Dinitrogen Complexes of Pincer-Ligated Iridium

Rajshekhar Ghosh, Mira Kanzelberger, Thomas J. Emge, Gene S. Hall, and
Alan S. Goldman*

*Department of Chemistry and Chemical Biology, Rutgers, the State University of New Jersey,
Piscataway, New Jersey 08854*

Received August 3, 2006

*Summary: Precursors of the fragment (PCP)Ir have been previously reported to react with dinitrogen to give the bridging dinuclear complex [(PCP)Ir]$_2$(N$_2$) (**2**), which was crystallographically characterized. We report that under N$_2$ atmosphere the only observable nitrogen complex in solution is actually the terminal dinitrogen complex (PCP)Ir(N$_2$). The mono- and dinuclear species are in equilibrium; the dinuclear complex more readily crystallizes from solution.*

Introduction

Since their discovery in 1965, transition metal dinitrogen complexes have been of great interest.[1] Dinitrogen complexes comprise one of the relatively few classes of compounds that can be formed from molecular nitrogen under mild conditions. They are clearly relevant both to nitrogen fixation by plants and to efforts to develop improved catalysts for the reduction of nitrogen.[1]

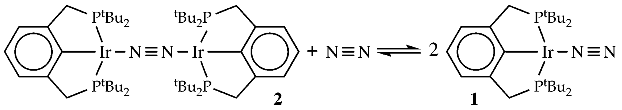
Dinitrogen complexes of almost every transition metal have now been prepared.[2] Some have found utility as synthetic precursors, largely due to the ease of displacing N$_2$, sometimes simply by applying a vacuum. Varied degrees of activation and several different bonding modes, both mono- and dinuclear, have been observed. Interest remains strong, although the potential for use of such complexes for catalytic fixation and functionalization of dinitrogen remains unrealized.[2]

The use of pincer ligands has seen dramatic growth in recent years.[3,4] Precursors of (PCP)Ir (PCP = κ^3-C$_6$H$_3$-2,6-(CH$_2$P^{t}Bu$_2$)$_2$) and derivatives have been found to be the most effective catalysts for alkane dehydrogenation reported to date.[4,5] However, a weakness of these systems is that, as reported by Jensen, catalytic activity is inhibited by nitrogen gas, even in trace amounts.[6] The formation of a bridging dinuclear dinitrogen complex, [(PCP)Ir]$_2$(N$_2$), which was crystallographically characterized,[6] was reported to be responsible for this inhibitory effect.

Results and Discussion

In the course of our work with (PCP)Ir complexes, a small, persistent peak was frequently observed in the ^{31}P{^{1}H} NMR spectrum with chemical shift δ 74.9−73.5 ppm in various solvents. This value is close to, but does not quite match, the value previously reported for [(PCP)Ir]$_2$(N$_2$) (δ 72.9 ppm in cyclohexane-d_{12}). To identify this species, we added N$_2$ (800 Torr) to a sample of (PCP)Ir(C$_6$H$_5$)(H) in *p*-xylene. Quantitative conversion to a single product (**1**) was observed in the ^{31}P{^{1}H} NMR (δ 72.9 ppm). After the sample was subjected to a freeze−pump−thaw cycle, however, a small peak at δ 74.7 ppm (**2**) appeared. To another sample of (PCP)Ir(C$_6$H$_5$)(H) in *p*-xylene we added approximately 0.25 equiv of N$_2$ (32 Torr). The ^{31}P{^{1}H} NMR signal at δ 74.7 ppm (**2**) grew in as the signal attributable to (PCP)Ir(C$_6$H$_5$)(H) diminished. Adding an additional 0.5 equiv of N$_2$ led to the complete disappearance of (PCP)Ir(C$_6$H$_5$)(H); while the signal at δ 74.7 ppm (**2**) was still dominant in the ^{31}P spectrum, the peak at δ 72.9 ppm (**1**) began to appear. Addition of 800 Torr of N$_2$ to this solution resulted in complete conversion to complex **1**.

These results strongly indicated that while complex **2** is the product of reaction with N$_2$, complex **1** results from the presence of a higher ratio of N$_2$ to (PCP)Ir. This could be readily explained by the equilibrium of eq 1 and the hypothesis that complexes **1** and **2** are the mononuclear terminal and bridging dinuclear dinitrogen complexes, respectively.



(1)

Addition of 800 Torr of N$_2$ to a benzene-d_6 solution of (PCP)Ir(NBE) (NBE = norbornene) results in quantitative appearance of the upfield (δ 72.5 ppm) resonance in the ^{31}P{^{1}H} NMR spectrum (**1**). This solution was allowed to slowly concentrate in hexane solvent in the glovebox. After 2−3 days amber-colored blocks were formed, which were suitable for X-ray diffraction. The structure of the complex (Figure 1) has hexane in the lattice but is otherwise very similar to that obtained by Jensen[7] for complex **2**. Selected bond lengths and angles are given in Table 1. Thus a solution of predominantly the species that we assigned as the mononuclear complex (PCP)Ir(N$_2$) (**1**) can yield crystals of dinuclear [(PCP)Ir]$_2$(N$_2$) (**2**), even under 800 Torr of N$_2$.

Slow evaporation of a solution of complex **1** also yielded crystals of complex **2**. However, complex **1** could be crystallized by preparing a saturated solution of **1** in hexane in an NMR tube and cooling this solution to −15 °C over 3−4 h under N$_2$ atmosphere (800 Torr). Large orange-red crystals were formed. X-ray analysis revealed that the crystalline material was indeed monomeric terminal dinitrogen complex (PCP)Ir(N$_2$) (**1**) (Figure

---

* Corresponding author. E-mail: alan.goldman@rutgers.edu.

(1) Allen, A. D.; Bottomley, F. *Acc. Chem. Res.* **1968**, *1*, 360−365.

(2) Fryzuk, M. D.; Johnson, S. A. *Coord. Chem. Rev.* **2000**, 200−202, 379−409.

(3) Albrecht, M.; van Koten, G. *Angew. Chem., Int. Ed.* **2001**, *40*, 3750−3781.

(4) van der Boom, M. E.; Milstein, D. *Chem. Rev.* **2003**, *103*, 1759−1792.

(5) Liu, F.; Pak, E. B.; Singh, B.; Jensen, C. M.; Goldman, A. S. *J. Am. Chem. Soc.* **1999**, *121*, 4086−4087.

(6) Lee, D. W.; Kaska, W. C.; Jensen, C. M. *Organometallics* **1998**, *17*, 1−3.

(7) Jensen and co-workers did the crystallization from cyclohexane, which likewise co-crystallized in the lattice (ref 6).

10.1021/om0607043 CCC: $33.50

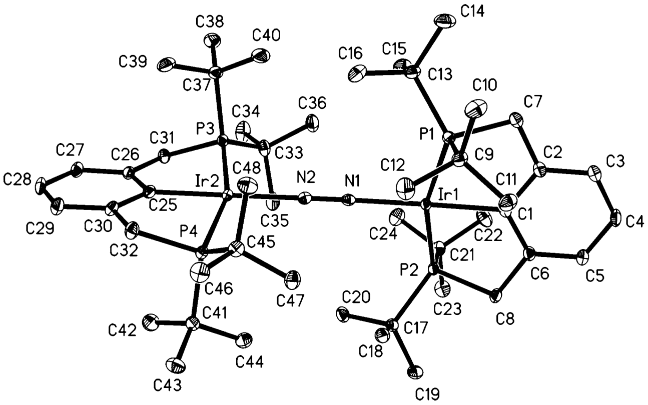


Figure 1. Complex **2** (similar to that reported by Jensen et al.[7]).

Table 1. Selected Bond Lengths and Bond Angles in Complex 2

	Bond Length (Å)		
Ir(1)−N(1)	2.0121(16)	Ir(2)−N(2)	2.0115(16)
Ir(1)−C(1)	2.0534(18)	Ir(2)−C(25)	2.0511(18)
Ir(1)−P(1)	2.2989(5)	Ir(2)−P(3)	2.2985(5)
Ir(1)−P(2)	2.3028(5)	Ir(2)−P(4)	2.3001(5)
N(1)−N(2)	1.134(2)		
	Bond Angles (deg)		
N(1)−Ir(1)−C(1)	179.29(6)	N(2)−Ir(2)−C(25)	179.57(7)
N(1)−Ir(1)−P(1)	100.35(4)	N(2)−Ir(2)−P(3)	99.07(4)
N(1)−Ir(1)−P(2)	99.00(4)	N(2)−Ir(2)−P(4)	100.28(4)
P(1)−Ir(1)−P(2)	160.630(16)	P(3)−Ir(2)−P(4)	160.623(16)
N(2)−N(1)−Ir(1)	178.97(15)	N(1)−N(2)−Ir(2)	179.64(16)

2a). Very few terminal Ir−N_2 complexes have been crystallographically characterized previously.[8]

The asymmetric unit of the crystal structure has four inequivalent molecules of **1** (Figure 2b). A list of bond lengths and bond angles seen in the four different structures are given in Table 2. The most notable difference among these inequivalent molecules involves the N−N−Ir bond angles, which are 176.0(2)° for N(2)−N(1)−Ir(1), as compared with the other three, which are in the range 178.8−179.6°.

It was reported that the solution IR spectrum of complex **2** (crystallographically characterized) contains a strong band (ν_{NN}) at 2078 cm^{-1}; however, such a band would not be expected of a centrosymmetric complex. The propensity of (PCP)Ir(N_2) (**1**) solutions to yield crystals of **2**, as noted above, easily explains this observation. In fact no bands were observed in the 2200−1800 cm^{-1} range in the infrared spectra of a solid sample of pure complex **2**. The Raman spectrum of complex **2**, however, shows a strong, sharp band at 1979 cm^{-1}, consistent with the presence of the bridging N≡N ligand.

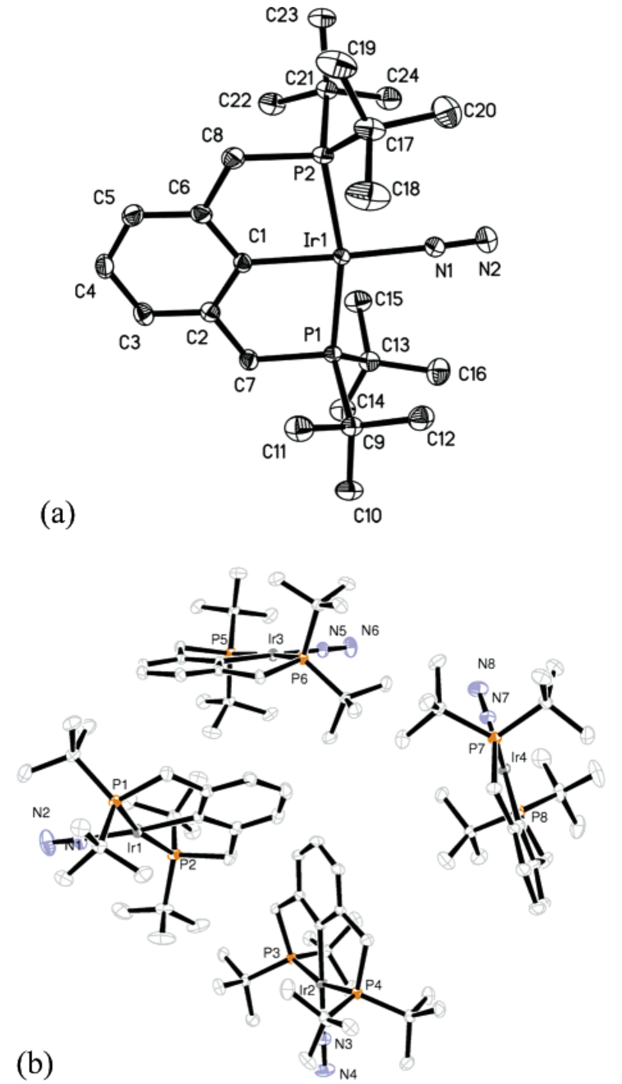


Figure 2. (a) Structure of (PCP)Ir(N_2) (**1**). (b) Asymmetric unit with four inequivalent molecules.

Table 2. Selected Bond Lengths and Angles in the Four Inequivalent Molecules of 1

	Bond Lengths (Å)		
Ir(1)−N(1)	1.9489(18)	Ir(2)−N(3)	1.9442(17)
Ir(1)−C(1)	2.0398(19)	Ir(2)−C(25)	2.0483(18)
Ir(1)−P(1)	2.2867(5)	Ir(2)−P(4)	2.2867(5)
Ir(1)−P(2)	2.2897(5)	Ir(2)−P(3)	2.2940(5)
N(1)−N(2)	1.107(3)	N(3)−N(4)	1.107(2)
Ir(3)−N(5)	1.9472(17)	Ir(4)−N(7)	1.9482(17)
Ir(3)−C(49)	2.0452(18)	Ir(4)−C(73)	2.0446(18)
Ir(3)−P(6)	2.2936(5)	Ir(4)−P(8)	2.2894(5)
Ir(3)−P(5)	2.2945(5)	Ir(4)−P(7)	2.2902(5)
N(5)−N(6)	1.107(2)	N(7)−N(8)	1.109(2)
	Bond Angles (deg)		
N(1)−Ir(1)−C(1)	175.51(8)	N(3)−Ir(2)−C(25)	179.79(6)
N(1)−Ir(1)−P(1)	97.24(5)	N(3)−Ir(2)−P(4)	97.20(5)
N(1)−Ir(1)−P(2)	96.93(5)	N(3)−Ir(2)−P(3)	97.38(5)
P(1)−Ir(1)−P(2)	165.807(18)	P(4)−Ir(2)−P(3)	165.110(17)
N(2)−N(1)−Ir(1)	176.0(2)	N(4)−N(3)−Ir(2)	179.20(19)
N(5)−Ir(3)−C(49)	179.14(7)	N(7)−Ir(4)−C(73)	178.16(7)
N(5)−Ir(3)−P(6)	97.16(5)	N(7)−Ir(4)−P(8)	97.32(5)
N(5)−Ir(3)−P(5)	97.47(5)	N(7)−Ir(4)−P(7)	97.07(5)
P(6)−Ir(3)−P(5)	165.370(17)	P(8)−Ir(4)−P(7)	165.541(17)
N(6)−N(5)−Ir(3)	179.63(18)	N(8)−N(7)−Ir(4)	178.84(19)

Terminal dinitrogen complex **1** is not centrosymmetric and exhibits signals in both the infrared and Raman spectra in the 2200−1800 cm^{-1} region. An infrared spectrum (ATR/FTIR) of crystals of complex **1** shows a strong band at 2076 cm^{-1} with a shoulder at 2084 cm^{-1}. Similarly, in the solid-state Raman spectrum two distinct signals with 1:1 intensities are observed at 2094 and 2077 cm^{-1}. A benzene solution of complex **1** shows only one signal in both the infrared and Raman spectra, at 2079 and 2083 cm^{-1}, respectively. A terminal molybdenum dinitrogen complex, [Mo(N_2)(dpepp)(dppm)] (dpepp = PhP($CH_2CH_2PPh_2$)$_2$; dppm = $Ph_2PCH_2PPh_2$), has previously been reported to have two Raman bands at 2003 and 1984 cm^{-1} in the solid state.[9] The two different signals in the solid-state infrared and Raman spectra may be due to coupling between different molecules in the asymmetric unit, as observed in the crystal structure.[10−12]

---

(8) (a) Bernskoetter, W. H.; Lobkovsky, E.; Chirik, P. J. *Chem. Commun.* **2004**, 764−765. (b) Tellers, D. M.; Bergman, R. G. *Organometallics* **2001**, *20*, 4819−4832. (c) Gutierrez-Puebla, E.; Monge, A.; Nicasio, M. C.; Perez, P. J.; Poveda, M. L.; Carmona, E. *Chem.−Eur. J.* **1998**, *4*, 2225−2236.

The significantly lower frequency of the N–N stretch of complex **2** (1979 cm^{-1}) as compared with **1** (2094 and 2077 cm^{-1}) can be attributed to the significantly greater combined $d\pi - p\pi$ back-bonding from two (PCP)Ir centers (cf. $\nu_{NN} = 2330$ cm^{-1} for free N_2). Accordingly, the crystal structures reveal that the N–N distance in **2**, 1.134(2) Å, is about 0.03 Å greater than that in **1**.

Both complexes **1** and **2** are pseudo-square planar (sums of the iridium–ligand angles are 359.97° and 359.99°, respectively). The coordinating phosphorus atoms are more "pulled back" in the dimer; P–Ir–P angles are 160.6° versus 165.1–165.8° in the monomer. This is likely due to repulsion between PCP units of the two components of the dimer (in spite of the arrangement in which the PCP units are mutually orthogonal). The symmetrical nature of the complexes is evident from the ^{1}H NMR and ^{13}C spectra. For both complexes, the methylene as well as *tert*-butyl groups each give a single signal in both the ^{1}H NMR and ^{13}C NMR spectra.

The monomer/dimer (**1**:**2**) equilibrium was measured. Nitrogen gas (200 Torr) was added to a J. Young NMR tube containing a benzene-d_6 solution of (PCP)Ir(Ph)H (34 mM); the tube was then shaken. The solution was subsequently allowed to equilibrate under 102 Torr of N_2, and the concentrations of complexes **1** and **2** were determined by inverse-gated ^{31}P NMR (33 and 1.0 mM) to yield an equilibrium constant for eq 1, $K_1 = 7.9$ M atm^{-1}. Alternatively, if dinitrogen is quantified as a solute rather than a gas, based on its solubility of 4.5 mM/atm,[13,14] we obtain $K_1 = 1800$. Dimer/monomer equilibrium measurements of a dinitrogen complex have previously been reported.[15,16] Milstein et al. obtained a ratio of 8:3 for [(^{iPr}PCP)-RhN_2] and [(^{iPr}PCP)$Rh)_2N_2$] under 1 atm of nitrogen (^{iPr}PCP = κ^3-C_6H_3-2,6-$(CH_2P^iPr_2)_2$).[16] The present system much more strongly favors the monomer; under 1 atm of N_2 we can extrapolate a monomer/dimer ratio of 21:1 with 0.4 M total iridium (the rhodium concentration in Milstein's case; with a more typical total iridium concentration of 40 mM, the ratio is 200:1). We suspect the difference between the equilibrium constants of the two systems is largely due to the greater steric bulk of the ^{tBu}PCP ligand, compared with ^{iPr}PCP, disfavoring dimer formation.

In conclusion, precursors of the (PCP)Ir fragment, including (PCP)IrPhH and (PCP)Ir(NBE), readily react with dinitrogen to give $[(PCP)Ir]_2(N_2)$ (**2**). In the presence of excess dinitrogen, mononuclear (PCP)Ir(N_2) (**1**) is formed predominantly, in equilibrium with small concentrations of dinuclear complex **2** (eq 1). Although monomer **1** is the major species in solution (ca. 99% under typical conditions at 1 atm of N_2), dimer **2** tends to selectively crystallize out at ambient temperature.

Experimental Section

General Experimental Methods. All reactions, recrystallizations, and routine manipulations were performed at ambient temperature in an argon-filled glovebox. Benzene, *p*-xylene, hexane, and deuterated solvents for use in NMR experiments were distilled from sodium/potassium alloy and vacuum-transferred under argon. (PCP)IrH_2 was synthesized according to published methods.[17] ^{1}H and $^{31}P\{^{1}H\}$ NMR spectra were obtained on a 400 MHz, Varian Inova-400 spectrometer. ^{1}H chemical shifts are reported in ppm downfield from tetramethylsilane and were referenced to residual protiated (^{1}H) or deuterated solvent. ^{31}P NMR chemical shifts were referenced to 85% H_3PO_4. Room-temperature (21 ± 1 °C) Raman spectra were obtained from a Renishaw (Renishaw Inc., Hoffman Estates, IL) System 1000 dispersive micro-Raman spectrometer. Room-temperature (21 ± 1 °C) attenuated total reflectance (ATR) FTIR spectra were recorded on a Bruker (Billerica, MA) Equinox55 spectrometer equipped with a DTGS detector and KBr beamsplitter. Additional spectroscopic details are in the Supporting Information.

(PCP)Ir(N_2). (PCP)IrH_2 (28 mg, 0.048 mmol) was dissolved in *p*-xylene (0.5 mL) containing 1.5 equiv of norbornene at room temperature in a J-Young NMR tube. This solution was freeze–pump–thawed, 950 Torr of N_2 was added, and the tube was shaken. After ca. 10 min the solvent was removed under vacuo to yield an orange-yellow compound. This was redissolved in hexane, the tube was freeze–pump–thawed, and 800 Torr of N_2 was added to it. On cooling this solution to −15 °C, orange-red crystals of (PCP)-Ir(N_2) suitable for X-ray diffraction were formed. For spectroscopic analysis a sample was prepared in a similar way in an NMR tube in benzene-d_6 and sealed under N_2 pressure; (PCP)Ir(N_2) was formed in 94% yield ($^{31}P\{^{1}H\}$ NMR). ^{31}P NMR (161.9 MHz, benzene-d_6): δ 72.5 (s). ^{31}P NMR (161.9 MHz, *p*-xylene-d_{10}): δ 72.9 (s). ^{1}H NMR (400 MHz, benzene-d_6): δ 7.03 (d, $J_{HH} = 7.4$ Hz, 2H, aromatic *H*), 6.91 (t, $J_{HH} = 7.8$ Hz, 1H, aromatic *H*), 3.07 (t, $J_{PH} = 3.9$ Hz, 4H, CH_2), 1.17 (t, $J_{PH} = 6.5$ Hz, 36H, $C(CH_3)_3$). ^{13}C NMR (100 MHz, benzene-d_6): δ 154.5 (t, $J_{CP} = 11.1$ Hz, Ar *C*-Ir), 123.6 (s, Ar), 120.0 (br, m), 36.6 (vt, $J_{CP} = 14.1$ Hz, CH_2P), 35.9 (vt, $J_{CP} = 10.3$ Hz, $PC(CH_3)_3$), 29.4 (s, $PC(CH_3)_3$). IR (solid, ATR/FTIR): $\nu_{NN} = 2084$, 2076 cm^{-1}. IR (C_6D_6): $\nu_{NN} = 2079$ cm^{-1}. Raman (solid): $\nu_{NN} = 2094$, 2077 cm^{-1}. Raman (C_6D_6): $\nu_{NN} = 2083$ cm^{-1}.

(PCP)Ir(N≡N)Ir(PCP). (PCP)IrH_2 (28 mg, 0.048 mmol) was dissolved in *p*-xylene (0.5 mL) containing 1.5 equiv of norbornene at room temperature in a J-Young NMR tube. This solution was freeze–pump–thawed, 1 atm of N_2 was added to it, and the tube was shaken. After ca. 10 min the solvent was removed under vacuo to yield an orange-yellow compound. This compound was redissolved in hexane and allowed to concentrate slowly in the glovebox. After 2–3 days large amber-colored blocks were formed, in 85%yield. ^{31}P NMR (161.9 MHz, benzene-d_6): δ 73.5 (s). ^{31}P NMR (161.9 MHz, *p*-xylene-d_{10}): δ 74.7 (s). ^{1}H NMR (400 MHz, benzene-d_6): δ 7.05 (d, $J_{HH} = 7.4$ Hz, 2H, aromatic *H*), 6.94 (t, $J_{HH} = 7.3$ Hz, 1H, aromatic *H*), 3.06 (t, $J_{PH} = 2.7$ Hz, 4H, CH_2), 1.26 (t, $J_{PH} = 6.2$ Hz, 36H, $C(CH_3)_3$). ^{13}C NMR (100 MHz, benzene-d_6): δ 153.1 (t, $J_{CP} = 9.9$ Hz, Ar *C*-Ir), 122.9 (s, Ar), 119.8 (br, m), 37.2 (vt, $J_{CP} = 14.4$ Hz, CH_2P), 35.1 (vt, $J_{CP} = 9.5$ Hz, $PC(CH_3)_3$), 30.5 (s, $PC(CH_3)_3$). Raman (solid): $\nu_{NN} = 1979$ cm^{-1}.

Monomer/Dimer Equilibrium (reaction 1). In a J-Young NMR tube, (PCP)IrH_2 (10 mg, 0.018 mmol) was dissolved in benzene-d_6 (0.5 mL) containing 1.5 equiv of norbornene at room temperature,

---

(9) Stephan, G. C.; Peters, G.; Lehnert, N.; Habeck, C. M.; Naether, C.; Tuczek, F. *Can. J. Chem.* **2005**, *83*, 385–402.

(10) Dows, D. A. *J. Chem. Phys.* **1960**, *32*, 1342–1347.

(11) Anson, C. E.; Jayasooriya, U. A. *Spectrochim. Acta, Part A* **1990**, *46A*, 861–869.

(12) Anson, C. E.; Jayasooriya, U. A. *Spectrochim. Acta, Part A* **1990**, *46A*, 967–974.

(13) Battino, R.; Cleve, H. L. *Chem. Rev.* **1966**, *66*, 395–463.

(14) Gjaldbaek, J. C.; Hildebrand, J. H. *J. Am. Chem. Soc.* **1949**, *71*, 3147–3150.

(15) (a) Bercaw, J. E. *J. Am. Chem. Soc.* **1974**, *96*, 5087–5095. (b) Yoshida, T.; Okano, T.; Thorn, D. L.; Tulip, T. H.; Otsuka, S.; Ibers, J. A. *J. Organomet. Chem.* **1979**, *181*, 183–201. (c) van der Boom, M. E.; Liou, S.-Y.; Ben-David, Y.; Shimon, L. J. W.; Milstein, D. *J. Am. Chem. Soc.* **1998**, *120*, 6531–6541. (d) Gusev, D. G.; Dolgushin, F. M.; Antipin, M. Y. *Organometallics* **2000**, *19*, 3429–3434.

(16) Cohen, R.; Rybtchinski, B.; Gandelman, M.; Rozenberg, H.; Martin, J. M. L.; Milstein, D. *J. Am. Chem. Soc.* **2003**, *125*, 6532–6546.

(17) (a) Gupta, M.; Hagen, C.; Flesher, R. J.; Kaska, W. C.; Jensen, C. M. *Chem. Commun.* **1996**, 2083–2084. (b) Zhu, K.; Achord, P. D.; Zhang, X.; Krogh-Jespersen, K.; Goldman, A. S. *J. Am. Chem. Soc.* **2004**, *126*, 13044–13053. (c) Goldman, A. S.; Ghosh, R. In *Handbook of C-H Transformations–Applications in Organic Synthesis*; Dyker, G., Ed.; Wiley-VCH: New York, 2005; pp 616–621.

to give a solution of (PCP)Ir(C_6D_5)(D). This solution was freeze−pump−thawed, 200 Torr of N_2 was added to it, and the tube was shaken. The tube was then equilibrated under 102 Torr of N_2, over 2 days, and the concentrations of **1** and **2** were measure by inverse-gated ^{31}P NMR. The ratio of [**1**]:[**2**] was found to be 32:1, implying respective concentrations of 0.0330 and 0.00103 M, to yield an equilibrium constant of 7.9 M atm^{-1}.

Acknowledgment. We thank the Division of Chemical Sciences, Office of Basic Energy Sciences, Office of Energy Research, U.S. Department of Energy, for support of this research.

Supporting Information Available: Crystallographic data for complexes **1** and **2** and Raman and IR spectroscopic details. This material is available free of charge via the Internet at http://pubs.acs.org.

OM0607043