of the sodium and cobalt compounds permitted assignment of the 2040 cm$^{-1}$ absorption to CO in the sodium salt. It should be noted that Cotton$^{49}$ had attributed a band at 2052 cm$^{-1}$ to CO in the very similar compounds $K_3Fe(CN)_5CO$ which displayed almost identical absorptions.

A new class of compounds in which all the anionic ligands are bound to the central metal by isocarbonyl bonds has been prepared by Burlitch et al.$^{50,51,53}$ The first compound in the series,$^{50}$ $A1[(h^5-Cp)W(CO)_3]_3\cdot3THF$ was synthesized by a metal exchange reaction of aluminium with $Hg[(h^5-Cp)W(CO)_3]_2$. A single x-ray crystal study of the product showed aluminium octahedrally coordinated to three THF molecules and three isocarbonyl bonds, one from each $(h^5-Cp)W(CO)_3$ entity, in a fac conformation. The W-C distances (1.85(2)Å) of the carbonyls which link tungsten to aluminium are systematically shorter than those of the terminal carbonyls (1.95(2)Å). Conversely, the corresponding C-O distances are 1.25(2)Å and 1.16(2)Å, respectively. These bond length changes are to be expected as electrons are withdrawn towards aluminium and away from tungsten. The Al-0 distances to three carbonyls (1.827(9)Å) are substantially shorter than to the THF ligands (1.94(2)Å) and also much shorter than the previously discussed $[(h^5-Cp)Fe(CO)_2]_2\cdot2AlEt_3$ case (1.98(2)Å).$^{29}$ All the W-C-O units are essentially linear (176(3)°) and all 0-Al-0 angles are orthogonal to within 3°. The Al-0-C angles vary from 140.4° to 162.9° and average 151°; Burlitch attributed this spread to packing forces. The shorter and presumably
stronger Al-0 bond to the carbonyl groups as opposed to the THF molecules is reflected in the fact that the infrared spectra in the solid state (Nujol) and in THF are identical, thereby implying no dissociation of the $[(h_5^5-Cp)W(CO)_3]^{-}$ anion from the complex in THF. In fact, only very strongly coordinating solvents such as dimethylformamide cause dissociation as evidenced by infrared spectroscopy. Chemically the compound behaves as though it is very ionic: it readily undergoes displacement by nucleophiles and is easily converted to HW($h_5^5-Cp$)(CO)$_3$ or CF$_3$COW($h_5^5-Cp$)(CO)$_3$. The infrared spectrum in Nujol is quite complicated, displaying four strong bands in the terminal $\nu_{CO}$ region and four others in the range 1570 - 1670 cm$^{-1}$ attributed to isocarbonyl interactions.

In a very recent paper,$^{51}$ this work has been extended to include derivatives of magnesium of the general formula $m_2$Mgpy$_4$, [$m = Co(CO)$_4$, ($h_5^5$-$Cp$)Mo(CO)$_3$, Mn(CO)$_5$, and ($h_5^5$-$Cp$)Fe(CO)$_2$]. The molybdenum and cobalt derivatives were prepared by reacting magnesium amalgam with the appropriate $m_2$Hg in a solution of pyridine and toluene, whilst the manganese and iron compounds were synthesized using the amalgam directly upon the metal carbonyl dimer in the same solvent mixture. (The iron required at least a trace of MgCl$_2$ to be present to promote the reaction). Alternatively the molybdenum compound was obtained by a metal exchange reaction with the corresponding $m_2$Hg in THF and recrystallization from pyridine. In all cases the complexes showed infrared absorptions (in pyridine, toluene or as a Nujol mull) in the region 1665 - 1720 cm$^{-1}$ indicative of an isocarbonyl link. The molybdenum compound was the subject of a single crystal x-ray determination which revealed an octahedrally coordinated magnesium with four equatorial pyridine groups and two axial isocarbonyl bonds. The Mg-0 distance (2.047(2)Å) is slightly longer than the analogous Al-0 length mentioned above$^{50}$ and apparently
this is reflected in less perturbation of the adjoining C-O bond now at 1.189(3) Å, but it is still significantly larger than the mean terminal C-O distance of 1.157 Å. The Mg-O-C angle is 155.0(2)°, whilst the Mo-C-O angles whether iso (177.2(1)°) or terminal (178.1(1)°) are both very close to linearity.

By analogy with the aluminium compound described above these magnesium derivatives behaved as strong nucleophiles with the added advantage, however, that the cobalt and manganese species were soluble in aromatic hydrocarbons. For example, Ph₃SiCl was converted in toluene to Ph₃SiMn(CO)₅ in 34% yield, a reaction which is inaccessible using NaMn(CO)₅ in THF.

Other workers⁵² have prepared almost identical magnesium derivatives using magnesium amalgam and metal carbonyl dimers in the presence of a base. The compounds they obtained have the general formula BₓMgₓm[ B=py or THF; m=(h⁵-Cp)Fe(CO)₂, Mn(CO)₄L, (h⁵-Cp)NiCO, Co(CO)₃L or Mo(CO)₂L (h⁵-Cp), where L = CO, or alkyl- or aryl-phosphine]; the value of x is two for a strongly nucleophilic anion and four for a weak nucleophile. On the basis of molar conductivities in THF they concluded that the magnesium-transition metal bond was not highly dissociated, moreover infrared measurements of the benzene solutions of the iron and cobalt (L = Ph₃P) complexes showed no bands below 1820 cm⁻¹. The absence of isocarbonyl bands contrasts strikingly with the results obtained by Burlitch.⁵⁰

Burlitch has extended his work on magnesium derivatives by employing manganese metal⁵³ in exchange reactions with m₂Hg to form compounds of the type m₂Mnpy₄[m = (h⁵-Cp)M(CO)₃, M = Cr, Mo, and W]. Infrared measurements showed three strong carbonyl absorptions, one of which was around 1650 cm⁻¹ and attributed to an isocarbonyl linkage.
In an attempt to form a covalent bond between aluminium and tungsten, two apparently different bonding modes were obtained in the ethyl and methyl species of the reaction.

\[
R_2AlH + HW(h^5-Cp)(CO)_3 \rightarrow R_2AlW(h^5-Cp)(CO)_3 + H_2
\]

Cryoscopic molecular weight determinations showed both compounds to be dimeric in benzene. In the 'H n.m.r., single peaks for both the \((h^5-Cp)\) ring and the methyl groups (for \(R=Me\)) which did not broaden or split even at -65°C removed the possibilities of ring substitution and methyl bridges respectively. The infrared spectrum showed considerably different absorptions: for \(R=Me\) in benzene strong bands at 2014 and 1926 \(\text{cm}^{-1}\) only occurred, whereas the ethyl derivative in methylcyclohexane displayed strong bands at 1986, 1692 and 1659 \(\text{cm}^{-1}\), typical of isocarbonyl behaviour. The quandary was partially resolved when an x-ray determination of the methyl compound was published later. In the solid state this compound also showed isocarbonyl behaviour as the compound consisted of a slightly puckered twelve membered ring containing Al-O-C-W bridges.

![Diagram of the compound](image)

The tungsten is roughly octahedrally coordinated whilst aluminium is four coordinated with a wide exocyclic C-Al-C angle, found in other ring systems (e.g. \((Me_2AlCl)_2\)).\(^{35}\) The Al-O distances are 1.83(3)Å and 1.79(3)Å, both very similar to that found by Burlitch in Al\([(h^5-Cp)W(CO)_3]\)_3·3THF\(^{50}\).
The same trend of longer W-C bonds in terminal carbonyls compared to the W-C length in the isocarbonyls is also observed in this structure.

The molecular structure of the ethyl derivative has not yet been reported; however, if it has a solid state geometry similar to that implied by its solution infrared spectrum, it could well be isostructural with the methyl analogue in the solid phase. The question remains as there appear to be no isocarbonyl linkages, how does the methyl compound exist in solution as a dimer? If a W-Al bond exists in solution, as shown in the figure below, then why does it not persist in the solid and why does not the ethyl complex adopt this bonding scheme? Unfortunately, the solution infrared spectra of the two complexes were not obtained in the same solvent (above); if this difference were responsible for the change in bonding a subtle lever would be provided for affecting the change of base sites.

\[
(h^5\text{-Cp})(\text{CO})_3W\rightarrow\text{AlMe}_2
\]

\[
\text{Me}_2\text{Al} \rightarrow W(h^5\text{-Cp})(\text{CO})_3
\]

It has been known for some time that organic carbonyls, such as ketones, interact through oxygen with Lewis acids.\(^{56}\) If the Lewis acid is a lanthanide shift reagent, specific structural information can often be gleaned from changes in the n.m.r. spectrum of the organic compound. It was reasonable, therefore, to use these paramagnetic shift reagents in an attempt to induce corresponding effects in the n.m.r. spectrum of metal carbonyl containing entities. Providing that the carbonyl oxygen was sufficiently basic, n.m.r. shifts were observed using Eu(fod)\(_3\) (fod = 1,1,2,2,3,3-heptafluoro-7,7-dimethyl-4,6-octanedionate) as the Lewis acid.\(^{57}\) For example, \((h^5\text{-Cp})\text{Fe(CO)}_2\text{Me}\) did not appear to interact, whereas the more basic bridging carbonyl of \([(h^5\text{-Cp})\text{Fe(CO)}_2]_2\) did, resulting in a downfield shift of up to
0.35 ppm of the (h^5-Cp) proton resonance. Marks et al.\textsuperscript{57} reported one new example of a shift in the proton resonances of a compound containing a terminal metal carbonyl as the base site, (phen) (Ph\textsubscript{3}P)\textsubscript{2}Mo(CO)\textsubscript{2}. This compound has low infrared stretching frequencies (1800s and 1729s cm\textsuperscript{-1}) for the carbonyl groups, a property that appears to be associated with good basicity. When the only base site of an organometallic compound is a terminal carbonyl group, the strength of the Lewis acid may be the limiting factor for adduct formation. Acid strength may be increased, however, by a suitable choice of ligands. These restrictions may limit use of this n.m.r. technique. It is worth mentioning that the p.m.r. spectra of inorganic compounds are rarely as complicated as those of organic species, consequently this interesting application possesses less potential for inorganic chemists.

Nuclear magnetic resonance spectroscopy was also used by Chatt and co-workers\textsuperscript{58,59} to determine the relative basicity of some compounds containing carbonyl and the isoelectronic dinitrogen as terminal ligands. Besides isolating 1:1 adducts with the Lewis acid Me\textsubscript{3}Al, they were able to measure the relative equilibrium constant, K, for the competition reaction:

\[
[L\text{-metal-}(X=Y)] + \text{Me}_3\text{Al} \cdot \text{Et}_2\text{O} \rightleftharpoons [L\text{-metal-}(X=Y) \cdot \text{AlMe}_3] + \text{Et}_2\text{O}
\]

where \(X = C, Y = O\) or \(X = Y = N\) and \(L = \) other ligands. The values of \(K\) were determined by relating the concentration of the species to their integrated peak heights in the proton n.m.r. spectrum of the equilibrated benzene solutions at 30°C. The values of \(K\) so obtained showed that all the M-X-Y species except one were more basic than diethyl ether. The exception had the highest \(\nu_{N-N}\) in the set, whereas the most basic had the lowest \(\nu_{N-N}\). Indeed, the most basic, trans(ReCl(N\textsubscript{2})(PMe\textsubscript{2}Ph\textsubscript{4})\textsubscript{2}) was the only
example for which there was the corresponding carbonyl available for comparison. Although the stretching frequency of the parent carbonyl is substantially lower, 1782 cm\(^{-1}\) relative to the parent dinitrogen at 1923 cm\(^{-1}\), the dinitrogen is far more basic having \(K = 70\) as opposed to \(K = 3.3\) for the carbonyl complex. This result is readily understood in terms of the greater effective nuclear charge of oxygen than nitrogen towards the lone pairs of electrons, which are available for adduct formation. By systematically changing the nature of \(L_2\) in trans ReCl\((N_2)\)\(L_4\) (\(L = \) a substituted phosphine), it was shown that the most basic ligand, \(L\), caused the greatest lowering in \(v_{N_2}\). "The implication of this is that the more electron density the ligating dinitrogen takes into its \(\pi^*\) orbitals from the metal d-orbitals, the more basic is the terminal nitrogen atom", Chatt remarked.

One of the earliest reported examples of a Lewis acid complex with a metal carbonyl is \((\text{Co}_2\text{CO})_8\cdot\text{AlBr}_3\). The molecular structure of dicobalt octacarbonyl in the solid state is such that the two cobalt atoms and the two bridging CO groups are not in the same plane, the molecule having only \(C_5\) symmetry. In solution, however, \(\text{Co}_2\text{CO})_8\) exists in two isomeric forms which are related by a temperature dependent equilibrium. One isomer, (I), corresponds to the crystalline substance whereas the other, (II), has no bridging CO groups, but only a cobalt-cobalt bond, i.e.

\[
\begin{align*}
\text{(OC)}_3\text{Co} & \quad \text{Co(OC)}_3 \quad \text{↔} \quad \text{(OC)}_4\text{Co} \quad \text{Co(OC)}_4 \\
\text{(I)} & \quad \text{(II)}
\end{align*}
\]

Chini and Ercoli suggested that the AlBr\(_3\) adduct they formed involving \(\text{Co}_2\text{CO})_8\) was coordinated via a three-centre-two-electron bond to the formally
bent cobalt-cobalt bond of isomer (I). Support for this structural proposal was the observation that the infrared spectrum (obtained with high resolution optics) of the adduct was virtually identical with that of the parent carbonyl in the CO stretching region. This result in itself is surprising, since reasoning of the type outlined previously leads one to expect that the carbonyl stretches of the adduct should occur at a somewhat higher frequency. Indeed, more recent work tends to refute the proposal that a three centre bond is involved. During a study of the effects of high temperature and high pressure upon the reaction between CO and Co\(_2\)(CO)\(_8\), Whyman found that Co\(_2\)(CO)\(_8\)-AlBr\(_3\), prepared according to Chini and Ercoli, displayed infrared bands in the region 1800 - 2200 cm\(^{-1}\), just as claimed, but also he observed a strong absorption at 1600 cm\(^{-1}\). The lowest band was suggested to result from possible isocarbonyl behaviour, although it was not specified whether this was of the bridging or terminal type.

Schmid and Bätzel were investigating the criteria for incorporating hetero atoms, (X), into the cluster unit, Co\(_3\)(CO)\(_9\)X, when they encountered the Co\(_2\)(CO)\(_8\)-AlBr\(_3\) adduct. Specifically, they had noticed that X could be sulphur, selenium, germanium or more commonly, carbon, but attempts to insert boron or silicon gave only compounds of the formula Co\(_3\)(CO)\(_9\)COSiR\(_3\) or Co\(_3\)(CO)\(_9\)COBH\(_2\)NR\(_3\) (where R = alkyl group). As a model for their studies they reacted Group IIIb and IVb halides with Co\(_2\)(CO)\(_8\), eg.

\[
4CCl\(_4\) + 9Co\(_2\)(CO)\(_8\) \rightarrow 4Co\(_3\)(CO)\(_9\)CCl + 36CO + 6CoCl\(_2\)
\]

and

\[
7Co\(_2\)(CO)\(_8\) + 4Cl\(_3\)BNR\(_3\) \rightarrow 4Co\(_3\)(CO)\(_9\)COBCl\(_2\)NR\(_3\) + 16CO + 2CoCl\(_2\)
\]

From the reaction of AlBr\(_3\) with Co\(_2\)(CO)\(_8\) they were able to isolate the adduct Co\(_2\)(CO)\(_8\)-AlBr\(_3\). Furthermore, they also noticed that earlier workers had overlooked a strong absorption at 1595 cm\(^{-1}\), which they assigned to a bridging
carbonyl of isomer I acting as an isocarbonyl unit. Heating this adduct in benzene ultimately led to a compound of the formula \( \text{Co}_3(\text{CO})_5\text{CoAlBr}_2\cdot\text{AlBr}_3 \), with the second AlBr\(_3\) providing a bromine bridging unit to coordinatively saturate the aluminium atoms in the structure given:

![Chemical structure](image)

The reaction was described to proceed according to the following equations:

\[
\begin{align*}
\text{Co}_2(\text{CO})_8 + \text{AlBr}_3 & \rightarrow \text{Co}_2(\text{CO})_8\cdot\text{AlBr}_3 \\
\text{Co}_2(\text{CO})_8\cdot\text{AlBr}_3 & \rightarrow 2\text{Co}(\text{CO})_4 + \text{AlBr}_3 \\
2\text{Co}_2(\text{CO})_8\cdot\text{AlBr}_3 + \text{Co}(\text{CO})_4 & \rightarrow \text{CoBr}_2 + 4\text{CO} + 2\text{Co}_2(\text{CO})_8\cdot\text{AlBr}_2 \\
\text{Co}_2(\text{CO})_8\cdot\text{AlBr}_2 + \text{Co}(\text{CO})_4 & \rightarrow (\text{CO})_3\text{Co}_3\text{CoAlBr}_2 + 2\text{CO} \\
(\text{CO})_3\text{Co}_3\text{CoAlBr}_2 + \text{AlBr}_3 & \rightarrow (\text{CO})_3\text{Co}_3\text{CoAlBr}_2\cdot\text{AlBr}_3
\end{align*}
\]

The proposal was made that Lewis acids initially engage in isocarbonyl bonding and hence are not incorporated into the cobalt cluster, but rather they remain oxygen bonded.

In a later more detailed study,\(^{68}\) it was shown that the terminal carbonyl stretching frequencies of \( \text{Co}_2(\text{CO})_8\cdot\text{AlBr}_3 \) have both increased in frequency by about 30 cm\(^{-1}\) and in number relative to the parent carbonyl, in addition to the band at 1600 cm\(^{-1}\). These results strongly favour the
oxygen bonded structure. (Attempts to form adducts employing aluminium alkyls and \( \text{Co}_2(\text{CO})_8 \) were unsuccessful.\(^{34} \) The cobalt carbonyl appeared to be destroyed by the \( \text{R}_3\text{Al} \) species. The substituted carbonyl \( \text{(Co(CO)}_3\text{PPh}_3)_2 \) showed no isocarbonyl behaviour either,\(^{34} \) although this compound exists in solution mostly as the non-bridged isomer.)

In the same study,\(^{68} \) Shriver presented evidence for 1:1 complex formation between \( [\text{(h}_5^\circ\text{-Cp})\text{Fe(CO)}]_2 \) and \( \text{BX}_3 \) (\( \text{X} = \text{F}, \text{Cl} \) or \( \text{Br} \)). In the case of the \( \text{BBF}_3 \) adduct, the infrared mull spectra showed the bridging carbonyl bands to be at 1849 and 1437 cm\(^{-1} \). Similarly both 1:1 and 1:2 adducts between \( [\text{(h}_5^\circ\text{-Cp})\text{FeCO}]_4 \) and \( \text{BX}_3 \) (\( \text{X} = \text{F}, \text{Cl} \) or \( \text{Br} \)) could be obtained. The infrared mull spectra revealed one new strong band in the 1300 - 1400 cm\(^{-1} \) region for the 1:1 adduct and two new bands for the 1:2 compound in the same region.

Spectra in the 1650 - 1750 cm\(^{-1} \) region for \( \text{CH}_2\text{Cl}_2 \) solutions of these adducts showed two bands for both the 1:1 and 1:2 complexes. These results are interesting in that the weaker Lewis acids \( \text{BX}_3 \) have caused a greater reduction in carbonyl stretching frequency than the aluminium alkyls which form 1:4 adducts with \( [\text{(h}_5^\circ\text{-Cp})\text{FeCO}]_4 \). It is worth noting that in the cases where it was possible to incrementally add Lewis acid it was never found that an intermediate adduct had a lower carbonyl absorption than the final complex. An explanation of the greater shift by \( \text{BX}_3 \) may be the more compatible sizes of the acceptor and donor orbitals of boron (2sp\(^3 \)) and oxygen (2sp\(^3 \)) respectively, as opposed to those for aluminium (3sp\(^3 \)) and oxygen. Better overlap and a stronger B-0 bond would result in a lower C-O stretching frequency. Another consequence might be that the remaining uncomplexed CO ligands become much less basic because of substantial charge withdrawal and so subsequent adduct formation is reduced; hence \( \text{BX}_3 \) only forms up to 1:2 adducts with \( [\text{(h}_5^\circ\text{-Cp})\text{FeCO}]_4 \).
One paper has been published dealing with the electronic spectra of an isocarbonyl compound. The species chosen for study was Mo(CO)$_2$(LL)(PPh$_3$)$_2$ (LL = phenanthroline or 5,6 dimethylphenanthroline), which has an intense charge transfer band centered at 693 nm (molar absorptivity: $7.7 \times 10^3$ mol$^{-1}$ cm$^{-1}$). Upon formation of the adduct with trialkylaluminium the colour changes from blue-green to deep red, resulting from a shift of the charge transfer (CT) band. The spectra of the complexes were described by a simple Hückel M.O. model which treats the fragment (LL)Mo(CO)$_2$. The charge transfer transition was assigned to the transition from a M.O. of $b_1$ symmetry mainly localized on Mo(CO)$_2$ to a $b_1$ symmetry M.O. which is mostly phenanthroline $\pi^*$ in character. The effect of a Lewis acid on the complex was introduced as a perturbation of the coulomb integral of the oxygen to which it is attached. A lowering of the Mo(CO)$_2$ donor orbital was found to result from this perturbation and thus increased the energy of the CT transition. Shriver pointed out that no account was made of Lewis acid influence upon changes in the $\sigma$ donation of CO toward molybdenum, which he regarded as less important than changes in $\pi$ bonding. Besides being able to calculate the energy of the band which agreed reasonably well with experiment (518 nm calc; 530 ± 10 nm found), it was shown that the charge shifted from oxygen to the Lewis acid decreased in the series Et$_3$Al > (i-Bu)$_3$Al > Me$_3$Ga; $\Delta q = 0.085; 0.080$ and $0.035$ e, respectively).

The latter result agrees with the known Lewis acidity of these Group IIIb alkyls, and although the numbers are not meant to be taken literally they offer an idea of the magnitude of electron transfer involved.

From this literature review it can be seen that the establishment and investigation of isocarbonyl linkages is very recent. Indeed, almost all
the work was published whilst our studies were in progress. This research was undertaken for a variety of reasons. At the start only aluminium alkyls were known to be sufficiently strong Lewis acids to induce isocarbonyl bonding. Earlier work\textsuperscript{20,50} had shown that Cp\textsubscript{3}Ln complexes form thermally stable 1:1 adducts with conventional Lewis bases such as Ph\textsubscript{3}P, NH\textsubscript{3}, C\textsubscript{6}H\textsubscript{11}NC and THF. Further, lanthanides are known to be hard acids. It therefore seemed feasible to determine whether the metals in compounds of the type Cp\textsubscript{3}Ln were sufficiently hard to interact with the oxygen of a metal carbonyl group. If this possibility proved to be the case, it would then be desirable to determine whether the shift of CO stretching frequency could be used as an approximate measure of acidity within the lanthanide series.\footnote{Strictly speaking, the change in stretching frequency of the carbonyl or nitrosyl band is not a measure of acidity, which is better described by thermodynamic functions which take account of changes within the donor and acceptor molecules themselves (such as bond lengthening). The variation in infrared band positions is more a reflection of the donor-acceptor bond interaction.} One would expect an increasing acidity as the metals contract in size, that is with increasing atomic weight. Conversely, by using one Cp\textsubscript{3}Ln compound it might be possible to use the same parameter to compare various metal carbonyl-containing molecules and obtain some guide towards their basicity. If metal carbonyl anions could be used as potential bases, the question would arise whether isocarbonyl behaviour or a lanthanide-transition element bond would prevail. Only one report of the latter possibility existed, that was for the species Er(Co(CO)\textsubscript{4})\textsubscript{3}·3C\textsubscript{6}H\textsubscript{6}O. This unique compound, prepared from Hg(Co(CO)\textsubscript{4})\textsubscript{2} and a 1% w/w Er/Hg mixture, has not been the subject of an x-ray study and
the assumption that it contains a metal-metal bond rests upon infrared data. Hence the reactions involving metal carbonyl anions were particularly intriguing.

The experiments involving nitrosyls were undertaken in order to determine the generality of the phenomenon and to compare NO with carbonyl ligands in this respect. Information of this type is useful, because it may lend insight into the mechanism of reactions between metal carbonyls or nitrosyls and strong Lewis acids.
2.2 EXPERIMENTAL

All reagents used were of reagent grade or comparable purity. The following chemicals were purchased from commercial suppliers: \( \text{C}_6\text{H}_7\text{Mn(CO)}_3 \), \([\text{h}^5\text{-C}_5\text{H}_5\text{Fe(CO)}_2]_2 \), \((\text{h}^5\text{-C}_5\text{H}_5\text{Fe(CO)}_2)_2\text{I} \), and \([\text{h}^5\text{-C}_5\text{H}_5\text{NiCO}]_2 \) from Alfa Inorganics and Co\(_2\text{(CO)}_8 \) from Pressure Chemical Company. The following chemicals were prepared according to literature procedures and their purity was ascertained by elemental analyses and/or melting point determinations: \((\text{h}^5\text{-C}_8\text{H}_8\text{Fe(CO)}_3)_7 \), \((\text{h}^5\text{-C}_5\text{H}_5\text{W}_2\text{H}_2)_7 \), \((\text{h}^5\text{-C}_5\text{H}_5\text{Cr(NO)}_2\text{Cl})_7 \), \(\text{Fe(CO)}_2\text{(NO)}_2 \), \((\text{h}^5\text{-C}_5\text{H}_5\text{Fe(CO)}_2\text{Cl})_7 \), \((\text{C}_5\text{H}_5)_2\text{Ln} \), \((\text{C}_6\text{H}_7)_2\text{LnCl} \), \((\text{C}_6\text{H}_7)_2\text{LnCl} \), \((\text{C}_6\text{H}_5)_2\text{Na}[(\text{h}^5\text{-C}_5\text{H}_5\text{M(CO)}_3)] \), \([\text{C}_6\text{H}_5\text{P}]_2\text{Ru(NO)}\text{Cl}_3 \), \([\text{h}^5\text{-C}_5\text{H}_5\text{Mn(CO)}\text{NO}]_2 \), \([\text{C}_6\text{H}_5\text{(CH}_3\text{)}\text{P}]_2\text{Fe(NO)}_2 \) was donated by Prof. W. Cullen. \([(\text{CH}_3)_2\text{NCS}_2]_2\text{FeNO} \) and \((\text{h}^5\text{-C}_5\text{H}_5\text{M(CO)}_2\text{NO}) \) (\(M = \text{Cr, Mo or W} \)) were prepared by our own methods (below). Lanthanide halides were purchased as hexahydrates (99.9% pure) from the Rare Earth Division, American Potash and Chemical Corporation. Dehydration was achieved by the method outlined below. All solvents were purified according to known methods. Solvents were degassed just prior to use; two methods were employed: the freeze-thaw method and a modification of this procedure by not freezing before each pumping and by finally immersing a sintered glass tube into the solvent through which nitrogen was bubbled for a few minutes. L-grade nitrogen was used throughout all experiments and for filling the dry box, which was a Vacuum Atmospheres Corporation Dri-Lab model He-43-2. Bench top operations were carried out under nitrogen.

Infrared spectra were recorded on a Perkin Elmer 457 spectrophotometer, using a polystyrene film as a calibrant. Proton magnetic resonance spectra were recorded on a Varian Associates T-60 spectrometer with tetra-
methylsilane being employed as an internal standard. Conductivity measurements were made using a Yellow Springs Instrument Company (YSI), Ohio, conductivity bridge model 31 equipped with a YSI 3403 conductivity cell. The conductivity bridge was initially calibrated against known resistances and then against a standard solution (a 101.47 g solution of distilled water containing 0.0756 g 'Analar' KCl) at 25°C. The standard solution was used to determine the cell constant, \( K = 1.015 \). Elemental analyses were carried out by Galbraith Laboratories, Knoxville, Tennessee, and by Mr. P. Borda of this department (see Appendix). Melting points of solids in sealed glass capillary tubes were recorded on a Gallenkamp Melting Point Apparatus.

**Preparation of bis(dimethyldithiocarbamato)nitrosyliron(I)**

In attempting to prepare derivatives of the formula \( R_2\text{NCS}_2\text{Fe(NO)}_2 \) \((R = \text{alkyl})\) from \( \text{Fe(CO)}_2(\text{NO})_2 \) and \( (\text{Fe(NO)}_2X)_2 \) \((X = \text{Br or I})\) we discovered a facile, high yield synthesis of \([\text{(CH}_3\text{)}_2\text{NCS}_2]_2\text{FeNO}\).

A solution containing \( \text{NaS}_2\text{CN(CH}_3\text{)}_2 \) \((0.60 \text{ g, 4.19 mmol})\) in \( \text{CH}_3\text{OH} \) \((50 \text{ ml})\) was added dropwise to \( \text{CH}_3\text{OH} \) \((35 \text{ ml})\) containing \( (\text{Fe(NO)}_2\text{Br})_2 \) \((1.09 \text{ g, 2.78 mmol})\). A precipitate formed immediately and was collected by filtration. The green solid was recrystallised from \( \text{CH}_2\text{Cl}_2\)-hexanes. Yield: 0.55 g (80%).

Analysis, calc. for \( \text{C}_6\text{H}_{12}\text{N}_3\text{O}_5\text{S}_4\text{Fe} \): C, 22.1; H, 3.68; N, 12.9.

Found: C, 22.1; H, 3.87; N, 12.4.

Infrared \((\text{CH}_2\text{Cl}_2)\): \( v_{\text{NO}}, 1717 \text{ cm}^{-1} \) and \( v_{\text{CN}}, 1535 \text{ cm}^{-1} \).

**Dehydration of lanthanide chloride hexahydrates**

In essence, this method is a variation of one used to dehydrate transition metal hydrates. The reaction is as follows:
The dehydration of SmCl$_3$.6H$_2$O is a typical example of this method.

Purified thionyl chloride$^{33}$ (40 ml) was added to finely ground SmCl$_3$.6H$_2$O (14.2 g) and refluxed with stirring for 24 h. Excess SOCl$_2$ was removed by evaporation at reduced pressure and then by heating to 80°C for 3 h at 10$^{-2}$ mm Hg. The solid was transferred to a dry box, ground to a fine powder and treated again with SOCl$_2$ (40 ml) at reflux for 24 h. After evaporation of SOCl$_2$, the solid was heated to 80°C for 16 h at 10$^{-2}$ mm Hg. Analysis for chlorine was satisfactory at this point, e.g. calc. for SmCl$_3$, Cl, 41.5; found Cl, 41.9.

Preparation of the cyclopentadienyldicarbonylnitrosylmetal compounds

The compounds (h$_5$-C$_5$H$_5$)M(CO)$_2$NO (M = Cr, Mo or W) were all synthesized in an identical manner. The method of preparation, using the chromium complex as a typical example, was as follows. Na[(h$_5$-C$_5$H$_5$)Cr(CO)$_3$] (1.77 g, 7.90 mmol) was suspended in diethyl ether (30 ml) and the mixture was cooled to 10°C. Then, N-methyl-N-nitroso-p-toluenesulphonamide (1.81 g, 8.5 mmol) dissolved in diethyl ether (10 ml) was added slowly to the suspension, whereupon the reaction mixture evolved gas and darkened in colour. After the addition was complete, the reaction mixture was stirred for a further 15 min at 10°C. The solvent was removed under vacuum and the remaining residue was sublimed (50°C, 10$^{-2}$ mm Hg) on to an ice-cooled probe. Bright orange crystals of the desired product were thus obtained in at least 60% yield.

Analysis, calc. for C$_7$H$_5$CrNO$_3$: C, 41.4; H, 2.5; N, 6.9.

Found: C, 41.3; H, 2.6; N, 6.8.
The molybdenum and tungsten compounds of comparable purity were obtained in similar yields. The physical and chemical properties of these complexes have been extensively described.84

Preparation of the tris(methylcyclopentadienyl)samariumoctacarbonyldicobalt 2:1 adduct

\((\text{C}_6\text{H}_7)_3\text{Sm} (1.59 \text{ g, 4.10 mmol})\) was dissolved in toluene (30 ml) to produce a bright orange solution, and \(\text{Co}_2(\text{CO})_8 (1.40 \text{ g, 4.10 mmol})\) was dissolved in toluene (15 ml) to produce a red-brown solution. The two solutions were filtered into a common flask and the mixture of filtrates was rapidly stirred. Within 20 min the solution became cloudy and a solid began to precipitate. After a further 2 h of stirring at room temperature, the reaction was filtered and the yellow orange solid thus obtained was washed thoroughly with toluene (5 x 20 ml) until the washings were colourless. The remaining bright yellow solid was dried overnight in vacuo. The yield (2.10 g) was virtually quantitative.

Analysis, calc. for \(\text{C}_{22}\text{H}_{21}\text{CoO}_4\text{Sm}\): C, 47.3; H, 3.8; Sm, 26.9. Found: C, 46.8; H, 4.0; Sm, 26.3.

The extremely air- and moisture-sensitive adduct is rapidly converted to a green solid if exposed to moist air and even decomposes over a period of several days in an atmosphere of prepurified nitrogen. It is insoluble in non-polar organic solvents such as benzene, toluene and hexane. It dissolves in polar solvents such as diethyl ether, tetrahydrofuran, dichloromethane, and acetonitrile only with attendant dissociation, as indicated by the appearance of the characteristic red-brown colour of \(\text{Co}_2(\text{CO})_8\) and the diagnostic infrared bands of this species in the CO-stretching region.
Preparation of the tris(methylcyclopentadienyl)samarium-bis(h⁵-cyclopentadienyl)dicarbonyliron 2:1 adduct

\[ [(\text{h}^{5}\text{-C}_5\text{H}_5)\text{Fe(CO)}_2]_2 (0.49 \text{ g}, 1.38 \text{ mmol}) \text{ dissolved in benzene (15 ml)} \text{ was added dropwise at room temperature to a stirred solution of } (\text{C}_6\text{H}_7)_3\text{Sm (1.01 g, 2.68 mmol)} \text{ dissolved in benzene (50 ml). Within a few minutes a solid began to precipitate. Stirring was continued for 2 h to ensure completion of the reaction. The reaction mixture was filtered to obtain a bright red solid which was washed thoroughly with pentane (3 x 10 ml) and dried in vacuo. The solid was recrystallized from a dichloromethane-hexane solution to obtain red microcrystals of the adduct in 70% yield.} \]

Analysis, calc. for \( \text{C}_{25}\text{H}_{26}\text{FeO}_2\text{Sm} \): C, 53.2; H, 4.6; Fe, 9.9. Found: C, 51.1; H, 4.6; Fe, 9.9. The low carbon value is not unexpected in the analysis of organolanthane complexes.⁵

The red compound is rapidly destroyed by air and moisture. It is thermally unstable above 120°C at 10⁻¹ mm Hg, and attempts at vacuum sublimation of the complex give only low yields of \( [(\text{h}^{5}\text{-C}_5\text{H}_5)\text{Fe(CO)}_2]_2 \). Further, the adduct is virtually insoluble in all common organic solvents except dichloromethane and tetrahydrofuran, but once in solution it experiences almost complete dissociation as shown by its infrared spectrum.

Preparation of the complexes \((\text{cp})_2\text{Ln}[\text{M(h}^{5}\text{-C}_5\text{H}_5)(\text{CO})_3]\), where \( \text{cp} = \text{C}_5\text{H}_5 \text{ or } \text{C}_6\text{H}_7, \text{Ln} = \text{Dy, Ho, Er, or Yb}, \text{ and M = Mo or W.} \)

Method A: Reaction of \((\text{cp})_2\text{LnCl} \) with \( \text{Na}[\text{M(h}^{5}\text{-C}_5\text{H}_5)(\text{CO})_3] \), \( \text{M = Mo or W.} \)

The preparation of \((\text{cp})_2\text{Yb} [\text{W(h}^{5}\text{-C}_5\text{H}_5)(\text{CO})_3] \) typifies the synthetic method employed to obtain all the \((\text{cp})_2\text{Ln}[\text{M(h}^{5}\text{-C}_5\text{H}_5)(\text{CO})_3] \) compounds. A solution containing \( \text{Na}[(\text{h}^{5}\text{-C}_5\text{H}_5)\text{M(CO)}_3] (1.00 \text{ g}, 2.81 \text{ mmol}) \) in THF (40 ml) was syringed into THF (40 ml) containing \( (\text{C}_5\text{H}_5)_2\text{YbCl} (0.956 \text{ g}, 2.82 \text{ mmol}). \)
A precipitate formed immediately, and the resultant brown mixture was stirred overnight at room temperature. The mixture was then centrifuged and the supernatant brown liquid was decanted from the solid matter. The solution was concentrated under reduced pressure until crystals began to form, at which point it was cooled in an ice-salt bath for 2 h. The golden crystals thus formed were collected by filtration, were washed with pentane (3 x 5 ml), and were dried in vacuo. The desired product was obtained in 75% yield.

Analytical data for the complexes are summarised below.

<table>
<thead>
<tr>
<th>Complex</th>
<th>Found</th>
<th>Calc.</th>
</tr>
</thead>
<tbody>
<tr>
<td>(C_5H_5)_2Yb[W(h^5-C_5H_5)(CO)_3]</td>
<td>C, 33.9; H, 2.4; Yb, 27.2</td>
<td>C, 34.0; H, 2.4; Yb, 27.2</td>
</tr>
<tr>
<td>(C_5H_5)_2Er[W(h^5-C_5H_5)(CO)_3]</td>
<td>C, 34.2; H, 2.7; Er, 26.4</td>
<td>C, 34.3; H, 2.4; Er, 26.5</td>
</tr>
<tr>
<td>(C_6H_7)_2Ho[W(h^5-C_5H_5)(CO)_3]</td>
<td>C, 36.1; H, 3.3</td>
<td>C, 36.6; H, 2.9</td>
</tr>
<tr>
<td>(C_6H_7)_2Dy[W(h^5-C_5H_5)(CO)_3]</td>
<td>C, 36.2; H, 3.0</td>
<td>C, 36.7; H, 2.9</td>
</tr>
</tbody>
</table>

Method B: Reaction of Mo(CO)_6 with (cp)_3Ln

The reaction of Mo(CO)_6 with (C_5H_5)_3Er is typical of this route where it is successful. A suspension of (C_5H_5)_3Er (1.025 g, 2.83 mmol) and Mo(CO)_6 (0.75 g, 2.86 mmol) in THF (15 ml) was refluxed overnight, by which time it had turned orange-red from pink. The solvent was removed under reduced pressure and any excess Mo(CO)_6, usually nil, was removed by sublimation at 10^{-2} mm Hg and 50°C for a few hours.

Analysis, calc. for C_{18}H_{15}O_{3}ErMo: C, 39.9; H, 2.79.

Found: C, 41.1; H, 4.00.

All of these complexes are air- and moisture-sensitive, and decompose at temperatures greater than 220°C. They are readily soluble in donor solvents such as THF and dimethylsulphoxide (DMSO), but are decomposed by halogenated solvents such as CH_2Cl_2.
Preparation of the complex Er[(h^-C_5H_5)Mo(CO)_3]_3.7H_2O

A solution containing Na[(h^-C_5H_5)Mo(CO)_3] (3.22 g, 12.0 mmol) in water (120 ml) was filtered into an aqueous solution (60 ml) containing ErCl_3.6H_2O (1.27 g, 3.30 mmol). A solid immediately deposited. After stirring at room temperature for 15 min, the solid was collected by filtration and was washed with water (3 x 15 ml). The resulting tan solid was dried over P_2O_5 in vacuo for one day. Yield, 1.65 g (48%).

Analysis, calc. for C_{24}H_{29}ErMo_{3}O_{16}: C, 28.0; H, 2.8. Found: C, 28.0; H, 2.4.

The product is totally insoluble in water or common organic solvents and it does not sublime. Moreover, it decomposes within minutes upon exposure to air to yield detectable amounts of [(h^-C_5H_5)Mo(CO)_3]_2.
2.3 RESULTS AND DISCUSSION

Evidence for the Lewis acid behaviour of the $R_3Ln$ complexes

We have utilized infrared and n.m.r. spectroscopy (as well as elemental analysis where possible) to provide evidence that $R_3Ln$ ($R = \text{Cp or MeCp}$) species can generally function as Lewis acids towards a variety of base sites. The following discussion is divided into sections dealing with each type of the electron donors investigated. The infrared data discussed are contained in Table I.

A) Terminal nitrosyl and carbonyl ligands

Upon complexation of $h^5\text{-CpCr(NO)}_2\text{Cl}$ and $R_3Ln$ in $\text{CH}_2\text{Cl}_2$ the infrared spectrum shows that both of the NO stretching frequencies are lowered (e.g. 1818 to 1786 and 1712 to 1686 cm$^{-1}$ for $\text{Cp}_3\text{Yb}$), thereby implying a weakening of the N-O bond as electrons are donated by the oxygen atom of the ligand to the lanthanide. In order to explain why both N-O stretching frequencies are lowered upon adduct formation, several possibilities must be considered: (a) $R_3Ln$ has attached to both nitrosyl groups. This conclusion cannot be correct because for a 1:1 stoichiometry no parent nitrosyl bands were observed using $\text{Cp}_3\text{Yb}$ or $\text{Cp}_3\text{Er}$ as acceptors. (b) Some sort of averaging is occurring with the $R_3Ln$ attaching and leaving each nitrosyl in turn. The time scale of the infrared measurement compared to that for a Lewis acid-base equilibrium, however, suggests that this explanation is unlikely. (c) Coupling of the complexed and non-complexed N-O vibrations occurs. Local symmetry of the adduct is so low, $C_1$, that this explanation is quite feasible:

The extent of complexation depends upon the lanthanide employed.
### Table I

Infrared spectra in the carbonyl and nitrosyl stretching region

<table>
<thead>
<tr>
<th>Lewis base</th>
<th>Lewis acid</th>
<th>CO and NO absorptions, cm⁻¹</th>
</tr>
</thead>
</table>

#### (A) Terminal nitrosyl and carbonyl ligands

**CH₂Cl₂ solutions**

<table>
<thead>
<tr>
<th>Lewis base</th>
<th>Lewis acid</th>
<th>Absorptions</th>
</tr>
</thead>
<tbody>
<tr>
<td>(h⁵-C₅)Cr(NO)₂Cl</td>
<td>&gt;2 (MeC₅)₃Sm</td>
<td>1818s, 1712s</td>
</tr>
<tr>
<td>(h⁵-C₅)Cr(NO)₂Cl</td>
<td>Cp₃Er</td>
<td>1818sh, 1784s, 1712sh, 1684s</td>
</tr>
<tr>
<td>(h⁵-C₅)Cr(NO)₂Cl</td>
<td>Cp₃Yb</td>
<td>1786s, 1688s</td>
</tr>
<tr>
<td>(h⁵-C₅)Cr(NO)₂Cl</td>
<td>Cp₂YbCl</td>
<td>1786s, 1686s</td>
</tr>
<tr>
<td>(h⁵-C₅)Cr(NO)₂Cl</td>
<td>(MeC₅)₂YbCl</td>
<td>1818s, 1712s</td>
</tr>
</tbody>
</table>

**C₆H₆ solutions**

<table>
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<tr>
<th>Lewis base</th>
<th>Lewis acid</th>
<th>Absorptions</th>
</tr>
</thead>
<tbody>
<tr>
<td>(h⁵-C₅)Cr(NO)₂Cl</td>
<td>(MeC₅)₃Sm</td>
<td>1820s, 1705s</td>
</tr>
</tbody>
</table>

**CH₂Cl₂ solutions**

<table>
<thead>
<tr>
<th>Lewis base</th>
<th>Lewis acid</th>
<th>Absorptions</th>
</tr>
</thead>
<tbody>
<tr>
<td>(h⁵-MeC₅)Mn(CO)₃</td>
<td>1 or 2 (MeC₅)₃Sm</td>
<td>2018s, 1928br,s, 1868m</td>
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<tr>
<td>(h⁵-MeC₅)Mn(CO)₃</td>
<td>Cp₃Er or Cp₃Yb</td>
<td>2018s, 1928br,s, 1868m</td>
</tr>
<tr>
<td>(h⁵-MeC₅)Mn(CO)₃</td>
<td>&gt;2 (MeC₅)₃Nd</td>
<td>2018s, 1928br,s, 1665m</td>
</tr>
<tr>
<td>(h⁵-MeC₅)Mn(CO)₃</td>
<td>Cp₂YbCl</td>
<td>2018s, 1928br,s</td>
</tr>
</tbody>
</table>
Table I (continued)

<table>
<thead>
<tr>
<th>Complex</th>
<th>Data</th>
</tr>
</thead>
<tbody>
<tr>
<td>((h^5\text{-Cp})\text{Cr(CO)}_2(\text{NO}))</td>
<td>2018s, 1945s, 1692s</td>
</tr>
<tr>
<td>((h^5\text{-Cp})\text{Cr(CO)}_2(\text{NO}))</td>
<td>2038s, 2018s, 1973s, 1945s, 1692s, 1635s</td>
</tr>
<tr>
<td>((h^5\text{-Cp})\text{Cr(CO)}_2(\text{NO}))</td>
<td>2038s, 2018s, 1973s, 1945s, 1692s, 1635s</td>
</tr>
<tr>
<td>((h^5\text{-Cp})\text{Cr(CO)}_2(\text{NO}))</td>
<td>2038s, 2018s, 1973s, 1945s, 1692s, 1635s</td>
</tr>
<tr>
<td>((h^5\text{-Cp})\text{Mo(CO)}_2(\text{NO}))</td>
<td>2016s, 1938s, 1662s</td>
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<tr>
<td>((h^5\text{-Cp})\text{Mo(CO)}_2(\text{NO}))</td>
<td>2035s, 2016s, 1968s, 1938s, 1662s, 1586s</td>
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<tr>
<td>((h^5\text{-Cp})\text{W(CO)}_2(\text{NO}))</td>
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<tr>
<td>((h^5\text{-Cp})\text{W(CO)}_2(\text{NO}))</td>
<td>2030s, 2000s, 1955s, 1923s, 1658s, 1580s</td>
</tr>
</tbody>
</table>

(B) Bridging carbonyl ligands

(a) **Nujol mulls**

<table>
<thead>
<tr>
<th>Complex</th>
<th>Data</th>
</tr>
</thead>
<tbody>
<tr>
<td>([(h^5\text{-Cp})\text{Fe(CO)}_2])_2</td>
<td>1955s, 1938s, 1752s</td>
</tr>
<tr>
<td>([(h^5\text{-Cp})\text{Fe(CO)}_2])_2</td>
<td>2024s, 1980br,s, 1700br,s</td>
</tr>
<tr>
<td>([(h^5\text{-Cp})\text{Fe(CO)}_2])_2</td>
<td>2020s, 1985br,s, 1700br,s</td>
</tr>
<tr>
<td>(\text{Co}_2(\text{CO})_8)</td>
<td>2035sh, 2015br,s, 1846sh, 1830br,s</td>
</tr>
<tr>
<td>(\text{Co}_2(\text{CO})_8)</td>
<td>2025vs, 1941br,s, 1841br,s, 1781br,s</td>
</tr>
</tbody>
</table>
Table I (continued)

(b) CH\textsubscript{2}Cl\textsubscript{2} solutions

<table>
<thead>
<tr>
<th>Compound</th>
<th>Wavenumbers</th>
</tr>
</thead>
<tbody>
<tr>
<td>[(h\textsubscript{5}-Cp)Fe(CO)\textsubscript{2}]\textsubscript{2}</td>
<td>1994s, 1953s, 1774s</td>
</tr>
<tr>
<td>[(h\textsubscript{5}-Cp)Fe(CO)\textsubscript{2}]\textsubscript{2}</td>
<td>2 (MeCp)\textsubscript{3}Sm, 1993s, 1952m, 1772s, 1700w</td>
</tr>
<tr>
<td>(h\textsubscript{5}-Cp)Ni(CO)\textsubscript{2}Fe(h\textsubscript{5}-Cp)(CO)</td>
<td>1995s, 1810s</td>
</tr>
<tr>
<td>(h\textsubscript{5}-Cp)Ni(CO)\textsubscript{2}Fe(h\textsubscript{5}-Cp)(CO)</td>
<td>&gt;2 (MeCp)\textsubscript{3}Ho, 2010s, 1738s</td>
</tr>
<tr>
<td>(h\textsubscript{5}-Cp)Ni(CO)\textsubscript{2}Fe(h\textsubscript{5}-Cp)(CO)</td>
<td>&gt;2 (MeCp)\textsubscript{3}Gd, 2010s, 1738s</td>
</tr>
<tr>
<td>[(h\textsubscript{5}-Cp)Ni(CO)]\textsubscript{2}</td>
<td>1886w, 1824s</td>
</tr>
<tr>
<td>[(h\textsubscript{5}-Cp)Ni(CO)]\textsubscript{2}</td>
<td>(MeCp)\textsubscript{3}Er, 1888m, 1824br,s, 1780m</td>
</tr>
<tr>
<td>[(h\textsubscript{5}-Cp)Ni(CO)]\textsubscript{2}</td>
<td>2 (MeCp)\textsubscript{3}Sm, 1888m, 1842br,s, 1780m</td>
</tr>
<tr>
<td>[(h\textsubscript{5}-Cp)Mn(CO)(NO)]\textsubscript{2}</td>
<td>1962s, 1785s, 1708s, 1510s</td>
</tr>
<tr>
<td>[(h\textsubscript{5}-Cp)Mn(CO)(NO)]\textsubscript{2}</td>
<td>2 Cp\textsubscript{3}Er, 1985br,s, 1790m, 1734s, 1708s, 1680s, 1525s</td>
</tr>
<tr>
<td>[(h\textsubscript{5}-Cp)Mn(CO)(NO)]\textsubscript{2}</td>
<td>3 Cp\textsubscript{3}Dy, 1990s, 1790m, 1735s, 1685s, 1525s</td>
</tr>
<tr>
<td>[(h\textsubscript{5}-Cp)Mn(CO)(NO)]\textsubscript{2}</td>
<td>4 Cp\textsubscript{3}Er, 1990s, 1790vw, 1735s, 1685s, 1525s</td>
</tr>
</tbody>
</table>
For example, even though \((\text{MeCp})_3\text{Sm}\) is present in excess, the spectral data indicate the presence of a small amount of the uncomplexed nitrosyl compound, whereas for \(\text{Cp}_3\text{Er}\) and \(\text{Cp}_3\text{Yb}\) complete complexation is observed as expected. Moreover, if an alternative solvent such as benzene is used, complete adduct formation with \((\text{MeCp})_3\text{Sm}\) still does not occur. The choice of solvents for these studies is limited by the solubility of the \(\text{R}_3\text{Ln}\) species to benzene, toluene and dichloromethane. Strongly coordinating solvents, such as THF and DMSO, prevent isocarbonyl formation and are obviously unsuitable. In fact, the \(\text{CH}_2\text{Cl}_2\) solutions shows signs of decomposition within a couple of hours for the least stable cases, that is, where \(\text{R} = \text{Cp}\) in \(\text{R}_3\text{Ln}\). When \(\text{R} = \text{MeCp}\) the organolanthanides are less susceptible to deterioration in chlorinated solvents and solutions can be stored up to two days in a nitrogen atmosphere.

It should also be noted that the magnitude of the shift to lower wave numbers of the NO frequencies is relatively constant for all the lanthanide complexes which form isonitrosyl linkages. Further, \(\text{Cp}_2\text{YbCl}\) and \((\text{MeCp})_2\text{YbCl}\) show no or very little adduct formation respectively. The slight complexation of the \((\text{MeCp})_2\text{YbCl}\) did not increase upon standing twenty-four hours nor upon addition of more Lewis acid up to a ratio of 1.5:1 for \((\text{MeCp})_2\text{YbCl}: (h^5\text{Cp})\text{Cr(NO)}_2\text{Cl}\). This observation is further supporting evidence for the existence of \(\text{R}_2\text{LnCl}\) as chlorine bridged dimers in non-donor solvents.\(^{77}\)

The interaction of the organolanthanides with the oxygen atom of a terminal carbonyl groups is weaker than that previously reported for various aluminium systems.\(^{44,46,50}\) Consistent with group theoretical predictions of lowered symmetry, three bands are observed in the carbonyl stretching region of the infrared spectrum when \((h^5\text{MeCp})\text{Mn(CO)}_3\) and \(\text{R}_3\text{Ln}\) are allowed to
react in a 1:1 ratio. Two of the bands are unchanged from those of the parent compound, but a third weaker band appears in all cases around 1868 cm$^{-1}$. (When aluminium is used as the acidic site in cpylidMo(CO)$_3$ the lowest absorption is around 1660 cm$^{-1}$.) No change in the spectrum occurs when the relative quantity of R$_3$Ln to (h$_5$-MeCp)Mn(CO)$_3$ is increased beyond 1:1. Once again R$_2$LnCl exhibit no behaviour attributable to the formation of an isocarbonyl linkage. The fact that the parent absorptions are unshifted and strong in the adduct whilst the new band is weaker may suggest that complexation is not complete up to the stoichiometry of 1:1. Upon complexation there is a loss of local symmetry of the Mn(CO)$_3$ group. Consequently, the stretching frequencies of the non-complexed carbonyls in the adduct may be coincident with those of the parent molecule, particularly if the interaction is weak.

In both the terminal nitrosyl and carbonyl cases, dilution of the adduct solution below ca. $10^{-3}$ M causes substantial dissociation. For this reason the infrared spectra were recorded at a concentration close to $5 \times 10^{-2}$ M.

The compounds (h$_5$-Cp)M(CO)$_2$NO (M = Cr, Mo or W) possess both terminal carbonyl and nitrosyl ligands. Our spectral data indicate that the nitrosyl ligand in these complexes is a better Lewis base than the carbonyl ligands, irrespective of the group VIA metal or the lanthanide involved. For example, (h$_5$-Cp)Cr(CO)$_2$NO, in the presence of an equimolar amount of (MeCp)$_3$Sm, exhibits new absorptions at 2038, 1973, and 1635 cm$^{-1}$ in addition to those normally observed for the parent compound. The lowest band in this region of the infrared spectrum clearly verifies the existence of an isonitrosyl linkage. The observations of two raised terminal carbonyl frequencies is consistent with the explanation offered earlier. (See section
2-1.) Again, an increase in the relative amount of $R_3Ln$ beyond the 1:1 stoichiometry does not cause complete complexation with any of the Group VIa compounds, and all of the adducts detected are exclusively of the iso-nitrosyl type.

B) Bridging carbonyl ligands

When $[(h_5^*-\text{Cp})\text{Fe}(\text{CO})_2]_2$ and $(\text{MeCp})_3\text{Sm}$ are reacted in a 1:2 ratio in benzene at room temperature, a bright red air-sensitive solid rapidly precipitates. The elemental analyses of the recrystallised solid are consistent with the complex being formulated as $[(h_5^*-\text{Cp})\text{Fe}(\text{CO})_2]_2.2\text{Sm}(\text{MeCp})_3$. The infrared spectrum of this solid as a Nujol mull indicates that iso-carbonyl linkages have been formed by the samarium atoms at each of the bridging carbonyl groups. The shift to higher frequencies of the terminal CO stretches and the shift to lower frequency of the bridging CO stretch relative to those observed for the uncomplexed iron compound are spectral features also exhibited by the known $[(h_5^*-\text{Cp})\text{Fe}(\text{CO})_2]_2.2\text{AlEt}_3$. These shifts are again smaller in magnitude for the samarium adduct than for the aluminium compound, but they do indicate that the two complexes are quite probably isostructural. The x-ray study of the Et$_3$Al adduct, which was discussed earlier (section 2-1), has conclusively shown the acidic aluminium atoms to be coordinated to the oxygen ends of the bridging carbonyl groups.

In donor (THF) or polar (CH$_2$Cl$_2$) solvents, the infrared spectrum shows $[(h_5^*-\text{Cp})\text{Fe}(\text{CO})_2]_2.2\text{Sm}(\text{MeCp})_3$ almost completely dissociated; however, in the case of CH$_2$Cl$_2$ the solubility is only slight. If $(h_5^*-\text{Cp})\text{Ni}(\text{CO})_2\text{Fe}(h_5^*-\text{Cp})(\text{CO})$ is employed as the Lewis base, only bridging isocarbonyl behaviour is observed for CH$_2$Cl$_2$ solutions containing greater than a twofold excess of
R₃Ln. The mixed nickel-iron complex thus forms adducts which are less susceptible to dissociation and appears to be a better donor of electrons than the isoelectronic iron compound, although these effects may accrue from increased solubility.

As mentioned earlier (section 2-1), Co₂(CO)₈ exists in solution in two isomeric forms: one containing bridging carbonyl groups whilst the other has only a metal-metal bond joining two Co(CO)₄ units. When Co₂(CO)₈ and (MeCp)₃Sm are reacted in a 1:1 ratio in toluene at room temperature, only a 1:2 adduct readily precipitates as an extremely air- and moisture-sensitive yellow solid. Its low resolution infrared spectrum (as a Nujol mull) is qualitatively different from that reported for the AlBr₃ adduct investigated by Cotton and Monchamp,⁶⁵ the only literature report at the time. That is to say, the spectrum exhibits a band which is characteristic of a bridging isocarbonyl linkage at 1781 cm⁻¹, plus an entirely different contour of higher frequency terminal carbonyl bands relative to Co₂(CO)₈. The presence of (MeCp)₃Sm displaces the Co₂(CO)₈ equilibrium completely to the form involving bridging CO ligands, the preferred sites of Lewis basicity. The >CO-Sm(MeCp)₃ bonds are established presumably because the hard lanthanide acid favours the harder oxygen of the CO groups over the softer metal-metal bond, although steric factors may also be operative during the formation of this compound. Regrettably, the adduct is not amenable to study in solution since it rapidly dissociates in those solvents in which it is soluble. Recently, this work has been substantiated by several investigators using other Group III Lewis acids.⁶⁶-⁶⁸ Once again a comparison of the magnitude of the shifts of carbonyl stretching frequencies shows that those of the aluminium system are greater for complexed and uncomplexed carbonyl groups than those of the organolanthanide adduct.
In light of the results with $\text{Co}_2(\text{CO})_8$ it was decided to use the structurally similar $\text{[(h}_5^5\text{-Cp})\text{NiCO]}_2$ as it offers both bridging carbonyls and a bent metal-metal bond as potential Lewis base sites in solution. In $\text{CH}_2\text{Cl}_2$ when $\text{[(h}_5^5\text{-Cp})\text{NiCO]}_2$ is treated with various $\text{R}_3\text{Ln}$ complexes, a new band appears in the infrared spectra at 1780 cm$^{-1}$ and the band at 1886 cm$^{-1}$ becomes slightly more intense. The spectra are invariant when the lanthanide concentration is increased beyond the 1:1 stoichiometry. In subsequent work Shriver$^{34}$ made the claim that the increased intensity of the higher frequency band upon complexation arises from the lack of a centre of symmetry in the 1:1 adduct. He pointed out that although the initial (NiCO)$_2$ group is not planar, the deviation is probably small since the dipole moment in benzene is not large (0.38D) and this would account for the weak symmetric stretch in the parent carbonyl. These spectral features strongly suggest, therefore, the formation of a 1:1 adduct and they confirm the preference of the lanthanides for the bridging carbonyl groups. Attempts to isolate the adducts from toluene solutions meet with failure.

The molecular structure of $\text{[(h}_5^5\text{-Cp})\text{Mn(CO)NO]}_2$ in the solid state is not yet known with certainty.$^{85}$ In solution the compound is thought to exist as a mixture of dissymmetric cis and trans isomers. Recent $^1\text{H}$ n.m.r. studies$^{86}$ indicate that rapid intramolecular positional exchange of CO and NO groups occurs. The $\text{CH}_2\text{Cl}_2$ solution infrared spectrum of the compound exhibits bands at 1962s (terminal $v$(CO)), 1785s (bridging $v$(CO)), 1708s (terminal $v$(NO)) and 1510s cm$^{-1}$ (bridging $v$(NO)). As progressively increasing amounts of $\text{R}_3\text{Ln}$ species are added to this solution, new bands appear and grow in intensity in the infrared spectrum while the absorptions of the parent carbonyl-nitrosyl gradually diminish in intensity. The limiting case is reached (Table I) at a mole ratio of base:acid = 1:4, when the following bands
are observed: 1990s, 1790vw, 1735s, 1680s, and 1525s cm⁻¹. This spectrum indicates that with [(h⁵-C₅H₅)Mn(CO)NO]₂ bridging isocarbonyl and terminal isonitrosyl bonds have been preferentially formed by the lanthanide element. This result is unexpected since, arguing by analogy with the purely carbonyl systems, one would have predicted the Lewis acid to add to the bridging nitrosyl ligand rather than the terminal one.

Not all carbonyl or nitrosyl ligands are sufficiently basic to form isocarbonyl or isonitrosyl linkages (as determined by infrared spectroscopy) with the acids under investigation. For example, Fe(CO)₂(NO)₂, (Ph₂MeP)₂Fe(NO)₂, (Me₂NCS)₂Fe(NO), (h⁵-Cp)Fe(CO)₂I, (h⁴-C₈H₈)Fe(CO)₃, (Ph₃P)₂Ru(NO)Cl₃, and [(h⁵-Cp)Mo(CO)₃]₂ exhibit no changes in their customary carbonyl and/or nitrosyl stretching frequencies when in solutions also containing various R₃Ln complexes. The [(h⁵-Cp)Mo(CO)₃]₂ compound is particularly interesting because, as mentioned earlier (section 2-1), C¹³ n.m.r. spectroscopy reveals no carbonyl transfer via a bridging intermediate, yet addition of (i-Bu)₃Al in heptane (at concentrations that are unattainable for the R₃Ln complexes) forms an equilibrium product whose infrared spectrum is consistent with two R₃Al-coordinated bridging carbonyls and four terminal carbonyls. Upon standing this equilibrium product is converted into a kinetic product with different carbonyl absorptions in the range 1990 - 1620 cm⁻¹, however, unlike the equilibrium product, addition of triethylamine does not regenerate [(h⁵-Cp)Mo(CO)₃]₂. The kinetic product is under further investigation according to Shriver who does not speculate upon its nature. It is worthwhile noting the similarity between the infrared spectrum of Al[(h⁵-Cp)W(CO)₃]₃.3THF (section 2-1) and Shriver's kinetic product as well as our own work (see below and Table III) with anions of the type [(h⁵-Cp)M(CO)₃]⁻ (M = Mo or W). The kinetic product may involve cleavage of
the Mo-Mo bond with the equilibrium product acting as an intermediate. This type of cleavage is not without precedent, for BCl$_3$ performs in this way$^{68}$ with [(h$_5$-Cp)Fe(CO)$_2$]$_2$ and almost certainly so does ytterbium metal with [(h$_5$-Cp)Mo(CO)$_3$]$_2$ (see Chapter III). Regardless of the true nature of these derivatives of [(h$_5$-Cp)Mo(CO)$_3$]$_2$, this is another example of organo-aluminiums being more reactive towards carbonyl-containing entities than R$_3$Ln.

Considering the accumulated infrared data (Table I) of R$_3$Ln interactions with the various carbonyl or nitrosyl ligands, it should be noted that the magnitude of the shift to lower wave numbers of the CO or NO frequency concerned is relatively constant for all the organolanthanides which form an isocarbonyl or isonitrosyl link. Consequently this spectral technique can only provide qualitative information about the degree of complexation and it cannot be used to establish a quantitative scale of acidities for the R$_3$Ln species. On the other hand our results do not imply that all R$_3$Ln are of comparable acidity, neither do our results suggest that infrared spectroscopy is insensitive to the differences in Lewis acidity of organolanthanides. For example, although (MeCp)$_3$Sm, (Cp)$_3$Er and (Cp)$_3$Yb all produce the same size shifts in the nitrosyl absorptions of (h$_5$-Cp)Cr(NO)$_2$Cl in CH$_2$Cl$_2$, in the case of (MeCp)$_3$Sm parent nitrosyl bands are also present, indicating incomplete complexation, even up to a ratio of base:acid = 1:2.15. Supposedly it is possible to determine at which point along the lanthanide series complete complexation occurs for a 1:1 stoichiometry; this was not pursued.

Interestingly, if other Lewis acids besides R$_3$Ln are utilized, shifts of varying magnitude are obtained for the same base. Unfortunately, a strict comparison is not available; however, a consideration of the data
involving \[(h^5\text{-Cp})\text{Fe(CO)}_2\]_2 with \(\text{BBR}_3\), \(\text{R}_3\text{Al}\) (\(\text{R} = \text{Et or i-Bu}\)) and \((\text{MeCp})_3\text{Sm}\) is illustrative (Table II). Although \((\text{MeCp})_3\text{Sm}\) did not form a 1:1 adduct with the designated base the isocarbonyl band appears not to vary for 1:1 or 1:2 stoichiometry in the case of \(\text{AlR}_3\). If this is generally true, a comparison of the shifts generated by the three acids upon complex formation can be made. In order of increasing shift they are 52 cm\(^{-1}\) \((\text{MeCp})_3\text{Sm}\), 112 cm\(^{-1}\) \((\text{R}_3\text{Al})\) and 345 cm\(^{-1}\) \((\text{BBR}_3)\). Clearly more detailed studies (such as similar ligands for all the acids), are necessary before conclusions can be drawn, however, the increasing size of the shift with decreasing atomic radius of the Lewis acid central atom is striking. On this basis, a similar trend might have been expected across the lanthanide series, but this appears not to be the case. Moreover, the decrease of the carbonyl shift with the increase of the molecular weight of the acid verifies that the lower vibrational frequency of the coordinated carbonyl is not caused solely by a mass effect.

Another general correlation that has been suggested is the connection between low \(\nu_{CO}\) and basicity of the carbonyl ligands, a reflection of the idea that a low \(\nu_{CO}\) corresponds to high electron density on the carbonyl. Attempts to plot \(\nu_{CO}\) (unshifted) versus \(\Delta\nu_{CO}\) for all reported cases showed no simple correlation, although this rule is worth bearing in mind as a general guide to those metal carbonyls likely to display basicity.

As an example of the difficulty involved in predicting a base site \((\text{cpylid})\text{Mo(CO)}_3\) forms complexes with \(\text{H}^+\) and \(\text{BF}_3\) bound to the metal, whereas \(\text{Me}_3\text{Al}\) attaches to the oxygen of a carbonyl group. Similarly, \(\text{H}^+\) adds to the metal in \([(h^5\text{-Cp})\text{Fe(CO)}_2)_2\], but \(\text{BBR}_3\), \(\text{R}_3\text{Al}\), and \(\text{R}_3\text{Ln}\) attach to the bridging carbonyl. Steric factors may well be a determining factor in the choice of the base site.
### TABLE II

Infrared spectra of adducts formed from \([\text{(h}^5\text{-Cp})\text{Fe(CO)}_2]_2\) and some Lewis acids

<table>
<thead>
<tr>
<th>Lewis base ([\text{(h}^5\text{-Cp})\text{Fe(CO)}_2]_2)</th>
<th>Lewis acid</th>
<th>Stoichiometry</th>
<th>CO Absorptions, cm(^{-1})</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\text{BBr}_3)</td>
<td>1:1</td>
<td>(\sim 2020,^a 1849, 1437)</td>
<td>68</td>
<td></td>
</tr>
<tr>
<td>(\text{R}_3\text{Al})</td>
<td>1:1</td>
<td>2026s, shm 1993(^b) 1983s, 1828m, 1682s</td>
<td>34</td>
<td></td>
</tr>
<tr>
<td>(\text{R}_3\text{Al})</td>
<td>1:2(^c)</td>
<td>2042s, 2009(^b), 2004s, 1682s</td>
<td>34</td>
<td></td>
</tr>
<tr>
<td>((\text{MeCp})_3\text{Sm})</td>
<td>1:2</td>
<td>2024s, 1980br,s, 1700br,s</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

*a*: The communication\(^{68}\) implies the terminal bands are more complex than a single absorption.

*b*: Probably arising from the trans form of the 1:2 adduct and in some spectra are not resolved - Shriver's footnote.\(^{34}\)

*c*: Nujol mull spectrum.

*d*: Heptane solution.
C) Other base sites

The interactions of the $R_3Ln$ complexes with Lewis bases can also be monitored by proton magnetic resonance as shown by the representative data displayed in Table III. This physical technique need not be hampered by the presence of an excess of Lewis base, and furthermore, it is quite sensitive; it can detect adduct formation for some complexes (e.g. $(h^8-C_8H_8)Fe(CO)_3$) whose infrared spectra do not change in the presence of $R_3Ln$. It is far more difficult, and in some cases not possible, to use n.m.r. as an independent determination of which base site is being utilized in a compound possessing a number of base sites. For several compounds such a distinction does not have to be made. For example, the $^1H$ n.m.r. spectrum of $(h^5-Cp)_2WH_2$ in a benzene solution also containing $(MeCp)_3Nd$ (particularly chosen because it does not broaden the observed resonances) shows upfield shifts of the cyclopentadienyl and hydride resonances. This effect can readily be ascribed to a paramagnetic shift of the signals resulting from a Lewis adduct in which the lone pair of electrons situated on tungsten forms a coordinate bond to neodymium. Similar compounds are known in which $R_3Al^{45,87,88}$ functions as the electron pair acceptor.

The observation that $(MeCp)_3Nd$ induces an upfield shift in the acetylenic proton resonance of phenylacetylene is quite interesting in that Tsutsui$^{17}$ has reported that $R_3Sm$ catalyzes the trimerization of the alkyne to 1,3,5-triphenylbenzene. Our result substantiates the role of the lanthanide as a coordination site for $\pi$-bases in such processes. Further, the $(h^5-Cp)Fe(CO)_2X$ ($X = Cl$ or $I$) compounds react with $(MeCp)_3Nd$ in benzene, although the iodide does so sufficiently slowly for an n.m.r. spectrum to be recorded. This spectrum shows an upfield shift of the cyclopentadienyl resonances. Coordination of the Lewis acid can, in principle, occur at
TABLE III

Changes induced by (MeCp)_3Nd in the proton magnetic resonance spectra of various Lewis bases.

<table>
<thead>
<tr>
<th>Lewis base</th>
<th>Concentration, M</th>
<th>( \tau^a ), ppm</th>
<th>Upfield shift(^b), ppm</th>
</tr>
</thead>
<tbody>
<tr>
<td>((h^5-MeCp)Mn(CO)_3)</td>
<td>10(^{-1})</td>
<td>5.74(^c); 8.34(^d)</td>
<td>0.36(^c); 0.26(^d)</td>
</tr>
<tr>
<td>((h^5-Cp)Cr(CO)_2(NO))</td>
<td>10(^{-1})</td>
<td>5.67</td>
<td>1.76</td>
</tr>
<tr>
<td>((h^4-C_8H_8)Fe(CO)_3)</td>
<td>10(^{-1})</td>
<td>5.14</td>
<td>0.28</td>
</tr>
<tr>
<td>([h^5-(Cp)]Ni(CO)]_2)</td>
<td>10(^{-1})</td>
<td>4.78</td>
<td>1.10</td>
</tr>
<tr>
<td>((h^5-Cp)Fe(CO)_2I)</td>
<td>10(^{-1})</td>
<td>5.96</td>
<td>1.09</td>
</tr>
<tr>
<td>((h^5-Cp)_2WH_2)</td>
<td>10(^{-1})</td>
<td>5.68(^c); 23.2(^e)</td>
<td>0.36(^c); 2.3(^e)</td>
</tr>
<tr>
<td>C_6H_5C=CH</td>
<td>10(^0)</td>
<td>7.20(^f)</td>
<td>0.11(^f)</td>
</tr>
</tbody>
</table>

All samples, except the one involving C_6H_5C=CH, were prepared with a saturated benzene solution of (MeCp)_3Nd such that the molar ratio of neodymium:base was 1:2.

\(^a\) Spectrum of pure compound relative to TMS (\( \tau = 10 \)).
\(^b\) Shift in resonances after adding (MeCp)_3Nd.
\(^c\) Cyclopentadienyl protons.
\(^d\) Methyl protons.
\(^e\) Hydride protons.
\(^f\) Acetylenic proton.
either the CO or the I ligand, but in view of the infrared results (which showed no isocarbonyl formation), the neodymium is probably attached at the halide site. Strong supporting evidence for this assignment comes from the work of Pankowski et al.,\textsuperscript{89a} who investigated the effects of Lewis acids such as AlX\textsubscript{3} (X = Cl, Br or I), FeCl\textsubscript{3}, and SbCl\textsubscript{5} upon the metal carbonyl halides Mn(CO)\textsubscript{5}X, (h\textsuperscript{5}-Cp)Fe(CO)\textsubscript{2}X, (Me\textsubscript{3}P)\textsubscript{2}Fe(CO)\textsubscript{2}X\textsubscript{2}, and (Me\textsubscript{3}P)\textsubscript{2}Ni(CO)I\textsubscript{2} (X = Cl, Br or I) in CH\textsubscript{2}Cl\textsubscript{2} solution. They concluded on the basis of infrared measurements that Lewis acid-base adduct formation occurred via the halogen of the metal carbonyl. They observed no lower carbonyl bands attributable to isocarbonyl linkages; in fact, the number of carbonyl bands was conserved in the complexes suggesting a retention of local symmetry. Some raising of the existing \( \nu_{\text{CO}} \) was observed upon complexation and this corroborates addition at the halogen site. Some recent studies by Cullen et al.\textsuperscript{89b} are also relevant to this discussion. They found that \([\text{SbCl}_3(\text{Fe(CO)}_2(\text{h}^5-\text{Cp})\text{Cl})_2]_2\) could be prepared either by mixing SbCl\textsubscript{3} and (h\textsuperscript{5}-Cp)Fe(CO)\textsubscript{2}Cl in ether or by the reaction of SbCl\textsubscript{3} with \([\text{(h}^5-\text{Cp})\text{Fe(CO)}_2]_2\) in CH\textsubscript{2}Cl\textsubscript{2}. A crystal structure determination of the isolated dimer revealed adduct formation via the chlorine attached to iron and no isocarbonyl linkages.

In recent work, Marks et al.\textsuperscript{57} have shown that Eu(fod)\textsubscript{3} can be used to shift the \( ^1\text{H} \) n.m.r. signals of appropriate compounds, since it also coordinates at various base sites, including carbonyl ligands (section 2-1). A direct comparison of the Eu(fod)\textsubscript{3} and (MeCp)\textsubscript{3}Nd shift reagents as chemical and structural probes is not possible, because of the different conditions existing in both sets of experiments. We would emphasize, however, that in spite of the substantial shifts induced by (MeCp)\textsubscript{3}Nd (Table III), it is not suitable for general use as a shift reagent because of (a) its low solubility in common organic solvents; (b) its sensitivity to air and moisture; (c) its
noticeable decomposition in chlorinated or acidic solvents, and (d) its reactivity with some substrates of interest. (A good illustration of the last handicap is the fact that (MeCp)$_3$Nd reacts rapidly with (Cp)$_2$Sn in benzene to yield a precipitate which leaves the supernatant solution devoid of proton resonances.) Remark (a) may be exemplified by the fact that a saturated solution of (MeCp)$_3$Nd in benzene is ca. $5 \times 10^{-2}$ M. The corresponding R$_3$Eu compound, which would be a more desirable shift reagent because of less broadening, is very difficult to desolvate reproducibly. The (Cp)$_3$Eu.THF adduct dissolved in benzene shows the THF proton resonances -29 ppm and at -63 ppm relative to TMS, indicating the ability of europium to generate large shifts.

Nevertheless, (MeCp)$_3$Nd can be employed to detect solution interactions which are difficult to determine otherwise, even at stoichiometries less than 1:1; in fact, nearly all the spectra in Table III were recorded at a base:acid ratio of 2:1. Although interactions with the stronger bases appear to produce the larger shifts, no accurate comment can be made without the limiting spectrum when the degree of complexation would be known with certainty. Studies involving the incremental addition of Lewis acid would also be useful in that the equilibrium constant for the complex formation could be determined.

Reactions involving metal carbonyl anions

The proton magnetic resonance evidence for the existence of a tungsten-neodymium bond in benzene solutions containing ($h^5$-Cp)$_2$WH$_2$ and (MeCp)$_3$Nd encouraged the investigation of the products of the reactions between R$_2$LnCl compounds and various metal carbonyl anions. As mentioned
earlier (section 2-1) two types of products were thought possible: those containing a discrete transition metal-lanthanide bond or those containing the lanthanide coordinated to the carbonyl fragment via an isocarbonyl linkage.

When \( \text{R}_2\text{LnCl} \) and \( \text{Na}[(\text{h}_5^5\text{-Cp})\text{W(CO)}_3] \) are reacted in a 1:1 ratio in THF (Method A) the analytically pure \( \text{R}_2\text{Ln}[W(\text{h}_5^5\text{-Cp})(\text{CO})_3] \) (Ln = Dy, Ho, Er or Yb) complexes can be isolated in good yields. Other carbonyl anions, however, do not produce analogous derivatives. For example, \( [\text{Co(CO)}_4]^− \) is not sufficiently nucleophilic\(^{90,91}\) to react with the organolanthanide compound. Indeed, stirring \( \text{Na}[\text{Co(CO)}_4] \) with \( (\text{MeCp})_2\text{YbCl} \) in THF for twenty hours at room temperature and three hours at reflux produces no change. On the other hand, use of the stronger nucleophiles \( [(\text{h}_5^5\text{-Cp})\text{Fe(CO)}_2]^− \) and \( [(\text{h}_5^5\text{-Cp})\text{Mo(CO)}_3]^− \) results in the contamination of the products with their corresponding neutral dimers.

The lanthanide-tungsten compounds are obtained as solvent-free crystals, which are thermally stable up to 220°C, soluble only in strongly donor solvents such as THF and DMSO, and decomposed by various halogenated solvents. The poor solubility of these compounds prevents obtaining an n.m.r. spectrum: sufficiently concentrated \( \text{d}^6\)-DMSO solutions have the consistency of a glassy syrup and display only very broad, weak absorptions. Spectra could probably be obtained in \( \text{d}^8\)-THF, however, this is a very expensive solvent. Conductivity values for dilute THF solutions of the holmium and ytterbium compounds plus a few \( \text{R}_3\text{Ln} \) (Ln = La, Gd, Ho and Yb) and \( (\text{MeCp})_2\text{HoCl} \) are listed in Table IV. The \( \text{R}_3\text{Ln} \) species have conductivities only slightly greater than that of the solvent, an observation made earlier by Birmingham and Wilkinson.\(^{3}\) The W-Ho and W-Yb compounds have
conductivities which are larger, suggesting that these compounds dissociate more than the almost entirely associated $R_3Ln$ and $(MeCp)_2HoCl$ in THF solution. The THF solution infrared spectra bear out this interpretation: the strong absorptions in the carbonyl stretching region for the tungsten derivatives and for Na[$(h^5-Cp)W(CO)_3$] are identical. A comparison of the mull spectra (Table V) of $R_2Ln[W(h^5-Cp)(CO)_3]$ and Na[$(h^5-Cp)W(CO)_3$], however, reveals that the former complexes exhibit additional bands at 2010m and ca. 1940s cm$^{-1}$ as well as a lowering of the lowest carbonyl stretching frequency to ca. 1565 cm$^{-1}$. These features can be interpreted as indicating the formation of some isocarbonyl bonds, and the large number of CO-stretching absorptions suggests a polymeric structure for these compounds. The existence of bridging carbonyl groups in this structure seems unlikely in view of the covalent radii of the metals involved. Moreover, such bridges would involve lanthanide-carbon sigma bonds which would have to cleave in solution. Generally, organolanthanide compounds thought to involve such $\sigma$-bonds, are very insoluble, polymeric materials, which are difficult to obtain in a pure state.$^5$ In addition, it might be noted that only very recently lanthanide (neodymium and ytterbium) carbonyls have been detected by infrared spectroscopy in argon matrices at 10°K;$^{12}$ this is the only report of lanthanide carbonyls. A structure which is consistent with the experimental observations is one in which the tungsten units are linked via a bridging framework of the type shown below:

\[
\begin{array}{ccccccc}
  \text{Cp} & \text{Cp} & \text{Cp} & \text{Cp} & \text{Cp} & \text{Cp} \\
  \text{Ln-OC-W-CO-Ln-OC-W-CO-Ln-OC-W-CO} \\
  \text{Cp} & \text{CO} & \text{Cp} & \text{CO} & \text{Cp} & \text{CO}
\end{array}
\]
<table>
<thead>
<tr>
<th>COMPOUND</th>
<th>CONCENTRATION (10^-2M)</th>
<th>RESISTANCE (10^5 ohm)</th>
<th>MOLAR CONDUCTIVITY (10^{-2} cm^2 ohms^{-1} mole^{-1})</th>
<th>TEMPERATURE (°C)</th>
</tr>
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<tbody>
<tr>
<td>Cp_3La</td>
<td>1.62</td>
<td>11.1</td>
<td>5.65</td>
<td>26.2</td>
</tr>
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<td></td>
<td>0.76</td>
<td>23.9</td>
<td>5.60</td>
<td>26.2</td>
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<tr>
<td>Cp_3Gd</td>
<td>1.50</td>
<td>10.6</td>
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</tr>
<tr>
<td></td>
<td>0.71</td>
<td>&gt;25</td>
<td>&lt;2.51</td>
<td>26.4</td>
</tr>
<tr>
<td>(MeCp)_3Ho</td>
<td>1.62</td>
<td>&gt;25</td>
<td>&lt;2.51</td>
<td>27.0</td>
</tr>
<tr>
<td>Cp_3Yb</td>
<td>1.60</td>
<td>12.6</td>
<td>5.03</td>
<td>25.6</td>
</tr>
<tr>
<td>(MeCp)_2HoCl</td>
<td>1.61</td>
<td>14.7</td>
<td>42.8</td>
<td>25.0</td>
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<tr>
<td>(MeCp)_2Ho[(h^5-Cp)W(CO)_3]</td>
<td>0.90</td>
<td>0.69</td>
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<td>(Cp)_2Yb[(h^5-Cp)W(CO)_3]</td>
<td>1.52</td>
<td>0.29</td>
<td>234</td>
<td>25.8</td>
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<td>COMPOUND</td>
<td>$\nu_{\text{CO}}$, cm$^{-1}$</td>
<td>Other absorptions, cm$^{-1}$</td>
<td></td>
<td></td>
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<tr>
<td>----------</td>
<td>-----------------</td>
<td>-----------------</td>
<td></td>
<td></td>
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<tr>
<td>$\text{Cp}_2\text{Yb}[\text{W}(h^5-\text{Cp})(\text{CO})_3]$</td>
<td>2010m, 1936s, 1890s, 1790s, 1740s</td>
<td>1045m, 1012m, 892w, 790m, 662w, 584m 505m, 484m</td>
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<td></td>
</tr>
<tr>
<td>in THF</td>
<td>as Nujol mull</td>
<td>2010m, 1984s, 1934s, 1890br,s, 1790br,s 1565br,s</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\text{(MeCp)}_2\text{Ho}[\text{W}(h^5-\text{Cp})(\text{CO})_3]$</td>
<td>2010m, 1936s, 1890s, 1790s, 1740s</td>
<td>1040m, 1010m, 780ms, 580m, 505m, 484m</td>
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<tr>
<td>in THF</td>
<td>as Nujol mull</td>
<td>2010m, 1976s, 1930br,s, 1880br,s 1750br,s, 1560br,s</td>
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<td>$\text{Cp}_2\text{Dy}[\text{W}(h^5-\text{Cp})(\text{CO})_3]$</td>
<td>2010m, 1980s, 1934br,s, 1890br,s 1770br,s, 1507br,s</td>
<td>1045w, 1012ms, 890w, 780ms, 690ms, 662mw, 580m, 505m, 484m</td>
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<td></td>
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<tr>
<td>as Nujol mull</td>
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<tr>
<td>$\text{Cp}_2\text{Er}[\text{W}(h^5-\text{Cp})(\text{CO})_3]$</td>
<td>2010m, 1980m, 1910br,s, 1780br,s, 1560br,s</td>
<td>1045w, 1010m, 780m, 505w</td>
<td></td>
<td></td>
</tr>
<tr>
<td>as Nujol mull</td>
<td></td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>$\text{Cp}_2\text{Er}[\text{Mo}(h^5-\text{Cp})(\text{CO})_3]^a$</td>
<td>2020m, 1940s, 1885br,s, 1770br,s 1690br,s</td>
<td>1045w, 1010m, 780m, 505w</td>
<td></td>
<td></td>
</tr>
<tr>
<td>as Nujol mull</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\text{Cp}_2\text{ErMo}(h^5-\text{Cp})(\text{CO})_3]^b$</td>
<td>2020m-s, 1940s, 1900br,m, 1790br,m, 1660br,m</td>
<td>1045w, 1010m, 780m, 505w</td>
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</table>
Table V (continued)

<table>
<thead>
<tr>
<th>Compound</th>
<th>Spectral Data</th>
<th>Preparative Method</th>
</tr>
</thead>
<tbody>
<tr>
<td>Er[$h^5$-CpMo(CO)$_3$]$_3$•7H$_2$O as Nujol mull</td>
<td>2020s, 1982s, 1940br,s, 1780br,w 1690br,ww</td>
<td>Prepared by Method A.</td>
</tr>
<tr>
<td>Na[$h^5$-CpW(CO)$_3$] in THF as Nujol mull</td>
<td>1936m, 1892br,s, 1790s, 1740s</td>
<td>Prepared by Method B.</td>
</tr>
<tr>
<td>Na[$h^5$-CpMo(CO)$_3$] in THF as Nujol mull</td>
<td>1940m, 1895s, 1790s, 1740s</td>
<td></td>
</tr>
<tr>
<td></td>
<td>1940w, 1895s, 1775s, 1690s</td>
<td></td>
</tr>
<tr>
<td></td>
<td>3600-3400br,m, 1010w, 810ms, 655m, 570m, 515w, 485m, 455w</td>
<td></td>
</tr>
<tr>
<td></td>
<td>805m, 585m, 515m, 505m</td>
<td></td>
</tr>
</tbody>
</table>
Such an arrangement satisfies the requirement that there be one or more isocarbonyls and one or more terminal carbonyls present.

The compounds \([(\eta^5-Cp)Mo(CO)_3]_2Mg(pyridine)_4\) and \(Al[W(CO)_3(\eta^5-Cp)].3THF\), by comparison are both shown to be monomers in the solid state from x-ray analysis (section 2-1). Both compounds are heavily solvated by good donor bases and manage to achieve octahedral coordination about the central metal. The lanthanide-tungsten complexes are not solvated and given the propensity of the rare-earths to high coordination number it is unlikely that a similar structure obtains. The central lanthanide element probably relieves its high positive charge in a polymeric structure, possibly of the type suggested above. Certainly the number of strong infrared bands in the carbonyl region cannot be conclusive since the above mentioned magnesium and aluminium compounds have three and six respectively, whilst the lanthanide species have five.

Unlike \(Na[(\eta^5-Cp)W(CO)_3]\) which rapidly smoulders in air, the \(R_2Ln[W(\eta^5-Cp)(CO)_3]\) salts turn deep red in dry air over a period of two days. Sublimation of this red solid yields pure \([(\eta^5-Cp)W(CO)_3]_2\) which can be identified by its elemental analysis, melting point and infrared spectrum. Indeed attempts to prepare the \(R_2Ln[Mo(\eta^5-Cp)(CO)_3]\) always yield some \([(\eta^5-Cp)Mo(CO)_3]_2\). Wilkinson\(^78\) has shown that \((\eta^5-Cp)W(CO)_3H\) also oxidises

\(^7\)The contamination by the molybdenum dimer could reflect the extremely air-sensitive character of the complexes or it could result from the presence of a Lewis acid site which promotes dimerization in the absence of air. It has been shown\(^15\) that the salts \([\text{Ph}_4\text{As}][(\eta^5-Cp)M(CO)_3]\) (M = Mo or W) react with \(BF_3\) in dichloromethane or dimethoxyethane to produce a mixture of \((\eta^5-Cp)M(CO)_3H\) and \([(\eta^5-Cp)M(CO)_3]_2\), even when all manipulations are made using a vacuum line. Presumably the lanthanide could act in a similar role to that of \(BF_3\).
in air to the dimer. This similarity in behaviour of the anion and the hydride suggested that it should be possible to nitrosylate the anion directly, thereby eliminating the intermediate conversion of the anion to the hydride during the preparation of \((\text{h}^5-\text{Cp})\text{M(CO)}_2\text{NO}\) (\(\text{M} = \text{Cr}, \text{Mo} \text{or W.}\)) In fact, good yields (>60% based on the anion) of the desired nitrosyls are obtained if the metal carbonyl anions are treated in diethyl ether with N-methyl-N-nitroso-p-toluenesulphonamide (Diazald). Only one other instance is known in which this nitrosylating agent converts a carbonyl anion to a nitrosyl, i.e. \([\text{Mn(CO)}_5]^-\) to \(\text{Mn(CO)}_4\text{NO}\).\(^{93}\) In addition, the lanthanide-Group VIA complexes can also be nitrosylated in THF with Diazald to produce \((\text{h}^5-\text{Cp})\text{M(CO)}_2\text{NO}\).

The similarity in chemical properties of \(\text{Na}[(\text{h}^5-\text{Cp})\text{M(CO)}_3]\) and \(\text{R}_2\text{Ln}[\text{M(h}^5-\text{Cp})(\text{CO})_3]\) salts suggested another synthetic route to the preparation of the latter. The direct reaction of \(\text{M(CO)}_6\) (\(\text{M} = \text{Cr}, \text{Mo} \text{or W.}\)) with \(\text{NaCp}\) in refluxing THF produces \(\text{Na}[(\text{h}^5-\text{Cp})\text{M(CO)}_3]\), hence the analogous reaction (Method B) was attempted:

\[
\text{R}_3\text{Ln} + \text{M(CO)}_6 \xrightarrow{\text{THF-reflux}} \text{R}_2\text{Ln(}\text{h}^5-\text{Cp})\text{M(CO)}_3 + 3\text{CO}
\]

\(\text{R} = \text{Cp} \text{or MeCp; M = Cr, Mo or W.}\)

The route is of interest because \(\text{R}_2\text{LnCl}\) compounds only exist for lanthanides heavier than neodymium, a peculiarity attributed to the lanthanide contraction.\(^{77}\) The previously described method (Method A) of preparing \(\text{R}_2\text{Ln}[(\text{h}^5-\text{Cp})\text{M(CO)}_3]\) is not accessible therefore, for all the rare earths. Of the Group VIA carbonyls only \(\text{Mo(CO)}_6\) reacts with \(\text{R}_3\text{Ln}\) under the conditions studied, namely, in the absence and presence of light and up to forty-eight hours refluxing in THF. The reactions were monitored by infrared spectroscopy,
and all the reaction mixtures were taken to dryness and checked for possible new products by sublimation. In the case of Mo(CO)$_6$ gas is evolved as expected and products can be isolated for Ln = La, Er and Ho. The analytical data for these products are all consistently high, suggesting incomplete conversion. The mull infrared spectra (Table V) exhibit the characteristic isocarbonyl absorptions also observed for the tungsten analogues prepared by the anion route. Further, the behaviour in air is identical with the other lanthanide-Group VIa derivatives, namely a slow darkening to a deep red solid, from which [(h$_5^\text{-Cp})M6(CO)$_3]$_2$ can be sublimed.

Finally, an attempt was made to prepare the totally substituted derivatives, LnA$_3$, (A = (h$_5^\text{-Cp})M(CO)$_3; M = Cr, Mo or W). A related compound, Tl[(h$_5^\text{-Cp})Mo(CO)$_3]$_3$ had been prepared by King. The infrared spectrum of this complex showed three bands in the terminal carbonyl region and none attributable to isocarbonyls. This compound was said to have a red-green dichroic appearance resembling certain sixteen electron square planar complexes of rhodium(I) (e.g. C$_5$H$_7$O$_2$Rh(CO)$_2$) and platinum(II) (e.g. Pt(NH$_3$)$_4$(PtCl)$_4$), which can form "stacked" polmeric crystal structures with metal-metal bonding on an axis perpendicular to the coordination square. Subsequently a single crystal x-ray structure determination was undertaken because of the potentially high electrical conductivity that this compound might display. The results have shown that the proposed "stacked" arrangement with Tl-Tl interactions is not confirmed. The molecule was found to have trigonal pyramidal coordination at thallium with an average Tl-Mo bond length of 2.965 Å, an average Mo-Tl-Mo angle of 119.7°, and the thallium atom displaced out of the plane of the three molybdenum atoms by 0.586 Å. At the time of our experiments, the x-ray result was not published, however, the other spectral and chemical evidence suggested a metal-metal bonded structure.
Consequently, an analogous reaction was undertaken to prepare a completely substituted lanthanide by employing the metathetical reactions:

\[
\text{LnCl}_3 + 3\text{NaA} \rightarrow \text{LnA}_3 + 3\text{NaCl}
\]

All of the Group VIa anions react rapidly in the expected manner, but in every case the product formed is an intractable air-sensitive solid, which is totally insoluble in water or common organic solvents† and does not sublimate. Only one such complex is reasonably pure, namely, \(\text{Er}[(\text{h}_5^5\text{-Cp})\text{Mo(CO)}_3]_3 \cdot 7\text{H}_2\text{O}\). This compound decomposes rapidly in air to produce the corresponding metal carbonyl dimer, as evidenced by infrared spectroscopy, an effect also noticed for the \(\text{R}_2\text{Ln}[(\text{h}_5^5\text{-Cp})\text{W(CO)}_3] \) and \(\text{Er}[\text{Co(CO)}_3]_3 \cdot 3\text{THF}\) complexes.

The infrared spectrum of the Er-Mo compound (Table V) verifies the presence of water and shows strong terminal CO bands and only weak lower frequency CO absorptions. It appears that \(\text{Er}[(\text{h}_5^5\text{-Cp})\text{Mo(CO)}_3]_3 \cdot 7\text{H}_2\text{O}\) is somewhat similar to \(\text{Er}[\text{Co(CO)}_3]_3 \cdot 3\text{THF}\) and \(\text{Tl}[(\text{h}_5^5\text{-Cp})\text{Mo(CO)}_3]_3\): In both of the erbium compounds in the solid state there may be some Er-transition metal bonding made possible by the substantial solvation of the lanthanide element. The strong carbonyl frequencies above the values observed for the corresponding sodium salts and the lack of strong isocarbonyl bands are consistent with this view. With the limited evidence available the assignment of a metal-metal bond is at best tentative and any analogies to the thallium compound are weak.

\[X \quad X \quad X \quad X\]

The evidence presented in this thesis (and the work of others)

†For example, in the case of \(\text{YbCl}_3 + \text{Na}[(\text{h}_5^5\text{-Cp})\text{W(CO)}_3]\) the product shows absolutely no extraction into acetone during a twenty four hour hot extraction using a Soxhlet apparatus.
documents isocarbonyl linkages as a valid bonding mode, however, the question remains as to what is occurring at an electronic level. Qualitatively there appears to be a donation of electrons from an oxygen lone pair orbital, if Purcell's explanation is accepted, (section 2-1) to the lanthanide involved. The role of the lanthanide must depend in large part upon the type of bonding in the initial Lewis acid complex. The organolanthanides whose bonding has been most intensively studied are the derivatives \( \text{Cp}_3\text{Ln} \). For example, work by Nugent et al.\(^1\) has shown the covalent character of the lanthanide-ring bonding to be no greater than 5% based upon the nephelauxetic parameter determined from absorption spectra. Further support for low covalency comes from another technique; the mass spectra of ionically bound dicyclopentadienyl metal sandwich compounds have been characterised as having the peak corresponding to the loss of one cyclopentadienyl group as the most intense.\(^9\) On the other hand relative abundancies in covalently bound complexes consistently showed the parent ion as the most intense peak. The lanthanide data are consistent with an ionic model.\(^19\) General chemical properties such as attack by halogenated solvents, solubility only in donor solvents and the instantaneously quantitative reaction with \( \text{FeCl}_2 \) to produce ferrocene\(^3\) confirm the highly ionic nature of these complexes.

Unfortunately no x-ray crystal structure determinations have been carried out upon \( \text{Cp}_3\text{Ln} \)-Lewis base systems. Moreover, only a single report of a structure of a \( \text{Cp}_3\text{Ln} \) compound exists.\(^9\) Apparently \( \text{Cp}_3\text{Sm} \) does not exist as a discrete molecule in the solid phase, but as infinite chains with a distorted tetrahedral geometry about Sm. This structure could be interpreted as \( \text{Cp}_3\text{Sm} \) acting as a Lewis acid and in so doing increasing its coordination by attracting part of a Cp ring of an adjacent molecule. If one assumes a \( C_{3v} \) or even
D$_3$h symmetry for the $\text{R}_3\text{Ln}$ part of a Lewis acid-base adduct the most likely vacant orbital on the lanthanide is the 5d$_{z^2}$, assuming the 4f orbitals have insufficient radial extension to enter the bonding. Whatever the orbital, the interaction between carbonyl oxygen and $\text{Cp}_3\text{Ln}$ is not as strong as for aluminium and boron complexes as judged by the shift in infrared absorptions (see above). Possibly the difference in size of the lanthanide and oxygen orbitals contributes to this observation. Hence the lanthanide-oxygen bond may be less covalent than the corresponding aluminium- and boron-oxygen bonds.

In the case of the species $m_2\text{Mgpy}_4$ (section 2-1) Burlitch believes that the Mg-isocarbonyl bond is predominantly ionic. The high reactivity of the $m^-$ anions and the fact that the average carbonyl stretching frequency is the same in these complexes and in the corresponding sodium salt lead him to this conclusion. Chemically the organolanthanides resemble Group IIa derivatives more closely than Group IIIa and so the results of the magnesium systems may well be relevant to our compounds.

In all probability the bonding between the lanthanide and the oxygen atom of a metal carbonyl or nitrosyl ligand is essentially ionic.
CHAPTER III
REACTIONS INVOLVING ELEMENTAL METALS

3.1 INTRODUCTION

The interaction of an elemental metal with an organic substrate is one of the oldest and most direct methods of preparing an organometallic compound. Indeed, the pioneering contribution of Frankland using zinc and the significance of Grignard's work fifty years later are well recognized. Electro-positive metals are most often employed in this type of reaction either alone or in an alloy. For example, one of the most common organometallic compounds, Et₄Pb, is prepared in this way.

$$4(Na/Pb) + 4EtCl \rightarrow Et_4Pb + 3Pb + 4NaCl$$

Instead of forming an alloy, metals can often be made to react more readily by reducing their particle size. Recently, Timms and other workers have found that low temperature co-deposition of metal atoms with organic species permits the formation of a variety of interesting compounds. Metals such as platinum or palladium (which are known for their "noble" character) can be used in this way in addition to more common transition elements. In this case chemical discoveries followed as a result of the development of a physical technique. Similarly the rare earth chemist has benefitted from the improved separation methods made available in the last twenty years. Consequently, highly purified lanthanide metal powders can now be obtained economically. Even so, the literature reports of organometallic compounds prepared directly from lanthanide metals are few.

The first attempt at such a reaction involved lanthanum metal, of unspecified size and quality, heated at 135°C with biphenylmercury in a sealed tube under nitrogen for 100 days. After treatment of the black liquid
product with carbon dioxide and extraction into benzene, the only isolable product was biphenyl in 15% yield. Whether the organic product was the result of the thermal decomposition of Ph₂Hg or was generated via interaction with lanthanum was not determined. In the same study Gilman found that iodobenzene and lanthanum metal in diethyl ether or benzene at room temperature did not react, even after four months.

The first substantial result using rare earth metals employed the fact that ytterbium and europium dissolve in liquid ammonia to form stable divalent cations. Fischer treated these solutions with cyclopentadiene to produce Cp₂Eu and Cp₂Yb, which were isolated by sublimation of the dried reaction mixture. Cp₂Eu is a yellow, paramagnetic (μ_{eff} = 7.6 BM) solid whose Debye-Scherrer pattern is identical to that of Cp₂Sr. The evidence supports an ionic bonding mode for europium. There is some controversy, however, regarding the species Cp₂Yb. The red diamagnetic solid which sublimed about 400°C, was said to be unsolvated Cp₂Yb. Calderazzo prepared Cp₂Yb via the liquid ammonia route and by the reduction of a Yb³⁺ species. He claimed Cp₂Yb to be emerald green when desolvated and that the red sublimate obtained by Fischer was not exclusively Cp₂Yb, but contained some Yb³⁺ as evidenced by ultraviolet spectroscopy. Later work by Hayes and Thomas on the liquid ammonia reaction revealed three sublimable products: at 150°C, a deep green solid assigned to be Cp₃Yb; at 170°C, a yellow solid formulated as a mixture of Cp₃Yb₂(NH₂)₂; and at 360°C, a red solid which was claimed to be Cp₂Yb. All formulations by Hayes and Thomas were based on detailed mass spectral and n.m.r. evidence. One component, [Cp₂YbNH₂]₂, of the ytterbium mixture subliming at 170°C, has also been observed by Muller. Liquid ammonia solutions of europium and ytterbium also react with
cyclooctatetraene to form COTEu and COTYb. Once again, the europium complex was shown to be paramagnetic and to display an e.s.r. signal consistent with the state Eu$^{2+}$. The diamagnetic ytterbium complex was characterised by metal analysis. Both compounds were readily solvated by strongly donor solvents.

Passage of propyne$^{10}$ through solutions of europium or ytterbium in liquid ammonia produced (CH$_3$-C≡C) Eu and the mixture (CH$_3$C≡C)$_2$Yb/Yb(NH$_2$)$_2$ according to elemental analysis. No properties other than the reaction with water to regenerate the alkyne were recorded.

Work, more closely related to our own, by Evans and coworkers$^{9,106}$ describes reactions of lanthanide metals with alkyl or aryl iodides in THF. It was found that ytterbium powder and europium ingots reacted readily at -15°C to give greater than 70% conversion to the corresponding Grignard-type species, RM$^{\text{II}}$I (M = Eu or Yb). Samarium powder required heating to 30°C and the conversion was never more than 50%. These reagents behaved towards aldehydes, ketones, R$_3$SiCl (R = alkyl or aryl group), and water as typical Grignard reagents. Magnetic susceptibilities as well as iodimetric and acidometric titrations helped to confirm the formulation as RM$^{\text{II}}$I. On the other hand gadolinium and erbium did not react even under vigorous conditions, whereas cerium ingots and lanthanum wire did show some reactivity towards alkyl and aryl iodides. On the basis of a Ce:I ratio of 1:1.5, these solutions were tentatively described as an equimolar mixture of R$_2$CeI and RCeI$_2$, or possibly a labile equilibrium of R$_3$Ce and CeI$_3$. Less data were reported for the lanthanum compounds except that much precipitation of LaI$_3$ occurred and the conversion was only about 25% compared to about 45% for the cerium species.
In summary then, the reactions used to prepare organolanthanides using elemental metals have been of the following types:

\[ M + nRH \rightarrow MR_n + n/2H_2 \quad \text{(i)} \]
\[ M + R' \rightarrow MR' \quad \text{(ii)} \]
\[ M + R''X \rightarrow R''MX \quad \text{(iii)} \]

(R = Cp or CH₃C≡C; R' = COT and R'' = alkyl or aryl group).

We were interested in reaction type (iii) where R is not an organic group, but rather a transition metal organometallic entity. That is to say, we were considering the formation of an organometallic Grignard-type reagent based upon the lanthanides. At the time the work was undertaken there were only two reports of similar species, both involving magnesium. Since then no further papers on this topic have appeared in the literature.

The first report of a transition metal-Grignard reagent was by Glocking.\(^{107}\) Two similar complexes were prepared by stirring \( (h^5\text{-Cp})(CO)_3MGeR_3 \) (M = Mo or W, Me or Et) with anhydrous MgBr₂ in THF for four days; the solvent was removed \textit{in vacuo} and, finally, the remaining solid was extracted and crystallized from benzene. The elemental analyses for both derivatives did not fit one formulation satisfactorily as there appeared to be some non-stoichiometric solvation by THF; the general formula \( (h^5\text{-Cp})M(CO)_3MgBr_x \text{THF} \) \( (x = 0+1) \) could be assigned to these complexes. A molecular weight determination of the tungsten compound showed it to be monomeric in benzene. In terms of reactivity both molybdenum and tungsten complexes were exothermally hydrolysed to the corresponding hydride and the tungsten reagent could not be converted into the \( \sigma \)-phenyl tungsten complex with bromobenzene. No conditions were specified for these conversion reactions.
The only use of elemental magnesium with a transition metal organometallic substrate was by Burlitch and Ulmer. They used three routes to prepare the Grignard-type reagents: (i) Magnesium powder reacted in THF at room temperature with Mn(CO)\(_5\)Br or \((h^5\text{-Cp})\text{Fe(CO)}_2\text{Cl}\) to produce highly coloured, air-sensitive solutions which reacted with \(\text{Ph}_3\text{SnCl}\) to give the corresponding Mn-Sn or Fe-Sn compound in greater than 70% yield. Using these reactive solutions with \(\text{MeI}\), it was shown by infrared measurements that Mn(CO)\(_5\)Me was obtained in 90% yield; (ii) An alternative method involved cleavage of a metal-metal bond in the presence of magnesium powder and \((\text{CH}_2\text{Br})_2\) in refluxing THF for 20 hours. The results are summarized below: (yields are in brackets)

\[
\begin{align*}
L-L + (\text{CH}_2\text{Br})_2 + \text{Mg} & \rightarrow "L-\text{Mg-Br}" \\
\text{(a)} (\text{CF}_3\text{CO})_2\text{O} & \rightarrow \text{CF}_3\text{COMn(CO)}_5 \\
\text{(b)} \text{HgCl}_2 & \rightarrow (h^5\text{-Cp})\text{Mo(CO)}_3\text{HgCl} \\
\text{(c)} \text{Ph}_3\text{SnCl} & \rightarrow \text{Ph}_3\text{Sn-R} \\
\text{(79%)} & >80% \quad (>70%) \\
\text{L} = \text{Mn(CO)}_5, \text{Fe(CO)}_2(h^5\text{-Cp}), \text{or Mo(CO)}_3(h^5\text{-Cp}), \text{R} = \text{Mn(CO)}_5, \text{Fe(CO)}_2(h^5\text{-Cp}).
\end{align*}
\]

This method is best regarded as a reaction of very reactive \(\text{MgBr}_2\), prepared \textit{in situ} by olefin elimination from \((\text{CH}_2\text{Br})_2\) and magnesium, with the metal dimers. The presence of halide was found to be essential for the formation of the Grignard-type species. The cleavage of \(\text{Mn}_2(\text{CO})_{10}\) by magnesium only did not occur. From the equations above it can be seen that besides using \(\text{Mn}_2(\text{CO})_{10}\) and \((h^5\text{-Cp})_2\text{Fe}_2(\text{CO})_4\), the Mo-Mo bond in \([((h^5\text{-Cp})\text{Mo(CO)}_3)]_2\) was cleaved. It was found that \(\text{Ph}_3\text{SnCl}\) did not react with the molybdenum-Grignard and this was attributed to the weakly nucleophilic character of the carbonyl containing group. Burlitch remarked that the lack of formation of the Sn-Mo bonded
compound was hardly surprising in so far as the compound isolated by Glooking was produced by a process which was essentially the reverse of reaction (c). Furthermore, the metal-metal bond in Co\(_2\)(CO)\(_8\) could not be cleaved with magnesium and (CH\(_2\)Br)\(_2\), since the carbonyl dimer rapidly decomposed in the presence of MgBr\(_2\); (iii) The final method was based upon mercury displacement from RHgCl species. For example, when a THF solution of (CO)\(_5\)MnHgBr was stirred with an excess of magnesium for two hours at room temperature a light yellow, highly air-sensitive solution was formed. Reaction of the solution with Ph\(_3\)SnCl gave a 93% yield of Ph\(_3\)SnMn(CO)\(_5\). This method was considered the cleanest route to "(CO)\(_5\)MnMgBr", however, the colour of the solution prepared in this way was different from the deep burgundy solution prepared using (CH\(_2\)Br)\(_2\). The analogous "Co(CO)\(_5\)MgBr" could be prepared similarly, but once again complete reaction with Ph\(_3\)SnCl was not achieved, presumably for the same reason as in the molybdenum case above. No spectral or other physical data were reported for the Grignard-type reagents, although it was noted that preliminary results suggested considerable covalent character in the magnesium-transition metal bond. This comment is interesting in the light of Burlitch's later work of preparing derivatives of the type \(m_2\text{Mgpy}_4\) (\(m =\) metal carbonyl anion, \(\text{py} =\) pyridine, section 2-1), where he found the bonding to be almost entirely ionic in nature.

The only reaction involving an elemental lanthanide with an organo-metallic complex is the reaction of a 1% w/w Er-Hg mixture with [(CO)\(_4\)Co]\(_2\)Hg to produce Er[Co(CO)\(_4\)]\(_3\)-4THF,\(^71\) which was discussed in detail earlier (section 2-1).

Our attempts to form lanthanide Grignard-type reagents were based upon the observations that Evans\(^9\) had prepared compounds of the type RM\(_{II}\)I and
that magnesium\textsuperscript{108} had been shown to produce reactive solutions, tentatively described as "L-Mg-X", with transition metal organometallic substrates in the presence of halide. It seemed reasonable to study the reactions of lanthanides which can exist in a +2 oxidation state, with suitable metal carbonyl halides. This approach may be regarded as another route to compounds containing transition metal-lanthanide bonds. In addition isocarbonyl bonding could be involved once more. Furthermore, results from our laboratory\textsuperscript{110} had shown that "RM\textsuperscript{II}I", formed from alkyl or aryl iodides according to Evans' method, did not always react with organic functional groups in a fashion similar to their magnesium analogues.

Although most of this work involved Mn(CO)\textsubscript{5}Br and (h\textsuperscript{3}-C\textsubscript{3}H\textsubscript{5})Fe(CO)\textsubscript{3}I, preliminary experiments were carried out using [(h\textsuperscript{5}-Cp)Mo(CO)]\textsubscript{2} and (h\textsuperscript{5}-Cp)Cr(CO)\textsubscript{3}HgCl. Cleavage of the Mo-Mo bond in the absence of halogen was also attempted.

The direct cleavage of a metal-metal bond by a metal other than a Group Ia element is also a field which has received little attention to date. For example, Robinson and coworkers\textsuperscript{111} have shown that thallium reacts with Co\textsubscript{2}(CO)\textsubscript{8} in benzene at room temperature to generate Tl[Co(CO)]\textsubscript{4}. Zinc and cadmium are known to insert into the metal-metal bond of Mn\textsubscript{2}(CO)\textsubscript{10}\textsuperscript{112} when refluxed in diglyme for 10 hours. McVicker and Matyas\textsuperscript{52} have shown that magnesium amalgam can effect the reductive cleavage of dimeric transition metal carbonyl complexes in the presence of a strong Lewis base such as pyridine or THF (see section 2-1 for preparative details).

\[
M-M + Mg(Hg)_{\text{base}} \rightarrow B_xMg(M)_{2}
\]

The species that result from metal carbonyl dimer cleavage are reported to have useful synthetic applicability. The Tl[Co(CO)]\textsubscript{4} formed above involved
a facile, high yield preparation, which avoided the use of large quantities of mercury and the formation of unwanted Hg[Co(CO)$_4$]$_2$, and produced a salt which is soluble in non-basic solvents such as CH$_2$Cl$_2$ and benzene. Further, Tl[Co(CO)$_4$] has sufficient stability towards the air to be weighed rapidly without the use of an inert atmosphere. Similarly, the reagents B$_x$Mg(M)$_2$ have excellent hydrocarbon solubility, unlike the sodium salts of metal carbonyl anions.

Aside from attempting to determine whether a lanthanide-transition metal bond could be formed, these studies using elemental rare earths held the possibility of generating synthetically useful reagents.
3.2 EXPERIMENTAL

The lanthanide metals used were of 99.9% purity and were purchased from Research Organic/Inorganic Chemical Corporation or the Research Chemicals Division of Nucor Corporation. Manganese, tin and iron were of 'Certified' purity from Fischer Scientific Company.

\[ \text{Mn}(	ext{CO})_5\text{Br} \text{ and } [(\text{h}^5-\text{C}_5\text{H}_5)\text{Mo}(	ext{CO})_3]_2 \]
were purchased from Strem Chemicals Incorporated, Mass. \( \text{Mn}_2(\text{CO})_{10}, \text{Fe}(	ext{CO})_5 \text{ and } \text{Mo}(	ext{CO})_6 \)
were purchased from Pressure Chemical Company, Pittsburgh.

\[ \text{NOCl}^{113}, \text{Mo}(	ext{NO})_2\text{Cl}_2,^{85} [(\text{h}^5-\text{C}_5\text{H}_5)\text{Cr}(	ext{CO})_3]\text{HgCl},^{114} (\text{h}^3-\text{C}_3\text{H}_5)\text{Fe}(	ext{CO})_3\text{I}^{124} \]
and \( \text{Mn}_2(\text{CO})_9\text{H}_2^{115} \)
were prepared according to literature methods.

For the reactions involving deactivated alumina, the deactivation was achieved by exposing Fisher adsorption alumina to the atmosphere for at least forty eight hours. For chromatography purposes Woelm neutral grade 1 alumina was used.

The purity of reagents was ascertained by elemental analysis and/or melting point determinations. All solvents were dried (if necessary), distilled, and degassed just prior to use, and all manipulations were performed in an atmosphere of prepurified nitrogen.

Infrared spectra were recorded on Perkin Elmer 457 and 710 spectrophotometers, and proton magnetic resonance spectra were recorded on a Varian Associates T-60 spectrometer with tetramethyilsilane or the solvent being used as internal standards. Electron spin resonance spectra were obtained with a Varian Associates E-3, X-band spectrometer, and visible and ultraviolet spectra were obtained with a Cary 14 recording spectrophotometer. Conductance measurements were made with a Yellow Springs Instrument Company (YSI) model 31 conductivity bridge using a calibrated YSI 3403 conductivity cell. Elemental analyses were carried out by Mr. P. Borda of this department.
3.2a REACTIONS INVOLVING MANGANESE CARBONYLS

Preparation of the red solution

Method A

An excess of manganese powder (0.32 g, 5.8 mmol) was vigorously stirred in a THF solution (30 ml) of Mn(CO)$_5$Br (1.15 g, 4.2 mmol) overnight at room temperature. The metal was allowed to settle and the supernatant liquid was decanted and filtered back onto the manganese. Stirring was continued for a further 2 days; the mixture was filtered to yield a deep red solution.

Other metals reacted similarly. For the more reactive elements such as ytterbium and samarium, the solution generally turned red within 12 h whereas the less reactive metals required up to 5 days of stirring in extreme cases.

Method B

Manganese powder (0.54 g, 9.9 mmol) was stirred in a refluxing THF solution (40 ml) of Mn$_2$(CO)$_{10}$ (0.80 g, 2.1 mmol) and (CH$_2$Br)$_2$ (2 ml, 23 mmol) for 24 h. The resultant red solution was filtered to remove excess metal. Ytterbium reacted in an identical manner.

Method C

Anhydrous MnCl$_2$ (0.26 g, 2.1 mmol) was stirred in a refluxing THF solution (40 ml) of Mn$_2$(CO)$_{10}$ (0.81 g, 2.1 mmol) for 3 days, by which time the solution had turned red. The solution was filtered before use. Anhydrous YbCl$_3$ did not react under similar conditions after 4 days of refluxing.
Method D

NaMn(CO)$_5$ (0.88 g, 4.0 mmol) [prepared by reduction of Mn$_2$(CO)$_{10}$ with a 1% Na-Hg amalgam in THF] and MnCl$_2$ (0.50 g, 4.0 mmol) were stirred overnight in THF (40 ml) at room temperature. The solution had turned red and was filtered. In order to obtain a solution whose infrared spectrum was qualitatively similar to the spectra exhibited by solutions prepared by other methods, this red solution was allowed to stir for several days or was diluted with THF.

All the red solutions, whatever the synthetic method employed, were monitored by infrared spectroscopy during their preparation. In the reactions described below, the actual preparative method of the red solution is generally of no consequence as far as the eventual success of the described typical syntheses is concerned. The origins of the red solutions are indicated in each description for the sake of completeness.

Reaction of the red solution with triphenyltin chloride

Solid (C$_6$H$_5$)$_3$SnCl (0.18 g, 0.47 mmol) was added to a stirred red solution prepared from Yb (0.17 g, 0.99 mmol) and Mn(CO)$_5$Br (0.13 g, 0.46 mmol) in THF (7 ml) according to Method A. The mixture was warmed to 50°C for 1 h, then hydrolyzed at 25°C with saturated aqueous NH$_4$Cl solution (10 ml), and washed with saturated aqueous NaCl solution (3 x 10 ml). The remaining brown THF solution was dried over anhydrous MgSO$_4$ and taken to dryness. The solid residue was extracted with hot hexane (3 x 15 ml), the extracts were combined and filtered, and the solvent was removed from the filtrate under reduced pressure to yield a pale yellow solid. Mn$_2$(CO)$_{10}$ was removed from the latter solid by sublimation (25°C, 10$^{-3}$ mm Hg), and the
remaining white solid was recrystallized from hexane to obtain \((\text{C}_6\text{H}_5)_3\text{SnMn(CO)}_5\). Yield 0.15 g, 59%. The identity of the product was confirmed by its infrared spectrum, melting point and elemental analysis. \(^{116}\) Anal. Calc for \(\text{C}_{27}\text{H}_{15}\text{O}_5\text{SnMn}\): C, 50.69; H, 2.75. Found: C, 50.99; H, 2.77.

Reaction of the red solution with methyl iodide

A THF solution (10 ml) of \(\text{CH}_3\text{I}\) (0.5 ml, 8.0 mmol) was added to a red solution prepared according to Method A from Sm (0.24 g, 1.6 mmol) and Mn(CO)\(_5\)Br (0.27 g, 0.98 mmol) in THF (8 ml). The reaction mixture was refluxed with stirring for 24 h, whereupon \(\text{H}_2\text{O}\) (10 ml) was added and the volume of the solution was reduced to 15 ml. The mixture was extracted with \(\text{CCl}_4\) (3 x 7 ml) and the combined extracts were concentrated. Proton magnetic resonance and infrared spectra \(^{117}\) revealed \(\text{CH}_3\text{Mn(CO)}_5\) to be present in the extracts. Yield \(\sim 10\%\).

Reaction of the red solution with allyl chloride

Allyl chloride (7.2 ml, 88.3 mmol) was syringed into a stirred red solution prepared according to Method D from MnCl\(_2\) (0.97 g, 7.7 mmol) and NaMn(CO)\(_5\) (1.68 g, 7.7 mmol) in THF (20 ml). The solution was stirred at room temperature overnight, by which time a precipitate had formed and the solution had turned yellow. The products were isolated by trap-to-trap distillation (0\(^\circ\)C, -35\(^\circ\)C and -78\(^\circ\)C) of the reaction mixture under vacuum. A small amount of Mn\(_2\)(CO)\(_{10}\) collected in the 0\(^\circ\)C trap, but the major carbonyl-containing product was a yellow liquid (1 ml) which collected in the -35\(^\circ\)C trap. Infrared and n.m.r. spectra showed the liquid to consist only of a
mixture of $^{1}$-C$_{3}$H$_{5}$Mn(CO)$_{5}$ and $^{3}$-C$_{3}$H$_{5}$Mn(CO)$_{4}$ in a ratio of 2.4:1. The yellow liquid was heated at 80 - 90°C for one hour and the n.m.r. spectrum of the resulting yellow solid revealed complete conversion to $^{3}$-C$_{3}$H$_{5}$Mn(CO)$_{4}$ as expected. The n.m.r. spectrum (C$_{6}$D$_{6}$) of $^{3}$-C$_{3}$H$_{5}$Mn(CO)$_{4}$ was $\tau$ 5.73 (m, 1 H), 7.72 (d, $J = 7$ Hz, 2 H), 8.62 (d, $J = 12$ Hz, 2 H).

Reaction of the red solution with benzoyl chloride

Benzoyl chloride (1.0 ml, 8.6 mmol) in THF (20 ml) was added dropwise to a red solution prepared according to Method A from Yb (0.90 g, 5.2 mmol) and Mn(CO)$_{5}$Br (1.11 g, 4.0 mmol) in THF (32 ml). No change was apparent after stirring for 2 h at room temperature, and the mixture was warmed to 65°C for 2 h, thereby causing a brown coloration to appear. The solvent was removed under reduced pressure at 25°C to yield an oil-covered orange solid which was extracted with light petroleum ether (3 x 45 ml). The combined extracts were reduced in volume and were transferred to an alumina column which was eluted with a light petroleum ether-diethyl ether solvent gradient. The two major products obtained by chromatography were Mn$_{2}$(CO)$_{10}$ (0.43 g, 55% yield) and C$_{6}$H$_{5}$CO$_{2}$(CH$_{2}$)$_{4}$Cl (0.41 g, 48% yield). The yields were based on Mn(CO)$_{5}$Br. The ester was identified spectroscopically: infrared (film), $\nu_{\text{max}}$ 1720, 1280, 1120, 720 cm$^{-1}$ [compare with Sadtler standard infrared spectrum 25038]; n.m.r. (CCl$_{4}$), $\tau$ 8.1 (m, 4 H), 6.43 (m, 2 H), 5.70 (m, 2 H), 2.81 - 2.40 (m, 3 H), 1.98 (m, 2 H) [compare with Sadtler standard n.m.r. spectrum 98444 M]; mass spectrum, m/e 214 ($M^{+}$, Cl$^{37}$), 212 ($M^{+}$, Cl$^{35}$), 77 (base peak).
Reaction of the red solution with sodium acetylacetonate

Sodium acetylacetonate (0.37 g, 3.0 mmol) was added to a red solution prepared according to Method A from Ho (0.71 g, 4.3 mmol) and Mn(CO)$_5$Br (0.66 g, 2.4 mmol) in THF (30 ml). The mixture was stirred at room temperature for 2 days and filtered to yield a golden brown solution which was taken to dryness under reduced pressure. The golden brown residue was extracted in a Soxhlet apparatus with refluxing diethyl ether (100 ml) for 4 h. The ether solution was reduced in volume to yield light brown crystals which were collected by filtration and washed with a small volume of pentane. Yield 0.12 g, 14%; infrared (Nujol), $\nu_{\text{max}}$ 2060(s), 2010(vs), 1975(s), 1925(s), 1910(s), 1620(sh), 1595(s), 1520(s), 1380(s), 1265(m), 1020(m), 930(w), 800(w) and 650(s) cm$^{-1}$; infrared (CH$_2$Cl$_2$), $\nu_{\text{max}}$ 2055(s), 2005(s), 1970(s), 1925(s), 1620(sh) and 1595(s) cm$^{-1}$.

Anal. Calc for C$_{23}$H$_{27}$O$_{14}$HoMn: C, 34.42; H, 3.37. Found: C, 34.42; H, 3.15.

The acetylacetonate complex [m.p. 78°C (decomp)] turns yellow upon exposure to air for a few hours, and Mn$_2$(CO)$_{10}$ can be sublimed from the oxidized product.

Reaction of the red solution with triphenylphosphine

A solution of (C$_6$H$_5$)$_3$P (3.9 g, 14.9 mmol) in THF (20 ml) was added dropwise at room temperature to a stirred red solution prepared according to Method D from NaMn(CO)$_5$Br (0.88 g, 4.0 mmol) and MnCl$_2$ (0.51 g, 4.0 mmol) in THF (15 ml) and diluted with THF (40 ml). After stirring from 20 minutes, the reaction mixture was taken to dryness under reduced pressure. The resi-
dual solid was extracted with hexane (5 x 20 ml), the combined extracts were filtered, and the resulting clear orange solution was reduced in volume under reduced pressure to 50 ml whereupon crystallization occurred. The orange crystals were collected by filtration, washed with a small volume of hexane, and dried in vacuo (10⁻³ mm Hg). The melting point and infrared spectrum of the crystals were found to be identical with those of Mn₂(CO)₈[P(C₆H₅)₃]₂.¹²⁰

**Anal.** Calc for C₄₄H₅₂O₈P₂Mn₂: C, 61.56; H, 3.52.

Found: C, 61.65; H, 3.79.

Further evidence for the dimeric (rather than the monomeric) nature of the product is its n.m.r. spectrum in CH₂Cl₂ which exhibits no broadening or shifting of the solvent peak, behaviour indicative of a diamagnetic species.

**Reaction of the red solution with 2,2'-bipyridyl**

A solution of 2,2'-bipyridyl (2.00 g, 12.8 mmol) in THF (10 ml) was added to a stirred red solution prepared according to Method D from MnCl₂ (0.50 g, 4.0 mmol) and NaMn(CO)₅ (0.88 g, 4.0 mmol) in THF (50 ml). This addition and subsequent manipulations of the reaction mixture were carried out in the absence of direct light. If Method A or B with Mn as the metal was used to prepare the red solution, MnBr₂·2 bipy (identified by elemental analysis) precipitated instantly upon the addition of the 2,2'-bipyridyl. If Method D was employed, however, no precipitate formed. In all three cases, the solution became deep purple after stirring at room temperature overnight. The purple solution was filtered, if necessary, and the solvent was removed under reduced pressure. The residue was extracted
with benzene (6 x 15 ml), and the combined extracts were filtered and concentrated until crystallization occurred. The purple-red crystals were collected by filtration and were washed with hexane (3 x 10 ml). Yield 0.43 g, 44%. The infrared spectrum and elemental analysis of the isolated product confirmed the formulation Mn$_2$(CO)$_8$(bipy).$^{115}$

Anal. Calc for C$_{16}$H$_8$O$_8$N$_2$Mn$_2$: C, 44.11; H, 1.64; N, 5.71. Found: C, 44.84; H, 1.63; N, 5.48.

Reaction of the red solution with N-methyl-N-nitroso-p-toluenesulphonamide (Diazald)

A solution of Diazald (0.40 g, 0.20 mmol) in THF (4 ml) was added dropwise at 0°C to a stirred red solution which was prepared according to Method A from Sm (0.50 g, 0.30 mmol) and Mn(CO)$_5$Br (0.06 g, 0.20 mmol) in THF (5 ml). The solution turned brown within 10 minutes and infrared spectroscopy revealed the appearance and growth of an absorption at 1752 cm$^{-1}$, characteristic of Mn(CO)$_4$NO.$^{121}$ A comparison of intensities of the initial and final Diazald bands in the infrared spectrum suggested a yield of ca. 40% of Mn(CO)$_4$NO.

Reaction of the red solution with iodine

Solid iodine (0.25 g, 2.0 mmol) was added at room temperature to a stirred red solution prepared according to Method A from Mn(CO)$_5$Br (0.57 g, 2.0 mmol) and Sm (0.45 g, 3.0 mmol) in THF (12 ml). An immediate color change to brown occurred and a precipitate formed. The mixture was stirred overnight and the solvent was removed under reduced pressure. The residual solid was extracted with benzene (3 x 20 ml), and the filtered extracts were
taken to dryness. The solid thus obtained was fractionally sublimed: at room temperature and $10^{-3}$ mm Hg, yellow and orange crystals formed; at 90°C and $10^{-3}$ mm Hg, deep red-brown crystals formed. The former sublimate was shown to be a mixture of Mn$_2$(CO)$_{10}$ and a small quantity of Mn(CO)$_5$I by infrared spectroscopy and a positive PdCl$_2$ spot test$^{126}$ for iodine. The higher temperature sublimate had an infrared spectrum identical with that of Mn$_2$(CO)$_8$I$_2$$^{122}$ and also gave a positive iodine spot test. Yield 40 mg, 6%.

Attempts to react the red solution with 1-butyne either by condensing the alkyne onto the cooled (-30°C) red solution and allowing the mixture to warm to room temperature, or by bubbling the gas through a red solution at 25°C were unsuccessful. Similarly, no reaction was apparent when CO or H$_2$ were bubbled through the red solution at room temperature; neither did cyclopentadiene give any detectable change in the red solution when heated to 60°C. All of these attempted reactions were monitored by infrared spectroscopy. If the red solution is taken to dryness and N,N-dimethylacetamide is introduced as the solvent, gas evolution can be detected, particularly upon warming the solution to 70°C.
3.2b REACTIONS INVOLVING ALLYTRICARBONYLIRON IODIDE

Preparation of the mauve solution from (h₃-C₃H₅)Fe(CO)₃I and a metal

Yb powder (0.47 g, 2.7 mmol) was vigorously stirred in a THF (17 ml) solution of (h₃-C₃H₅)Fe(CO)₃I (0.62 g, 2.0 mmol) at room temperature until the solution turned mauve, normally about 1.5 - 2 h. The mauve solution was filtered and used immediately.

If the solution was left to stir after it had achieved the mauve color, it turned brown within 1 h and after about 12 h it had turned black. The black solution was filtered to yield an intractable black solid and a clear black solution which, when taken to dryness by solvent evaporation under reduced pressure, did not redissolve in common organic solvents. Infrared (black solid from black solution taken to dryness), (Nujol), \( \nu_{max} \): 2010(sh), 1965(br,s), 1030(s) and 875(s) cm⁻¹.

Samarium, manganese and yttrium reacted similarly.

The reaction of allyltrimcarbonyliron iodide with deactivated alumina

(a) In benzene: (h₃-C₃H₅)Fe(CO)₃I (0.21 g, 0.7 mmol) was stirred with deactivated alumina (10 g) in benzene (10 ml) for 1 min, by which time the color was mauve. An infrared spectrum was recorded of this solution, the remaining mauve solution was diluted (benzene, 10 ml) and the infrared spectrum was recorded once more. A further dilution (benzene, 20 ml) was performed and the mixture was allowed to stand until it had turned green (35 mins); a final infrared spectrum was recorded (see Figure 3-3).

(b) In THF: the above procedure was repeated using THF as the solvent. The same color changes were obtained within the same time periods; the reaction
was monitored by infrared spectroscopy (see Figure 3-3).

A mauve solution, prepared from \((\text{h}_3\text{-C}_3\text{H}_5)\text{Fe(CO)}_3\text{I}\) (0.41 g, 1.3 mmol) and deactivated alumina 20 g in THF (30 ml) was treated with dropwise addition of Diazald (0.29 g, 1.3 mmol) in THF (6 ml). Immediately the solution turned brown and an infrared spectrum of the reaction mixture showed the following bands, \(v_{\text{max}} 2040(\text{s}), 1977(\text{s}), \) and \(1756(\text{s}) \text{ cm}^{-1}\).

**Reaction of the mauve solution with Diazald**

Diazald (0.40 g, 1.9 mmol) in THF (8 ml) was added dropwise at 0°C, to a stirred, light-protected mauve solution which was prepared according to the above procedure from Yb (0.45 g, 2.6 mmol), and \((\text{h}_3\text{-C}_3\text{H}_5)\text{Fe(CO)}_3\text{I}\) (0.61 g, 2.0 mmol) in THF (16 ml). After stirring 5 min, the solution was concentrated to ca. 5 ml by solvent removal under reduced pressure. The remaining red solution was transferred to a neutral alumina chromatography column, which was eluted with pentane. The first red fraction was collected and separated by trap to trap distillation (15°C, -35°C, -78°C), under vacuum. A red solution collected in the -35°C trap, upon warming to room temperature the solid melted to a red oil. Infrared and n.m.r. measurements showed the oil to be \((\text{h}_3\text{-C}_3\text{H}_5)\text{Fe(CO)}_2\text{NO}\). N.m.r. \((\text{C}_6\text{H}_6), \tau 6.88 \ (d, J = 11 \text{ Hz}, 2 \text{ H}), 6.02 \ (d, J = 5.5 \text{ Hz}, 2 \text{ H}) \) and \(5.62 \ (m, 1 \text{ H})\). Infrared (pentane), \(v_{\text{max}} 2040, 1977 \) and \(1756 \text{ cm}^{-1}\) in the CO and NO region.

Yield: 0.16 g (37%).

**Reaction of the mauve solution with iodine.**

Solid iodine (0.14 g, 0.6 mmol) was added to a 5 ml aliquote of mauve solution prepared from Yb (0.47 g, 2.7 mmol) and \((\text{h}_3\text{-C}_3\text{H}_5)\text{Fe(CO)}_3\text{I}\)
(0.62 g, 2.0 mmol) in THF (17 ml). Immediately the solution turned brown. The infrared spectrum in the carbonyl region displayed only the bands at 2090s, 2040vs, and 2020sh cm$^{-1}$, characteristic of (h$_3$C$_3$H$_5$)Fe(CO)$_3$I.\textsuperscript{124}

Reaction of the mauve solution with triphenylphosphine

Ph$_3$P (2.60 g, 9.9 mmol) in THF (12 ml) was added dropwise to a stirred mauve solution prepared from Yb (0.53 g, 3.1 mmol) and (h$_3$C$_3$H$_5$)Fe(CO)$_3$I (0.60 g, 1.9 mmol) in THF (17 ml) by the method described above. Immediately the solution turned green-brown; after stirring at room temperature for 15 mins the solution was filtered. The solvent was removed from the filtrate under reduced pressure to yield a green solid. The solid was recrystallized from THF-hexane and then from toluene at -78°C. The green crystals were washed with hexane (5 ml) and were dried at room temperature under vacuum (10$^{-2}$ mm Hg). Yield 0.73 g.

The air-sensitive green solid is slightly soluble in CCl$_4$ and CH$_3$CN, but fairly soluble in benzene and CH$_2$Cl$_2$; infrared (CH$_2$Cl$_2$), $\nu_{\text{max}}$ 1960s and 1885s cm$^{-1}$; (Nujol) $\nu_{\text{max}}$ 1955s, 1875s(br,vs), 1440s, 1095m, 750m, 710m, 700s, and 640m. N.m.r. (C$_6$D$_6$), $\tau$ 2.82(m).m.pt.: 89°C (dec).

$^{57}$Fe Mossbauer (Figure 3-4): (solid at 77°K):

- Q.S.$\textsubscript{14}$, 2.64 mms$^{-1}$; I.S.$\textsubscript{14}$, -0.09 mms$^{-1}$;
- Q.S.$\textsubscript{23}$, 0.59 mms$^{-1}$; I.S.$\textsubscript{23}$, +0.12 mms$^{-1}$. I.S. quoted relative to Fe foil.

Anal: C, 60.13; H, 4.16; I, 11.27.

Reactions using cyclopentadienyldicarbonyliron halide

(h$_5$Cp)Fe(CO)$_2$I (1.54 g, 5.1 mmol) and Yb (1.05 g, 6.1 mmol) in THF (70 ml) were stirred at -5°C for 1 h, then allowed to warm to room temper-
ature. Solid Ph$_3$SnCl (1.8 g, 4.7 mmol) was added to the filtered solution, and stirring was continued for 1.5 h. The mixture was hydrolyzed with 50 ml aqueous NH$_4$Cl solution and was washed with aqueous NaCl solution (2 x 25 ml). The THF layer was dried over anhydrous MgSO$_4$ and the solvent was removed under reduced pressure. The remaining solid was extracted with CH$_2$Cl$_2$ (3 x 25 ml), filtered and hexane added to induce crystallization. The dark mauve crystals were recrystallized from CH$_2$Cl$_2$/hexane. The infrared spectrum and m.pt. (191 - 192, lit 194°C) were identical to those of [(h$_5$-Cp)Fe(CO)$_2$].$^{125}$ Yield 0.61 g (68%).

Similar results were obtained using (h$_5$-Cp)Fe(CO)$_2$Cl and ytterbium.

Other attempted reactions

Nitrosylation of the mauve solution using a dropwise addition of NOCl in THF was unsuccessful. Although the solution turned brown, the infrared spectrum revealed only the presence of (h$_3$-C$_3$H$_5$)Fe(CO)$_3$I. Several attempts were made to react Ph$_3$SnCl with the mauve solution; in each case a small quantity of a brown tarry solid was obtained, [infrared (hexane) $\nu_{\text{max}}$ 2050s, 1978s, and 1960s cm$^{-1}$; n.m.r. (CCl$_4$), $\tau$ 2.57 (m, 15 H), 7.31 (d, J = 5.0 Hz, 2 H)- and 7.90 (d, J = 12.2 Hz, 2 H)] and much unreacted Ph$_3$SnCl.
3.2c REACTIONS USING CYCLOPENTADIENYLTETRACARBONYLMOLYBDENUM DIMER AND YTTERBIUM METAL

(a) In the presence of 1,2-dibromoethane

Yb (0.42 g, 2.4 mmol) was stirred in a refluxing THF (30 ml) solution of [(h^5-Cp)Mo(CO)]_2 (0.700 g, 1.4 mmol) and (CH_2Br)_2 (0.25 ml, 2.7 mmol) for 26 h. The solution turned red-brown and an infrared spectrum of the filtered solution was recorded.

The red-brown solution was treated with the dropwise addition of Diazald (1.0 g, 4.7 mmol) in THF (10 ml) at room temperature. After stirring for 30 mins, the solvent was removed under reduced pressure and the remaining solid was sublimed at 50°C (10^-2 mm Hg). Orange crystals collected. The infrared spectrum and m.pt. (86 - 87°C). lit 85.2 - 85.7°C confirmed the formulation (h^5-Cp)Mo(CO)_2N.78 Yield 0.26 g (37%).

A similarly prepared solution from Yb, (CH_2Br)_2 and [(h^5-Cp)Mo(CO)]_2 in THF did not react with Ph_3SnCl at 60°C after 1 h, as evidenced by infrared spectroscopy.

(b) In the absence of 1,2-dibromoethane

Yb (0.54 g, 3.1 mmol) was stirred in a refluxing THF (30 ml) solution of [(h^5-Cp)Mo(CO)]_2 (0.960 g, 2.0 mmol) for 20 h. The solution turned brown, it was filtered and the infrared spectrum was recorded.

The brown solution was treated as follows:

(i) addition of iodine

Solid iodine (0.25 g, 1.0 mmol) was added to 5 ml of the above solution. After stirring at room temperature for 20 mins the solvent was
removed under reduced pressure. The remaining solid was twice recrystallized from CH$_2$Cl$_2$/C$_6$H$_{14}$ to yield a ruby red solid, whose infrared and n.m.r. spectra confirmed the assignment (h$_5$-Cp)Mo(CO)$_3$I. Yield 0.28 g (26%).

(ii) addition of H$_2$O

Introduction of H$_2$O (0.1 ml, 5.6 mmol) to the remainder of the above solution (8 ml) caused a dark brown jelly to form immediately. The solvent was removed under reduced pressure and the remaining solid was sublimed at 60°C (10^{-2} mm Hg). Light yellow crystals collected. The infrared and n.m.r. spectra and m.pt. (51 - 52°C, lit 50 - 52°C) were found to be identical to those of (h$_5$-Cp)Mo(CO)$_3$H. Yield 0.21 g (36%).
3.2d REACTIONS INVOLVING MERCURY COMPOUNDS AND YTTERBIUM METAL

(i) (Cyclopentadienyltricarbonylchromium)mercury chloride and ytterbium

\[ [(\text{h}_5^5\text{-Cp})\text{Cr(CO)}_3]_2\text{Hg} \ (0.51 \text{ g, 0.8 mmol}) \text{ and } \text{HgCl}_2 \ (0.22 \text{ g, 0.8 mmol}) \text{ were dissolved in THF (20 ml) and stirred for 30 min before the addition of Yb powder (0.39 g, 2.3 mmol)}. \text{ Immediately the solution turned green; within 10 min it was pink-brown and a grey deposit had formed. The mixture was filtered and the solvent was removed under reduced pressure to yield 0.6 g of pink-green solid. The filtered solid contained visible globules of a metallic liquid and gave a positive mercury spot test after digestion in \text{c.HNO}_3. \text{ A portion of the dried filtrate was sublimed at 110^\circ C 10^{-2} \text{ mm Hg to yield a small quantity of green-blue solid, whose infrared spectrum and m.pt. (164 dec, lit 163-168^\circ C dec) were identical to those of } [(\text{h}_5^5\text{-Cp})\text{Cr(CO)}_3]_2. \text{ The remaining dried filtrate was redissolved in THF (15 ml) and was treated with 0.37 g (1.0 mmol) solid Ph}_3\text{SnCl. The mixture was heated to 55^\circ C for 1 h; the solvent was removed under reduced pressure to yield a solid which was extracted with \text{CCl}_4 (5 \times 10 \text{ ml}) and filtered. Crystals formed as the solvent was removed slowly under reduced pressure. The m.pt. (215 - 217^\circ C, lit 219 - 221^\circ C) and infrared and n.m.r. spectra confirmed the assignment (h^5\text{-Cp})\text{Cr(CO)}_3\text{SnPh}_3. \text{ Yield 0.16 g.}} \]

(ii) Phenylmercuric chloride and ytterbium

\text{PhHgCl (0.65 g, 2.1 mmol) and Yb (0.52 g, 3.0 mmol) were stirred in THF for 2 days at room temperature. An air-stable grey solid was deposited and the mixture was filtered. The solvent was removed under reduced pressure from the filtrate to yield an air-stable white solid. The grey solid gave}
positive mercury and chloride spot tests and could not be extracted with CH₂Cl₂. The white solid was extracted with HCCl₃ (2 x 20 ml), these extracts were washed with water (2 x 20 ml), and the HCCl₃ was allowed to evaporate. Thin layer chromatography (silica gel) developed with 10% benzene-hexane) showed the resulting white solid to contain only one component. The white solid was sublimed at 120°C 10⁻¹ mm Hg. The white sublimate was found to have an m.pt. (123 - 4, lit 125°C), infrared and n.m.r. spectra consistent with the formulation Ph₂Hg. Furthermore, the sublimate showed a positive mercury spot test and a negative halide test. Yield 0.3 g (41%).
3.3 RESULTS

3.3a REACTIONS INVOLVING MANGANESE CARBONYLS

(1) Methods of preparing and factors affecting formation of the red solution

Method A: Metal + Mn(CO)\textsubscript{5}Br

We have found that certain lanthanide metals (Y, Pr, Sm, Dy, Ho, Er and Yb) and manganese react with Mn(CO)\textsubscript{5}Br in THF under ambient conditions to produce red, air- and moisture-sensitive solutions. Those lanthanides which are known to possess a stable +2 oxidation state, ytterbium and samarium, react more rapidly than the other metals. [In all probability, europium would react similarly or faster than ytterbium, but this metal is rather expensive and was not used.] Common to all the metals, however, is the increased reactivity associated with a smaller particle size and the need for good agitation of the reaction mixture. For the less reactive metals, careful filtration of the solution (as described in the experimental section, 3.2a) after one day's stirring is beneficial. Some dark, air-unstable solid is removed by this process, the metal surface becomes more reactive, and the reaction proceeds smoothly. Iodine, when added in trace amounts, is not an effective initiating agent, but concentration of the solutions by solvent removal under reduced pressure, is often helpful to avoid a sluggish reaction.

Other than the metals mentioned previously, lanthanum, gadolinium, tin and iron show some reaction with Mn(CO)\textsubscript{5}Br in THF at room temperature. Although the red solution does not develop, an infrared spectrum of the carbonyl-stretching region is identical for all four metals. In addition to bands which can be attributed to Mn(CO)\textsubscript{5}Br, the spectrum exhibits two lower
frequency absorptions at 1964m and 1930m cm\(^{-1}\). The lack of conversion to the red solution may be attributed to particle size in the cases of lanthanum and gadolinium which were only available as ingots.

Despite the experimental difficulties associated with this synthetic method, it is reproducible for the indicated metals, and since the reaction conditions involved are quite mild, it is the method of choice for a general preparation of the red solution. The other routes to this reactive solution have been less thoroughly investigated; they are described below.

**Method B: Metal + Mn\(_2\)(CO)\(_{10}\) + (CH\(_2\)Br)\(_2\)**

Both manganese and ytterbium produce the red solution when stirred in a refluxing THF solution of Mn\(_2\)(CO)\(_{10}\) and (CH\(_2\)Br)\(_2\) for at least 16 h.

**Method C: MnCl\(_2\) + Mn\(_2\)(CO)\(_{10}\)**

The red solution can be obtained by refluxing a THF solution of MnCl\(_2\) and Mn\(_2\)(CO)\(_{10}\) for three days. The extent of conversion, however, is not great. In contrast, YbCl\(_3\) does not react with Mn\(_2\)(CO)\(_{10}\), as evidenced by infrared spectroscopy, even after four days of stirring in a refluxing THF solution.

**Method D: MnCl\(_2\) + NaMn(CO)\(_5\)**

After stirring a 1:1 mixture of MnCl\(_2\) and NaMn(CO)\(_5\) in THF overnight, a solid precipitates and the solution turns red. This solution exhibits the characteristic bands in the carbonyl region of its infrared spectrum (see below). However, this spectrum also reveals that the solution generated in this manner contains a greater proportion of anionic (e.g. [Mn(CO)\(_5\)]\(^-\))
components than those prepared by the other synthetic methods. Stirring the solution for a longer period of time causes an intensity decrease of the infrared bands attributable to the anions and an increase of some of the higher frequency absorptions. If, on the other hand, the originally precipitated solid is removed, the remaining red solution deposits more solid within a matter of hours and the higher frequency bands increase in intensity at the expense of the lower frequency absorptions in the infrared spectrum. Similar spectral changes occur when the original red solution is diluted (Figure 3-1).

(2) Properties of the red solution

(a) Infrared spectrum

The following seven bands are observed in the carbonyl region of the infrared spectrum regardless of the mode of preparation of the red solution: (I) 2040, (II) 2005, (III) 1965, (IV) 1930, (V) 1885, (VI) 1850 and (VII) 1820 cm⁻¹. The relative intensities of the seven bands reflect the preparative route employed. For example, bands (V) and (VI), which are also observed in the infrared spectrum of NaMn(CO)₅, are initially quite intense for a red solution prepared by Method D, but they diminish in intensity with time and dilution (see Figure 3-1) as the simultaneous growth in bands (I), (III) and (IV) occurs. Band (II) is generally strong, whereas band (VII) is usually of medium intensity.

(b) Ultraviolet spectrum

A concentrated red solution prepared with Yb shows a weak band at 10,250 cm⁻¹ which can be attributed to a \(^{2}F_{7/2} \rightarrow ^{2}F_{5/2}\) transition\(^{13}\) and is
indicative of at least a part of the lanthanide being in a +3 oxidation state.

(c) **Ionic dissociation in solution**

Electrical conductivity measurements in THF at 25°C indicate that the red solutions are electrically conducting. Tables VI and VII show that the conductivity of the red solution, whatever its mode of preparation, is substantially greater than Mn(CO)₅Br or Mn₂(CO)₁₀. The extent of ionization is apparently not great since attempts to isolate any carbonyl anions with (Ph₃P)₂NCl are unsuccessful.

(d) **Electron spin resonance spectrum**

Preliminary e.s.r. data of the red solution derived from manganese are consistent with the presence of Mn²⁺ (i.e. the expected six-line spectrum is observed). However, as outlined above, dilution appears to affect the composition of the solution, and consequently care must be taken in interpreting these results.

(e) **The solid remaining after removal of THF**

A red-brown, air- and moisture-sensitive solid can be obtained by taking the red solution to dryness under reduced pressure and allowing the mixture to cool in the process. If Method A is used for the preparation of the red solution, the weight of the solid thus isolated is greater than that of the original Mn(CO)₅Br (e.g. by a factor of ~1.4 for samarium). Sublimation of the red-brown solid at 10⁻³ mm Hg and room temperature causes some Mn₂(CO)₁₀ to collect on the water-cooled probe. The solid which does not sublime exhibits a positive halide test and upon exposure to air it slowly
The red solution prepared by method D after 2 days

(a) Diluted 100% 
(b) Diluted a further 50% 
(c) Diluted a further 67% = solution A 
(d) Solution A left 24 hours

The solutions were stirred for a few hours after dilution of stages (b), (c) and (d), before the i.r. spectra were recorded.
TABLE VI
Conductivity Results for Manganese Carbonyl Reactions

<table>
<thead>
<tr>
<th>METHOD OF PREPARATION&lt;sup&gt;a&lt;/sup&gt;</th>
<th>METAL USED</th>
<th>INITIAL MOLAR (x10^-2) CONCN. &quot;Mn(CO)₅&quot;</th>
<th>MEASURED RESISTANCE R, Ω x 10&lt;sup&gt;3&lt;/sup&gt;</th>
<th>CALCULATED CONDUCTIVITY κ=K/R, ohm&lt;sup&gt;-1&lt;/sup&gt;cm&lt;sup&gt;-1&lt;/sup&gt; x 10&lt;sup&gt;-5&lt;/sup&gt;&lt;sup&gt;b&lt;/sup&gt;</th>
<th>TEMPERATURE °C</th>
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</thead>
<tbody>
<tr>
<td>A</td>
<td>Mn</td>
<td>4.4</td>
<td>34.0</td>
<td>2.98</td>
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<tr>
<td>A</td>
<td>Sm</td>
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<tr>
<td>B</td>
<td>Mn</td>
<td>4.6</td>
<td>23.0</td>
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<tr>
<td>D</td>
<td>-</td>
<td>4.5</td>
<td>2.90</td>
<td>35.0</td>
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<sup>a</sup> see section 3.2a

<sup>b</sup> K = 1.015 cm<sup>-1</sup>
<table>
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<tr>
<th>COMPOUND</th>
<th>MOLAR (x10^{-2}) CONCN. OF &quot;Mn(CO)_5&quot;</th>
<th>MEASURED RESISTANCE R, ohm x 10^3</th>
<th>CALCULATED CONDUCTIVITY ( \kappa = K/R ), ohm^{-1}cm^{-1}x 10^{-5}</th>
<th>TEMPERATURE °C</th>
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<tr>
<td>Mn(CO)_5Br</td>
<td>10.0</td>
<td>5.0 x 10^2</td>
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<td></td>
<td>4.1</td>
<td>6.0 x 10^2</td>
<td>1.69 x 10^{-1}</td>
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<td></td>
<td>1.7</td>
<td>11.2 x 10^2</td>
<td>9.07 x 10^{-2}</td>
<td>25</td>
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<tr>
<td>Mn_2(CO)_10</td>
<td>19.8</td>
<td>&gt; 25 x 10^2</td>
<td>&lt;&lt; 4 x 10^{-2}</td>
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<td></td>
<td>7.8</td>
<td>&gt; 25 x 10^2</td>
<td>&lt; 4 x 10^{-2}</td>
<td>25</td>
</tr>
<tr>
<td>NaMn(CO)_5</td>
<td>9.9</td>
<td>7.58 x 10^{-1}</td>
<td>1.34 x 10^2</td>
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<tr>
<td></td>
<td>6.6</td>
<td>12.25 x 10^{-1}</td>
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<td>4.11</td>
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<tr>
<td>THF</td>
<td>Neat</td>
<td>&gt; 25 x 10^2</td>
<td>4 x 10^{-2}</td>
<td>24</td>
</tr>
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</table>
turns yellow. More Mn₂(CO)₁₀ can then be sublimed from this oxidized species.

Metal analyses of the red-brown solid derived from red solutions prepared from lanthanide metals and Mn(CO)₅Br have so far been obstructed by mutual cross-interference of the metals during the analytical process. At room temperature, the red-brown solid is soluble in acetone, THF and CH₂Cl₂, although it decomposes within an hour in the last solvent. In N,N-dimethylacetamide, however, the solid dissolves upon warming with concomitant gas evolution.

(3) Reactions of the red solution

(a) Halide displacement reactions

Treatment of the red solution with Ph₃SnCl at 50°C for one h affords Ph₃SnMn(CO)₅ in up to 60% yield. In a similar manner, allyl chloride reacts smoothly with the red solution at room temperature overnight to produce a mixture of (h⁴-C₅H₅)Mn(CO)₅ and (h³-C₃H₅)Mn(CO)₄ in a ratio of 2.4:1. Methylation of the red solution by MeI, on the other hand, proceeds slowly and incompletely to give a low yield (≈ 10%) of MeMn(CO)₅ even after refluxing for 24 h.

A derivative containing the lanthanide metal may be isolated if the red solution, prepared using holmium, is treated with sodium acetylacetonate for two days at room temperature. After appropriate work up of the reaction mixture, a brown, air-sensitive solid, whose elemental analysis is consistent with the formulation [Mn(CO)₅]₂Ho(C₅H₇O₂)·2Et₂O is obtained. The mull infrared spectrum of this solid exhibits both metal carbonyl absorptions and the bands characteristic of the acetylacetonate ligand.
(b) Carbonyl substitution reactions

Addition of good Lewis bases such as 2,2'-bipyridyl and triphenylphosphine to the red solution at room temperature and in the absence of light produces fair yields of the substituted manganese carbonyls \([\text{Mn}(\text{CO})_4\text{L}]_2\) (\(\text{L} = \text{PPh}_3\) or 1/2(bipy)). [If manganese is used to prepare the red solution via Method A or B, \(\text{MnBr}_2\cdot2\text{bipy}\) can be isolated as a by-product of the bipy reaction.]

(c) Other reactions

The red solution reacts smoothly with Diazald at 0°C to produce \(\text{Mn}(\text{CO})_4\text{NO}\) in fair yield as evidenced by infrared spectroscopy. Reaction with benzoyl chloride at 65°C for two h does not lead to the expected acyl derivative of manganese pentacarbonyl, but cleavage of the THF solvent occurs instead. The major organic product of this latter reaction is \(\text{C}_6\text{H}_5\text{CO}_2(\text{CH}_2)_4\text{Cl}\) (48% yield) and the principal metal carbonyl entity is \(\text{Mn}_2(\text{CO})_{10}\) (55% yield).

Iodine reacts with the red solution to give low yields (< 5%) of \(\text{Mn}(\text{CO})_5\text{I}\) and \([\text{Mn}(\text{CO})_4\text{I}]_2\). The red solution does not react with CO, \(\text{H}_2\), \(\text{C}_5\text{H}_6\) or simple olefins under ambient conditions.
3.3b THE MAUVE SOLUTION FROM ALLYTRICARBONYLIRON IODIDE AND A METAL

(1) Preparation

An air- and moisture-sensitive mauve solution can be readily produced at room temperature within two hours by vigorously stirring ytterbium, yttrium, samarium, or manganese with \( \text{(h}^3\text{-C}_3\text{H}_5)\text{Fe(CO)}_3\text{I} \) in THF. Other metals have not been investigated. The mauve solution must be used as soon as the infrared spectrum indicates complete disappearance of the parent carbonyl (see below). If stirring is continued, the solution turns black eventually and a large quantity of precipitate forms. The black supernatant liquid still contains some metal carbonyl entities. However, upon solvent removal the small amount of solid that remains does not redissolve completely in common organic solvents.

(2) Infrared measurements

The formation of the mauve solution can be monitored by infrared spectroscopy (Figure 3-2). A THF solution of the parent carbonyl, \( \text{(h}^3\text{-C}_3\text{H}_5)\text{Fe(CO)}_3\text{I} \), displays only two bands in the carbonyl stretching region of the infrared spectrum: 2085s and 2030br,s cm\(^{-1}\). As the reaction proceeds the higher band diminishes, ultimately to zero absorbance when the solution is mauve and ready to be used. The lower band at 2030 cm\(^{-1}\) broadens and develops a shoulder at 1995 cm\(^{-1}\). Separation of these absorptions finally occurs to give two bands at 2050s and 1995br,s cm\(^{-1}\). Meanwhile, a new peak develops at 1950 cm\(^{-1}\). The final mauve solution has the following bands: 2050s, 1995br,s and 1950vs cm\(^{-1}\). Upon dilution these peaks change as follows (Figure 3-3): the 1950 band weakens; the 1995 absorption splits into one at
Figure 3-2  Formation of the mauve solution.

\[(h^3-C_3H_5)Fe(CO)_3I\] in THF = solution 1

Solution 1 + Yb

(a) after 50 mins.
(b) after 78 mins.
(c) after 136 mins.
(d) (mauve)
Figure 3-3  Dilution of the mauve solution

I. Prepared with Ytterbium in THF

[Graph showing spectra with labels (a), (b), (c)]

(a) Mauve solution
(b) Mauve solution diluted 100%
(c) Diluted a further 40%

II. Prepared with deactivated Alumina in Benzene

[Graph showing spectra with labels (a), (b), (c), (d)]

(a) Solution 1 + Alumina after 5 mins, mauve
(b) Mauve solution diluted 100% (5 min)
(c) Mauve solution diluted 100% (70 min)

III. Prepared from deactivated Alumina in THF

[Graph showing spectra with labels (a), (b), (c)]

(a) Solution 1 diluted 100%
(b) Solution 1 after 5 min = Solution 1
(c) Diluted a further 50%, (50 min)
1995, which increases in intensity relatively, and one at 2018 cm\(^{-1}\); the 2050 peak remains constant as the weakest band. The final solution has the following bands: 2050m, 2015m-s, 1995s and 1950s cm\(^{-1}\).

The formation of the radical-dimer equilibrium,

\[ 2 \left( \text{h}^3\text{C}_3\text{H}_5 \right) \text{Fe(CO)}_3 \rightleftharpoons \left[ \left( \text{h}^3\text{C}_3\text{H}_5 \right) \text{Fe(CO)}_3 \right]^2 \]

by dehalogenation of \((\text{h}^3\text{C}_3\text{H}_5)\text{Fe(CO)}_3\)I using deactivated alumina has been described previously.\(^{130}\) Using THF and benzene as solvents and the method above\(^{130}\) it is possible to study the effect of dilution on the infrared spectrum as outlined earlier (Figure 3-3). Regardless of the solvent, the characteristic mauve colour develops within 5 mins and the infrared spectrum has three bands at 2050s, 1995br,s and 1950vs cm\(^{-1}\). Dilution causes similar behaviour to that noted for the mauve solution prepared using ytterbium (Figure 3-3), namely diminishing intensity of the 1950 cm\(^{-1}\) band and splitting of that at 1995 cm\(^{-1}\). If the dilute solution is allowed to stand over the alumina for over one hour, the only remaining bands are those at 1995vs and 2015 cm\(^{-1}\) and the solution is a pale green colour.

Further, addition of Diazald to the mauve solution prepared from alumina and \((\text{h}^3\text{C}_3\text{H}_5)\text{Fe(CO)}_3\)I causes an immediate colour change; the resultant solution has an infrared spectrum identical to that of \((\text{h}^3\text{C}_3\text{H}_5)\text{Fe(CO)}_2\text{NO}\).

(3) Reactions

The mauve solution reacts smoothly under ambient conditions with Diazald to form \((\text{h}^3\text{C}_3\text{H}_5)\text{Fe(CO)}_2\text{NO}\) in 37% yield. Another feasible route to this compound, the action of NOCl upon the mauve solution, did not give any of the expected product according to the infrared spectrum.
The reaction with solid iodine to produce \( \left( \text{h}^3\text{-C}_3\text{H}_5 \right) \text{Fe(CO)}_3\text{I} \) is instantaneous and judging from the infrared spectrum, probably quantitative. After the addition of triphenylphosphine to the mauve solution, an air- and moisture-sensitive green solid can be isolated. To date this green solid has been incompletely characterised by infrared, \(^{57}\text{Fe Mossbauer}\), and n.m.r. spectroscopy and elemental analysis of the carbon, hydrogen and iodine content. The n.m.r. data show only phenyl proton resonances, however, other protons present may not have been detected because the solid is not very soluble in \( \text{d}^6\)-benzene. The \(^{57}\text{Fe Mossbauer}\) spectrum (Figure 3-4) is complex with four peaks; this result indicates that there are at least two iron sites, which are equally populated. The broadness of peak 3 may be caused by decomposition of the sample or alternatively it may result from a third iron site in the compound. Repeated attempts to isolate a product from the reaction of the mauve solution with \( \text{Ph}_3\text{SnCl} \) yield only a small quantity of a tarry brown solid, whose infrared spectrum shows three bands in the metal carbonyl region and whose n.m.r. spectrum displays phenyl proton and two higher field doublet resonances.

By comparison, the halides, \( \left( \text{h}^5\text{-Cp} \right) \text{Fe(CO)}_2\text{X} \) (\( \text{X} = \text{Cl} \) or \( \text{I} \)), react with ytterbium to produce \( \left[ \left( \text{h}^5\text{-Cp} \right) \text{Fe(CO)}_2 \right]_2 \) in ca. 70% yield. Addition of \( \text{Ph}_3\text{SnCl} \) to the reaction solution does not produce any \( \left( \text{h}^5\text{-Cp} \right) \text{(CO)}_2\text{Fe-SnPh}_3 \).
Figure 3-4  Mössbauer Spectrum of green solid from mauve solution and Triphenylphosphine.
3.3c CYCLOPENTADIENYLTRICARBONYLMOLYBDENUM DIMER REACTIONS

Ytterbium reacts with \([(h^5\text{-Cp})\text{Mo(CO)}_3]\)_2 in THF either in the presence or absence of (CH$_2$Br)$_2$ to produce two reactive solutions, whose infrared spectra differ in the studied range 2100 - 1500 cm$^{-1}$. The solution prepared using (CH$_2$Br)$_2$ shows bands attributable to the parent carbonyl plus the following: $\nu_{\text{max}}$ 2025sh, 1925sh, 1875sh, 1850m, and 1585m cm$^{-1}$. If (CH$_2$Br)$_2$ is not employed the resulting brown solution has a completely new infrared spectrum in comparison to \([(h^5\text{-Cp})\text{Mo(CO)}_3]\)_2, namely: $\nu_{\text{max}}$ 2025m, 1925sh, 1910s, 1815vs, 1790sh, 1745m, 1675br,s, and 1580m cm$^{-1}$.

The species prepared in the presence of (CH$_2$Br)$_2$ reacts with Diazald to form the corresponding nitrosyl \((h^5\text{-Cp})\text{Mo(CO)}_2\text{NO}\) (37% yield), but attempts to form a Sn-Mo bond with Ph$_3$SnCl are not successful. On the other hand, the brown solution prepared in the absence of (CH$_2$Br)$_2$ reacts smoothly with iodine and water to form \((h^5\text{-Cp})\text{Mo(CO)}_3\text{I}\) and \((h^5\text{-Cp})\text{Mo(CO)}_3\text{H}\) respectively, in fair yields.
3.3d **REACTIONS WITH MERCURY COMPOUNDS**

Ytterbium displaces mercury from \((\text{h}^5\text{-Cp})\text{Cr(CO)}_3\text{HgCl}\) to generate a reactive mixture, one of whose minor components can be identified as \([\text{(h}^5\text{-Cp})\text{Cr(CO)}_3\text{]}_2\). An infrared spectrum (Nujol mull) of the reactive solution, after solvent removal, displays the following peaks: \(v_{\text{max}}\) 2010s, 1935sh, 1925s, 1905s, 1808s, 1678s, 1664s, 1010m, 862m, 710m, 656m, and 620m cm\(^{-1}\). The reactive solution combines smoothly at 55°C with \(\text{Ph}_3\text{SnCl}\) to yield \(\text{Ph}_3\text{Sn-Cr(h}^5\text{-Cp})(\text{CO})_3\).

The analogous reaction using \(\text{PhHgCl}\) with ytterbium produces only \(\text{Ph}_2\text{Hg}\) in 41% yield.
3.4 DISCUSSION

3.4a REACTIONS INVOLVING MANGANESE CARBONYLS

The red solution resulting from the activation of Mn(CO)$_5$Br by elemental metals in THF (as well as from other synthetic routes) exhibits a variety of interesting physical and chemical properties. It undergoes halide displacement reactions to produce the derivatives RMn(CO)$_5$ (R = Ph$_3$Sn, Me or C$_3$H$_5$), but it does so less efficiently than the sodium salt, Na[Mn(CO)$_5$] in terms of yields and reaction conditions.\textsuperscript{116,118}

It is worth noting that according to Dessy et al.\textsuperscript{131} the yields of reactions to form metal-metal bonds from anions appear to be dependent upon the counter cation. Specifically, in the formation of (CO)$_5$Mn-SnPh$_3$ from Na[Mn(CO)$_5$] an 81% yield is obtained,\textsuperscript{116} whereas using (C$_4$H$_9$)$_4$N[Mn(CO)$_5$] the yield is only 30 - 40%.\textsuperscript{131}

On the other hand, the red solution permits the preparation of the carbonyl-substituted compounds [Mn(CO)$_4$L]$_2$ (L = PPh$_3$ or 1/2(2,2'-bipyridyl)) under much milder experimental conditions than those previously employed. For example, it has been reported that [Mn(CO)$_4$PPh$_3$]$_2$ can be prepared from Mn$_2$(CO)$_{10}$ and PPh$_3$ by either ultraviolet irradiation of a cyclohexane solution for twelve hours or by heating both in a sealed tube for four hours at 130°C.\textsuperscript{120} Similar forcing conditions are necessary for the preparation of the 2,2'-bipyridyl-substituted product.\textsuperscript{115}

The unexpected product, C$_6$H$_5$CO$_2$(CH$_2$)$_4$Cl, and the unusually high yield of Mn$_2$(CO)$_{10}$ isolated from the reaction with benzoyl chloride are intriguing in that they give an indication of species possibly present in the red solution. Two mechanisms have been proposed for similar reactions. The
first proposal involves the cleavage of the solvent (diethyl ether) by 'C₆H₅MgBr' in the presence of benzoyl chloride and cobaltous chloride to produce many products including the ester, ethyl benzoate.¹³² This result can be rationalized in terms of the free radical mechanism summarized below:

\[
\begin{align*}
C₆H₅MgBr + MCl_x & \rightarrow C₆H₅MCl_{x-1} + MgCl \hspace{1cm} \text{[M = Co and x = 2 in the particular reaction being considered.]} \\
2 C₆H₅MCl_{x-1} & \rightarrow C₆H₅-C₆H₅ + 2\cdot MCl_{x-1} \\
C₆H₅COCl + MCl_{x-1} & \rightarrow C₆H₅CO^+ + MCl_x \\
C₆H₅CO^+ + (C₂H₅)₂O & \rightarrow C₆H₅CO₂C₂H₅ + C₂H₅.
\end{align*}
\]

By comparison, 'C₆H₅YbI' reacts with C₆H₅COCl in THF in the absence of other metal halides to produce n-propylbenzoate as a by-product.¹¹⁰ It is, therefore, conceivable that a free radical mechanism involving a lower halide of the lanthanide plays a role in the reaction of the red solution with benzoyl chloride. Possible supporting evidence for this view is the substantial yield of Mn₂(CO)₁₀ which could result from radical coupling of -Mn(CO)₅ units.

Ethers can also be cleaved by acyl chlorides in the presence of a Lewis acid to produce esters.¹³³ The suggested mechanism is an ionic one, involving the benzoyl cation as shown below:

\[
\begin{align*}
R'COCl + LA & \rightarrow R'CO^+ + LACl^- \\
R-O + R'CO^+ & \rightarrow R-O-C-R' \\
R^+O-C-R' + LACl^- & \rightarrow RC1 + LA + R-O-C-R'.
\end{align*}
\]

[LA = Lewis acid.]
If such a mechanism were operative during the reaction of the red solution with benzoyl chloride, then cleavage of the cyclic ether (THF) would lead to $C_6H_5CO_2(CH_2)_4Cl$, the identified organic product. Moreover, the Lewis acidity of the lanthanide elements in an organic environment has been established (eg. see Chapter II). Obviously, the exact nature of the lanthanide in the red solution is presently not known with certainty; however, formation of the potentially acidic halides $LnX_2$ or $LnX_3$ from $Mn(CO)_5X$ and $Ln$ could also explain the production of $Mn_2(CO)_{10}$.

Some other work which may be relevant to this ether cleavage reaction involves the species $R_3MMgX$ ($R$ = aryl or alkyl group; $M$ = Si or Ge; $X$ = Cl or Br). Although these compounds have never been isolated there is strong evidence from coupling, hydrolysis, and carbonation reactions to confirm their postulated formula. They also undergo cleavage reactions with THF to produce $R_3M(CH_2)_4OH$. This alcohol is not the analogous product to our benzoyl chloride reaction, but it does illustrate the ability of this general class of reagent to cleave THF. However, the capability of ether cleavage may be more related to the coordinative power of magnesium (or ytterbium) than to the nature of the $R$ group in $"RMgX"$. Some support for this last viewpoint is that $Ph_3GeLi$ only affords a 23% yield of $Ph_3Ge(CH_2)_4OH$, whereas "$Ph_3GeMgCl"$ produces an 83% yield of the same compound under similar conditions.

The red solution is readily nitrosylated with Diazald to give $Mn(CO)_4NO$. Diazald has previously been employed for the conversion of $[Mn(CO)_5]^-$ or $HMn(CO)_5$ to the isoelectronic carbonylnitrosyl. The infrared spectrum of the red solution exhibits strong absorptions characteristic of $[Mn(CO)_5]^-$ (ie. 1885 and 1850 cm$^{-1}$) but not of $HMn(CO)_5$. Nitrosylation of
the red solution, therefore, presumably occurs via the anionic species.

The infrared spectrum of the red THF solution in the carbonyl-stretching region shows seven bands of which six are strong at one concentration or another. The large number of bands, their variance in intensity with dilution and the coincidence of some of the absorptions with those exhibited by [Mn(CO)₅]⁻ suggest that a number of carbonyl-containing species are present in the red solution. It can be noted that red solutions of manganese carbonyl complexes in THF have been prepared by utilizing irradiation techniques, but the entities present in these solution have been assigned the compositions \(-\text{Mn(CO)}\)\textsubscript{5}\textsuperscript{135} and \([\text{H}_2\text{Mn}_3\text{(CO)}\text{\textsubscript{12}}]\)\textsuperscript{136}, neither of which has an infrared spectrum similar to the one prepared here.

Another possible explanation concerning the nature of the red solution is a manganese carbonyl anion-hydride equilibrium, with the hydride formed perhaps by proton abstraction from the solvent. Hieber et al.\textsuperscript{115} has shown that \(\text{Mn}_2\text{(CO)}\text{\textsubscript{9}}\text{H}_2\) can react with chlorinated solvents under ultraviolet irradiation to produce \(\text{Mn(CO)}\text{\textsubscript{5}}\text{Cl}\) and \([\text{Mn(CO)}\text{\textsubscript{4}}\text{Cl}_2]\), and under unspecified conditions with 2,2'-bipyridyl to form \(\text{Mn}_2\text{(CO)}\text{\textsubscript{9}}\text{(bipy)}\). Moreover, the preparation of \([\text{Mn}_2\text{(CO)}\text{\textsubscript{9}}]\)\textsuperscript{2⁻} from \(\text{Mn}_2\text{(CO)}\text{\textsubscript{10}}\) and \(\text{NaBH}_4\) also generates \([\text{Mn(CO)}\text{\textsubscript{5}}]\)\textsuperscript{⁻} in approximately equal amounts. We have repeated Hieber's work and found that the mixture of anions is red, but has no infrared absorptions above 1900 cm\textsuperscript{-1}. Those peaks below 1900 cm\textsuperscript{-1} are identical to bands observed for the red solution. Acidification of Hieber's anionic mixture permits ultimate isolation of \(\text{Mn}_2\text{(CO)}\text{\textsubscript{9}}\text{H}_2\) whose infrared spectrum in THF shows bands at 2050s, 2035ms, 1995s, and 1960m-s cm\textsuperscript{-1}. The positions and relative intensities of these bands do not match those of the red solution at the equivalent or any other concentration, nor does the infrared spectrum\textsuperscript{138} of \(\text{Mn(CO)}\text{\textsubscript{5}}\text{H}\) give a better fit.
The pertinent question is whether or not a metal carbonyl hydride can exist in the presence of lanthanide metals without metallation occurring. The answer is not yet known, but it seems unlikely that our solution contains a hydride, although the presence of both anions, $[\text{Mn(CO)}_5]^{-}$ and $[\text{Mn}_2(\text{CO})_9]^{2-}$, is a possibility.

The ultraviolet spectrum of the ytterbium-containing red solution indicates that some of the lanthanide is present in the trivalent state. However, 'RYbI' solutions in which the metal is formally divalent display magnetic properties indicative of the presence of some Yb$^{3+}$. Consequently, the existence of Yb$^{2+}$ in the red solution cannot be ruled out. A compound containing the trivalent lanthanide can be isolated after treatment of the holmium-containing red solution with sodium acetylacetonate. This compound, whose elemental analysis is consistent with the formulation $[\text{Mn(CO)}_5]_2\text{Ho(C}_5\text{H}_7\text{O}_2)_2\text{Et}_2\text{O}$, exhibits an infrared spectrum in the carbonyl region unlike that of other complexes which are known to possess metal-Mn(CO)$_5$ interactions either through direct metal-metal bonds or isocarbonyl linkages.

If manganese is used as the activating metal, the e.s.r. spectrum of the red solution and the products of its reaction with 2,2'-bipyridyl (e.g. MnBr$_2$·2 bipy) strongly suggest the presence of Mn$^{2+}$.

In summary, the fact that the red solution can be prepared in a variety of ways, the fact that it undergoes a number of diverse reactions, and the fact that it displays an infrared spectrum rich in carbonyl bands suggest that the red solution consists of a mixture of complexes. The physical properties and some of the reactions undergone by the red solution suggest the presence of an anionic component, possibly $[\text{Mn(CO)}_5]^{-}$. Moreover, other reaction products such as $[\text{Mn(CO)}_4\text{PPh}_3]_2$ imply the existence of a binuclear manganese carbonyl entity which readily undergoes substitution of the carbonyl.
ligands and is, therefore, unlikely to be anionic in nature.\textsuperscript{139} Such a binuclear species, which could give rise to the higher frequency absorptions in the infrared spectrum, may be a radical although reaction of the red solution with iodine gives only low yields of Mn\textsubscript{2}(CO)\textsubscript{8}I\textsubscript{2}. 
3.4b REACTIONS INVOLVING ALLYLTRICARBONYLIRON IODIDE

The mauve solution prepared from \((\text{h}^3\text{-C}_3\text{H}_5)\text{Fe(CO)}_3\text{I}\) and any of the metals, ytterbium, samarium, yttrium or manganese appears to contain the equilibrium mixture:

\[2(\text{h}^3\text{-C}_3\text{H}_5)\text{Fe(CO)}_3 \rightleftharpoons [(\text{h}^3\text{-C}_3\text{H}_5)\text{Fe(CO)}_3]^2\]

The reasons for arriving at this conclusion are based upon comparative infrared measurements on an authentic sample of the monomer-dimer equilibrium mixture and the mauve solution; the similar reaction of this sample and the mauve solution with Diazald; the short lived nature of the mauve solution under an inert atmosphere; the effect of iodine upon the mauve solution; and a comparison with the products obtained from the reaction of the analogous \((\text{h}^5\text{-Cp})\text{Fe(CO)}_2\text{X}\) \((\text{X} = \text{Cl} \text{ or } \text{I})\) compounds with ytterbium.

Each of these points will be considered in order. The mauve solution prepared using ytterbium has the same three carbonyl absorptions in the infrared spectrum as the solution prepared using alumina according to Murdoch (Figure 3-3), namely, 2050, 1995, and 1950 cm\(^{-1}\). The behaviour upon dilution is similar (Figure 3-3), that is, appearance and growth of a band at 2015 cm\(^{-1}\), whilst the 1950 cm\(^{-1}\) absorption diminishes and a concomitant increase in intensity of the 1995 cm\(^{-1}\) peak occurs. The bands due to the monomeric radical are presumably observed at 2015 and 1995 cm\(^{-1}\); it then leaves those at 2050 and 1950 cm\(^{-1}\) to be assigned to the dimer. The results of the infrared dilution studies of the mauve solution are identical, regardless of the solvent or method of preparation used. Although these results agree qualitatively with those of Murdoch, there is some discrepancy regarding exact band positions and assignments. Murdoch's work was carried out in an unspecified hydrocarbon solvent and this may account for the difference in the
(h$_3$-C$_3$H$_5$)Fe(CO)$_2$NO can be obtained from the mauve solution prepared from alumina or ytterbium and treated with Diazald. This result is interesting because Diazald is known to react with metal carbonyl hydrides$^{78}$ and metal carbonyl anions$^{93}$ (section 2-2) to produce the corresponding isoelectronic nitrosyls. It now appears that this reagent also reacts with metal carbonyl radicals. The mauve solution does not react with NOCl, although NOCl has been observed to form nitrosyls with metal carbonyl anions such as [Mn(CO)$_5$]$^\cdot$$^{140}$

This indication, plus the fact that the anion [(h$_3$-C$_3$H$_5$)Fe(CO)$_3$]$^-$ gives a different infrared spectrum$^{141}$ in THF solution (ie. 1910 and 1855 cm$^{-1}$) from the mauve solution, strongly suggests that there is no anion present in the mauve solution.

The mauve solution prepared from ytterbium does not retain its colour beyond three hours, after which time it darkens with accompanying solid deposition. This behaviour is consistent with the presence of a free radical which may be undergoing reaction with the solvent or other species in solution.

According to the infrared spectrum, the addition of iodine to the mauve solution quantitatively regenerates (h$_3$-C$_3$H$_5$)Fe(CO)$_3$I, again this is identical to the behaviour Murdoch observed for the (h$_3$-C$_3$H$_5$)Fe(CO)$_3$ radical.$^{130}$

Finally, the corresponding iron halides (h$_5$-Cp)Fe(CO)$_2$X (X = Cl or I) react with ytterbium to form the dimer [(h$_5$-Cp)Fe(CO)$_2$]$_2$ for which the analogous monomer dimer equilibrium presumably is not known because the radical, if it exists in solution, is very short lived. Hence the allyl system is anomalous since a stable free radical can be formed in this case. The function of ytterbium is the same in both instances, to abstract halogens.
On the basis of this accumulated evidence the active component in the mauve solution is assigned to the free radical \((\text{h}_3^3\text{C}_3\text{H}_5)\text{Fe(CO)}_3\).

In reactions involving \(\text{Ph}_3\text{SnCl}\) and the mauve solution limited evidence for a new product consists of the infrared and n.m.r. spectra, recorded on the very small quantity of impure material obtained. By comparison with the changes in the carbonyl region of the infrared spectrum for the conversion of \((\text{h}^5\text{-Cp})\text{Mo(CO)}_3\text{I}\) to \((\text{h}^5\text{-Cp})\text{Mo(CO)}_3\text{SnPh}_3\), the spectrum obtained from the mauve solution reaction is qualitatively similar: a shift to lower wave numbers of the three observed bands by about 40 cm\(^{-1}\) is observed in both instances. The n.m.r. spectrum displays a strong signal in the phenyl proton region and two doublets at higher field. Normally a \(\pi\)-bonded allyl group shows three resonances in the n.m.r. spectrum, two doublets, each of intensity equivalent to two protons, and a multiplet at lower field, equivalent in intensity to one proton. It is conceivable that the lower field multiplet, arising from the sole proton of the central carbon atom of the allyl group, was not observed because the sample was not sufficiently concentrated. The two observed higher field doublets have coupling constants of the same order of magnitude as those reported for \((\text{h}^3\text{-C}_3\text{H}_5)\text{Fe(CO)}_2\text{NO}\) and \((\text{h}^3\text{-C}_3\text{H}_5)\text{Fe(CO)}_3\text{I}\). These two physical measurements are consistent with the formulation \((\text{h}^3\text{-C}_3\text{H}_5)\text{(CO)}_3\text{Fe-SnPh}_3\), however, the assignment and existence of this compound are only tentatively suggested. Interestingly, the reaction of the anion \([[(\text{h}^3\text{-C}_3\text{H}_5)\text{Fe(CO)}_3]]^-\) with \(\text{Ph}_3\text{SnCl}\) does not produce the Sn-Fe bonded compound, but instead \(\text{Ph}_6\text{Sn}_2\) is formed in 87% yield. Other attempts to replace bromine in \((\text{h}^3\text{-C}_3\text{H}_5)\text{Fe(CO)}_3\text{Br}\) by transition-metal-containing anions, such as \([\text{Mn(CO)}_5]^-\) and \([[(\text{h}^5\text{-Cp})\text{Fe(CO)}_2]]^-\), have only led to the establishment of the aforementioned equilibrium,
(ie. $2 \text{(h}_3\text{-C}_3\text{H}_5\text{)}\text{Fe(CO)}_3 \rightleftharpoons [(\text{h}_3\text{-C}_3\text{H}_5\text{)}\text{Fe(CO)}_3]_2$) and not to the desired metal-metal bonded products.

The product obtained from the action of Ph$_3$P upon the mauve solution is somewhat puzzling. For the analogous reaction of Ph$_3$P with the equilibrium mixture of $(\text{h}_3\text{-C}_3\text{H}_5\text{)}\text{Fe(CO)}_3$ and its dimer, Murdoch$^{130}$ obtained a compound for which he reported only infrared and e.s.r. spectral data: the benzene solution infrared spectrum of the carbonyl region had two bands at 1956 and 1893 cm$^{-1}$; the e.s.r. signal recorded for the Nujol solution of the compound displayed a doublet (17.1 gauss separation) attributed to $^{31}$P hyperfine splitting. Murdoch interpreted the e.s.r. result to mean that only one Ph$_3$P group was present in the radical and taken in conjunction with the infrared spectrum that there was no doubt the species was the radical $(\text{h}_3\text{-C}_3\text{H}_5\text{)}\text{Fe(CO)}_2\text{PPh}_3$. In contrast, the compound prepared here has similar infrared spectral values for the carbonyl stretching frequencies (1960 and 1885 cm$^{-1}$ (CH$_2$Cl$_2$), 1955 and 1875 cm$^{-1}$ (Nujol), but elemental analyses reveal a substantial presence of iodine and an n.m.r. spectrum displays no paramagnetic broadening of its only resonance situated in the usual position for phenyl protons. Even if the solution used to record the n.m.r. spectrum was too dilute to reveal the allyl group protons, the species is not $(\text{h}_3\text{-C}_3\text{H}_5\text{)}\text{Fe(CO)}_2\text{PPh}_3\text{I}$, which is a different colour, brown, and has different infrared carbonyl bands at 1965 and 2015 cm$^{-1}$, (HCCl$_3$ as solvent).$^{143}$ The elemental analyses can best be fitted by the formulation Fe$_2$(CO)$_5$(PPh$_3$)$_2$I (calc C, 60.7; H, 3.90; I, 10.90. Found: C, 60.13; H, 4.16, I, 11.27).

Mössbauer ($^{57}\text{Fe}$) measurements are similar to quadrupole splitting and isomer shift values for monomeric iron carbonyls containing Ph$_3$P$^{149}$ (eg. Fe(CO)$_4$PPh$_3$, Q.S.: 2.54 mms$^{-1}$, I.S. Fe: -0.088 mms$^{-1}$, and Fe(CO)$_3$(PPh$_3$)$_2$, Q.S.: 2.76 mms$^{-1}$, I.S. Fe: -0.098 mms$^{-1}$) or iodine$^{149}$ (eg. Fe(CO)$_4$I$_2$, Q.S.: 0.38 mms$^{-1}$, I.S. Fe: +0.14 mms$^{-1}$). The quadrupole splittings for monomeric iron carbonyls contain-
ing an allyl group are generally quite different from those of the compound isolated here (eg. \( \text{(H}_3\text{C}_3\text{H}_5)\text{Fe(CO)}_2\text{PPh}_3\text{Br} \), Q.S.: 1.60 mm/s\(^{-1}\), I.S.\(_\text{Fe}\): +0.19 mm/s\(^{-1}\)) and \((\text{H}_3\text{C}_3\text{H}_5)\text{Fe(CO)}_3\text{Br} \), Q.S.: 1.50 mm/s\(^{-1}\), I.S.\(_\text{Fe}\): +0.10 mm/s\(^{-1}\)).

Amongst dimeric iron carbonyls, \((\text{OC})_4\text{Fe(PMe}_2)_2\text{Fe(CO)}_4 \) and \((\text{OC})_3\text{Fe(PMe}_2)_2\text{Fe(CO)}_3 \) have similar parameters (Q.S.: 2.58 mm/s\(^{-1}\), I.S.\(_\text{Fe}\): -0.032 mm/s\(^{-1}\)) and Q.S.: 0.685 mm/s\(^{-1}\), I.S.\(_\text{Fe}\): -0.043 mm/s\(^{-1}\)) respectively) to those of the newly prepared species, whereas \(\text{I(OC)}_3\text{Fe(PMe}_2)_2\text{Fe(CO)}_3\text{I} \) (Q.S.: 0.99 mm/s\(^{-1}\), I.S.\(_\text{Fe}\): -0.001 mm/s\(^{-1}\)) has somewhat different values. The compound prepared here may have one iron site which is five coordinate because the quadrupole splitting of lines 1 and 4 is of the right magnitude, that is ca. 2.5 mm/s\(^{-1}\). Furthermore, the n.m.r. evidence taken in conjunction with the Mossbauer spectrum suggests the absence of an allyl group. Finally, the infrared spectrum indicates only terminal carbonyl absorptions, which leaves one to speculate upon the existence of an iron-iron bond or iodine bridges, since there are at least two iron sites in the compound.
3.4c REACTIONS INVOLVING CYCLOPENTADIENYLTRICARBONYLMOLYBDENUM DIMER

The reactive species prepared from \([\text{(}h^5\text{-Cp})\text{Mo(CO)}_3\text{)]_2\) and ytterbium in the absence of \((\text{CH}_2\text{Br})_2\) displays an infrared spectrum in THF reminiscent of that of \(\text{Al}[\text{(}h^5\text{-Cp})\text{W(CO)}_3\text{)]_3\cdot3\text{THF}\) (section 2.1). The large number of bands in the range 2100 - 1500 cm\(^{-1}\) strongly suggests isocarbonyl bonding. Furthermore, the ready reaction with water or iodine is characteristic of the anion \([\text{(}h^5\text{-Cp})\text{MoCO}_3\text{]}^-\), a property also found for the above mentioned aluminium complex. It should not be overlooked, however, that iodine reacts instantly with \([\text{(}h^5\text{-Cp})\text{Mo(CO)}_3\text{]}_2\) in HCCl\(_3\) to produce the corresponding iodide in 20 - 70% yield.\(^{144}\) It is conceivable, therefore, that any unreacted dimer would also combine with iodine to yield \((\text{h}^5\text{-Cp})\text{Mo(CO)}_3\text{I}\). A comparison with the infrared spectra of the molybdenum dimer, however, shows the presence of this compound to be negligible in the reactive mixture.

The infrared spectrum of the red-brown solution prepared from ytterbium and \([\text{(}h^5\text{-Cp})\text{Mo(CO)}_3\text{]}_2\) in the presence of \((\text{CH}_2\text{Br})_2\) shows an absorption at 1585 cm\(^{-1}\) and a new band at 1850 cm\(^{-1}\), whilst the rest of the carbonyl region bears a strong resemblance to the parent dimer. It is possible that the band at 1585 cm\(^{-1}\), is caused by either an isocarbonyl link or by a multiply-bridging carbonyl resulting from metal-cluster formation. A review of the known molybdenum carbonyl cluster compounds, however, reveals no similar infrared band.

The conversion of the red-brown solution to \((\text{h}^5\text{-Cp})\text{Mo(CO)}_2\text{NO}\) with Diazald, together with the lower frequency carbonyl bands suggest some anionic or radical character of the \((\text{h}^5\text{-Cp})\text{Mo(CO)}_3\) group.

Furthermore, the lack of reaction of the red-brown solution with Ph\(_3\)SnCl is not surprising, because the corresponding magnesium compound pre-
pared by Burlitch did not react either. The exact reason for the lack of reactivity by \([h^5\text{-Cp} \text{Mo(CO)}_3]^−\) towards \(\text{Ph}_3\text{SnCl}\) is not known. The nucleophilicity of \([\text{Mn(CO)}_5]^−\) is similar to that of \([h^5\text{-Cp} \text{Mo(CO)}_3]^−\), as measured by the rate of displacement of iodide from methyl iodide, and so it might be expected that the two anions would react similarly. A more salient point could be the change in coordination number in forming the neutral species: from five to six for \([\text{Mn(CO)}_5]^−\) and from six to seven for \([h^5\text{-Cp} \text{Mo(CO)}_3]^−\). Presumably, octahedral geometry is preferred and hence \([\text{Mn(CO)}_5]^−\) reacts whilst \([h^5\text{-Cp} \text{Mo(CO)}_3]^−\) does not (see below for further comment).

\[\text{Assuming } (h^5\text{-Cp}) \text{ occupies three coordination sites.}\]
3.4d REACTIONS INVOLVING MERCURY COMPOUNDS

The two preliminary results involving ytterbium with RHgCl species (R = Ph and \((h^5\text{-Cp})\text{Cr(CO)}_3\)) indicate that it is possible to generate a reactive anionic organometallic ligand, whereas the purely organic "R" group prefers to be attached to mercury. These results probably reflect the stability of the two anions "R" in THF.

Interestingly, chromium has a much lower nucleophilicity than molybdenum in the anions \([(h^5\text{-Cp})M(CO)_3]^{-}\) (M = Cr or Mo), according to Dessy et al.\(^91\) By using the mercury salt method, however, it is possible to obtain \(\text{Ph}_3\text{Sn-Cr(h}^5\text{-Cp})(\text{CO})_3\). An explanation of this result might be that a more anionic species is generated by the mercury route. Evidence for this conclusion is the mull infrared spectrum of the reactive chromium solution taken to dryness: the many strong carbonyl stretching frequencies in the region 1600 - 2050 cm\(^{-1}\) suggest an isocarbonyl anion (Chapter II). The attempts to prepare a Sn-Mo bond were made using the solution prepared using \((\text{CH}_2\text{Br})_2\) and the infrared spectrum of this solution did not show as many strong bands in the range 1600 - 1850 cm\(^{-1}\), suggesting less anionic character than the chromium counterpart.

As the work progressed, our aim shifted slightly from a desire to isolate an \(\text{RM}^{II}X\) species to investigating the synthetic utility of the reactive solutions we could generate. It was for this reason that we were interested in the generality of synthesis of the red manganese carbonyl solution and in turn it led us to begin using other metals as starting materials.

Finally, it is obviously necessary to perform further experiments to determine the nature of the synthetically versatile, red manganese solu-
tion; to ascertain the changes in oxidation state of the metals during its formation, and to discover how these results relate to the data that we have obtained by utilizing other metal carbonyl and organometallic complexes as precursors.
CHAPTER IV

CONCLUDING REMARKS

It would not be amiss to make a few general comments in order to place these studies in the context of what is known and to indicate where these results might lead. The specific conclusions, which are to be found within each chapter, will not be reiterated.

The object of these investigations was to gain some insight into the chemistry of the rare earth elements in organic media. The first part of the project demonstrated that a wide range of substrates were receptive to some form of interaction with the Lewis acids $R_3Ln$ ($R = \text{MeCp or Cp}$). The establishment of isocarbonyl linkages between neutral as well as anionic bases and a lanthanide has helped to determine the generality of this recently discovered bonding mode for the carbonyl ligand. Furthermore, it was shown that the Lewis acidity of $R_3Ln$ could be used to form isonitrosyl or metal-lanthanide bonds (ie. with $(h^5-\text{Cp})\text{WH}_2$) and also to support the involvement of organolanthanides in the trimerization of PhC≡CH. In each of these cases no definitive evidence existed regarding the role of the rare earth. Clearly further studies of the isolated complexes using other physical techniques, such as x-ray diffraction, would be useful.

The results obtained from the reactions employing elemental metals indicate that this is an area worthy of more detailed study. It is conceivable that synthetically versatile reagents could be developed from this preparative route. In addition, the exact nature of these solutions requires considerable further examination, in particular by spectral methods.

One aim of these studies was to isolate a compound containing a lanthanide-transition metal bond. In spite of using various approaches, this
end has not been achieved. Often the rare earth appeared to prefer to form isocarbonyl bonds, whereas in other cases the lanthanide acted as a halogen abstractor.

Although the possibilities of forming new organolanthanides may be limited, the role of rare earths in organometallic chemistry should not be viewed similarly. These investigations have shown that the properties of organolanthanides and the metals themselves can produce a wide range of effects.
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APPENDIX

The Determination of Lanthanides in Organometallic Complexes
by the Closed Oxygen Flask Method

INTRODUCTION

The work reported in this appendix is almost entirely that of Mr. P. Borda. It has been included, however, for two reasons. The development of this analytical technique was essential to characterize several solids that were isolated, hence the nature of the problems involved in the project are more fully displayed. Secondly, this information is vital for other workers entering this field.

The quantitative determination of the lanthanide content in organometallic compounds becomes a necessity for those species whose characterization by common physical techniques is hampered by various factors. The total or very poor solubility of organolanthanides is the major reason that prompted this work. Since all organolanthanides are air- and moisture-sensitive to varying degrees, the customary procedures involved in metal estimation, the dry combustion of a sample in oxygen to the corresponding metal oxide or the wet degradation of the sample by an appropriate acid medium in a Kjeldahl flask, become extremely cumbersome. Moreover, the dry combustion technique is totally inapplicable if metals other than the rare earths are also present in the compound to be analyzed. It was, therefore, necessary to develop a method of lanthanide determination which can be carried out simply, accurately and rapidly if the analytical sample is initially decomposed by means of the oxygen flask.
Since 1955 considerable attention has been focused on the analysis of non-metals by Schöninger's oxygen flask method. However, despite its apparent utility for the analogous determination of metals, this combustion technique has only been infrequently employed during the estimation of both main group (eg. Mg, Ca, Ba and Sn) and transition metals (eg. Zn, Cd, Hg, Mn and Co). Furthermore, the metal-containing species which were studied were primarily air-stable coordination compounds. True organometallic complexes (ie. those containing direct metal-carbon bonds) have largely been neglected. The present studies represent the first extensive application of the oxygen-flask technique during the analysis of a class of these latter compounds.

Accounts of the basic principles, methods and problems of metal analysis by the Schöninger method have been published.
EXPERIMENTAL MATERIALS AND METHODS

Reagents and Apparatus

All reagents used were of analytical grade or comparable purity. The titrations were carried out with either a Gilmont micrometer burette (Cole-Parmer catalog number 7876) having a 2.5000 ml capacity and capable of measuring to 0.0001 ml, or a Mettler E457 micrometer burette having a 5.000 ml capacity and capable of measuring to 0.001 ml, as required. The hydrogen-ion concentration in the various solutions was monitored by an Orion model 801 digital pH meter.

Procedure

Since all of the compounds examined were sensitive in differing degrees to both air and moisture, all manipulations of the solid species prior to combustion were performed in a glove bag filled with prepurified nitrogen. Analytical samples were prepared by placing 5-10 mg of the organo-lanthanide derivative into pre-weighed adhesive cellulose containers fitted with a filter paper lining. The containers were then sealed and their weight was determined either by the procedure outlined by Pickhardt and co-workers, or by direct weighing in the nitrogen atmosphere on a Cahn electronic balance. The samples were then ignited in a 500-ml oxygen flask charged with 10 ml of either 1N HCl or 1N HNO₃ as the absorbent solution. After combustion was complete, the flask was shaken thoroughly for ten minutes, and then the stopper and platinum gauze were rinsed with distilled water. During this operation it was noted that the solubilities of the lanthanide residues in the absorbent solutions diminished as the atomic weight of the metal increased. Thus, for
example, the La, Sm and Gd oxides readily dissolved in the acid solution whereas the corresponding Dy, Er and Yb species required gentle heating to effect complete dissolution. Once the metal oxides were dissolved, the contents of the oxygen flask were then washed into a 150 ml beaker, the total volume of the solution at this stage being approximately 50 ml.

The most rapid and simple means of final determination involved the titrimetric evaluation of the lanthanides with 0.01 N or 0.005 N EDTA. Two types of titration environments were utilized and the end points of the titrations were ascertained by the three methods outlined below.

A. A basic medium with Eriochrome Black T as indicator

The hydrochloric acid absorbent solution was neutralized at room temperature with 1N NH₄OH, with sodium tartrate being added at pH 6 to prevent precipitation of hydroxide derivatives of the metals. An appropriate NH₄Cl-NH₄OH buffer solution was next introduced to maintain the pH of the solution in the optimum range of 8.3 - 8.6. The solution was then heated to ~80°C, and was titrated directly at this temperature in the presence of Eriochrome Black T. Throughout this titration, stringent adherence to a specified pH range (narrower than that previously reported for analogous determinations^3), was found to be mandatory because the indicator was very sensitive to changes in the hydrogen-ion concentration, especially when small amounts of metals such as ytterbium were being titrated. For example, at pH 8.8 the end points were attained very slowly and the recoveries of the heavier lanthanides were never quantitative. Below pH 8.3, on the other hand, the color change of the indicator near the end point was very poor.
B. An acidic medium with Xylenol Orange as indicator

The pH of the hydrochloric acid absorbent solution was adjusted to approximately 4 with 1N \( \text{NH}_4\text{OH} \). While the solution was gently warmed, an appropriate \( \text{CH}_3\text{COONa} - \text{CH}_3\text{COOH} \) buffer was added to maintain the pH of the solution in the range 4.8 - 5.5. This environment was found to be the most satisfactory of all for obtaining good end points in the direct titration of the warm solution with Xylenol Orange as indicator. If the pH was allowed to increase above 5.8, not only were repeated false end points prematurely observed, but also the reddish tint of the indicator itself obscured the desired color change at the true end point. Our findings thus substantiated recent reports [cf. 5] that the true working pH range of Xylenol Orange in such complexometric titrations is actually lower than had been claimed previously\(^6\).

C. An acidic medium with the end point being detected potentiometrically

One normal nitric acid was used as the absorption medium during the initial combustion. The pH of the final absorbent solution was adjusted to 4.3 - 5.0 with 1N NaOH. Then 5 ml of an acetate buffer (pH 4.8) and four drops of a \( 10^{-3} \) M solution of the mercury-EDTA complex were added. The resultant solution was heated to 80\(^\circ\)C and was titrated while hot with EDTA, the end point being detected potentiometrically with a mercury electrode\(^10,11\). A calomel electrode filled with a saturated solution of KNO\(_3\) was employed as a reference.

No difficulties were experienced with this method and all titrations were easily performed. Moreover, the presence of chlorine in the organo-
lanthanide sample did not interfere with the mercury indicator electrode. Hence, because of its general applicability, especially when very small (<1 mg) amounts of metal were to be determined, and less rigorous experimental conditions, this procedure eventually became the method of choice.

The closed oxygen flask technique was also successfully utilized during the analysis of more complex organometallic compounds. For instance, the compounds which contained both tungsten and a lanthanide were initially burned in the usual manner. The absorbent solution was then simply boiled, the tungstic acid was removed from the hot solution by filtration, and the lanthanide content of the filtrate was determined by one of the methods described previously.
RESULTS AND DISCUSSION

Good precision end points were obtained with all the methods of final determination as shown by the representative data displayed in the Table.

The results indicate that the closed oxygen flask method provides a general means of decomposing very reactive compounds which contain direct metal-carbon bonds. Moreover, the flask method expedites the desired metal analyses in those cases for which a rapid final method of determination is known or can be developed. In this connection it should be noted that when small amounts (ie. 1-3 mg) of metals are being analyzed, conditions different from those employed for larger-scale determinations may be required. For example, these studies reveal that for the use of Eriochrome Black T as an indicator in lanthanide-EDTA titrations, the hydrogen-ion concentration range in which the indicator-metal complex is not too inert and the protonated form of the indicator does not interfere is, unexpectedly, quite small when micro-determinations of metal are performed.

Certainly the closed oxygen flask method is invaluable as the first step during analysis of the lanthanide content of all types of organolanthanide complexes.
## TABLE

Analysis of Various Organolanthanide Complexes

<table>
<thead>
<tr>
<th>Compound</th>
<th>% Lanthanide</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Theoretical</td>
<td>Found</td>
</tr>
<tr>
<td>Tris(cyclopentadienyl)lanthanum, (C\textsubscript{5}H\textsubscript{5})\textsubscript{3}La</td>
<td>41.56</td>
<td>41.47</td>
</tr>
<tr>
<td>Tris(cyclopentadienyl)samarium, (C\textsubscript{5}H\textsubscript{5})\textsubscript{3}Sm</td>
<td>43.51</td>
<td>43.21</td>
</tr>
<tr>
<td>Tris(methylcyclopentadienyl)samarium\textsuperscript{b}, (C\textsubscript{6}H\textsubscript{7})\textsubscript{3}Sm</td>
<td>38.79</td>
<td>38.64</td>
</tr>
<tr>
<td>Tris(methylcyclopentadienyl)gadolinium, (C\textsubscript{6}H\textsubscript{7})\textsubscript{3}Gd</td>
<td>39.84</td>
<td>39.81</td>
</tr>
<tr>
<td>Tris(methylcyclopentadienyl)dysprosium, (C\textsubscript{6}H\textsubscript{7})\textsubscript{3}Dy</td>
<td>40.64</td>
<td>40.69</td>
</tr>
<tr>
<td>Tris(cyclopentadienyl)erbium, (C\textsubscript{5}H\textsubscript{5})\textsubscript{3}Er</td>
<td>46.12</td>
<td>46.34</td>
</tr>
<tr>
<td>Bis(cyclopentadienyl)erbium chloride, (C\textsubscript{5}H\textsubscript{5})\textsubscript{2}ErCl</td>
<td>50.23</td>
<td>50.47</td>
</tr>
<tr>
<td>Bis(cyclopentadienyl)ytterbium chloride\textsuperscript{a}, (C\textsubscript{5}H\textsubscript{5})\textsubscript{2}YbCl</td>
<td>51.08</td>
<td>51.31</td>
</tr>
<tr>
<td>Tricarbonyltris(cyclopentadienyl)erbiumtungsten\textsuperscript{b} (C\textsubscript{5}H\textsubscript{5})\textsubscript{2}ErW(C\textsubscript{5}H\textsubscript{5})(CO)\textsubscript{3}</td>
<td>26.54</td>
<td>26.42</td>
</tr>
<tr>
<td>Tricarbonyltris(cyclopentadienyl)tungstenytterbium\textsuperscript{a} (C\textsubscript{5}H\textsubscript{5})\textsubscript{2}YbW(C\textsubscript{5}H\textsubscript{5})(CO)\textsubscript{3}</td>
<td>27.20</td>
<td>27.04</td>
</tr>
</tbody>
</table>

\textsuperscript{a} Determined by Method A;

\textsuperscript{b} Determined by Method B;

All others determined by Method C.
APPENDIX REFERENCES