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Anita Palepu, MD, MPH

Co-editor , Open Medicine

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Division of Internal Medicine

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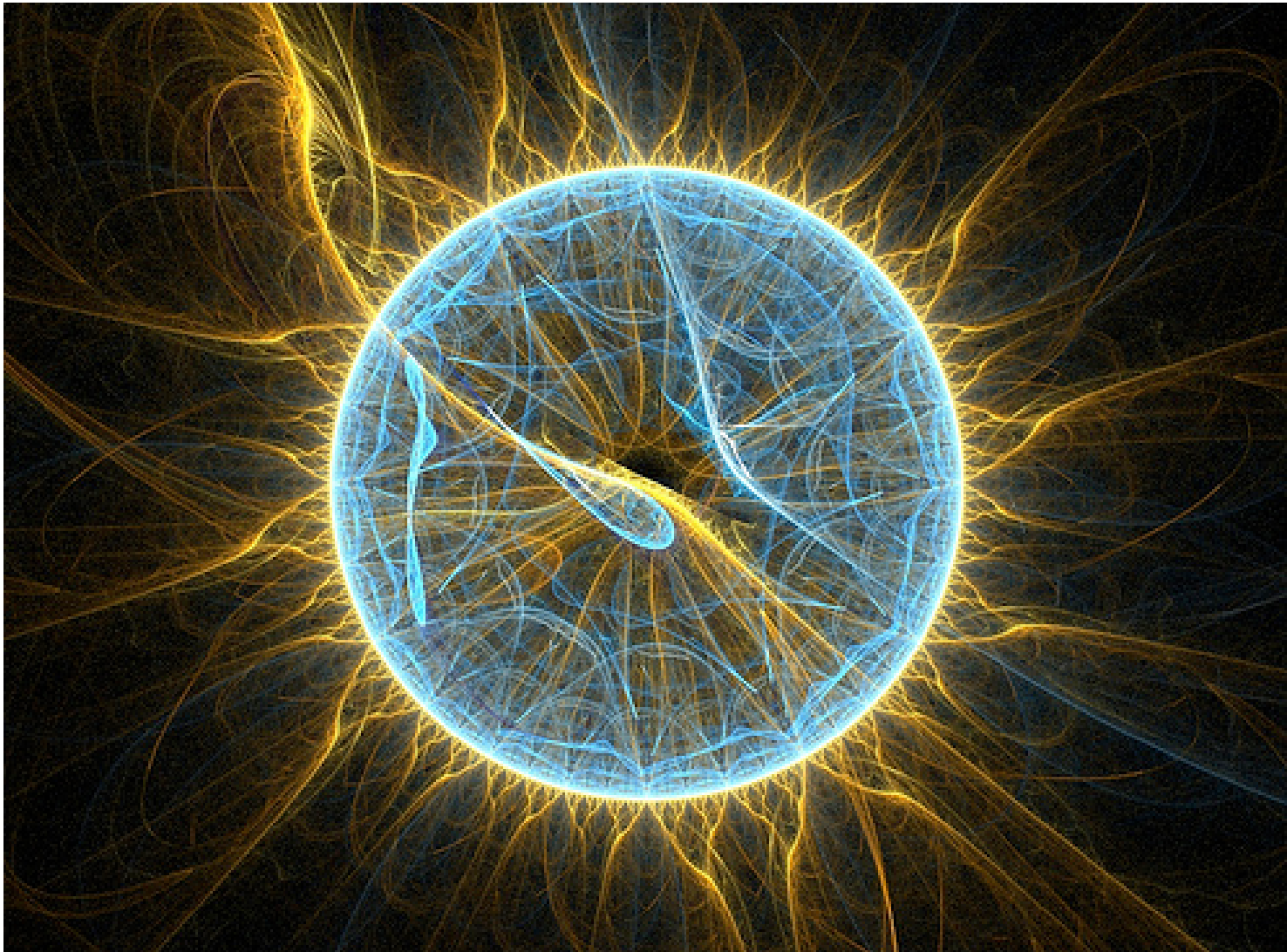
Open Medicine Roadmap

- Where we came from
- What we are
- Our impact
- Our future

Acknowledgement

- Claire Kendall, Deputy Editor, OM
- Dean Giustini, UBC Health Librarian and OM Blogger
- MJ Suhonos, Sage Advisor, Public Knowledge Project

Where did we come from?



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Open Medicine

What is Open Medicine?

- Peer-reviewed, independent, open-access general medical journal
- Examines issues relevant to health and clinical medicine both in Canada and internationally

What is Open Medicine?

- Collaborative team
- Unique venture
- *A new model* of scholarly publishing

What is Open Medicine?



Open Medicine

What is Open Medicine?

- Collaborative team
- Unique venture
- *A new model* of scholarly publishing

Unique venture: Two key drivers

1. Editorial independence

2. The internet changes everything

Unique venture

The internet changes everything

- Cheap
- Fast
- Global
- Search and retrieval

What is Open Medicine?

- Collaborative team
- Unique venture
- *A new model of scholarly publishing*

A new model - 4 principles

- Freedom
- Transparency
- Creativity
- Community

Freedom

Our goal is to make Open
Medicine itself a publicly
available resource

Freedom

PKP

PUBLIC
KNOWLEDGE
PROJECT

Open Medicine

Freedom

Open Journal Systems

- Open source Journal management and publishing system
- Goal to expand and improve access to research
- Active participant in the development of ideas and code

Freedom

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Freedom





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“If you have an apple and I have an apple and we exchange these apples then you and I will have each one apple. But if you have an idea and I have an idea and we exchange these ideas, then each of us have two ideas.”

George Bernard Shaw

Quinone-Annulated N-Heterocyclic Carbene–Transition-Metal Complexes:
Observation of π -Backbonding Using FT-IR Spectroscopy and Cyclic Voltammetry

Matthew D. Sanderson, Justin W. Kamplain, and Christopher W. Bielawski*

Department of Chemistry and Biochemistry, The University of Texas at Austin, Austin, Texas 78712

Received October 19, 2006; E-mail: bielawski@cm.utexas.edu

Since Arduengo's seminal isolation of 1,3-diadamantyl-imidazolidene,¹ N-heterocyclic carbenes² (NHCs) have found extraordinary utility for modulating the activities of transition metals³ and as versatile catalysts for promoting organic reactions.⁴ We have recently launched a program that utilizes NHCs as building blocks for organometallic polymers, with an emphasis on tuning the electronic interactions between NHCs and their ligated transition metals.⁵

The complexation of NHCs to transition metals is strongly governed by σ -donation from the carbene to the metal center. π -Backbonding from the metal to the p-orbital of the carbene has historically been considered to be negligible owing to competing π -overlap of the electron-rich N atoms adjacent to the carbene.^{6,7} However, recent theoretical analyses and synthetic advances have challenged this view. By corroborating computational models with key bond distances and angles observed in select ranges of metal–NHC X-ray crystal structures, Light, Meyer, Frenking, and Jacobsen concluded that π -backbonding contributes up to 30% of the overall bonding character.⁸ However, Heinicke⁹ demonstrated that metal complexes formed with carbo- and heterocyclic annulated NHCs did not adhere to these models. As a result, the nature of the NHC–metal interaction, including the existence of π -backbonding, remains controversial.¹⁰

The discrepancies between the aforementioned studies can be traced to challenges associated with separating σ - and π -contributions in NHC–metal complexes. An NHC featuring a functional group in conjugation with the carbene atom and sensitive to π -effects would be ideal for identifying π -backbonding in its respective metal complexes. We envisioned this could be accomplished by fusing a *p*-quinone moiety to the 4,5-positions of an imidazolidene. With two carbonyl groups formally conjugated to the p-orbital at the carbene atom, a quinone-annulated NHC was anticipated to offer three distinct advantages for studying metal–NHC interactions: (1) Carbonyl stretching frequencies are sensitive to minute electronic changes in π -systems and can be conveniently measured using IR spectroscopy.¹¹ (2) The electron-withdrawing nature of the quinone should result in increased propensities for π -backbonding upon ligation to a transition metal. (3) *p*-Quinones exhibit reduction potentials that are sensitive to subtle electronic changes on their peripheries.¹² Collectively, this enables the use of IR spectroscopy and cyclic voltammetry to observe structural and electronic changes, including deconvoluting σ - versus π -effects, on the NHC ligand upon complexation. Herein, we report the synthesis of the first NHC annulated to a quinone and present evidence for π -backbonding in its respective transition-metal complexes.

Imidazolium salt **1** was synthesized in 74% isolated yield by reacting commercially available 2,3-dichloro-1,4-naphthoquinone with *N,N*-dimethylformamide under mildly basic conditions (Scheme 1).¹³ A signal assigned to the iminium proton was found at 12.8 ppm in the ¹H NMR spectrum (CDCl₃). To the best of our knowledge, this is the largest downfield shift reported for any known imidazolium compound and reflects the highly electron-withdrawing nature of the quinone moiety. Free carbene **2** was obtained in 73%

yield by deprotonating **1** with sodium hydride (facilitated by adding a catalytic amount of potassium *tert*-butoxide). NHC **2** exhibited a signal at 232 ppm in the ¹³C NMR spectrum (C₆D₆), which was similar to known benzimidazolidenes and other annulated carbenes.⁹ Combined with the ¹H NMR data for **1**, this result highlights the subtleties in using NMR spectroscopy to isolate σ - from π -effects in NHCs. To confirm the molecular structure of **2**, a crystal was obtained by slowly cooling a hot, saturated toluene solution and analyzed using X-ray diffraction analysis. The molecular structure of **2** revealed a planar ring system, relatively long N–C bond lengths (1.392(8) Å), and a narrow N–C–N bond angle (102.1°)¹⁴ which suggested that the π -system of the quinone moiety was effectively conjugated to the carbene.

Scheme 1. Synthesis of an NHC Annulated to a Quinone and its Rh Complexes

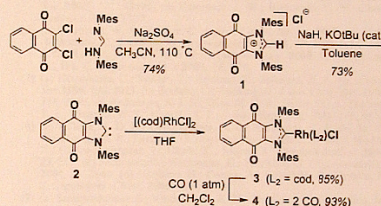


Table 1. Summary of Selected Physical Data for Compounds 1–5

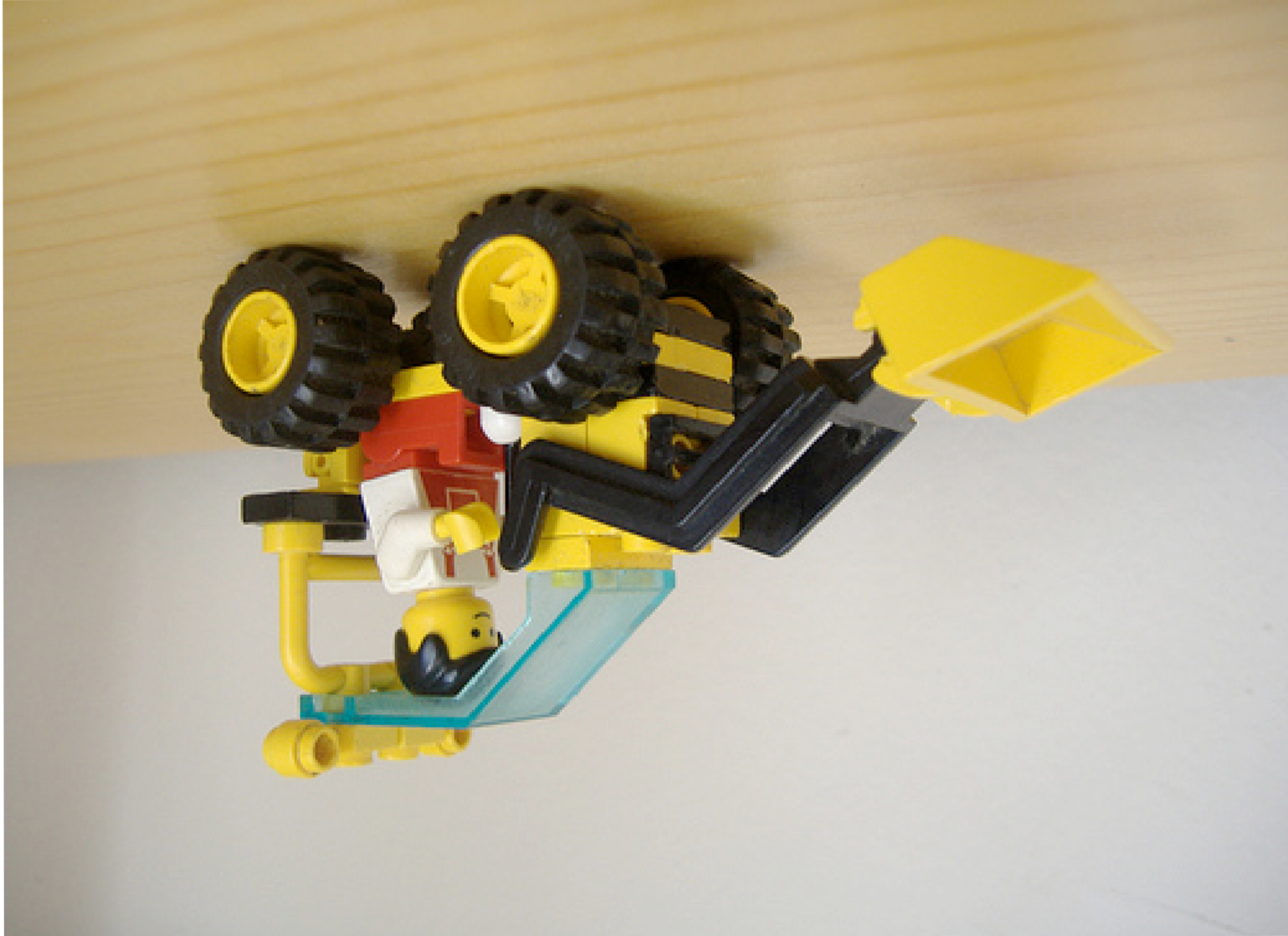
compd	¹³ C (ppm) ^a	N–C (Å) ^b	C=O (cm ^{−1}) ^c	E _{1/2} (V) ^d
1	142	1.336(2)	1685 (1690)	−0.24
2	232	1.392(8)	1671 (°)	e
3	200	1.379(6)	1670 (1675)	−0.55
4	191	e	1680 (1680)	−0.49
5	193	1.352(4)	1681 (1683)	−0.49

^a Chemical shift of the carbene atom found in its respective ¹³C NMR spectrum (C₆D₆). ^b Distance between the carbene atom and adjoining nitrogen atom. For **2**, the data reflects the longer N–C bond; the shorter N–C bond = 1.385(8) Å. All other compounds showed symmetric N–C bond lengths. ^c Carbonyl stretching frequencies were determined using IR spectroscopy for compounds in the solid-state (KBr); parenthetical values were determined for compounds in solution (CHCl₃). Values are ± 1 cm^{−1}.

^d First reduction potentials as determined using cyclic voltammetry in CH₃CN, 1 mM analyte, 0.1 M (Bu₄N)(PF₆) as electrolyte, referenced to Fc^{+/0}/Fc (1 mM) at 507 mV vs Ag/AgCl/KCl (saturated) electrode; scan rate = 0.2 V s^{−1}. Values are ± 0.01 V. ^e Not evaluated.

After isolation and characterization of **2**, its utility in the synthesis of organometallic complexes was investigated. With the goal of evaluating π -backbonding characteristics in mind, a metal complex was needed with ancillary ligands that were exchangeable without disrupting other physical characteristics of the complex (oxidation state, geometry, coordination number, etc.). In particular, we desired a system where a ligand with relatively little π -backbonding capability (e.g., an olefin) could be substituted with a ligand that is highly capable (e.g., carbon monoxide). Ancillary ligand exchange







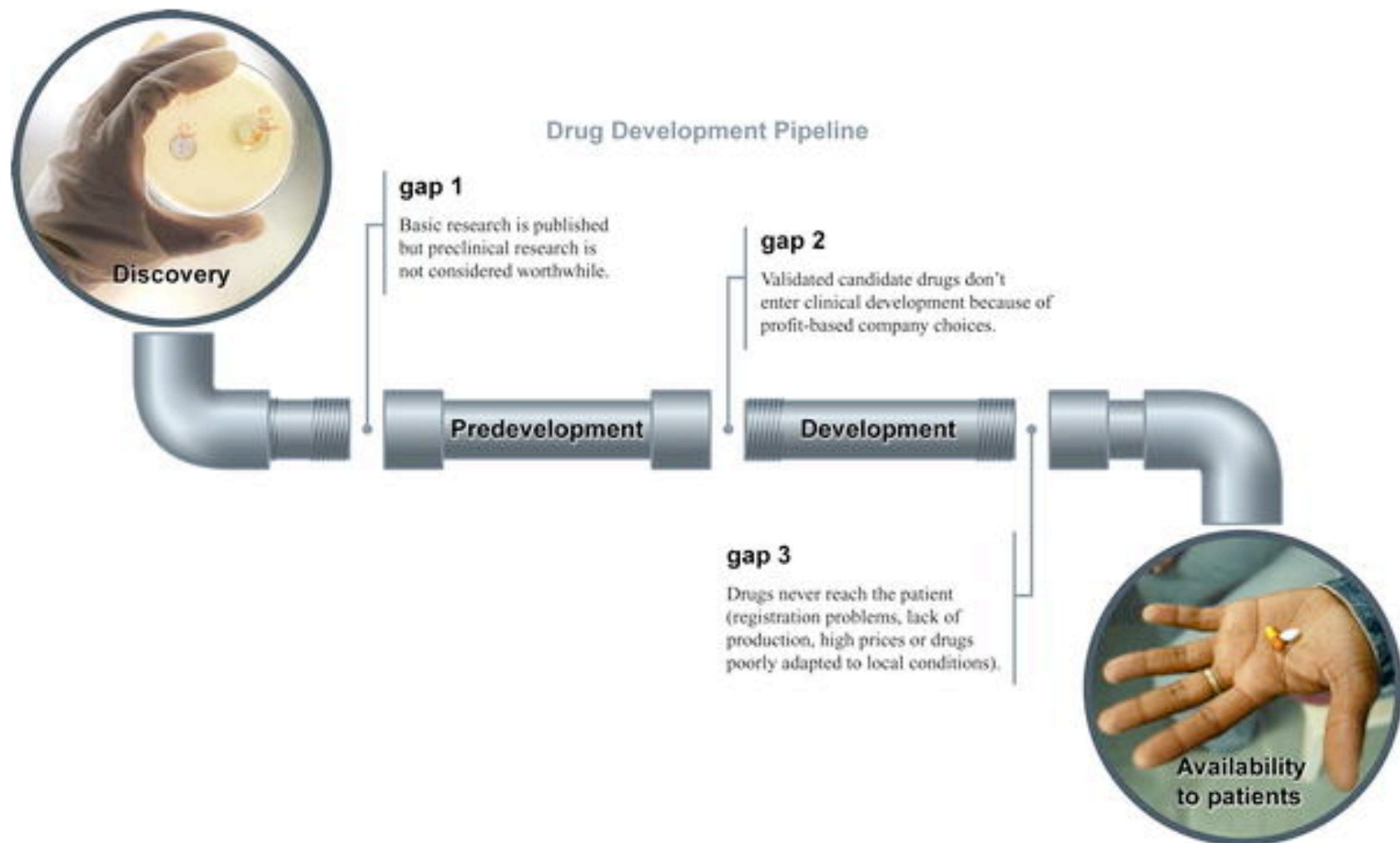


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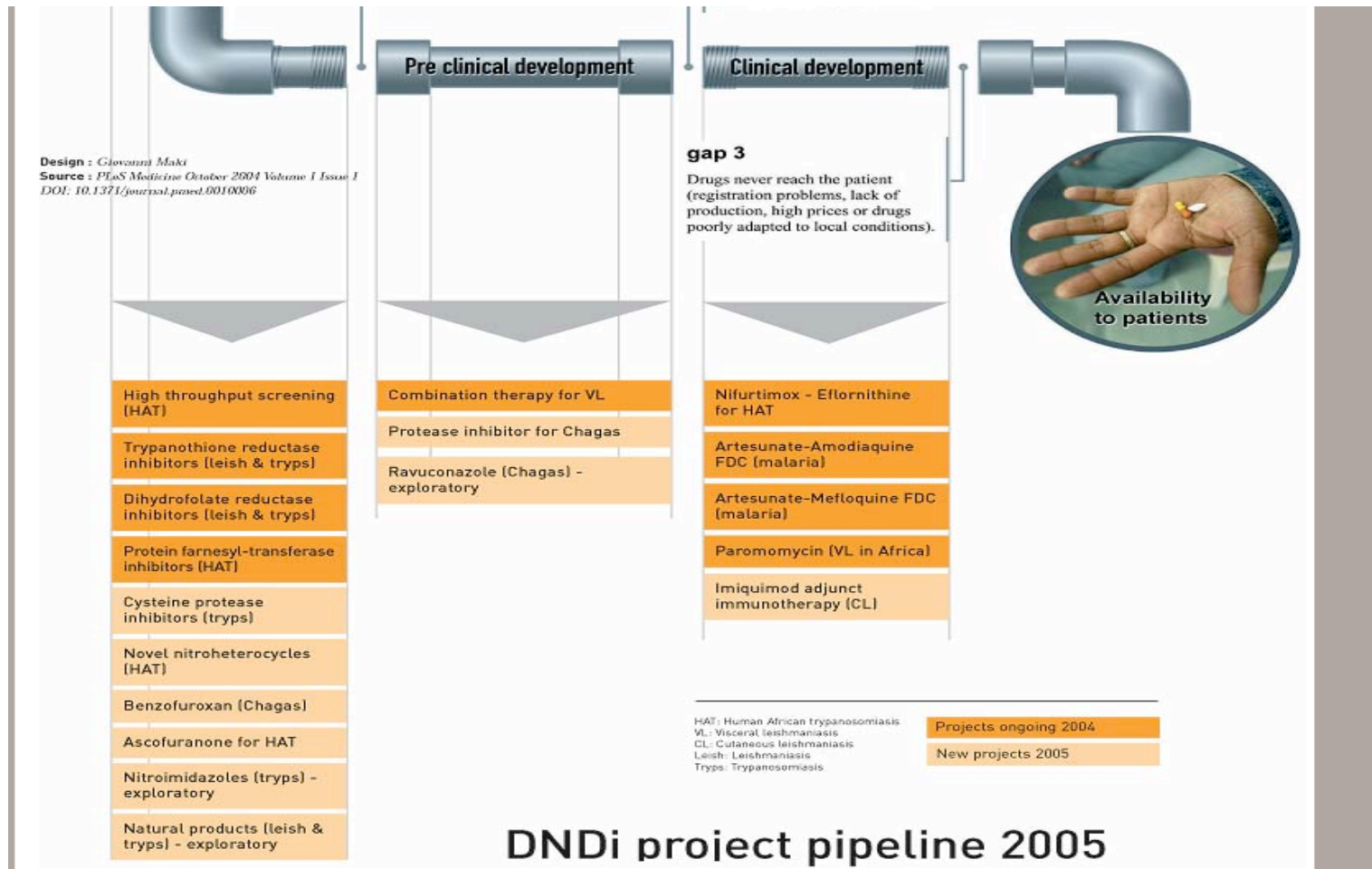


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PLoS Image



Re-mix



Transparency

Political

- Governance with Board of Directors

Financial

- Advertising policy - no pharma
- Sponsorship policy
- Means thinking about new economic models

Transparency

- Content
 - No embargo policy
 - Data sharing
 - Competing interest policy
 - Editors
 - Reviewer
 - Authors

Creativity

- Rolling TOC
- Audio podcast
- Editorial workflow (Lemon8, XML-based layout)
- Reader involvement
 - Post a comment, linking to Pubmed, Google, Open Medicine blog
- *Low cost*

Creativity- Audio podcast

Open Medicine

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A conversation with Richard Smith



Richard Smith discusses haggis, Tim Berners-Lee, the future of medical publishing and much, much more...

Listen to “Can the Public Trust Medical Journals?”—a fun, provocative and thoroughly entertaining conversation with Richard Smith, former editor-in-chief of the British Medical Journal and author of *The Trouble With Medical Journals*. This Open Medicine event was recorded live at the University of Toronto on November 21,

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12. JOHN HOEY - CONCLUSION

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Community

Open Medicine has a desire to contribute back to the communities we are involved with and supported by:

- Open Source Community
- Scholarly Community
- Library Community

Open Medicine, Vol 1, No 2 (2007)

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ANALYSIS AND COMMENT

Science and ideology

STEPHEN W. HWANG

Stephen W. Hwang is a research scientist at the Centre for Research on Inner City Health, the Keenan Research Centre in the Li Ka Shing Knowledge Institute of St. Michael's Hospital, Toronto, Ont., and is an associate professor of medicine in the Division of General Internal Medicine, Department of Medicine, University of Toronto.

More than 130 prominent Canadian physicians, scientists and public health professionals have endorsed this commentary. They are listed at:

http://www.gim.utoronto.ca/Research/Research/inner_city_health/Hwang_SW.htm

Competing interests: None declared.

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SCIENCE AND IDEOLOGY: A COMMENTARY BY DR. STEPHEN HWANG

August 21, 2007

["Science and Ideology"](#) written by Dr. Stephen Hwang, Associate Professor of Medicine, University of Toronto has been published in the peer-reviewed, independent, open-access scientific journal [Open Medicine](#). More than 130 prominent Canadian physicians, scientists, and public health professionals have endorsed Dr. Hwang's commentary, and their names are listed below. Institutional affiliations are provided for identification purposes only; no endorsement by any of these institutions is intended or should be inferred.

1. Barry Adam, PhD, University of Windsor
2. Alix Adrien, MD, CM, MSc, Direction de santé publique de Montréal
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11. Cecilia Benoit, PhD, University of Victoria
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Reader Comments

The Pot Calling the Kettle Black

DR Colin Richard Mangham (2007-08-28)

[EMAIL REPLY](#) [POST REPLY](#) [DELETE THIS COMMENT](#)

Dr. Hwang seems to assert that those disagreeing with the philosophy and approach of harm reduction in the form it has taken in Canada ignore science in favour of ideology. I strongly challenge this line of... [Read more](#)

Time for Reasoned Academic Debate on Safer Injection Facilities

Evan Wood (2007-09-07)

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As the external evaluators of the Vancouver medically supervised safer injection facility (SIF), we read the commentary by Dr. Stephen Hwang (REF Open Medicine Commentary) and... [Read more](#)

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Homelessness and Addictions

by Sandra Kiume
September 4, 2007

[Bums](#) by Peter Bagge is a great comic e-book (it's short, just four pages) with some of the most all-around rational views on homelessness I've ever read. Includes a description of the Housing First approach, which is to get people sleeping indoors and *then* work on treatment.

In Vancouver, BC the [InSite safe injection site](#) illustrates a major roadblock in dealing with homelessness: moral judgments and ideology obstructing science and clinical mental health care. A [letter published in Open Medicine](#) signed by 134 doctors, scientists, politicians, police members and community workers protests the federal government's

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the letter:

Policy-makers may legitimately decide on ethical, moral, political, or economic grounds to severely restrict or even prohibit the use of an intervention, such as Vancouver's supervised injection site, that careful scientific inquiry has shown to have significant health benefits. In these situations, however, policy-makers must provide cogent reasons for their decision and make the basis for their actions explicit and transparent. Such decisions must not be justified by resorting to deceptive claims that cast doubt on the effectiveness of the intervention, or that raise unsupported fears of harmful side effects.

At the same time, physicians, scientists, and public health professionals must be willing to speak out in the public arena when the accumulated body of research evidence clearly supports a health intervention that faces resistance because of entrenched beliefs. As stated in a declaration by Scientists and Engineers for America, a grassroots organization that counts 15 Nobel laureates among its board of advisors, "[t]he principal role of the science and technology community is to advance human understanding. But there are times when this is not enough. Scientists and engineers have a right, indeed an obligation, to enter the political debate when the nation's leaders systematically ignore scientific evidence and analysis, [or] put ideological interests ahead of scientific truths."

Vancouver isn't even close to adopting a Housing First

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[Steve Higgins](#) is a psychology graduate student at an online university. He hopes that the three weeks and \$29.95


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Bums and Conservatives

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Posted on: September 5, 2007 8:00 AM, by [Sandra Klume](#)

[Bums](#) by Peter Borge is a great comic book (it's short - just four pages) with some of the


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Comments

And with the current crop of conservatives in power at the municipal, provincial, and federal level, there will be no further progress in dealing with homelessness and addiction in Vancouver (or other Canadian cities).

#1

Posted by: [Richard](#) | [September 5, 2007 12:03 PM](#)

Yeah, its a shame to see Canada, who has done some stuff at least better than we in the states, have crap like this happen.

#2

Honestly, it's almost like some people have a kind of cultural suicide wish - they wish to deny anything that'd actually help people for some sick reason.

Posted by: [DragonScholar](#) | [September 5, 2007 1:25 PM](#)

Sad but true, both comments.

#3

Posted by: [Sandra](#) | [September 5, 2007 3:41 PM](#)

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Harper Continues To Ignore Evidence Around Safe Injection Site

August 22, 2007

OTTAWA - Prime Minister Stephen Harper must put his personal ideologies aside and heed the scientific evidence that supports Canada's only safe injection site, Liberal Health Critic Bonnie Brown and Senator Larry Campbell said today.

"Today we had a group of 130 prominent doctors, scientists and public health professionals condemning the Harper government for putting political ideology ahead of scientific evidence when considering the future of Vancouver's Insite," said Ms. Brown.

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