

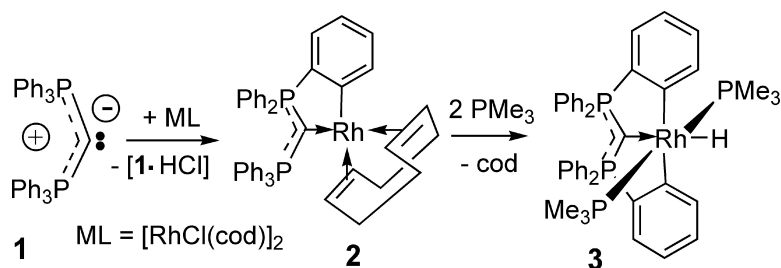
Communication

**Chelate and Pincer Carbene Complexes of Rhodium and Platinum
 Derived from Hexaphenylcarbodiphosphorane, PhPCPPh**

Kazuyuki Kubo, Nathan D. Jones, Michael J. Ferguson, Robert McDonald, and Ronald G. Cavell

J. Am. Chem. Soc., **2005**, 127 (15), 5314-5315 • DOI: 10.1021/ja0502831 • Publication Date (Web): 22 March 2005

Downloaded from <http://pubs.acs.org> on March 25, 2009



More About This Article

Additional resources and features associated with this article are available within the HTML version:

- Supporting Information
- Links to the 2 articles that cite this article, as of the time of this article download
- Access to high resolution figures
- Links to articles and content related to this article
- Copyright permission to reproduce figures and/or text from this article

[View the Full Text HTML](#)



ACS Publications
 High quality. High impact.

Chelate and Pincer Carbene Complexes of Rhodium and Platinum Derived from Hexaphenylcarbodiphosphorane, $\text{Ph}_3\text{P}=\text{C}=\text{PPh}_3$

Kazuyuki Kubo,[†] Nathan D. Jones,[‡] Michael J. Ferguson,[‡] Robert McDonald,[‡] and Ronald G. Cavell^{*‡}

Department of Chemistry, Graduate School of Science, Hiroshima University, Higashi-Hiroshima, 739-8526 Japan, and Department of Chemistry, University of Alberta, Edmonton, AB, Canada T6G 2G2

Received January 16, 2005; E-mail: ron.cavell@ualberta.ca

Cyclometalated “pincer” complexes (Chart 1, A) have become important in the last 30 years,¹ both in the variety of known compounds and in the range of their catalytic applications.² Reaction types now include diverse transformations: alkane dehydrogenation,^{2a,b} activation of small molecules (e.g., CO_2 ^{2c} and N_2 ^{2d}), C–X bond formation^{2e} and activation^{2f,g} (X = C, N, O), polymerization of alkynes^{2h} and alkenes,^{2i,j} and transfer hydrogenation catalysis.^{2k} Applications as sensors^{1a,2l} and “molecular switches”^{2m} have also emerged.

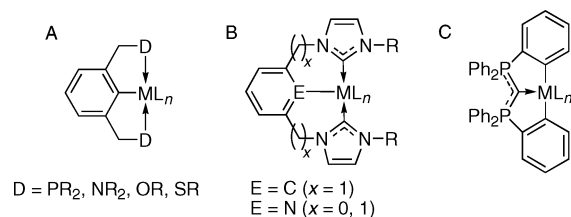
A few cyclometalated pincer N-heterocyclic carbenes (NHCs) (Chart 1, B; E = C) have recently been reported by Crabtree³ and Danopoulos.⁴ Related *C,N,C* (NHC) pincers (Chart 1, B; E = N) have been used as catalysts in alkene oligomerization and polymerization,^{2i,j} Heck,^{3a–c,5} Sonogashira,⁶ transfer hydrogenation,^{3e,4b} and oxidative cleavage^{3e} reactions.

In extending our studies of phosphorus-stabilized pincer carbene complexes of the late metals,^{7,8} we have investigated the chemistry of the carbodiphosphoranes, $\text{R}_3\text{P}=\text{C}=\text{PR}_3$ ($\text{R}_3\text{P}^+-\text{C}^{2-}-\text{PR}_3$). Although a formal carbene resonance form (six valence electrons on C) cannot be drawn for these compounds, we feel that they have strong (and underappreciated) parallels^{9,10} with Bertrand- and Arduengo-type carbenes in that they are stable, neutral, two-electron σ -donors, with bent structures in the solid state, and have ylidic resonance forms that place eight valence electrons on the “carbenic” carbon. While the NHCs are recognized as “push–push” carbenes¹¹ and the Bertrand-type (phosphanyl–silyl) carbenes as “push–pull”,¹¹ carbodiphosphoranes may be conceptualized as a “pull–pull” variety considering that the positively charged phosphonium substituents withdraw electron density from the central, formally C^{2-} atom to give it a distinct carbenic character. Here, we describe new members of the small class of *C,C,C* pincer complexes and introduce a unique category of pincer carbenes (Chart 1, C) which, unlike B, incorporates only a single carbene donor and two, as opposed to one, cyclometalated phenyl rings. Rh(III) and Pt(II) prototypes are presented, with the Rh case also yielding a Rh(I) *C,C* bidentate carbene intermediate.

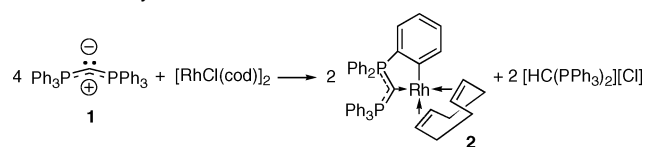
Treatment of $[\text{RhCl}(\text{cod})]_2$ (cod = 1,5-cyclooctadiene) with $\text{Ph}_3\text{P}=\text{C}=\text{PPh}_3$ (**1**)¹² gave $(\text{cod})\text{Rh}[\eta^2-\text{C}\{\text{P}(\text{C}_6\text{H}_4)\text{Ph}_2\}\{\text{PPh}_3\}]$ (**2**) in 78% yield and the phosphonium salt, $[\text{HC}(\text{PPh}_3)_2][\text{Cl}]$ (Scheme 1). Complex **2** is air sensitive but is thermally stable under an inert atmosphere to at least 60 °C. We propose an initial bridge splitting coordination of **1** to Rh followed by phenyl orthometalation at one end of the ligand to form a putative hexacoordinated Rh(III)–hydride intermediate which is dehydrohalogenated by free **1**.

Structural characterization of **2** (Figure 1) shows a Rh(I) atom in a characteristic distorted square–planar coordination geometry. The C(1) center is trigonal planar (sum of angles = 360.0°),

Chart 1



Scheme 1. Synthesis of **2**



indicative of sp^2 hybridization. The Rh–C(1) bond (2.165(2) Å) is longer than those reported for Rh–NHC complexes (2.00–2.10 Å)¹³ and can be regarded as a single bond. The C(1)–P(1) and C(1)–P(2) distances are indistinguishable despite the asymmetry of the ligand. Complex **2** can be formulated as a 16-electron Rh(I) complex wherein the central C atom acts as a net neutral, 2-electron, σ -donor. The bidentate carbene ligand in **2** is reminiscent of our *C,N*-bidentate bis(phosphoranimine) carbene complex of Pt (see Supporting Information, Figure S1).⁷

Reaction of **2** with 2 equiv of PMe_3 gave the Rh(III) *C,C,C* pincer carbene complex, $\text{HRh}(\text{PMe}_3)_2[\eta^3-\text{C}\{\text{Ph}_2\text{P}(\text{C}_6\text{H}_4)\}_2]$ (**3**), in 85% yield (Scheme 2) by replacement of the cod ligand and a second phenyl orthometalation event on the free PPh_3 end of the ligand. Complex **3** represents a distinctly new class of pincer complexes (Chart 1, C) and is the first example of a pincer carbene complex derived from **1**. The second orthometalation step is probably facilitated by (i) a strong σ -donor contribution from PMe_3 and (ii) displacement of cod to alleviate the requirement for the mutual cis orientation of ancillary ligands. Such *C,C,C* pincer systems are rare;

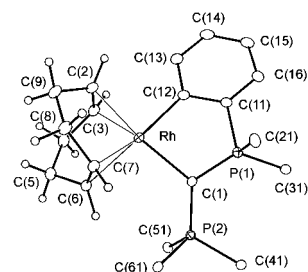


Figure 1. ORTEP illustration of the molecular structure of **2** (20% ellipsoids) showing only cod H atoms and only the *ipso* carbon atoms of the phenyl rings, except for those in the orthometalated ring. Selected bond lengths (Å) and angles (°): Rh–C(1) 2.165(2), Rh–C(12) 2.072(2), C(1)–P(1) 1.692(2), C(1)–P(2) 1.693(2), P(1)–C(1)–P(2) 124.50(13).

[†] Hiroshima University.

[‡] University of Alberta.

Scheme 2. Synthesis of 3

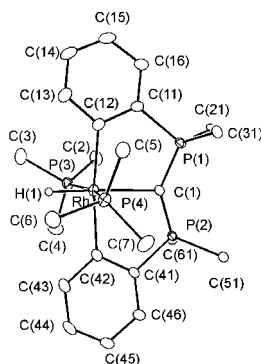
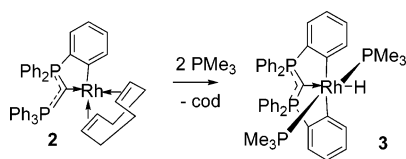
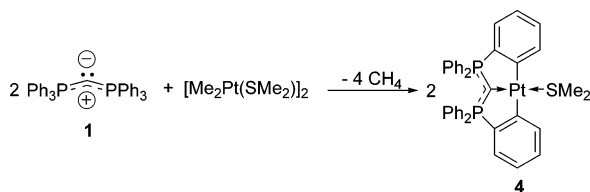


Figure 2. ORTEP representation of the molecular structure of **3** (20% ellipsoids). Only the hydride H atom is shown. All but the *ipso* C atoms of the phenyl rings are omitted except for those on the orthometalated rings. Selected bond lengths (Å) and angles (°): Rh–C(1) 2.202(3), C(1)–P(1) 1.672(3), C(1)–P(2) 1.675(3), P(1)–C(1)–P(2) 138.32(18).

Scheme 3. Synthesis of 4



we know of only two other reported types: a Pt complex of ours⁸ (Figure S1) and three substitutional variants of a group of Pd–NHC complexes of type B (E = C) from the groups of Crabtree^{3a} and Danopoulos.^{4c}

The Rh center in **3** has a distorted octahedral geometry (Figure 2). The Rh–C(1) bond (2.202(3) Å) is slightly longer than that in **2**. The sum of the angles around C(1) is 359.83°, indicative once again of sp² hybridization. We formulate **3** as an 18-electron Rh(III) species in which the central carbon atom, again, acts as a neutral, 2-electron, σ-donor.

Although the C(1)–P bonds in **2** and **3** are in the range previously reported for L_nM–C(PPh₃)₂ complexes (M = Re, Ni, Cu, Au; 1.66–1.78 Å),¹⁴ those in **2** (av 1.693(2) Å) are slightly longer than those in **3** (av 1.674(3) Å), indicating lower C(1)–P bond orders in **2**. The stronger Rh–C(1) bond in **2** may act to reduce the negative charge on C(1) and, consequently, the π-donation from C(1) to P. The P(1)–C(1)–P(2) angle (138.32(18)°) in **3** is the greatest throughout the range of complexes of **1** (123.1–136.0°),¹⁴ including **2** (124.50(13)°).

Reaction of **1** with [Me₂Pt(SMe₂)₂] gave an analogous C,C,C pincer carbene complex of Pt(II) (**4**) directly via double orthometalation with elimination of 2 equiv of CH₄ (Scheme 3). No intermediate species were observed. The complex is stable in the same fashion as **2**. Full details are given in the Supporting Information.

Preliminary DFT electronic structure calculations¹⁵ using the model complex, HRh(PH₃)₂[η³-C{H₂P(C₆H₄)₂}]₂ (**3'**), revealed one net bonding MO of σ symmetry with respect to the Rh–C_{carbene} axis, which is best described as a bonding overlap between an sp²-hybridized orbital on C and a d-orbital on Rh. The HOMO is predominantly a C_{carbene} p_z-orbital with a small antibonding d-orbital

contribution on Rh (Figure S2). This picture is similar to that given by Le Floch and co-workers for the HOMO of the S,C,S pincer carbene complex, (Ph₃P)Pd[C{Ph₂P=S}]₂.¹⁶ Calculated Mulliken charges for **3'** are Rh +0.26, C_{carbene} –0.87, P +0.40 (including H atoms), and C_{phenyl} +0.17. Detailed calculations are in progress as are reactivity studies of these new pincer carbene complexes.

Acknowledgment. We thank the Natural Sciences and Engineering Research Council of Canada and ACS-PRF (35314-AC3) for financial support. K.K. thanks the Japan Ministry of Education, Culture, Sports, Science and Technology for an Overseas Visiting Scholarship. N.D.J. thanks the Killam Trust for a postdoctoral fellowship.

Supporting Information Available: Synthetic and characterization data for **2**, **3**, and **4**, crystallographic data in CIF for **2**·2.5C₆H₆ and **3**, calculation details, and selected MO representations for **3'**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

References

- (1) (a) Albrecht, M.; van Koten, G. *Angew. Chem., Int. Ed.* **2001**, *40*, 3750–3781. (b) van der Boom, M. E.; Milstein, D. E. *Chem. Rev.* **2003**, *103*, 1759–1792. (c) Slagt, M. Q.; van Zwielen, D. A. P.; Moerkerk, A. J. C. M.; Gebbink, R. J. M. K.; van Koten, G. *Coord. Chem. Rev.* **2004**, *248*, 2275–2282.
- (2) (a) Liu, F.; Pak, E. B.; Singh, B.; Jensen, C. M.; Goldman, A. S. *J. Am. Chem. Soc.* **1999**, *121*, 4086–4087. (b) Jensen, C. *Chem. Commun.* **1999**, 2443–2449. (c) Lee, D. W.; Jensen, C. M.; Morales-Morales, D. *Organometallics* **2003**, *22*, 4744–4749. (d) Vignalok, A.; Ben-David, Y.; Milstein, D. *Organometallics* **1996**, *15*, 1839–1844. (e) Beletskaya, I. P.; Cheprakov, A. V. *Chem. Rev.* **2000**, *100*, 3009–3066 and references therein. (f) Liou, S.-Y.; van der Boom, M. E.; Milstein, D. *Chem. Commun.* **1998**, 687–688. (g) Gandelman, M.; Milstein, D. *Chem. Commun.* **2000**, 1603–1604. (h) Yao, J.; Wong, W. T.; Jia, G. J. *Organomet. Chem.* **2000**, *598*, 228–234. (i) McGuinness, D. S.; Gibson, V. C.; Steed, J. W. *Organometallics* **2004**, *23*, 6288–6292. (j) McGuinness, D. S.; Gibson, V. C.; Wass, D. F.; Steed, J. W. *J. Am. Chem. Soc.* **2003**, *125*, 12716–12717. (k) Dani, P.; Karlen, T.; Gossage, R. A.; Gladiali, S.; van Koten, G. *Angew. Chem., Int. Ed.* **2000**, *39*, 743–745. (l) Albrecht, M.; Gossage, R. A.; Lutz, M.; Spek, A. L.; van Koten, G. *Chem.–Eur. J.* **2000**, *6*, 1431–1445. (m) Steenwinkel, P.; Grove, D. M.; Veldman, N.; Spek, A. L.; van Koten, G. *Organometallics* **1998**, *17*, 5647–5655.
- (3) (a) Gründemann, S.; Albrecht, M.; Loch, J. A.; Faller, J. W.; Crabtree, R. H. *Organometallics* **2001**, *20*, 5485–5488. (b) Peris, E.; Loch, J. A.; Mata, J.; Crabtree, R. H. *Chem. Commun.* **2001**, 201–202. (c) Loch, J. A.; Albrecht, M.; Peris, E.; Mata, J.; Faller, J. W.; Crabtree, R. H. *Organometallics* **2002**, *21*, 700–706. (d) Crabtree, R. H. *Pure Appl. Chem.* **2003**, *75*, 435–443. (e) Poyatos, M.; Mata, J. A.; Falomir, E.; Crabtree, R. H.; Peris, E. *Organometallics* **2003**, *22*, 1110–1114. (f) Peris, E.; Crabtree, R. H. *Coord. Chem. Rev.* **2004**, *248*, 2239–2246.
- (4) (a) Tulloch, A. A. D.; Danopoulos, A. A.; Tizzard, G. J.; Coles, S. J.; Hursthouse, M. B.; Hay-Motherwell, R. S.; Motherwell, W. B. *Chem. Commun.* **2001**, 1270–1271. (b) Danopoulos, A. A.; Winston, S.; Motherwell, W. B. *Chem. Commun.* **2002**, 1376–1377. (c) Danopoulos, A. A.; Tulloch, A. A. D.; Winston, S.; Eastham, G.; Hursthouse, M. B. *J. Chem. Soc., Dalton. Trans.* **2003**, 1009–1015. (d) Danopoulos, A. A.; Tsoureas, N.; Wright, J. A.; Light, M. E. *Organometallics* **2004**, *23*, 166–168. (e) Danopoulos, A. A.; Wright, J. A.; Motherwell, W. B.; Ellwood, S. *Organometallics* **2004**, *23*, 4807–4810.
- (5) Crudden, C. M.; Allen, D. P. *Coord. Chem. Rev.* **2004**, *248*, 2247–2273.
- (6) Mas-Marza, E.; Segarra, A. M.; Claver, C.; Peris, E.; Fernandez, E. *Tetrahedron Lett.* **2003**, *44*, 6595–6599.
- (7) Jones, N. D.; Lin, G.; Gossage, R. A.; McDonald, R.; Cavell, R. G. *Organometallics* **2003**, *22*, 2832–2841 (erratum 5378).
- (8) Lin, G.; Jones, N. D.; Gossage, R. A.; McDonald, R.; Cavell, R. G. *Angew. Chem., Int. Ed.* **2003**, *42*, 4054–4057.
- (9) Schmidbaur, H.; Hasslberger, G.; Deschler, U.; Schubert, U.; Kappenstein, C.; Frank, A. *Angew. Chem., Int. Ed. Engl.* **1979**, *18*, 408–409.
- (10) Bruce, A. E.; Gamble, A. S.; Tonker, T. L.; Templeton, J. L. *Organometallics* **1987**, *6*, 1350–1352.
- (11) Bourissou, D.; Guerret, O.; Gabbai, F. P.; Bertrand, G. *Chem. Rev.* **2000**, *100*, 39–91.
- (12) Ramirez, F.; Desai, N. B.; Hansen, B.; McKelvie, N. J. *J. Am. Chem. Soc.* **1961**, *83*, 3539–3540.
- (13) Despagnet, E.; Miqueu, K.; Gornitzka, H.; Dyer, P. W.; Bourissou, D.; Bertrand, G. *J. Am. Chem. Soc.* **2002**, *124*, 11834–11835.
- (14) Vicente, J.; Singhal, A. R.; Jones, P. G. *Organometallics* **2002**, *21*, 5887–5900 and references therein.
- (15) B3LYP/LANL2DZ. Frisch, M. et al. *Gaussian 98*, 2002. For full citation, see the Supporting Information.
- (16) Cantat, T.; Mézailles, N.; Ricard, L.; Jean, Y.; Le Floch, P. *Angew. Chem., Int. Ed.* **2004**, *43*, 6382–6385.

JA0502831