Oxidative Addition and Reductive Elimination Reactions of *trans*-[Ir(PPh_3)$_2$(CO)(NC_4H_4)] and *trans,cis*-[Ir(PPh_3)$_2$(H)$_2$(CO)(NC_4H_4)], Including N−H Bond-Forming Reductive Elimination of Pyrrole

Michael S. Driver and John F. Hartwig*

Department of Chemistry, Yale University, P.O. Box 208107, New Haven, Connecticut 06520-8107

Received November 28, 1997

The complex *trans*-(PPh_3)$_2$(CO)Ir(NC_4H_4) (**1**) has been synthesized and is an analogue of metal−aryl complexes, but with a nitrogen of the heteroaromatic group covalently bonded to the transition metal. Compound **1** readily undergoes initial reaction with a variety of substrates at the metal center rather than at the pyrrolyl nitrogen, allowing for the study of reactions between the pyrrolyl group and accompanying covalent ligands. These reactions ultimately produce *N*-substituted pyrroles, X-NC_4H_4 (X = C(O)CH_3, C(O)$C_6H_4CH_3$, H, $SnMe_3$, $SiMe_3$, $SiEt_3$, Bcat). Compound **1** undergoes oxidative addition of H_2 to form the stable Ir(III) product (PPh_3)$_2$(CO)Ir(H)$_2$(NC_4H_4) (**2**). When pure **2** is heated, it undergoes simple elimination of H_2 to regenerate **1**; however, if **2** is heated for longer times under H_2 in the presence of PPh_3, it undergoes reductive elimination of pyrrole and forms (PPh_3)$_3$(CO)Ir(H). Qualitative analysis of the mechanism of this reaction suggests that it occurs by either direct reductive elimination from the octahedral complex or rate-determining ligand dissociation, followed by rapid reductive elimination of pyrrole. Reductive elimination of pyrrole from **2** was also observed to occur photochemically by initial irreversible dissociation of a dative ligand.

Introduction

Oxidative addition and reductive elimination reactions involving the C−C and C−H bonds of organic substrates are among the fundamental transformations of organometallic chemistry. The mechanisms of these transformations have been studied extensively and have provided a detailed understanding of how these processes occur. Such mechanistic information has been instrumental in the development of homogeneous catalytic reactions resulting in C−H and C−C bond formation.[1] Recently, there has been an increasing interest in parallel oxidative addition and reductive elimination reactions involving the H-heteroatom (N, O, and S) and C-heteroatom bonds of organic compounds. It is important to understand how these transformations occur in order to apply them to the development of catalytic reactions involving the cleavage and formation of H−X and C−X bonds. The catalytic hydrogenation of ketones,[2−11] imines,[2,12−29] and nitriles[30,31] is thought to proceed via metal−alkoxo and metal−amido intermediates. The proposed mechanistic cycle for these hydrogenation reactions invokes O−H and N−H bond-forming reductive eliminations to form the final alcohol and amine products; likewise, the reverse reaction,

(1) Collman, J. P.; Hegedus, L. S.; Norton, J. R.; Finke, R. G. *Principles and Applications of Organotransition Metal Chemistry*, 2nd ed.; University Science Books: Mill Valley, CA, 1987; pp 322−333.
(2) Bakos, J.; Toth, I.; Heil, B.; Szalontai, G.; Parkanyi, L.; Fulop, V. *J. Organomet. Chem.* **1989**, *370*, 263.
(3) Delgado-Lieta, E.; Luke, M. A.; Jones, R. F.; Cole-Hamilton, D. J. *Polyhedron* **1982**, *1*, 839.
(4) Jung, C. W.; Garrou, P. E. *Organometallics* **1982**, *1*, 658.
(5) Sanchez-Delgado, R. A.; Valencia, N.; Rosa-Linda, M. S.; Antida, A.; Medina, M. *Inorg. Chem.* **1986**, *25*, 1106.
(6) Tani, K.; Suwa, K.; Tanigawa, E.; Yoshida, T.; Okano, T.; Otsuka, S. *Chem. Lett.* **1982**, 261.
(7) Tani, K.; Tanigawa, E.; Tatsuno, Y.; Otsuka, S. *J. Organomet. Chem.* **1985**, *279*, 87.
(8) Tani, K.; Tanigawa, E.; Tatsuno, Y.; Otsuka, S. *Chem. Lett.* **1986**, 737.
(9) Noyori, R.; Takaya, H. *Acc. Chem. Res.* **1990**, *23*, 345.
(10) Takahashi, H.; Sakuraba, S.; Takeda, H.; Achiwa, K. *J. Am. Chem. Soc.* **1990**, *112*, 5876.
(11) Kawano, H.; Y. I.; Saburi, M.; Uchida, Y. *J. Chem. Soc., Chem. Commun.* **1988**, 87.
(12) Amrani, Y.; Lecomte, L.; Simou, D.; Bakos, J.; Toth, I.; Heil, B. *Organometallics* **1989**, *8*, 542.
(13) Bakos, J.; Toty, I.; Heil, B.; Marko, L. *J. Organomet. Chem.* **1985**, *279*, 23.
(14) Bakos, J.; Orosz, A.; Heil, B.; Laghmari, M.; Lhoste, P.; Sinou, D. *J. Chem. Soc., Chem. Commun.* **1991**, 1684.
(15) Becalski, A. G.; Cullen, W. R.; Fryzuk, M. D.; James, B. R.; Kang, G. J.; Rettig, S. J. *Inorg. Chem.* **1991**, *30*, 5002.
(16) Burk, M. J.; Feaster, J. E. *J. Am. Chem. Soc.* **1992**, *114*, 6266.
(17) Chan, Y. N. C.; Osborn, J. A. *J. Am. Chem. Soc.* **1990**, *112*, 9400.
(18) Cullen, W. R.; Fryzuk, M. D.; James, B. R.; Kutney, J. P.; Kang, G. J.; Herb, G.; Thorburn, I. S.; Spogliarich, R. *J. Mol. Catal.* **1990**, *62*, 243.
(19) Fryzuk, M. D.; Piers, W. E. *Organometallics* **1990**, *9*, 986.
(20) For a recent review see: James, B. R. *Chem. Ind.* **1995**, *62*, 167.
(21) Kang, G. J.; Cullen, W. R.; Fryzuk, M. D.; James, B. R.; Kutney, J. P. *J. Chem Soc., Chem. Commun.* **1988**, 1466.
(22) Longley, C. J.; Goodwin, T. J.; Wilkinson, G. *Polyhedron* **1986**, *5*, 1625.
(23) Ng, Y.; Chan, C.; Meyer, D.; Osborm, J. A. *J. Chem. Soc., Chem. Commun.* **1990**, 869.
(24) Spindler, F.; Pugin, B.; Blaser, H. U. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 558.
(25) Vastag, S.; Bakos, J.; Toros, S.; Takach, N. E.; King, R. B.; Heil, B.; Marko, L. *J. Mol. Catal.* **1984**, *22*, 283.
(26) Willoughby, C. A.; Buchwald, S. L. *J. Am. Chem. Soc.* **1992**, *114*, 7562.
(27) Willoughby, C. A.; Buchwald, S. L. *J. Org. Chem.* **1993**, *58*, 7627.

S0276-7333(97)01049-2 CCC: $15.00
Publication on Web 02/24/1998

dehydrogenation of alcohols, may involve the oxidative addition of an O−H bond.[4,32] In a similar manner, the alcoholysis of organohalides[33] is believed to proceed through metal−alkoxide complexes to form the ether products. The hydration of olefins has also been observed to occur by olefin insertion into a metal−hydroxide bond.[34] Another catalytic process which has recently been reported leads to the addition of aniline across an olefin via oxidative addition of the aniline to form a metal−amido intermediate.[35,36]

Recently, there has been a significant amount of research conducted on C−N bond-forming reductive eliminations of amines. Much of this work has been conducted in combination with the development of palladium-catalyzed aryl halide amination chemistry.[37−41] Mechanistic analysis of the original amination reaction involving aminostannanes[42,43] and analysis of C−N bond-forming reductive-elimination reactions to form amines[44,45] provided insights that led to substantial improvements in the catalytic amination chemistry. These improvements included the replacement of toxic, air-sensitive aminostannanes with free amines and an alkoxide base[46,47] and the use of catalytic species containing chelating phosphines. These developments have dramatically increased substrate specificity and compatibility.[48−50] N−H bond cleavage chemistry is crucial to the amination using amines as substrates.

The reactivity of N−H bonds with late-transition-metal complexes remains scarce. Although there have been reports of oxidative addition[30,35,51−64] and reductive elimination[65,66] reactions of N−H bonds with late-transition-metal complexes, no clear mechanistic understanding of these transformations has emerged. Earlier studies conducted on the reductive elimination of amine and alcohol from $(C_5Me_5)(PPh_3)Ir(X)(H)$ (X = NHPh, OEt)[66] showed the formation of an intermediate but did not directly probe the O−H and N−H bond-forming steps. The introduction of a ligand (L = CO, C_2H_4, $CNBu^t$, PPh_3, PPh_2Me) to a solution of $(C_5Me_5)(PPh_3)Ir(X)(H)$ induced reductive elimination of either aniline or ethanol. Results from a detailed mechanistic analysis of these reactions ruled out pathways including dative ligand association, dative ligand dissociation, ligand homolysis to form radicals, dissociation of the anionic ligand, ligand migration to the Cp* ring, formation of an ethanol or aniline σ-complex, as well as direct elimination. A pathway involving a ring slip of the Cp* ligand from an η^5- to η^3-bonding mode followed by trapping of this intermediate by PPh_3 was the most probable mechanism. Further information on O−H and N−H bond-forming reductive eliminations in other systems is needed to provide a general view on how this class of reaction occurs.

We report here the preparation and reactivity of an iridium−pyrrolyl complex. Little organometallic reaction chemistry of η^1-pyrrolyl or indolyl ligands has been published. The synthesis of a related Ir(I) η^1-indolyl from Vaska's complex was reported during the course of the work described here, but the only reaction chemistry included in this paper was protonation of the indolyl ligand with triflic acid.[67] We report that the pyrrolyl complex *trans*-$(PPh_3)_2(CO)Ir(NC_4H_4)$ undergoes oxidative addition and reductive elimination reactions with a variety of substrates to ultimately produce *N*-substituted pyrroles. In one of these reactions, the pyrrolyl complex oxidatively adds H_2 to form a stable Ir(III)−pyrrolyl dihydride. When heated in the presence of free PPh_3 and H_2, the Ir(III) complex undergoes reductive elimination of pyrrole. The reductive elimination of pyrrole was also induced photochemically. The mechanism of these reductive eliminations is not clearly defined, but it appears to involve irreversible ligand dissociation.

Results and Discussion

Synthesis and Characterization of Iridium Pyrrolyl Complexes. The synthesis of *trans*-$(PPh_3)_2(CO)$-

(28) Willoughby, C. A.; Buchwald, S. L. *J. Am. Chem. Soc.* **1994**, *116*, 11703.
(29) Willoughby, C. A.; Buchwald, S. L. *J. Am. Chem. Soc.* **1994**, *116*, 8952.
(30) Armor, J. N. *Inorg. Chem.* **1978**, *17*, 203.
(31) Yoshida, T.; Okano, T.; Otsuka, S. *J. Chem. Soc., Chem. Commun.* **1979**, 870.
(32) Morton, D.; Cole-Hamilton, D. J. *J. Chem. Soc., Chem. Commun.* **1987**, 248.
(33) Milstein, D. *J. Chem. Soc., Chem. Commun.* **1986**, 817.
(34) Ganguly, S.; Roundhill, D. M. *J. Chem. Soc., Chem. Commun.* **1991**, 639.
(35) Casalnuovo, A. L.; Calabrese, J. C.; Milstein, D. *J. Am. Chem. Soc.* **1988**, *110*, 6738.
(36) Dorta, R.; Egli, P.; Zürcher, F.; Togni, A. *J. Am. Chem. Soc.* **1997**, *119*, 10857.
(37) Kosugi, M.; Kameyama, M.; Migita, T. *Chem. Lett.* **1983**, 927.
(38) Kosugi, M.; Kameyama, M.; Sano, H.; Migita, T. *Nippon Kagaku Kaishi* **1985**, *3*, 547.
(39) Paul, F.; Patt, J.; Hartwig, J. F. *J. Am. Chem. Soc.* **1994**, *116*, 5969.
(40) Guram, A. S.; Buchwald, S. L. *J. Am. Chem. Soc.* **1994**, *116*, 7901.
(41) For a review, see: Hartwig, J. F. *Synlett* **1996**, 329.
(42) Louie, J.; Hartwig, J. F. *J. Am. Chem. Soc.* **1995**, *117*, 11598.
(43) Louie, J.; Paul, F.; Hartwig, J. F. *Organometallics* **1996**, *15*, 2794.
(44) Driver, M. S.; Hartwig, J. F. *J. Am. Chem. Soc.* **1995**, *117*, 4708.
(45) Driver, M. S.; Hartwig, J. F. *J. Am. Chem. Soc.* **1997**, *119*, 8232.
(46) Louie, J.; Hartwig, J. F. *Tetrahedron Lett.* **1995**, *36*, 3609.
(47) Guram, A. S.; Rennels, R. A.; Buchwald, S. L. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1348.
(48) Driver, M. S.; Hartwig, J. F. *J. Am. Chem. Soc.* **1996**, *118*, 7217.
(49) Wolfe, J. P.; Wagaw, S.; Buchwald, S. L. *J. Am. Chem. Soc.* **1996**, *118*, 7215.
(50) Louie, J.; Driver, M. S.; Hamann, B. C.; Hartwig, J. F. *J. Org. Chem.* **1997**, *62*, 1268.
(51) Hillhouse, G. L.; Bercaw, J. E. *J. Am. Chem. Soc.* **1984**, *106*, 5472.
(52) Samat, A.; Sala-Pala, J.; Guglielmetti, R.; Guerchais, J. *Nouv. J. Chem.* **1978**, *2*, 13.
(53) Casalnuovo, A. L.; Calabrese, J. C.; Milstein, D. *Inorg. Chem.* **1987**, *26*, 971.
(54) Hsu, G. C.; Kosar, W. P.; Jones, W. D. *Organometallics* **1994**, *13*, 385.
(55) Ladipo, F. T.; Merola, J. S. *Inorg. Chem.* **1990**, *29*, 4172−4173.
(56) Fornies, J.; Green, M.; Spencer, J. L.; Stone, F. G. *J. Chem. Soc., Dalton Trans.* **1977**, 1006.
(57) Jones, W. D.; Dong, L.; Myers, A. W. *Organometallics* **1995**, *14*, 855.
(58) Hedden, D.; Roundhill, D. M.; Fultz, W. C.; Rheingold, A. L. *J. Am. Chem. Soc.* **1984**, *106*, 5014.
(59) Lin, Y.; Mayr, A.; Knobler, C. B.; Kaesz, H. D. *J. Organomet. Chem.* **1984**, *272*, 207.
(60) Bryan, E. G.; Johnson, B. F. G.; Lewis, J. *J. Chem. Soc., Dalton Trans.* **1977**, 1328−1330.
(61) Johnson, B. F. G.; Lewis, J.; Odiaka, T. I.; Raithby, P. R. *J. Organomet. Chem.* **1981**, *216*, C56.
(62) Rauchfuss, T. B.; Roundhill, D. M. *J. Am. Chem. Soc.* **1974**, *96*, 3098.
(63) Park, S.; Hedden, D.; Roundhill, D. M. *Organometallics* **1986**, *5*, 2151.
(64) Hedden, D.; Roundhill, D. M. *Inorg. Chem.* **1986**, *25*, 9.
(65) Yamamoto, T.; Sano, K.; Yamamoto, A. *Chem. Lett.* **1982**, 907.
(66) Glueck, D. S.; Winslow, L. J.; Bergman, R. G. *Organometallics* **1991**, *10*, 1462.
(67) Chen, S.; Noll, B. C.; Peslherbe, L.; Rakowski DuBois, M. *Organometallics* **1997**, *16*, 1089.

Table 1. Infrared Spectra of Selected Iridium Complexes

Ir(I) complexes	ν_{CO}, cm^{-1}	Ir(III) complexes	ν_{CO}, cm^{-1}	$\nu_{IrH/D}$, cm^{-1}
$(PPh_3)_2(CO)Ir(NC_4H_4)$	1964[a]	$(PPh_3)_2(CO)Ir(H)_2(NC_4H_4)$	2075[a]	2142, 2183[a]
$(PPh_3)_2(CO)IrCl$	1950[b]	$(PPh_3)_2(CO)Ir(H)_2Cl$	1975[b]	2100, 2190[b]
$(PPh_3)_2(CO)IrBr$	1955[b]	$(PPh_3)_2(CO)Ir(H)_2Br$	1982[b]	2105, 2200[b]
$(PPh_3)_2(CO)IrI$	1975[b]	$(PPh_3)_2(CO)Ir(H)_2I$	1995[b]	2100, 2225[b]
		$(PPh_3)_2(CO)Ir(D)_2(NC_4H_4)$	2017[a]	1553[a]
		$(PPh_3)_2(CO)Ir(D)_2Cl$	1995[b]	1572[b]

[a] KBr pellet. [b] Reference 64.

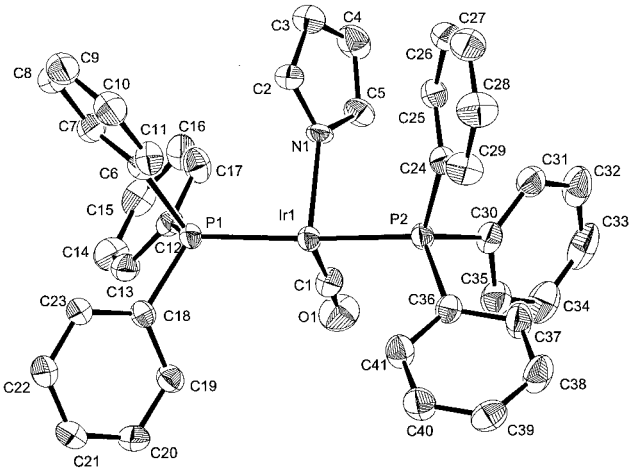
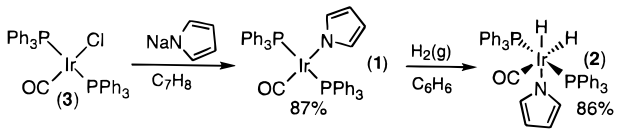


Figure 1. ORTEP drawing of **2**. Hydrogen atoms were omitted for clarity. The two iridium hydrides were not located.

Scheme 1



$Ir(NC_4H_4)$ (**1**) and $(PPh_3)_2(CO)Ir(H)_2(NC_4H_4)$ (**2**) are summarized in Scheme 1. Addition of $NaNC_4H_4$ to a THF solution of *trans*-$(PPh_3)_2(CO)IrCl$ (**3**) led to the formation of **1** in 87% isolated yield. Subsequently, **2** was prepared in 86% isolated yield by addition of ~2 atm of H_2 to **1** at room temperature for 36 h. Complexes **1** and **2** were characterized by ^1H, $^{13}C\{^1H\}$, and $^{31}P\{^1H\}$ NMR and IR spectroscopy, as well as elemental analysis. Complex **2** was also characterized by X-ray diffraction, as discussed below. The $^{31}P\{^1H\}$ NMR spectrum of **1** consisted of a singlet at δ 20.7, upfield from the resonance for Vaska's complex **3** (δ 24.8), while the $^{31}P\{^1H\}$ NMR signal for the pyrrolyl dihydride **2** was located even further upfield at δ 7.0. The hydride resonances for **2** appeared as two doublets of triplets (δ −15.84, −6.89, J = 5.0, 16.7 Hz), indicating that the hydrides are cis to one another, inequivalent, and located cis to the two equivalent phosphine ligands, as shown in Scheme 1. In the IR spectrum, the ν_{CO} for **1** appeared at 1964 cm^{-1}, a higher stretching frequency than the ν_{CO} for Vaska's complex (1950 cm^{-1}). The CO ligand of **2** vibrates at a slightly higher frequency, 1967 cm^{-1} (see Table 1).

X-ray Structure of 2. Crystals of **2** suitable for an X-ray diffraction study were obtained by layering a toluene solution of **2** with pentane. An ORTEP drawing of **2** is provided in Figure 1; data on crystal parameters, data collection, and refinement are provided in Table 2, while selected bond distances and angles are given in Tables 3 and 4. The structure of **2** showed a pseudo-octahedral geometry. The two metal hydrides were not located, but are clearly present in the two vacant cis sites. The pyrrolyl ligand maintains planarity; the sum of the three bond angles at nitrogen is exactly 360°. The plane of the pyrrolyl ligand is slightly skewed from the plane of the two hydrides, the CO, and the iridium. The C(1)−Ir−N−C(5) torsional angle is 26.8(4)°. Most notably, the iridium−nitrogen distance is 0.074 Å longer than the Ir−indolyl distance in a PPh_3-ligated Ir(I) indolyl complex[67] but only 0.02 Å longer than that in a related tris-PMe_3 Ir(III) indolyl complex.[55]

Table 2. Data Collection and Refinement Parameters for the Structure of 2

A. Crystal Data	
empirical formula	$C_{43.50}H_{34}NOP_2Ir$
fw	840.92
cryst color, habit	yellow, prismatic
cryst dimens	0.19 × 0.25 × 0.40 mm
cryst syst	triclinic
lattice type	primitive
lattice params	a = 9.470(1)Å
	b = 12.123(1) Å
	c = 17.531(1) Å
	α = 79.208(6)°
	β = 74.742(5)°
	γ = 71.834(8)°
	V = 1832.7(3) Å^3
space group	$P\bar{1}$ (No. 2)
Z value	2
D_{calc}	1.524 g/cm^3
F_{000}	834.00
μ(Mo Kα)	37.74 cm^{-1}
no. of reflns measd	total 7682
	unique 7428 (R_{int} = 0.024)
corrections	Lorentz−polarization abs (transmission factors 0.7283 − 1.0000)
no. of observations ($I > 3.00\sigma(I)$)	6426
no. of variables	427
residuals: R; R_w	0.034; 0.042

Table 3. Selected Bond Lengths (Å) for 2

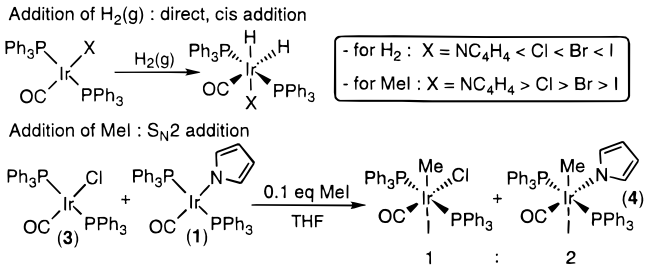
Ir(1)−P(1)	2.323(1)	Ir(1)−P(2)	2.338(1)
Ir(1)−N(1)	2.154(4)	Ir(1)−C(1)	1.916(6)
O(1)−C(1)	1.147(7)	N(1)−C(2)	1.354(6)
N(1)−C(5)	1.344(6)	C(2)−C(3)	1.366(8)
C(3)−C(4)	1.399(9)	C(4)−C(5)	1.373(8)

Table 4. Selected Bond Angles (deg) for 2

P(1)−Ir(1)−P(2)	169.76(4)	P(1)−Ir(1)−N(1)	90.8(1)
P(1)−Ir(1)−C(1)	92.7(2)	P(2)−Ir(1)−N(1)	90.1(1)
P(2)−Ir(1)−C(1)	97.3(2)	N(1)−Ir(1)−C(1)	96.5(2)
Ir(1)−N(1)−C(2)	126.2(3)	Ir(1)−N(1)−C(5)	126.1(3)
C(2)−N(1)−C(5)	107.7(4)	Ir(1)−C(1)−O(1)	174.6(5)
N(1)−C(2)−C(3)	110.1(5)	C(2)−C(3)−C(4)	105.8(5)
C(3)−C(4)−C(5)	107.3(5)	N(1)−C(5)−C(4)	109.1(5)

Oxidative Addition Reactions of H_2 and MeI to 1. Complex **1** undergoes oxidative addition reactions similar to those observed for Vaska's complex **3** and the

Scheme 2



other halide derivatives of **3**.[68] As discussed above, **1** oxidatively adds H_2 to form **2**. Qualitative studies of the addition of H_2 to **1** indicated that the reaction is not inhibited by the addition of free phosphine, disfavoring a mechanism involving initial, reversible dissociation of PPh_3. As is the case for Vaska's complex, the addition of H_2 to **1** is reversible. When a benzene solution of **2** was heated under vacuum at 95 °C, H_2 was eliminated to regenerate **1**. Due to these similarities in reactivity and in the geometries of the two addition products, the addition of H_2 to **1** most likely proceeds through the same mechanism of concerted, direct cis addition as observed for Vaska's complex.[68] In qualitative comparisons of the rates of H_2 addition, pyrrolyl complex **1** reacted much slower than did Vaska's complex.

Complex **1** also underwent oxidative addition of MeI to form $(PPh_3)_2(CO)Ir(CH_3)(I)(NC_4H_4)$ (**4**), as shown in Scheme 2. The formation of **4** was indicated by a large upfield shift in the $^{31}P\{^1H\}$ NMR spectrum from δ 20.7 for **1** to δ −14.8. The Me resonance appeared in the ^1H NMR spectrum as a triplet at δ 1.26 (J = 4.9 Hz), indicating that the Me group is located cis to the two equivalent phosphine ligands. This reactivity of MeI at the metal center contrasts that of late-transition-metal amido complexes which undergo *N*-alkylation of the amido ligand.[69−75] In a competition study, equimolar amounts of **1** and Vaska's complex were mixed with 0.1 equiv of MeI. The ratio of **4**: $(PPh_3)_2(CO)Ir(CH_3)(I)(Cl)$ was 2:1. Since the addition of MeI is thought to be an S_N2 mechanism,[68] the preferential reactivity of **1** with MeI indicates that **1** possesses a more nucleophilic Ir center than does Vaska's complex.

The relative rates for H_2 and MeI additions to **1** can be interpreted along with the relative rates for addition of these substrates to $(PPh_3)_2(CO)IrX$ (X = Cl, Br, I). For example, the relative rates for MeI addition are NC_4H_4 > Cl > Br > I, as shown in Scheme 2.[68] This trend suggests that the Ir center is the most nucleophilic in the case of pyrrolyl complex **1**. It is well-known that the relative rates for addition of H_2 to the various halide versions of Vaska's complex are the opposite of those for the addition of MeI.[68,76] Again, pyrrolyl complex **1** falls at the end of the spectrum of rates, I > Br > Cl > NC_4H_4 (Scheme 2). However, the ν_{CO} values do not seem to follow the same trend. The pyrrolyl complex falls in the middle of the halides: Cl > Br > NC_4H_4 > I. The origins of the subtle σ and π effects on the ν_{CO} are complex and are still evolving.[77,78] Perhaps the trends in oxidative addition reaction rates are a better measure of the electron density of the metal centers than ν_{CO} in this case.

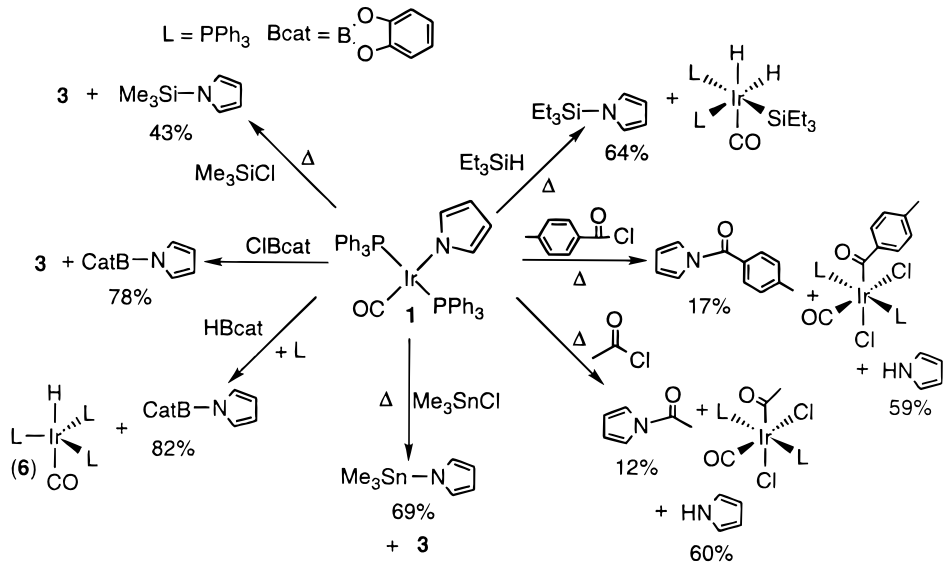
Oxidative Addition and Reductive Elimination Reactions of 1 Resulting in *N*-Substituted Pyrroles. Complex **1** undergoes reaction with a variety of substrates to produce *N*-substituted pyrroles, as shown in Scheme 3. The formation of an *N*-substituted pyrrole is indicative of a pathway initiated by oxidative addition of the substrate to the Ir center followed by reductive elimination of the corresponding pyrrole. A pathway of external nucleophilic attack would result in a 2-substituted pyrrole, since the α-carbon is the most nucleophilic site on the pyrrolyl ligand. The formation of a 2-substituted pyrrole has been observed previously in our laboratory from the addition of CD_3I to (DPPE)Pd-$(CH_3)(NC_4H_4)$[79] to give 2-methyl-d_3-pyrrole,[75] and the indolyl complex reported by Rakowski DuBois[67] is protonated at the 3-position.

When the methyl iodide oxidative-addition product **4** was heated at 95 °C for 18 h, no *N*-methylpyrrole was observed; only the formation of pyrrole was detected. No other organic products were identified, and no CH_4 or C_2H_6 was observed. The proton source is unknown. However, the addition of MeI to *trans*-$(PPh_3)_2(CO)Ir(OMe)$[80] gave a similar formation of MeOH with no Me_2O.

Complex **1** underwent oxidative addition with acetyl chloride to form the new Ir(III) species $(PPh_3)_2(CO)Ir[C(O)CH_3](Cl)(NC_4H_4)$ (**5**). Again, the $^{31}P\{^1H\}$ NMR spectrum showed a large upfield shift for the Ir(III) species (δ −15.4), and a new acetyl peak appeared at δ 1.39 in the ^1H NMR spectrum. Attempts to isolate this Ir(III) complex were unsuccessful due to decomposition of this acetyl halide adduct. However, when the reaction of 2 equiv of acetyl chloride with **1** was monitored by NMR spectrometry in benzene-d_6, it was observed that all of **1** was converted to the Ir(III) species **5**. Heating the complex generated *in situ* at 70 °C resulted in the formation of *N*-acetyl pyrrole (12%) and pyrrole (60%).[81] The only metal product observed by $^{31}P\{^1H\}$ NMR spectroscopy was $(PPh_3)_2(CO)Ir[C(O)CH_3](Cl)_2$ (δ −18.8). Similar reactivity was observed upon addition of *p*-toluoyl chloride to **1**. The addition of 2 equiv of *p*-toluoyl chloride to a toluene-d_8 solution of **1**, however, did not result in the formation of an Ir(III) complex at room temperature. Instead, addition of *p*-toluoyl chloride followed by heating of the sample at 80 °C led to the formation of *N*-*p*-toluoylpyrrole (17%) and pyrrole (59%). The identities of the *N*-substituted pyrroles were

(68) Chock, P. B.; Halpern, J. *J. Am. Chem. Soc.* **1966**, *88*, 3511.
(69) Bryndza, H. A.; Fultz, W. C.; Tam, W. *Organometallics* **1985**, *4*, 939.
(70) Bryndza, H. E.; Tam, W. *Chem. Rev.* **1988**, *88*, 1163 and references therein.
(71) Cowan, R. L.; Trogler, W. C. *J. Am. Chem. Soc.* **1989**, *111*, 4750.
(72) Fryzuk, M. D.; Montgomery, C. D. *Coord. Chem. Rev.* **1989**, *95*, 1−40 and references therein.
(73) Dewey, M. A.; Bakke, J. M.; Gladysz, J. A. *Organometallics* **1990**, *9*, 1349.
(74) Dewey, M. A.; Knight, A.; Arif, A.; Gladysz, J. A. *Chem. Ber.* **1992**, *125*, 815.
(75) Driver, M. S. Ph.D. Thesis, Yale University, 1997.
(76) Strohmeier, W. *J. Organomet. Chem.* **1971**, *32*, 137.
(77) Poulton, J. T.; Sigalas, M. P.; Folting, K.; Streib, W. E.; Eisenstein, O.; Caulton, K. G. *Inorg. Chem.* **1994**, *33*, 1476.
(78) Abu-Hasanayn, F.; Goldman, A. S.; Krogh-Jespersen, K. *Inorg. Chem.* **1994**, *33*, 5122.
(79) DPPE = 1,2-bis(diphenylphospino)ethane.
(80) Bernard, K. A.; Atwood, J. D. *Organometallics* **1987**, *6*, 1133.
(81) Yields measured by ^1H NMR spectroscopy using an internal standard.

Scheme 3

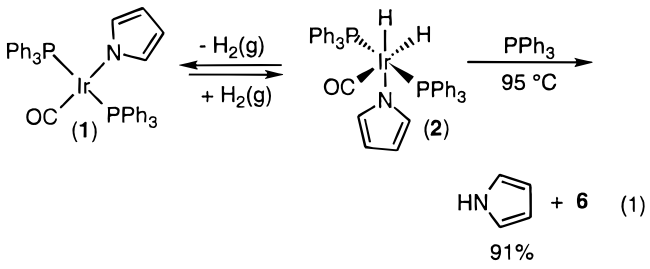


confirmed by generation of an authentic sample by addition of acetyl chloride or *p*-toluoyl chloride to sodium pyrrolyl.

Electrophilic substrates containing Sn, Si, and B were reacted with **1** to explore the scope of its oxidative addition/reductive elimination reactions with main-group reagents. Heating a sample of Me_3SnCl with **1** in benzene-d_6 at 80 °C for 14 h led to the formation of *N*-(trimethylstannyl)pyrrole in 69% yield. Vaska's complex **3** was the only Ir product observed by $^{31}P\{^1H\}$ NMR spectroscopy. None of the Ir(III) oxidative addition product was detected either at room temperature or throughout the course of the reaction. Silanes and chlorosilanes also reacted with **1**. Heating a benzene-d_6 solution of Me_3SiCl with **1** at 80 °C for 14 h gave *N*-(trimethylsilyl)pyrrole in 43% yield. Again, **3** was the only Ir product observed by $^{31}P\{^1H\}$ NMR spectroscopy. When a benzene-d_6 solution of Et_3SiH and **1** was heated at 80 °C for 18 h, *N*-(triethylsilyl)pyrrole was formed in 64% yield. The iridium product was the known $(PPh_3)_2(CO)Ir(SiEt_3)(H)_2$[82] (66%). Again, no Ir(III) pyrrolyl species was observed either at room temperature or throughout the course of the reactions with silanes. The reactions of **1** with chloroboronate esters occurred rapidly, even below room temperature. Addition of ClBcat[83] to a room-temperature solution of **1** led to the rapid formation of 2-pyrrolyl-1,3,2-benzodioxaborole in 78% yield and **3** in 89% yield. Similarly, addition of 1 equiv of HBcat[84] to a solution of **1** with added PPh_3 gave 2-pyrrolyl-1,3,2-benzodioxaborole in 82% yield. $(PPh_3)_3(CO)Ir(H)$[85] (**6**) was the dominant Ir product (ca. 90%) observed by $^{31}P\{^1H\}$ NMR spectroscopy. When an excess amount of HBcat was used, the product **6** was observed to react with HBcat to form an unidentified Ir complex. With both boronate esters, formation of the *N*-substituted pyrrole occurred directly upon mixing of the samples at room temperature and no Ir(III) species was detected. Even addition of the boronate esters at −80 °C led to the formation of the *N*-substituted pyrrole too rapidly to observe an Ir(III) oxidative addition product. The identity of the *N*-substituted pyrroles was confirmed by generation of an authentic sample by addition of either Me_3SiCl, Me_3SnCl, or ClBcat to sodium pyrrolyl.

Free pyrrole reacts with electrophiles at the carbons of the aromatic ring. The addition of alkyl halides leads to the formation of a mixture of 2- and 3-alkylpyrroles, while the addition of acyl halides gives 2-acylpyrrole.[86] As mentioned above, palladium pyrrolyl complexes that do not undergo oxidative additions give reactions at the pyrrolyl carbons, and the indolyl complex reported by Rakowski DuBois[67] is protonated at the 3-position. The key to formation of *N*-substituted pyrroles from **1** is the initial reaction of the substrate with the Ir(I) center to give the Ir(III) oxidative addition intermediate with subsequent N−E (E = B, Si, Sn) reductive elimination to form the respective pyrrole products.

Reductive Elimination of Pyrrole from 2. As discussed previously, **1** oxidatively adds H_2 to form **2**. When a solution of **2** was heated at 95 °C, it reductively eliminated H_2 to regenerate **1**. Thus, an equilibrium between **2** and **1** + H_2 exists, and the equilibrium constant K_{eq} between **2** and **1** + H_2 (eq 1) at 95 °C, which is the temperature of the mechanistic studies presented below, was measured to be 500 M^{-1} at 95 °C. The ratio



of **2**:**1** was 6.2:1 at the approximately 2 atm of H_2 employed during the studies of pyrrole elimination. At room temperature, only **2** existed in measurable quantities under 2 atm of H_2.

(82) Chalk, J. *J. Chem. Soc., Chem. Commun.* **1969**, 1207.
(83) ClBcat = 2-chloro-1,3,2-benzodioxaborole.
(84) HBcat = 1,3,2-benzodioxaborole.
(85) Yagupsky, G.; Wilkinson, G. *J. Chem. Soc. A* **1969**, 725.
(86) Jones, R. A.; Bean, G. P. *The Chemistry of Pyrroles*; Academic Press: London, 1977; Vol. 34.

In contrast to this result, heating a solution of **2** with added PPh_3 under 2 atm of H_2 for several days led to N−H bond-forming reductive elimination of pyrrole (91%) and the formation of **6**, as shown in eq 1. N−H bond-forming reductive elimination has also been observed in a few other systems. The elimination of aniline has been observed from $(C_5Me_5)(PPh_3)Ir(H)(NHPh)$,[66] while the addition of π-acids to succinimido−hydride complexes of Ni, Pd, and Pt induced the elimination of succinimide.[65] By understanding the N−H bond-forming reductive elimination of amines, insight can be also be gained on the reverse reaction, the oxidative addition (activation) of the N−H bond of amines. The activation of amine N−H bonds has been observed in a handful of systems. Some early-transition-metal systems have been observed to activate ammonia[51] and pyrroles.[52] Although often accompanied by further chemistry, products resulting from some type of oxidative addition of amines to late-transition-metal complexes have been isolated from reactions with ammonia,[53] pyrroles,[54−56,57] aryl and alkylamines,[35,59,60,63] as well as imides.[65,87]

Mechanism of Pyrrole Reductive Elimination. The activation of amines to form reactive metal−amido complexes is a key step in catalytic pathways for the functionalization of amines. A better understanding of N−H reductive elimination and oxidative addition reactions is necessary for the further development of such catalysis. We studied the N−H bond-forming reductive elimination of pyrrole from **2** in order to elucidate the mechanism of this transformation. These studies were hampered by difficulties in obtaining reproducible rate constants, but we were able to show that the usual mechanism for C−H bond-forming reductive eliminations from octahedral compounds that involves reversible predissociation of a phosphine ligand is an unlikely pathway.

Previous studies conducted on other Ir(III) complexes revealed C−H bond-forming reductive eliminations that preceded by initial, reversible ligand dissociation. The carborane complex $Ir(H)(Cl)(\sigma\text{-carb})(CO)(PPh_3)_2$[88] reductively eliminated carborane after initial PPh_3 dissociation.[89] In a similar manner, the complex $Ir(H)(\sigma\text{-}CHCH_2C(O)OC(O)](\sigma\text{-carb})(CO)(PhCN)(PPh_3)$ first dissociated PhCN to generate a five-coordinate intermediate, which underwent C−H bond-forming reductive elimination to form succinic anhydride.[90] The Rh(III) complex $(PMe_3)_3Rh(H)(Cl)[CH_2C(O)CH_3]$ reductively eliminated acetone after dissociation of a PMe_3 ligand.[91] The O−H bond-forming reductive elimination of $(PEt_3)_3Ir(H)(OMe)Cl$ to form MeOH was reported to proceed by direct elimination from the six-coordinate Ir(III) complex;[92] yet, a mechanism involving irreversible phosphine loss is also consistent with the kinetic data presented.

Reaction rates were measured by ^1H NMR spectrometry under H_2 with excess PPh_3 added. Because of the partial formation of **1** under the reaction conditions, the reactions were allowed to stand at room temperature for a minimum of 3 h before obtaining ^1H NMR spectra to allow all of the iridium−pyrrolyl species to return to **2** and to, therefore, allow $[Iridium]_{total}$ to simply equal [**2**]. Quantitative studies were hampered by difficulties in reproducing the rate constants for these reactions, and the half-lives for reactions varied by as much as a factor of 2. However, qualitative studies involving added phosphine, CO, H_2, and pyrrole showed that reaction rates were independent of the concentration of all these species. Further, no noticeable difference in the reaction rates was observed between reactions in THF and reactions in toluene.

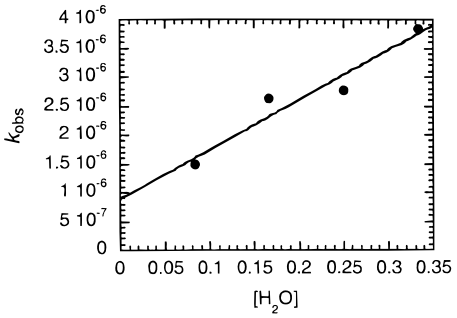


Figure 2. Linear plot of k_{obs} vs $[H_2O]$ ($R = 0.97$) with a y-intercept of $8.9 \times 10^{-7} \pm 3.7$, demonstrating the presence of two concurrent pathways for formation of pyrrole from **2**.

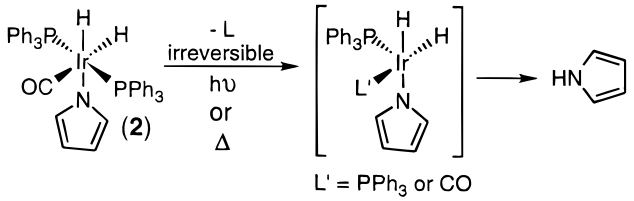
Reversible dissociation of phosphine, followed by reductive elimination of pyrrole, would lead to reaction rates that are retarded by increasing concentrations of phosphine. The lack of rate dependence on $[PPh_3]$ rules out this path. Similarly, the absence of an effect of added CO rules out reversible CO dissociation. The absence of an effect of pyrrole concentration on reaction rates also shows that the lack of ligand dependence does not result from reversible ligand dissociation that is followed by reversible reductive elimination and irreversible ligand association. A mechanism involving dissociation of a pyrrolyl group to generate a cationic hydride, which is deprotonated by the pyrrolyl anion, would be related to the ionic mechanism for oxidative addition of alkyl halides to Vaska's complex. This mechanism was ruled out by the absence of a significant solvent effect on the rates of the reaction.

A mechanism involving reductive elimination catalyzed by adventitious water could occur by protonation of the pyrrolyl ligand to form pyrrole and an Ir(III) hydrido hydroxide intermediate. Indeed, we did find that water catalyzed the reductive elimination. A plot of k_{obs} vs $[H_2O]$ for reactions conducted with varying amounts of added water (Figure 2) was linear and had a positive slope. However, this plot also had a nonzero y-intercept, and this y-intercept corresponds to the rate constant with $[H_2O]$ equal to zero. The value of this y-intercept was within the range of rate constants we obtained in the absence of added water. Thus, a mechanism catalyzed by adventitious water could be ruled out, at least as the dominant pathway for reactions without purposefully added water.

Instead, mechanisms involving irreversible phosphine dissociation or direct reductive elimination are more likely. Isotope effects, which would distinguish direct

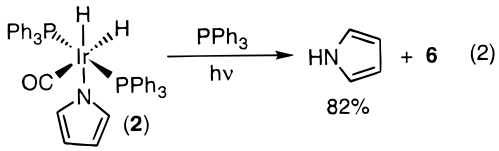
(87) Roundhill, D. M. *Inorg. Chem.* **1970**, *9*, 254.
(88) carb = 7-C_6H_5-1,7-$C_2B_{10}H_{10}$.
(89) Basato, M.; Morandini, F.; Longato, B.; Bresadola, S. *Inorg. Chem.* **1984**, *23*, 649.
(90) Basato, M.; Longato, B.; Morandini, F.; Bresadola, S. *Inorg. Chem.* **1984**, *23*, 3972.
(91) Milstein, D. *Acc. Chem. Res.* **1984**, *17*, 221.
(92) Blum, O.; Milstein, D. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 229.

Scheme 4



reductive elimination from elimination after irreversible phosphine dissociation, were not large enough to evaluate confidently from our data. However, the photochemical experiments described below suggest that elimination occurs after irreversible dissociation of a ligand, as shown in Scheme 4.

Photochemically Induced Reductive Elimination of Pyrrole from 2. We investigated potential reductive elimination from **2** after photochemically induced ligand dissociation. As shown in eq 2, complex **2** underwent reductive elimination of pyrrole in 82% yield upon irradiation in benzene solution with a medium-pressure Hg arc lamp. The hydride complex



6 was the only Ir species observed by either ^{1}H or ^{31}P-{^{1}H} NMR spectroscopy. Irradiation of a solution of **2** with free PPh_3 under a pressure of CO again led to the formation of pyrrole in 88% yield. In this case, the Ir product observed by ^{1}H and ^{31}P{^{1}H} NMR spectroscopy was $(PPh_3)_2(CO)_2Ir(H)$.[85]

Qualitative studies indicated that the conversion of **2** to pyrrole at various reaction times was unaffected by added PPh_3 or CO. Also, side-by-side reactions of **2-*d*$_2$** and **2** showed no apparent isotope effect, suggesting that the Ir−H bond is broken after an irreversible photochemical step. This irreversible step is likely to be ligand dissociation. Thus, reductive elimination of pyrrole is likely to occur rapidly after irreversible photochemical dissociation of PPh_3 or CO (Scheme 4). Because the rate of elimination was unaffected by either added PPh_3 or CO, our data does not reveal which ligand is lost before elimination occurs; however, it is well-known that irradiation of Ir(III) derivatives of Vaska-type complexes leads to facile CO dissociation. Previous studies conducted on the photochemically induced elimination of H_2 from Ir(III) dihydrides[93] $(PPh_3)_2(CO)Ir(H)_2Cl$ and $(PPh_3)_3Ir(H)_2Cl$ occurred by formation of a common intermediate $(PPh_3)_2IrCl$, which was not the result of secondary photolysis of the expected square-planar Ir(I) products. Thus, CO was preferentially lost from the Ir(III) starting complex $(PPh_3)_2(CO)Ir(H)_2Cl$, which is analogous to **2**, to give $(PPh_3)_2Ir(H)_2Cl$. The pentacoordinate Ir(III) complex $(PPh_3)_2Ir(H)_2Cl$, which is analogous to the potential intermediate $(PPh_3)_2Ir(H)_2(NC_4H_4)$, then undergoes elimination of H_2 to give $(PPh_3)_2IrCl$.

Thus, we suggest that the photochemically induced reductive elimination of pyrrole occurs via irreversible dissociation of CO rather than PPh_3 from the photochemically excited state of **2**. These data, in conjunction with our qualitative kinetic data on the thermal chemistry of **2**, suggest that the thermal reductive elimination occurs after irreversible dissociation of ligand. Considering that phosphine dissociation is typically more rapid than CO dissociation under thermal conditions with these systems, we tentatively conclude that thermal reductive elimination occurs after irreversible PPh_3 dissociation. These mechanistic conclusions are consistent with the previously determined mechanisms for C−H bond-forming reductive elimination from Ir(III), as described above.

Conclusions

The Ir(I) pyrrolyl complex $(PPh_3)_2(CO)Ir(NC_4H_4)$ (**1**) undergoes oxidative addition reactions with substrates such as MeI and H_2 in a manner similar to Vaska's complex, $(PPh_3)_2(CO)IrCl$. Complex **1** also undergoes initial oxidative addition and reductive elimination reactions with a variety of substrates to form *N*-substituted pyrroles, $X-NC_4H_4$ (X = $C(O)CH_3$, $C(O)C_6H_4CH_3$, H, $SnMe_3$, $SiMe_3$, $SiEt_3$, Bcat). This reactivity differs from that seen for free pyrrole and strongly suggests that the Ir center is directly involved in the formation of the *N*-substituted pyrroles. Complex **1** reversibly adds H_2 to form the Ir(III) dihydride $(PPh_3)_2(CO)Ir(H_2)(NC_4H_4)$ (**2**). When **2** is heated in the presence of PPh_3 under an atmosphere of H_2, it undergoes N−H bond-forming reductive elimination to give pyrrole and the Ir(I) hydride **6**. The pyrrole is formed through a mechanism that does not involve reversible phosphine dissociation before reductive elimination. Instead, reductive elimination more likely occurs by irreversible dissociation of CO or PPh_3 or without any ligand dissociation. The observation of photochemically induced reductive elimination, which does not show any isotope effect, suggests that elimination of pyrrole can proceed after irreversible ligand dissociation and that this pathway may be occurring in both the thermal and photochemically induced reductive elimination.

Experimental Section

General Methods. Unless otherwise noted, all reactions and manipulations were performed in an inert atmosphere glovebox or by using standard Schlenk techniques. All ^{31}P-{^{1}H} NMR chemical shifts are reported in parts per million relative to an 85% H_3PO_4 external standard. Shifts downfield of the standard are reported as positive. Benzene, toluene, THF, ether, and pentane solvents were distilled from sodium/benzophenone prior to use. Methylene chloride was degassed and dried over calcium hydride. Acetyl chloride was purified by literature procedures.[94] Triphenylphosphine was sublimed prior to use in kinetic reactions. Vaska's complex was prepared according to published methods.[95] Sodium pyrrolyl was prepared by the addition of sodium hydride to a pentane solution of pyrrole and isolated as a white powder. Catecholborane was vacuum distilled prior to use. All other chemicals were used as received from commercial suppliers.

Preparation of *trans*-$(PPh_3)_2(CO)Ir(NC_4H_4)$. Into a 20 mL vial was weighed 88.6 mg (0.114 mmol) of *trans*-$(PPh_3)_2$-

(93) Wink, D. A.; Ford, P. C. *J. Am. Chem. Soc.* **1986**, *108*, 4838.

(94) Perrin, D. D.; Armarego, W. L. F. *Purification of Laboratory Chemicals*, 3rd ed.; Pergamon Press: Oxford, 1988.

(95) Collman, J. P.; Sears, C. T.; Varieze, K.; Kubota, M. *Inorg. Synth.* **1990**, *28*, 92.

(CO)IrCl. The solid was dissolved in 8 mL of THF with stirring. $NaNC_4H_4$ (10.7 mg, 0.120 mmol) was added as a solid. The reaction was stirred at room temperature for 2 h, after which time the solvent was removed under vacuum. The residue was dissolved in 5 mL of CH_2Cl_2 and filtered through Celite. The resulting solution was concentrated, layered with Et_2O, and cooled at −35 °C for 12 h to obtain 80.1 mg (87%) of yellow crystalline material. ^{1}H NMR (C_6D_6): δ 6.41 (t, 1.6 Hz, 2H), 6.44 (t, 1.6 Hz, 2H), 6.97−7.03 (m, 18H), 7.51−7.54 (m, 12H). $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ 107.3 (s), 127.6 (s), 128.2 (s), 130.3 (s), 132.3 (br), 134.4 (s), 179.7 (s). $^{31}P\{^1H\}$ NMR (C_6H_6): δ 20.6 (s);.IR (cm^{-1}), (KBr): 3059 (m), 2969 (w), 2923 (w), 2859 (w), 1964 (s, ν_{CO}), 1919 (w), 1668 (w), 1586 (m), 1567 (m), 1479 (m), 1434 (s), 1311 (w), 1261 (w), 1183 (m), 1167 (m), 1091 (s), 1048 (s), 1039 (m), 1027 (m), 999 (m), 812 (m), 749 (s), 722 (s), 693 (s), 621 (w), 605 (m), 569 (w), 520 (s). Anal. Calcd for $C_{41}H_{34}NIrOP_2$: C, 60.65; H; 4.22; N, 1.73. Found: C, 60.51; H, 4.29; N, 1.61.

Preparation of $(PPh_3)_2(CO)Ir(H)_2(NC_4H_4)$. *trans*-$(PPh_3)_2$(CO)Ir($NC_4H_4$) (260 mg, 0.32 mmol) was dissolved in 40 mL of benzene and transferred to a flask fused to a Kontes vacuum adapter. The solution was frozen in N_2(l), and the flask was evacuated. A pressure of 400 Torr of H_2 was added to the cooled flask to provide a H_2 pressure of ∼2 atm at room temperature. The flask was sealed, and the solution was thawed. The reaction was stirred at room temperature for 36 h, over which time the solution turned pale yellow. The final reaction solution was transferred to a 50 mL round-bottomed flask, and the benzene was removed under vacuum. The product was recrystallized from THF/Et_2O to give 223 mg (86%) of $(PPh_3)_2(CO)Ir(H)_2(NC_4H_4)$. ^{1}H NMR ($C_6D_6$): δ −15.84 (dt, 4.9, 15.3 Hz, 1H), −6.89 (dt, 4.9, 17.6 Hz, 1H), 6.37 (t, 1.5 Hz, 2H), 6.63 (t, 1.5 Hz, 2H), 6.95−7.10 (m, 18H), 7.52−7.60 (m, 12H). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 108.9 (s), 128.4 (t, 5.2 Hz), 130.3 (s), 134.3 (t, 5.5 Hz), 134.4 (t, 28.7 Hz), 134.5 (s), 177.6 (t, 7.1 Hz). $^{31}P\{^1H\}$ NMR (C_6H_6): δ 7.0. IR (cm^{-1}, KBr): 3051 (m), 2917 (w), 2183 (m, ν_{Ir-H}), 2142 (m, ν_{Ir-H}), 2075 (s, ν_{CO}), 1978 (m), 1966 (s), 1482 (s), 1464 (w), 1433 (s), 1390 (w), 1334 (w), 1308 (w), 1266 (w), 1190 (m),1169 (m), 1161 (m), 1095 (s), 1071 (w), 1046 (m), 1033 (m), 999 (m), 970 (w), 928 (w), 894 (m), 854 (m), 836 (s), 820 (m), 805 (m), 748 (s), 715 (s), 706 (s), 691 (s), 649 (m), 618 (w), 544 (w), 523 (s), 512 (s). Anal. Calcd for $C_{41}H_{36}NIrOP_2$: C, 60.58; H, 4.46; N, 1.72. Found: C, 60.50; H, 4.79; N, 1.62.

Addition of MeI to *trans*-$(PPh_3)_2(CO)Ir(NC_4H_4)$. *trans*-$(PPh_3)_2$(CO)Ir(NC_4H_4) (100 mg, 0.123 mmol) was weighed into a 20 mL vial and dissolved in 12 mL of THF with stirring. MeI (8.4 μL, 0.135 mmol) was added to the vial by syringe. The vial was capped, and the reaction was allowed to stir at room temperature for 10 h. The THF was concentrated and layered with Et_2O. The vial was cooled at −35 °C for 12 h to obtain 84 mg (72%) of a white crystalline material of $(PPh_3)_2$(CO)Ir(Me)(NC_4H_4)I. ^{1}H NMR (C_6D_6): δ 1.26 (t, 4.9 Hz, 3H), 6.47 (m, 2H), 6.91−7.10 (m, 20H), 7.36 (m, 12H). $^{31}P\{^1H\}$ NMR (C_6H_6): δ −14.8 (s). IR (cm^{-1}, KBr): 3140 (w), 3125 (w), 3076 (w), 3053 (w), 2919 (w), 2849 (w), 2015 (s, ν_{CO}), 1589 (w), 1572 (w), 1483 (m), 1454 (w), 1429 (m), 1393 (w), 1317 (w), 1247 (m), 1189 (m), 1162 (m), 1093 (s), 1032 (m), 1000 (m), 822 (m), 744 (s), 728 (s), 691 (s). Anal. Calcd for $C_{42}H_{37}NIrOP_2I$: C, 52.94; H, 3.91; N, 1.47. Found: C, 53.17; H, 4.22; N, 1.44.

Addition of MeI to *trans*-$(PPh_3)_2(CO)Ir(NC_4H_4)$ and *trans*-$(PPh_3)_2(CO)IrCl$. *trans*-$(PPh_3)_2$(CO)Ir(NC_4H_4) (9.9 mg, 0.012 mmol) was weighed into vial and dissolved in 1.0 mL of THF. *trans*-$(PPh_3)_2$(CO)Ir(NC_4H_4) (9.5 mg, 0.012 mmol) was weighed into another vial and dissolved in 1.0 mL of THF. The two THF solutions were combined in a 5 mL vial. A 10 μL amount of MeI was diluted with 2.0 mL of THF to make a 0.080 M solution. An aliquot of the MeI solution (15.2 μL, 0.0012 mmol) was added to the combined Ir solutions. The reaction vial was capped and stirred at room temperature for 12 h. A $^{31}P\{^1H\}$ NMR spectrum of the reaction solution was taken. Integration of the spectrum gave a ratio of products $(PPh_3)_2(CO)Ir(Me)(NC_4H_4)$I:$(PPh_3)_2(CO)Ir(Me)(Cl)$I of 2:1.

Thermolysis of $(PPh_3)_2(CO)Ir(H)_2(NC_4H_4)$. $(PPh_3)_2$(CO)-$Ir(H)_2(NC_4H_4)$ (7.4 mg, 0.0091 mmol) was weighed into a small vial and dissolved in 0.6 mL of THF. The solution was transferred to an NMR tube. The NMR tube was then equipped with a vacuum adapter, frozen in N_2(l), evacuated, and flame-sealed. The solution was thawed, and the sample was heated at 95 °C for 4 h. A $^{31}P\{^1H\}$ NMR spectrum of the reaction solution showed complete conversion of the starting material to $(PPh_3)_2(CO)Ir(NC_4H_4)$.

Thermolysis of $(PPh_3)_2(CO)Ir(Me)(NC_4H_4)$I. $(PPh_3)_2$-(CO)Ir(Me)(NC_4H_4)I (10.1 mg, 0.0106 mmol) was weighed into a small vial and dissolved in 0.6 mL of THF. The solution was transferred to an NMR tube. The NMR tube was then equipped with a vacuum adapter, frozen in N_2(l), evacuated, and flame-sealed. The solution was thawed, and then the reaction was heated at 130 °C for 12 h. A $^{31}P\{^1H\}$ NMR spectrum of the reaction solution showed complete conversion of the starting material to $(PPh_3)_2(CO)IrI$ (δ 25.1). A GC/MS of the reaction solution indicated that free pyrrole was the only organic product formed. Upon repeating the reaction in benzene-d_6, no formation of methane or ethane was observed by ^{1}H NMR spectroscopy.

Reaction of *trans*-$(PPh_3)_2(CO)Ir(NC_4H_4)$ with Acetyl Chloride. *trans*-$(PPh_3)_2$(CO)Ir(NC_4H_4) (7.2 mg, 0.0089 mmol) was weighed into a vial containing a small amount (<2 mg) of trimethoxybenzene. The solids were dissolved in benzene-d_6 and transferred to an NMR tube. Initial ^{1}H and $^{31}P\{^1H\}$ NMR spectra were taken. The NMR tube was then equipped with a vacuum adapter, frozen in N_2(l), and evacuated. Acetyl chloride (1.4 mg, 0.018 mmol) was transferred into the tube as a gas using a bulb of known volume. The tube was flame-sealed and thawed. The reaction mixture was left at room temperature for 1 h, and a $^{31}P\{^1H\}$ NMR spectrum was taken. All of the starting complex had been converted to the oxidative-addition product $(PPh_3)_2(CO)Ir(NC_4H_4)[C(O)CH_3](Cl)$ (δ = −15.4). The reaction was heated at 70 °C for 3 h. The ^{1}H NMR spectrum indicated the formation of pyrrole (60%) and *N*-acetylpyrrole (11.7%). $(PPh_3)_2(CO)Ir[C(O)CH_3](Cl)_2$ (δ = −18.8) was the only phosphorus-containing iridium product observed by $^{31}P\{^1H\}$ NMR spectroscopy.

Reaction of *trans*-$(PPh_3)_2(CO)Ir(NC_4H_4)$ with *p*-Toluoyl Chloride. *trans*-$(PPh_3)_2$(CO)Ir(NC_4H_4) (5.2 mg, 0.0064 mmol) was weighed into a vial and dissolved in toluene-d_8 containing some pentane, which was used as an internal standard. The solution was transferred to an NMR tube. An initial ^{1}H NMR spectrum was taken. *p*-Toluoyl chloride (2.1 mg, 0.014 mmol) was added to the NMR tube. The tube was heated at 80 °C for 15 h. The ^{1}H spectrum indicated the formation of pyrrole (59%) and *N*-*p*-toluoylpyrrole (16.7%).

General Reaction of *trans*-$(PPh_3)_2(CO)Ir(NC_4H_4)$ with Sn- and Si-Containing Substrates. *trans*-$(PPh_3)_2$(CO)Ir-(NC_4H_4) was weighed into a vial and dissolved in benzene-d_6 containing a small amount of Et_2O, which was used as an internal standard. Initial ^{1}H and $^{31}P\{^1H\}$ NMR spectra were taken. The main-group reagent was then added to the NMR tube. The reaction was left at room temperature for 2 h. The $^{31}P\{^1H\}$ NMR spectrum indicated no reaction. The tube was heated at 80 °C for 14 h. A ^{1}H NMR spectrum was taken at the end of the reaction to determine the organic products formed. The yields of the products were measured relative to an internal Et_2O standard. A combination of ^{1}H and $^{31}P\{^1H\}$ NMR spectra were used to identify the final Ir product.

Reaction of 2 with Trimethyltin Chloride. The general procedure using 7.1 mg (0.0088 mmol) of **2** and 0.012 mmol of trimethyltin chloride gave *N*-(trimethylstannyl)pyrrole in 69% yield. $(PPh_3)_2(CO)Ir(Cl)$ was the only metal product observed.

Reaction of 2 with Trimethylsilyl Chloride. The general procedure using 7.6 mg (0.0094 mmol) of **2** and 3.0 mg of

trimethylsilyl chloride (0.028 mmol) gave *N*-(trimethylsilyl)-pyrrole (43%) along with $(PPh_3)_2(CO)Ir(Cl)$ (47%).

Reaction of 2 with Triethylsilane. The general procedure using 10.7 mg (0.0132 mmol) of **2** and 3.1 mg (0.026 mmol) of triethylsilane gave *N*-(triethylsilyl)pyrrole in 64% yield along with $(PPh_3)_2(CO)Ir(H)_2(SiEt_3)$ in 66% yield.

Reaction of *trans*-$(PPh_3)_2(CO)Ir(NC_4H_4)$ with 2-Chloro-1,3,2-benzodioxaborole. *trans*-$(PPh_3)_2(CO)Ir(NC_4H_4)$ (6.0 mg, 0.0074 mmol) was weighed into a vial and dissolved in benzene-d_6 containing some toluene, which was used as an internal standard. The solution was transferred into an NMR tube. Initial ^1H and $^{31}P\{^1H\}$ NMR spectra were taken. 2-Chloro-1,3,2-benzodioxaborole (2.6 mg, 0.017 mmol) was added to the NMR tube. The tube was left at room temperature for 1 h. The ^1H NMR spectrum indicated the formation of 2-pyrrolyl-1,3,2-benzodioxaborole (78%) (^{11}B NMR $\delta = 24$) with $(PPh_3)_2(CO)Ir(Cl)$ (89%). No other metal products were observed in the $^{31}P\{^1H\}$ NMR spectrum.

Reaction of *trans*-$(PPh_3)_2(CO)Ir(NC_4H_4)$ with 1,3,2-Benzodioxaborole. *trans*-$(PPh_3)_2(CO)Ir(NC_4H_4)$ (5.6 mg, 0.0069 mmol) and PPh_3 (2.8 mg, 0.011 mmol) were weighed into a vial and dissolved in benzene-d_6 containing some toluene, which was used as an internal standard. The solution was transferred into an NMR tube. Initial ^1H and $^{31}P\{^1H\}$ NMR spectra were taken. 1,3,2-Benzodioxaborole (1.1 mg, 0.0094 mmol) was added to the NMR tube. The tube was left at room temperature for 1 h. The ^1H NMR spectrum indicated the formation of 2-pyrrolyl-1,3,2-benzodioxaborole (82%) (^{11}B NMR $\delta = 24$). $(PPh_3)_3(CO)Ir(H)$ was the only metal product observed in the $^{31}P\{^1H\}$ NMR spectrum.

Thermal Reductive Elimination of Pyrrole from $(PPh_3)_2(CO)Ir(H)_2(NC_4H_4)$. $(PPh_3)_2(CO)Ir(H)_2(NC_4H_4)$ (7.8 mg, 0.0096 mmol) was weighed into a vial. PPh_3 (12 mg, 0.041 mmol) was weighed into another vial and dissolved in 0.6 mL of THF. The phosphine solution was transferred into the vial containing the Ir complex. Upon dissolution, the solution was transferred to a medium-walled NMR tube. The NMR tube was equipped with a vacuum adapter in the drybox, frozen in N_2(l), evacuated, and charged with 500 Torr of H_2. The tube was flame-sealed, and then the reaction solution was thawed. The reaction was heated at 130 °C until all of the starting material had been converted to $(PPh_3)_3(CO)Ir(H)$ by $^{31}P\{^1H\}$ NMR spectroscopy (approximately 3 days). A GC/MS of the reaction mixture indicated the formation of free pyrrole. Upon repeating the reaction in toluene-d_8, ^1H NMR spectroscopy using dimethoxyethane as an internal standard indicated the formation of pyrrole in 91% yield.

Kinetic Analysis of the Thermal Reductive Elimination of $(PPh_3)_2(CO)Ir(H)_2(NC_4H_4)$. $(PPh_3)_2(CO)Ir(H)_2(NC_4H_4)$ (23.5 mg, 0.0289 mmol) was weighed into a vial and dissolved in 1.4 mL of toluene-d_8. Dimethoxyethane (2.3 μL, 0.0066 mmol) was added to the solution as an internal standard. PPh_3 was weighed into a vial, and a 0.3 mL aliquot (0.0062 mmol) of the Ir solution was added to the vial. When used, the pyrrole (0.8 μL, 0.01 mmol) was added by syringe at this point. The solution was then transferred into a medium-walled NMR tube. The tubes were frozen in N_2(l), evacuated, and charged with 500 Torr of H_2. The tubes were then flame-sealed. The sample was immersed in a 95 °C constant-temperature water bath, and ^1H NMR spectra were obtained after heating for 10 h and standing at room temperature for a minimum of 3 h to convert all of the Ir material from **1** to **2**. The concentration of **2** was monitored throughout the course of the reaction by integration of a pyrrolyl resonance relative to the dimethoxyethane internal standard.

Solvent Effect. Two samples of $(PPh_3)_2(CO)Ir(H)_2(NC_4H_4)$ (7.2 mg, 0.0089 mmol) were weighed into separate vials. PPh_3 (11 mg, 0.042 mmol) was weighed into each vial. The solids were dissolved in 0.3 mL of toluene and THF, respectively. The solutions were transferred to medium-walled NMR tubes. The NMR tubes were equipped with a vacuum adapter, frozen in N_2(l), evacuated, and charged with 500 Torr of H_2. The tube was flame-sealed, and the sample was thawed. The samples were immersed in a 95 °C constant-temperature water bath. The progress of the reaction was followed by $^{31}P\{^1H\}$ NMR spectroscopy. Qualitative comparison of the NMR spectra indicated no significant difference in the rates of reaction.

Qualitative Comparison of Reaction Rates of Pyrrole Elimination from $(PPh_3)_2(CO)Ir(H)_2(NC_4H_4)$ with Added CO. Into a vial was weighed 26.1 mg (0.032 mmol) of $(PPh_3)_2(CO)Ir(H)_2(NC_4H_4)$ and 42.2 mg (0.161 mmol) of PPh_3. The solids were dissolved in 2.3 mL of toluene to make a stock solution. Aliquots (0.5 mL, 0.007 mmol of **2**) of the stock solution were transferred by syringe to two medium-walled NMR tubes. The tubes were equipped with vacuum adapters, frozen in N_2(l), and evacuated. One tube was charged with 250 Torr of H_2 and flamed-sealed. A second tube was charged with a mixture of 250 Torr of H_2 and 250 Torr of CO (gases mixed in the vacuum line) and flame-sealed. The tubes were thawed, and $^{31}P\{^1H\}$ NMR spectra were taken. The tubes were heated simultaneously at 95 °C in a constant-temperature water bath, and $^{31}P\{^1H\}$ NMR spectra were obtained at approximately 10 h intervals.

Measurement of K_{eq} for the Loss of H_2 from $(PPh_3)_2(CO)Ir(H)_2(NC_4H_4)$ at 95 °C. $(PPh_3)_2(CO)Ir(H)_2(NC_4H_4)$ (8.4 mg, 0.010 mmol) was weighed into a small vial and dissolved in 0.4 mL of toluene-d_8. The solution was transferred to a medium-walled NMR tube. The NMR tube was equipped with a vacuum adapter, frozen in N_2(l), evacuated, and charged with 500 Torr of H_2. The tube was flame-sealed, and the sample was thawed. A ^1H NMR spectrum was obtained. The NMR tube was heated at 95 °C in the NMR probe for 1 h. A ^1H NMR spectrum was obtained at 95 °C. The concentrations of $(PPh_3)_2(CO)Ir(H)_2(NC_4H_4)$, $(PPh_3)_2(CO)Ir(H)_2(NC_4H_4)$, and H_2 were determined relative to an internal Et_2O standard. The K_{eq} was calculated to be 2.0×10^{-3} M.

Reaction of $(PPh_3)_2(CO)Ir(H)_2(NC_4H_4)$ with H_2O. $(PPh_3)_2(CO)Ir(H)_2(NC_4H_4)$ (26.6 mg, 0.0328 mmol) was weighed into a vial along with 60.1 mg (0.229 mmol) of PPh_3. The solids were dissolved in 1.8 mL of toluene-d_8 to make a stock solution. A small amount of dimethoxyethane was added to the solution for use as an internal standard. Aliquots (0.4 mL, 0.00728 mmol of **2**) of the stock solution were transferred to each of four medium-walled NMR tubes by syringe. The tubes were sealed with rubber septa and removed from the drybox. Degassed water (0.6 μL, 0.036 mmol; 1.2 μL, 0.073 mmol; 1.8 μL, 0.10 mmol; 2.4 μL, 0.13 mmol) was added to the NMR tubes. The tubes were equipped with a vacuum-line adapter, frozen in N_2(l), and evacuated. Each of the NMR tubes was charged with 500 Torr of H_2 and flame-sealed. The reaction was conducted at 95 °C in a constant-temperature water bath. ^1H NMR spectra were obtained after heating the samples for 4 h and then standing at room temperature for 2 h. The concentration of **2** was monitored throughout the course of the reaction by integration of the pyrrolyl resonance relative to the dimethoxyethane internal standard.

Photochemical Reductive Elimination of $(PPh_3)_2(CO)Ir(H)_2(NC_4H_4)$. Reaction in the Presence of Excess PPh_3. $(PPh_3)_2(CO)Ir(H)_2(NC_4H_4)$ (6.8 mg, 0.0084 mmol) and PPh_3 (6.1 mg, 0.023 mmol) were weighed into a vial and dissolved in 0.5 mL of benzene-d_6 containing some toluene, which was used as an internal standard. An initial ^1H NMR spectrum was taken. The sample was irradiated with a 450 W Hg arc lamp for 1 h. The ^1H NMR spectrum indicated the formation of pyrrole in 85% yield. $(PPh_3)_3(CO)Ir(H)$ was the only metal product observed in the $^{31}P\{^1H\}$ NMR spectrum.

Reaction in the Presence of Excess CO and PPh_3. $(PPh_3)_2(CO)Ir(H)_2(NC_4H_4)$ (8.1 mg, 0.010 mmol) and PPh_3 (4.2 mg, 0.016 mmol) were weighed into a vial and dissolved in 0.5 mL of benzene-d_6 containing some toluene, which was used as an internal standard. The solution was transferred into an NMR tube, which was frozen in N_2(l), evacuated, and

charged with 300 Torr of CO. The tube was flame-sealed and thawed. An initial ^{1}H NMR spectrum was taken. The sample was irradiated with a 450 W Hg arc lamp for 1 h. The ^{1}H NMR spectrum indicated the formation of pyrrole in 87% yield. $(PPh_3)_2(CO)_2Ir(H)$ was the only metal product observed in the $^{31}P\{^1H\}$ NMR spectrum.

Dependence of Conversion on [PPh_3]. $(PPh_3)_2(CO)Ir(H)_2(NC_4H_4)$ (14.6 mg, 0.0180 mmol) was weighed into a vial and dissolved in 1.3 mL of benzene-d_6. Into two vials was weighed PPh_3 (9.1 mg, 0.035 mmol or 27.2 mg, 0.104 mmol). The phosphine was dissolved in a 0.5 mL aliquot of the reaction solution. The solutions were transferred into two NMR tubes. The samples were irradiated with a 450 W Hg arc lamp with ^{1}H NMR spectra obtained periodically. The concentration of the starting complex was monitored by the integration of a pyrrolyl resonance relative to a pentane internal standard.

Dependence of Conversion on CO. $(PPh_3)_2(CO)Ir(H)_2(NC_4H_4)$ (15.1 mg, 0.0186 mmol) was weighed into a vial and dissolved in 1.3 mL of benzene-d_6. A 0.5 mL aliquot of the solution was transferred into two NMR tubes. The samples were frozen in N_2(l), and CO was added (200 or 500 Torr at 77 K). The tubes were flame-sealed and thawed. The samples were irradiated with a 450 W Hg arc lamp with ^{1}H NMR spectra obtained periodically. The concentration of the starting complex was monitored by the integration of a pyrrolyl resonance relative to a pentane internal standard.

Isotope Effect Measurement. $(PPh_3)_2(CO)Ir(H)_2(NC_4H_4)$ (6.4 mg, 0.0079 mmol) or $(PPh_3)_2(CO)Ir(D)_2(NC_4H_4)$ (6.2 mg, 0.0076 mmol) was weighed into a vial and dissolved in 0.5 mL of toluene-d_8. PPh_3 (10.3 mg, 0.039 mmol) was weighed into a separate vial and dissolved in each of the reaction solutions. The solution was transferred into an NMR tube. The samples were irradiated with a 450 W Hg arc lamp with ^{1}H NMR spectra obtained periodically. The concentration of starting complex was monitored by the integration of a pyrrolyl resonance relative to a pentane internal standard.

X-ray Structure of 2. The structure of **2** was solved by methods described previously.[45] A yellow prismatic crystal of $C_{41}H_{34}NOP_2Ir\cdot C_{2.5}$ having approximate dimensions of 0.19 × 0.25 × 0.40 mm was mounted on a glass fiber. All measurements were made on an Enraf-Nonius CAD4 diffractometer with graphite-monochromated Mo Kα radiation. Cell constants and an orientation matrix for data collection, obtained from a least-squares refinement using the setting angles of 25 carefully centered reflections in the range $10.27 < 2\theta < 17.98°$, corresponded to a primitive triclinic cell. For $Z = 2$ and fw = 840.92, the calculated density was 1.52 g/cm^3. On the basis of a statistical analysis of the intensity distribution and the successful solution and refinement of the structure, the space group was determined to be $P\bar{1}$ (No. 2).

The data were collected at a temperature of −90 ± 1 °C. Of the 7682 reflections that were collected, 7428 were unique ($R_{int} = 0.024$). No decay correction was applied. An empirical absorption correction based on azimuthal scans of several reflections was applied, which resulted in transmission factors ranging from 0.73 to 1.00. The data were corrected for Lorentz and polarization effects.

The structure was solved by heavy-atom Patterson methods and expanded using Fourier techniques. Most non-hydrogen atoms were refined anisotropically, while the disordered solvent molecule atoms were refined isotropically. The pentane molecule was located on a crystallographic inversion center (refining in P_1 did not remove this disorder) with the terminal carbon refined at 50% occupancy in either position. Hydrogen atoms were included but not refined. The final cycle of full-matrix least-squares refinement was based on 6426 observed reflections ($I > 3.00\sigma(I)$) and 427 variable parameters and converged (largest parameter shift was 0.00 times its esd) with unweighted and weighted agreement factors of $R = \sigma||F_o| - |F_c||/\sigma|F_o| = 0.034$, $R_w = [(\sigma w(|F_o| - |F_c|)^2/\sigma w F_o^2)]^{1/2} = 0.042$. The standard deviation of an observation of unit weight was 2.32. The maximum and minimum peaks on the final difference Fourier map corresponded to 2.31 and −1.45 e$^-$/Å^3, respectively. All calculations were performed using the teXsan crystallographic software package of Molecular Structure Corp.

Supporting Information Available: Text giving the full experimental details for the structure solution of **2** and tables of experimental details, atomic coordinates, anisotropic displacement parameters, bond lengths, bond angles, tension angles, and nonbonded contacts (16 pages). Ordering information is given on any current masthead page.

OM971049P