# Synthesis of a Hetero-bimetallic Complex with an Inorganic Cyclic Framework Using a Bis(iminophosphorane)iron Complex as a Chelating Ligand

Kazuyuki Kubo, Takashi Akimoto, Tsutomu Mizuta, and Katsuhiko Miyoshi*
*Department of Chemistry, Graduate School of Science, Hiroshima University,*
*1-3-1 Kagamiyama, Higashi-Hiroshima 739-8526*

(Received October 25, 2007; CL-071183; E-mail: kmiyoshi@sci.hiroshima-u.ac.jp)

An iron–rhodium bimetallic complex bearing a six-membered metallacycle was synthesized from a lithium bis(iminophosphorane)iron complex, which served as an anionic chelating ligand carrying a bis(iminophosphorano)methanide-like inorganic framework. The metallacycle complex takes a peculiar boat shape, in which the two metal centers are in close proximity and the carbonyl ligand on the iron atom overhangs the rhodium atom, giving a considerably low-frequency IR absorption and assuming a slightly bent structure.

Coordination chemistry of metallochelates has owed its recent developments to the utility of $\beta$-diketiminate **I** (Chart 1), which serves as an efficient chelating ligand toward a wide range of metals to stabilize their unusual oxidation state or coordinatively unsaturated geometry.[1] Such a prominent feature of this type of ligands allows them to find numerous utilities especially in a wide range of catalyses, and a variety of their topological congeners have been extensively investigated to date. Above all, a phosphorus analogue **II**, i.e., bis(iminophosphorano)methanide, is one of the current focuses of attention, and a large number of its metal complexes have been recently exploited, with main group and transition metals including f-block metals.[2] In this paper, we report the synthesis of an Fe–Rh hetero-bimetallic complex using an anionic bis(iminophosphorane)iron complex as a new chelating ligand of the type **III**, that is, a metallic variant of the bis(iminophosphorano)methanide. This *metalloligand* is readily coordinated toward a second metal complex fragment to provide an inorganic six-membered metallacycle, the structure of which is also discussed here.

To our knowledge, only a few bimetallic complexes containing a related metalloligand moiety have been studied up to date; Gray and Kraihanzel[3] and Powell et al.[4] reported the reactions of dianionic complexes of the type **IV**, while Nagashima et al. reported electrically neutral phosphinoamide complexes, which served as metallophosphine ligands **V** toward several late transition metals.[5] As a new inorganic chelating ligand bearing a bis(iminophosphorano)methanide-like framework, the monoanionic bis(imonophosphorane) complex **III** will offer facile and convenient access to stable homo- and hetero-bimetallic complexes exhibiting interesting properties.[2]

Deprotonation of $[Cp^*(CO)Fe\{P(OMe)_2N(H)Ph\}_2]PF_6$ (**1**) with an equimolar amount of MeLi as a base led to a neutral complex, $Cp^*(CO)Fe\{P(OMe)_2N(H)Ph\}\{P(OMe)_2NPh\}$ (**2**), in 76% yield (Scheme 1; Cp* stands for $\eta^5$-$C_5Me_5$). The IR spectrum of **2** has a CO absorption band at $1943\,cm^{-1}$. In the $^{31}P\{^1H\}$ NMR spectrum, the sole singlet was observed at 152.3 ppm, showing the two phosphorus fragments are apparently equivalent, probably because of the rapid proton migration between the two imino nitrogen atoms. The complex **2** was further treated with another equiv of MeLi to give the lithiated metalloligand, $Cp^*(CO)Fe\{P(OMe)_2NPh\}_2Li$ (**3**). In the $^{31}P\{^1H\}$ NMR spectrum of the reaction mixture, a singlet attributable to **3** was observed at a magnetic field (145.7 ppm) slightly higher than that of **2**, suggesting that **3** is better described not as an ion pair but as a neutral Fe–Li bimetallic complex.

Since the lithium chelate **3** was quite air- and/or moisture-sensitive and any efforts to isolate it were unsuccessful, it was used without isolation for the following reaction. The chelate **3** generated in situ was treated with a dimeric rhodium complex, $[Rh(cod)Cl]_2$ (cod = 1,5-cyclooctadiene). The reaction proceeded smoothly to yield yellow powder of the Fe–Rh bimetallic complex, $Cp^*(CO)Fe\{P(OMe)_2NPh\}_2$-$\kappa N,\kappa N'$-Rh(cod) (**4**), in moderate yield (65%).[6] In the $^{31}P\{^1H\}$ NMR spectrum, a doublet with Rh–P coupling of $J_{RhP} = 6.7\,Hz$ was observed at a slightly lower magnetic field (155.5 ppm) than the corresponding singlet of **2**. In the IR spectrum, a terminal CO absorption band was observed at an unexpectedly lower wavenumber of 1919 $cm^{-1}$ than that of **2** ($1943\,cm^{-1}$).

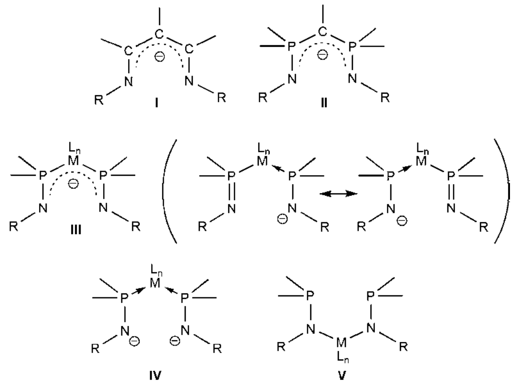
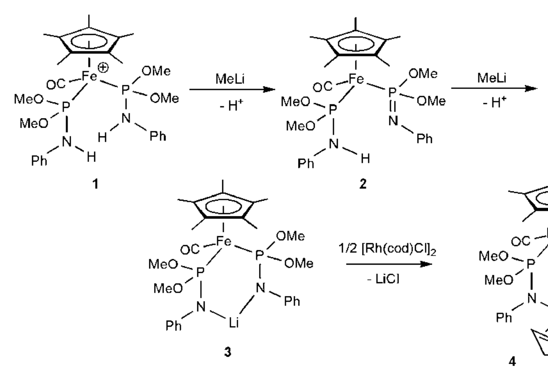


**Chart 1.**



**Scheme 1.**

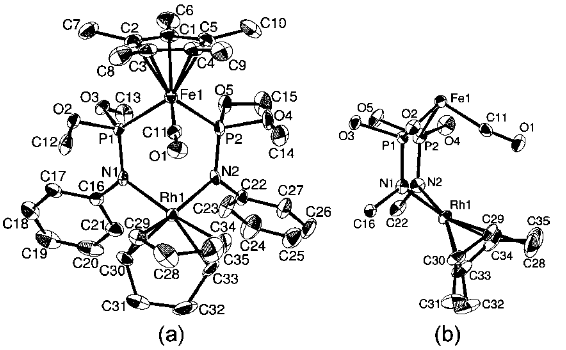


**Figure 1.** (a) ORTEP drawing of **4** with the non-hydrogen atoms as 50% probability thermal ellipsoids with a numbering scheme. (b) Side view of the core structure of **4**.

The X-ray crystallographic study[7] revealed that the iron fragment in **4** has two iminophosphorane groups bonded to the Rh atom to form a six-membered metallacycle (Figure 1). The rhodium fragment has a square-planar geometry characteristic of $d^8$ $Rh^I$ complexes. Both imino nitrogen atoms have a planar geometry probably because of the favorable $\pi$ interaction between the filled $\pi^n$(N) and the empty $\sigma^*$(P) orbitals. Indeed, the two P–N bonds similar in length (P(1)–N(1) = 1.610(5) Å, P(2)–N(2) = 1.614(5) Å) are shorter than the formal P–N single bond in the related complex, $[Cp^*(CO)_2Fe\{P(OMe)_2NHPh\}]PF_6$ (1.672(2) [1.658(2)] Å).[8] These structural aspects are consistent with the resonance structures assumed for this ligand system **III** shown in Chart 1.

The six-membered metallacycle takes a boat form, which makes the two metal centers close to each other and the CO ligand on the iron atom overhang the Rh atom (Figure 1b). Although this conformation seems to be due to a subtle steric balance leading to minimum strain and repulsion on the metallacycle skeleton, it is worth noting that in some related metallacycles there arise additional intramolecular interactions encouraged by the particular conformation adopted; Nagashima et al. reported that the Cl ligand on the Ru atom in $(O)Ti\{N^tBuPPh_2\}_2$-$\kappa P,\kappa P'$-($\mu$-Cl)RuCp* donates its lone-pair electrons to the Ti atom to bridge the two metal atoms,[5b] and more interestingly, the Pt atom in $Cl_2Ti\{N^tBuPPh_2\}_2$-$\kappa P,\kappa P'$-$PtX_2$ (X = Cl, Me or *p*-tol) donates some electron density toward the Ti atom to result in a Pt → Ti dative bond.[5a] Considering the rather long Rh···Fe bond (3.8154(7) Å) in **4**, there seems to be no bonding interaction between them. On the other hand, the Rh atom is located relatively close to the C atom of the CO ligand (Rh···C = 3.176(4) Å), which is slightly bent back at the carbon atom with the Fe–C–O angle of 169.9(4)° away from the Rh center. Although this nonlinearity could merely come from the steric repulsion with the rhodium fragment, some orbital interactions might be responsible for it. For example, Caulton et al. pointed out that the M–C–O moiety can be bent in some cases to diminish the electronic repulsion between the CO lone pair and a filled d orbital.[9] For bimetallic complexes, another interaction is also probable between the CO and the metal center to which the carbonyl is not directly coordinated. A square-planar $d^8$ complex serves as an electron donor,[10] while the CO acts as an acceptor via its $\pi^*$ orbitals, and thus the donor–acceptor interaction between them will make the M–C–O moiety angular with the C–O bond concomitantly weakened. In fact, the CO absorption band of **4** is observed at an unexpectedly lower frequency in the IR spectrum (vide supra). Although such direct orbital interaction looks, if any, very feeble in **4** as judged from the long Rh–C bond and also from a lack of the $J_{CRh}$ coupling in the $^{13}C$ NMR spectrum,[6] the boat-shaped conformation could endue the adjacent Fe and Rh metals with some synergistic reactivity expected to play a unique role in the activation of small molecules.

The coordination compounds of the alkali metals have been of interest because of their extensive utilities for the synthetic purposes. In this context, the lithiated chelate **III** will serve as a versatile building block for metal-containing molecules, such as not only homo- and hetero-bimetallic complexes but inorganic macrocycles as well as inorganic coordination polymers.

This work was financially supported in part by Grant-in-Aids for Scientific Research (Nos. 19550066, 19350032, and 19550067) and by that on Priority Areas (No. 19027041, Synergy of Elements) from the Ministry of Education, Culture, Sports, Science and Technology, Japan.

## References

1 L. Bourget-Merle, M. F. Lappert, J. R. Severn, *Chem. Rev.* **2002**, *102*, 3031.

2 For recent examples, see: a) S. A. Ahmed, M. S. Hill, P. B. Hitchcock, *Organometallics* **2006**, *25*, 394, and references cited therein. b) T. K. Panda, P. W. Roesky, P. Larsen, S. Zhang, C. Wickleder, *Inorg. Chem.* **2006**, *45*, 7503, and references cited therein.

3 G. M. Gray, C. S. Kraihanzel, *J. Organomet. Chem.* **1978**, *146*, 23.

4 a) J. Powell, M. Gregg, A. Kuksis, P. Meindl, *J. Am. Chem. Soc.* **1983**, *105*, 1064. b) J. Powell, M. R. Gregg, P. E. Meindl, *Organometallics* **1989**, *8*, 2942.

5 a) H. Nagashima, T. Sue, T. Oda, A. Kanemitsu, T. Matsumoto, Y. Motoyama, Y. Sunada, *Organometallics* **2006**, *25*, 1987. b) Y. Sunada, T. Sue, T. Matsumoto, H. Nagashima, *J. Organomet. Chem.* **2006**, *691*, 3176. c) T. Sue, Y. Sunada, H. Nagashima, *Eur. J. Inorg. Chem.* **2007**, 2897.

6 Analytical data for **4**: IR ($\nu_{CO}$, in THF): 1919 $cm^{-1}$. $^1H$ NMR ($\delta$, in $C_6D_6$) 1.37 (m, 2H, cod), 1.63 (s, 15H, $C_5(CH_3)_5$), 1.66 (m, 2H, cod), 2.11 (br, 2H, cod), 2.69 (br, 2H, cod), 3.27 (t, $J_{HP}$ = 5.1 Hz, 6H, $OCH_3$), 3.53 (br, 2H, cod), 3.64 (t, $J_{HP}$ = 5.9 Hz, 6H, $OCH_3$), 4.20 (br, 2H, cod), 7.02–7.98 (m, 10H, $C_6H_5$). $^{13}C\{^1H\}$ NMR ($\delta$, in $C_6D_6$): 9.6 (s, $C_5(CH_3)_5$), 29.8 (s, cod), 30.8 (s, cod), 50.0 (s, $OCH_3$), 53.4 (t, $J_{CP}$ = 3.8 Hz, $OCH_3$), 78.0 (d, $J_{CRh}$ = 12.3 Hz, cod), 81.1 (d, $J_{CRh}$ = 13.7 Hz, cod), 95.8 (s, $C_5(CH_3)_5$), 121.1 (s, $C_6H_5$), 127.7 (t, $J_{CP}$ = 4.7 Hz, $C_6H_5$), 128.3 (s, $C_6H_5$), 152.9 (t, $J_{CP}$ = 7.9 Hz, $C_6H_5$), 222.9 (t, $J_{CP}$ = 33.7 Hz, CO). $^{31}P\{^1H\}$ NMR ($\delta$, in $C_6D_6$): 155.5 (d, $J_{PRh}$ = 6.7 Hz). Anal. Calcd for $C_{35}H_{49}N_2FeO_5P_2Rh$: C, 52.65; H, 6.19; N, 3.51%. Found: C, 52.42; H, 6.38; N, 3.42%.

7 Crystallographic data for **4** have been deposited with Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-664797. Copies of the data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge, CB2 1EZ, UK; fax: +44 1223 336033; or deposit@ccdc.cam.ac.uk).

8 K. Kubo, H. Nakazawa, H. Inagaki, K. Miyoshi, *Organometallics* **2002**, *21*, 1942.

9 M. Ogasawara, S. A. Macgregor, W. E. Streib, K. Folting, O. Eisenstein, K. G. Caulton, *J. Am. Chem. Soc.* **1995**, *117*, 8869.

10 G. Aullón, S. Alvarez, *Inorg. Chem.* **1996**, *35*, 3137.