Stereoselective Decarbonylation of Methanol to Form a Stable Iridium(III) *trans*-Dihydride Complex

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Thermolysis of the known cationic iridium complex [(PNP)Ir(C_6H_5)H]PF_6 (PNP = 2,6-bis-(di-*tert*-butylphosphinomethyl)pyridine) in methanol results in reductive elimination of benzene and stereoselective methanol decarbonylation to form the new iridium(III) *trans*-dihydride carbonyl complex [(PNP)Ir(CO)-H_2]PF_6 (***trans*-2**). The iridium(III) dihydride complex [(PNP)Ir$(H)_2$]PF_6 (**3**) is formed as a minor product. *cis*-[(PNP)Ir(CO)H_2]PF_6 (***cis*-2**) has been independently prepared by the reaction of dihydride **3** with CO and undergoes reductive elimination of hydrogen at room temperature to form the iridium(I) carbonyl [(PNP)Ir(CO)]PF_6 (**4**), demonstrating that ***cis*-2** is not an intermediate in the decarbonylation reaction.

Introduction

Homogeneously catalyzed dehydrogenation of alcohols is an attractive synthetic route for the preparation of aldehydes and ketones. A number of transition metal complexes have been shown to catalyze the dehydrogenation of primary and secondary alcohols.[1] However, this reaction can be complicated by decarbonylation of the alcohol or aldehyde, forming a stable metal-carbonyl product.[1c−e,g,i,2] Such alcohol decarbonylation reactions date back to Vaska's work, where evidence was provided that the carbonyl ligand in the complex Ir(Cl)$(PPh_3)_2$-(CO) was derived from ethylene glycol.[3]

Iridium complexes of anionic tridentate "pincer" ligands are popular catalysts for alkane dehydrogenation,[4] and recently these same iridium complexes have proven to be active in alcohol dehydrogenation.[5] The complex (PCP^{tBu})IrH_2 (PCP^{tBu} = 1,3-bis-(di-*tert*-butylphosphinomethyl)benzene) was shown to catalyze the transfer dehydrogenation of primary and secondary alcohols with *tert*-butylethylene to form the corresponding aldehydes and ketones and *tert*-butylethane. When methanol was employed as the substrate, however, stoichiometric decarbonylation of the alcohol was observed with formation of the iridium(I) carbonyl complex (PCP^{tBu})Ir(CO).[5]

Herein we report a different type of iridium product from methanol decarbonylation using a very closely related iridium pincer complex. Thermolysis of the known cationic iridium complex [(PNP)Ir(C_6H_5)H]PF_6[6] (PNP = 2,6-bis-(di-*tert*-butylphosphinomethyl)pyridine) in methanol results in reductive elimination of benzene and formation of the new iridium(III) *trans*-dihydride carbonyl complex [(PNP)Ir(CO)H_2]PF_6 (***trans*-2**) as the major product. A small amount of the five-coordinate iridium(III) dihydride complex [(PNP)Ir$(H)_2$]PF_6 (**3**) also forms. A mechanism is proposed for this reaction, and evidence is presented that the formation of ***trans*-2** is the result of stereoselective decarbonylation of methanol.

Results and Discussion

The known cationic iridium complex bearing a neutral tridentate ligand [(PNP)Ir(C_6H_5)H]PF_6 (**1**) (PNP = 2,6-bis(di-*tert*-butylphosphinomethyl)pyridine) was heated in methanol at 80 °C for 20 h. Reductive elimination of benzene and the formation of the *trans*-dihydride iridium(III) carbonyl complex [(PNP)Ir(CO)H_2]PF_6 (***trans*-2**) was observed (eq 1). A minor product of this reaction was the five-coordinate iridium(III) dihydride complex [(PNP)Ir$(H)_2$]PF_6 (**3**). Both iridium products are quite thermally stable and exhibited no further reactivity when heated at 80 °C in methanol for an additional 48 h.

The $\{^1H\}^{31}P$ NMR spectrum of ***trans*-2** (acetone-d_6) shows a singlet at 70.46 ppm, arising from the two equivalent *trans* phosphorus atoms on the ligand, and a heptet for free PF_6 at −142.61 ppm. The ^1H NMR spectrum (acetone-d_6) shows a single virtual triplet for the *tert*-butyl protons on the ligand at 1.48 ppm (J_{H-P} = 6.0 Hz), indicating an environment of C_{2v} symmetry. This symmetry is also evident in the hydride resonance, which appears as a triplet at −6.63 ppm ($^2J_{H-P}$ = 12.3 Hz), integrating to 2H. The IR spectrum of ***trans*-2** reveals a sharp band arising from the C−O stretch at 2008 cm^{-1}, as well as a weaker band for the Ir−H stretch at 1805 cm^{-1}.

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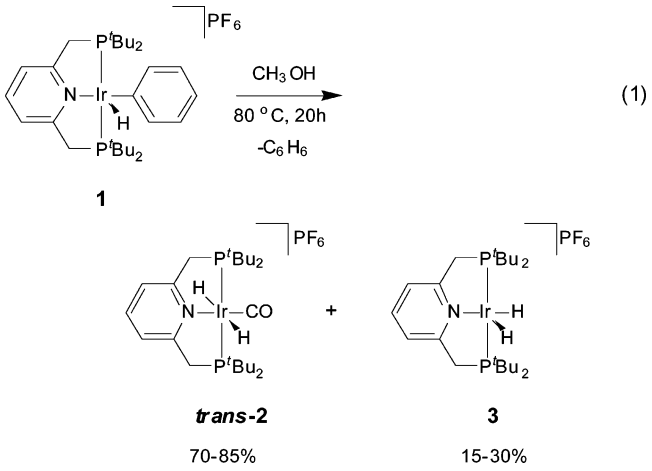
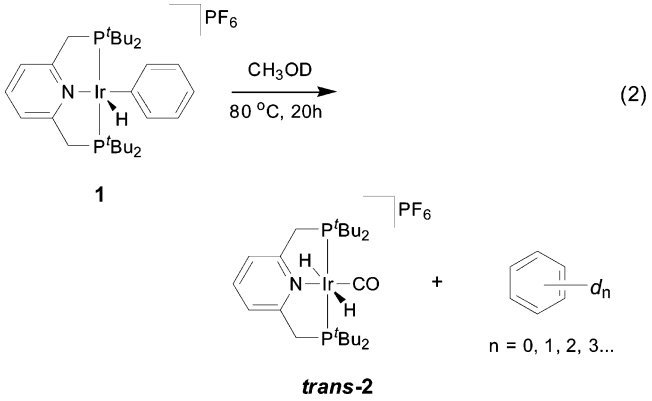


The structure of ***trans*-2** was confirmed by X-ray crystallography (Figure 1). Crystals were grown from a concentrated methanol solution at room temperature. The carbonyl group is located in the plane of the PNP ligand, with the hydride ligands positioned *trans* to one another. The quality of the data set allowed for the location of hydride 1a, while hydride 1b was constrained to an equivalent geometry. Although *trans*-dihydride complexes are traditionally thought to be rare due to the destabilizing influence of having the two strong sigma donor hydride ligands located *trans* to each other,[7] a reasonable number of these complexes have been observed.[1b,7−9] In a related pincer iridium case, the *trans* isomer has even been shown to be thermodynamically favored over the *cis* compound.[7]

When the thermolysis of **1** was conducted in CD_3OD with an internal standard of toluene, a 70−85% yield of [(PNP)Ir(CO)D_2]PF_6 (***trans*-2-d_2**) was determined. The remainder of the material (15−30%) was the five-coordinate dideuteride complex [(PNP)Ir$(D)_2$]PF_6 (**3-d_2**) (identified by comparison with a sample of [(PNP)Ir$(H)_2$]PF_6 (**3**), which was independently synthesized, vide infra). When the synthesis was conducted in CH_3OD, the observed ***trans*-2** product contained no deuterium (eq 2), demonstrating that the hydride ligands originate from the C−H bonds of the methanol substrate.



Labeling studies in both CD_3OD and CH_3OD also revealed that multiple deuterium were incorporated into the benzene released (eq 2). Upon completion of the thermolysis in either solvent, analysis of the volatiles from the reaction mixture by GC-MS revealed that approximately 85% of the benzene produced consisted of benzene-d_1 and higher isotopomers. If the thermolysis of **1** was stopped prior to completion (after 3 h), and the iridium species examined by ^{2}H NMR spectroscopy, deuterium was observed in both the phenyl and hydride positions on **1**. The deuterium exchange into the hydride position likely proceeds by the deprotonation of five-coordinate phenyl hydride complex **1**.[10] Consistent with this proposal, in a separate experiment the addition of 1 equiv of triethylamine to a solution of **1** in CD_3OD catalyzed complete deuterium exchange into the hydride position at room temperature, as determined by both ^{1}H and ^{2}H NMR spectroscopy. Deuterium incorporation into the phenyl positions on **1** may occur through reductive coupling between the hydride and phenyl ligands, as has been reported with other phenyl hydride/arene complexes.[11]

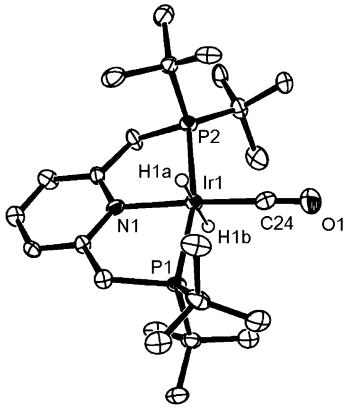


Figure 1. Thermal ellipsoid drawing of the molecular cation of *trans*-[(PNP)Ir$(CO)H_2$]PF_6 (***trans*-2**). (Thermal ellipsoids at 50% probability; nonhydridic H atoms omitted for clarity.) Select bond distances (Å) and angles (deg): Ir1−C24 = 1.848(8), Ir1−N1 = 2.106(6), Ir1−P1 = 2.322(2), Ir1−P2 = 2.329(2), Ir1−H1a = 1.73-(8), C24−O1 = 1.139(8), P1−Ir1−P2 = 165.40 (6), N1−Ir1−C24 = 176.1(3), P1−Ir1−N1 = 82.9(2), P2−Ir1−N1 = 82.6(2).

A reasonable mechanism for the formation of ***trans*-2** is shown in Scheme 1. In the first step, the phenyl hydride complex **1** reductively eliminates benzene and activates the O−H or C−H bond of the methanol solvent (oxidative addition of the O−H bond is shown in Scheme 1). Both O−H and C−H bond activation has been observed with closely related Ir(I) species.[12,13] It is likely that reductive coupling of benzene from phenyl hydride complex **1** occurs prior to methanol oxidative addition. This would be consistent with the observed H/D scrambling described above. In addition, it is noted that the analogous five-coordinate dihydride complex **3** does not reductively eliminate hydrogen or decarbonylate methanol when

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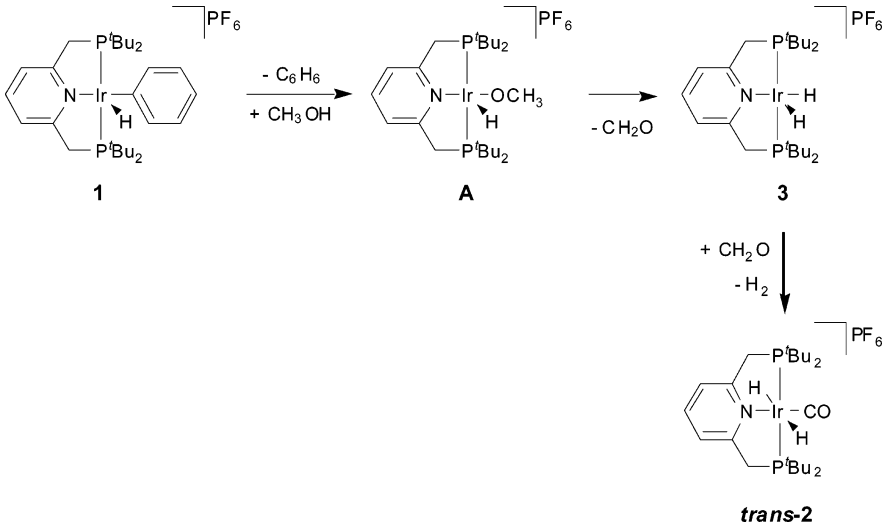
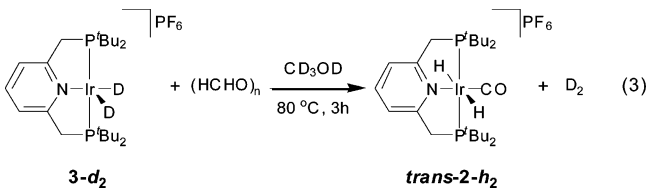
Scheme 1



heated under the same reaction conditions used to form ***trans*-2**. This reactivity pattern is similar to the (PCP$^{t\mathrm{Bu}}$)Ir system, where (PCP$^{t\mathrm{Bu}}$)Ir(H)$_2$ is stable at room temperature, but reversible benzene reductive elimination was observed for (PCP$^{t\mathrm{Bu}}$)Ir(C$_6$H$_5$)H.[13] Mechanistic studies provided evidence that for the PCP$^{t\mathrm{Bu}}$ complex the reaction proceeds by dissociative loss of the benzene and formation of the active three-coordinate species (PCP$^{t\mathrm{Bu}}$)Ir.[13]

In the second step of the mechanism (Scheme 1), β-hydride elimination from **A** leads to formaldehyde and dihydride complex **3**. Dihydride complex **3** reacts with formaldehyde, eliminating hydrogen and activating the aldehyde C−H bond. This reaction of **3** with formaldehyde has been independently demonstrated. When a solution of the five-coordinate dideuteride complex ***3*-d_2** in CD_3OD was heated with an excess of paraformaldehyde at 80 °C for 3 h, quantitative conversion to ***trans*-2-h_2** was observed (eq 3). No H_2 or HD gas was observed as a product of this reaction. This experiment establishes that both of the hydride ligands in the product ***trans*-2-h_2** were derived from the paraformaldehyde. This formation of exclusively ***trans*-2-h_2** argues against aldehyde C−H bond oxidative addition preceding reductive elimination of D_2 from ***3*-d_2**, as partial deuterium incorporation in the ***trans*-2** product of this reaction would be expected. However, association of formaldehyde likely occurs before reductive elimination of hydrogen from **3** (or deuterium from ***3*-d_2**), since as noted above complex **3** was stable in the absence of paraformaldehyde and did not reductively eliminate hydrogen when heated in methanol at 80 °C. Promotion of hydrogen reductive elimination by ligand association has previously been noted with d^6 five-coordinate hydride species.[14] In addition, as discussed below, six-coordinate ***cis*-2** undergoes facile H_2 reductive elimination.



(3)

In the final step of the mechanism, the aldehyde activation is followed by deinsertion of CO (migration of the hydride) to produce specifically the *trans*-dihydride complex ***trans*-2**. This last step of the reaction is intriguing, as it appears to be a stereoselective migration resulting in the formation of the *trans*- rather than the *cis*-dihydride complex. This is similar to the report that the neutral iridium(I) amido phosphine complex Ir(COE)N(SiMe$_2$CH$_2$PPh$_2$)$_2$ decarbonylates paraformaldehyde, generating the iridium(III) carbonyl *trans*-dihydride complex Ir(N(SiMe$_2$CH$_2$PPh$_2$)$_2$)CO(H)$_2$.[8] This process was proposed to proceed by activation of the aldehyde C−H bond, followed by a stereospecific migratory deinsertion. In contrast, although a similar set of reaction steps (formaldehyde C−H activation followed by CO migratory insertion) was proposed in the methanol decarbonylation reaction involving the (PCP$^{t\mathrm{Bu}}$)Ir system, the formation of (PCP$^{t\mathrm{Bu}}$)Ir(CO) was observed.[5] The formation of the Ir(I) carbonyl implies that either the migratory deinsertion reaction proceeds stereospecifically to the *cis*-dihydride isomer or *trans*-to-*cis* isomerization occurs following migratory deinsertion, since reductive elimination of H_2 to generate the iridium(I) carbonyl must occur from the *cis*-dihydride, *cis*-(PCP$^{t\mathrm{Bu}}$)Ir(CO)H$_2$. In the closely related Ir pincer system where the *t*-Bu group is replaced by an *i*-Pr group, it was found that *cis*-(PCP$^{i\mathrm{Pr}}$)Ir(CO)H$_2$ isomerizes to *trans*-(PCP$^{i\mathrm{Pr}}$)Ir(CO)H$_2$ when heated under hydrogen at 90 °C.[7] This result would appear to support the former option of stereospecific migratory deinsertion to form the *cis* isomer, as the *trans* isomer was shown to be thermodynamically preferred in the *i*-Pr-substituted system. However, it is possible that the steric difference between *i*-Pr and *t*-Bu substitution could influence the *cis*−*trans* equilibrium.[15]

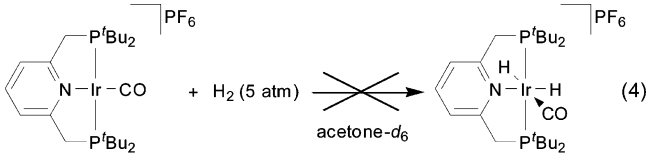
To investigate whether we were in fact observing a true stereospecific migratory deinsertion and not a thermodynamic consequence, we attempted to prepare *cis*-[(PNP)Ir(CO)H$_2$]PF$_6$ (***cis*-2**) and examine its reactivity, in particular with respect to its ability to undergo isomerization. Our first attempt to prepare ***cis*-2** was by the reaction of the PNP iridium(I) carbonyl complex [(PNP)Ir(CO)]PF$_6$ (**4**) with hydrogen. Compound **4** was prepared by the addition of 1 atm of CO to a solution of the known complex [(PNP)Ir(COE)]PF$_6$[6] and was characterized by ^{1}H and {^{1}H}^{31}P NMR and IR spectroscopy, as well as elemental analysis. The IR spectrum of this complex shows a sharp band

(14) West, N. W.; Reinartz, S.; White, P. S.; Templeton, J. L. *J. Am. Chem. Soc.* **2006**, *128*, 2059−2066.

(15) Alternatively, a referee suggested that the PCP case could proceed through a fluxional iridium(V) intermediate that allows a *cis* configuration of hydrides to occur. An iridium(V) intermediate may not be accessible with the weaker donor set of the PNP ligand.

$\nu_{CO} = 1962\ cm^{-1}$, indicating a greater degree of back-bonding to CO than in the iridium(III) carbonyl *trans*-dihydride ***trans*-2**.

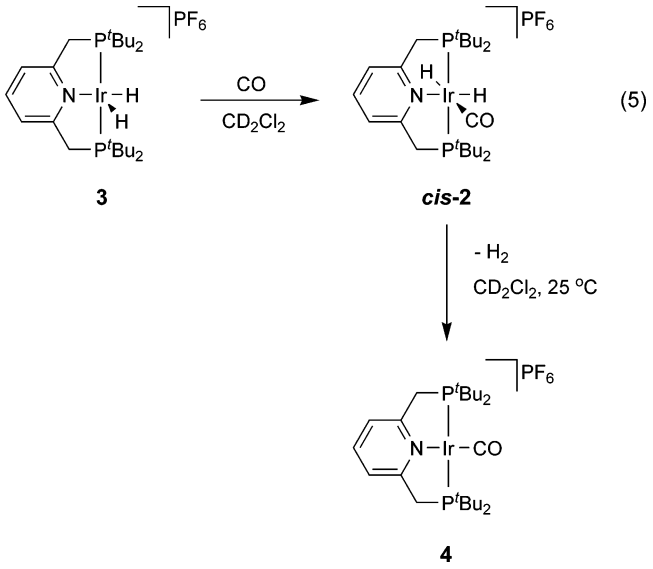
The oxidative addition of hydrogen to both neutral and cationic iridium(I) complexes has been extensively studied[16] and in most cases proceeds under mild conditions (room temperature or below, 1 atm hydrogen) to form *cis*-dihydride iridium(III) complexes. Surprisingly, treatment of a methanol solution of the iridium(I) carbonyl complex **4** with an atmosphere of hydrogen resulted in no reaction. No conversion to ***cis*-2** occurred, even when the solution of **4** was heated at 100 °C for 24 h or when a solution of **4** was pressurized with 5 atm of hydrogen at room temperature (eq 4).



4 ***cis*-2**

As hydrogen did not add to the iridium(I) carbonyl, ***cis*-2** was synthesized by an alternative method. The iridium(III) dihydride complex $[(PNP)Ir(H)_2]PF_6$ (**3**) was prepared by addition of an atmosphere of hydrogen to an acetone solution of $[(PNP)Ir(COE)]PF_6$. The ^1H NMR spectrum of **3** (298 K, CD_2Cl_2) shows a single virtual triplet for the *tert*-butyl groups on the ligand (1.28 ppm, $J_{P-H} = 7.5$ Hz), indicating an environment of C_{2v} symmetry. The resonance for the hydride ligands appears as a broad triplet at −28.65 ppm ($^2J_{P-H} = 12.5$ Hz), integrating to 2H. Variable-temperature ^1H NMR spectroscopy reveals that **3** is fluxional in solution. A dynamic process renders the two hydride ligands equivalent and creates the apparent additional plane of symmetry in the molecule.

Addition of an atmosphere of CO to a methylene chloride solution of **3** results in an immediate color change and quantitative formation of the *cis*-dihydride carbonyl complex $[(PNP)Ir(CO)H_2]PF_6$ (***cis*-2**) (eq 5). The ^1H NMR spectrum of ***cis*-2** (CD_2Cl_2) shows two virtual triplet resonances corresponding to the *tert*-butyl groups on the ligand at 1.43 ppm ($J_{P-H} = 7.0$ Hz) and 1.27 ppm ($J_{P-H} = 7.0$ Hz). Each of these virtual triplets integrates to 18H, indicating a different environment above and below the plane of the ligand. Two distinct signals are evident in the hydride region, a doublet of triplets at −8.87 ppm ($^2J_{P-H} = 16.8$ Hz, $^2J_{H-H} = 3.0$ Hz), integrating to 1H, and a second doublet of triplets at −17.75 ppm ($^2J_{P-H} = 11.7$ Hz, $^2J_{H-H} = 3.0$ Hz), also integrating to 1H. This pattern is consistent with two mutually coupled inequivalent hydride ligands, both located *cis* to the phosphorus atoms of the ligand. The IR spectrum of *cis*-2 reveals a sharp band at 2000 cm^{-1}, arising from the C−O stretch, and two weaker Ir−H bands at 2133 and 1969 cm^{-1}.[17]



cis-Dihydride ***cis*-2** is not stable in solution at room temperature. Even under an atmosphere of hydrogen, this complex undergoes reductive elimination of hydrogen over the course of 4.5 h to yield the iridium(I) carbonyl **4** quantitatively (eq 5). This observed reactivity of ***cis*-2** establishes that ***cis*-2** is not generated as an intermediate in the formation of ***trans*-2** and that the decarbonylation reaction discussed above proceeds stereospecifically.

Conclusions

The stoichiometric decarbonylation of methanol by $[(PNP)Ir(C_6H_5)H]PF_6$ proceeds stereoselectively to generate the novel *trans*-dihydride ***trans*-2**. This is in contrast to a similar methanol decarbonylation involving a closely related PCP^{tBu} iridium complex, where the iridium(I) carbonyl complex is obtained as the sole product. That the iridium(I) carbonyl is formed in the PCP^{tBu} system implies that the *cis*-dihydride iridium(III) complex is on the reaction pathway. We have provided evidence that the corresponding *cis*-dihydride, ***cis*-2**, is never formed in the PNP iridium system and that ***trans*-2** is the kinetic product of this reaction. The formation of ***trans*-2**, rather than ***cis*-2**, implies that the migratory deinsertion reaction of the formyl ligand proceeds stereoselectively. Thus, a subtle ligand modification is found to have a profound effect on the stereoselectivity of this reaction.

Experimental Section

General Considerations. All reactions were carried out under a dry nitrogen atmosphere using standard glovebox and Schlenk techniques. Di-*tert*-butylphosphine was purchased from Strem. Deuterated solvents were purchased from Cambridge Isotope Laboratories and stored over CaH_2 (CD_2Cl_2), $CaSO_4$ (acetone-d_6), or activated molecular sieves (CD_3OD). THF, pentane, diethyl ether, benzene, and toluene were dried by passage through activated alumina and molecular sieve columns. CH_3OH was distilled from Mg/I_2. All other reagents were purchased from Aldrich and used as received. NMR spectra were obtained at room temperature on Bruker DPX200, AV300, or AV500 MHz spectrometers. ^1H NMR spectra were referenced to residual solvent peaks, with chemical shifts (δ) reported in ppm downfield of tetramethylsilane. $^{31}P\{^1H\}$ NMR spectra were referenced externally to 85% H_3PO_4. $[(PNP)Ir(COE)]PF_6$ and $[(PNP)Ir(C_6H_5)H]PF_6$ were prepared according to published procedures.[6] Elemental analyses were performed by Atlantic Microlab Inc. of Norcross, GA.

(16) For representative examples, see: (a) Mazet, C.; Smidt, S. P.; Meuwly, M.; Pfaltz, A. *J. Am. Chem. Soc.* **2004**, *126*, 14176−14181. (b) Paterniti, D. P.; Francisco, L. W.; Atwood, J. D. *Organometallics* **1999**, *18*, 123−127. (c) Kimmich, B. F. M.; Somsook, E.; Landis, C. R. *J. Am. Chem. Soc.* **1998**, *120*, 10115−10125. (d) Deutsch, P. P.; Eisenberg, R. *Chem. Rev.* **1988**, *88*, 1147−1161. (e) Johnson, C. E.; Eisenberg, R. *J. Am. Chem. Soc.* **1985**, *107*, 3148−3160. (f) Chin, C. S.; Park, H. *Polyhedron* **1985**, *4*, 1673−1675. (g) Park, S.; Park, H.; Chin, C. S. *Inorg. Chem.* **1985**, *24*, 1120−1122. (h) Crabtree, R. *Acc. Chem. Res.* **1979**, *12*, 331−337. (i) Crabtree, R.; Felkin, H.; Morris, G. E. *J. Chem. Soc., Chem. Commun.* **1976**, 716−717. (j) Vaska, L.; Catone, D. L. *J. Am. Chem. Soc.* **1966**, *88*, 5324−5325.

(17) Data are similar to those reported for *cis*-$(PCP^{iPr})Ir(CO)(H)_2$, $\nu_{CO} = 1950\ cm^{-1}$, $\nu_{Ir-H} = 2066, 1965\ cm^{-1}$; see ref 7.

Table 1. Crystallographic Data Collection Parameters for *trans*-2

empirical formula	$C_{24}H_{45}IrNOP_2F_6P'$
fw	762.72
T (K)	130(2)
wavelength (Å)	0.71703
cryst descrip	plate
space group	$P\bar{1}$
unit cell dimens	$a = 8.3180(2)$ Å
	$b = 12.5200(4)$ Å
	$c = 15.4940(5)$ Å
	$\alpha = 104.9640(15)°$
	$\beta = 104.7720(15)°$
	$\gamma = 93.2510(14)°$
V (Å^3)	1494.30(8)
Z, ρ (mg/m^3)	2, 1.695
μ (mm^{-1})	4.684
F(000)	760
cryst size	0.24 × 0.17 × 0.05
no. of reflns for indexing	253
θ range (deg)	2.50 to 28.31
index ranges	$-10 \le h \le 11$
	$-16 \le k \le 16$
	$-20 \le l \le 17$
no. of reflns collected, unique	10 982, 6754
completeness to θ	96.1%
absorp corr	semiempirical from equivalents
refinement method	full-matrix least squares on F^2
goodness of fit on F^2	$S = 0.982$
R_1	0.0528
R_w ($I > 2\sigma I$)	0.1105

***trans*-[(PNP)Ir(CO)H$_2$]PF$_6$ (*trans*-2).** [(PNP)Ir(C_6H_5)H]PF_6 (9.5 mg, 0.012 mmol) was added to a resealable Teflon-valve NMR tube. CH_3OH (0.44 mL) was added by vacuum transfer, and the tube was placed under an atmosphere of nitrogen. The reaction was heated at 80 °C for 20 h, during which time the color changed from pale orange to pale yellow. After cooling to room temperature, pale yellow crystals of ***trans*-2** precipitated from solution. When the thermolysis was conducted in CD_3OD with a more dilute solution (0.014 M), all species remained in solution. ***trans*-2-*d*$_2$** was formed in 70−85% yield, as judged by integration against an internal standard. Dideuteride complex **3-*d*$_2$** was also formed in 15−30% yield. ***trans*-2**: ^{1}H NMR (acetone-d_6, 300 MHz): δ 7.99 (t, 1H, $J = 9.6$ Hz, Py), 7.68 (d, 2H, $J = 7.5$ Hz, Py), 4.30 (vt, 4H, $J = 4.2$ Hz, CH_2), 1.48 (vt, 36H, $J = 6.0$ Hz, C(CH_3)$_3$), −6.63 (t, 2H, $^2J_{H-P} = 12.3$ Hz, Ir-*H*). ^{31}P{^{1}H} NMR (acetone-d_6): δ 70.46 (s, Ir-*P*), −142.61 (h, $^1J_{F-P} = 709$ Hz, *P*F_6). IR (thin film): $\nu_{CO} = 2008$ cm^{-1}, $\nu_{Ir-H} = 1805$ cm^{-1}. Anal. Calcd for $C_{24}H_{45}F_6IrNOP_3$: C, 37.79; H, 5.95; N, 1.84. Found: C, 37.89; H, 5.83; N, 1.91.

[(PNP)Ir(H)$_2$]PF$_6$ (3). In a glass vessel fitted with a Teflon stopcock, [(PNP)Ir(COE)]PF_6 (0.150 g, 0.178 mmol) was dissolved in acetone (5 mL). One atmosphere of hydrogen was admitted to the reaction vessel. After stirring for 1.5 h, the color of the reaction mixture changed from deep red to a pale orange. The solvent was removed under vacuum, leaving an orange solid. The solid was washed with pentane (2 × 5 mL) and dried under vacuum to yield 0.102 g (78%). The product was recrystallized from a concentrated acetone solution at room temperature. ^{1}H NMR (CD_2Cl_2, 500 MHz): δ 7.95 (t, 1H, $J = 7.5$ Hz, Py), 7.68 (d, 2H, $J = 8.0$ Hz, Py), 3.94 (vt, 4H, $J = 3.5$ Hz, CH_2), 1.28 (vt, 36 H, $J = 7.5$ Hz, C(CH_3)$_3$), −28.65 (t, 2H, $^2J_{P-H} = 12.5$ Hz, Ir-*H*). ^{31}P{^{1}H} NMR (CD_2Cl_2): δ 75.62 (s, Ir-*P*), −143.87 (h, $^1J_{F-P} = 709$ Hz, *P*F_6). Anal. Calcd for $C_{23}H_{45}F_6IrNP_3$: C, 37.60; H, 6.17; N, 1.91. Found: C, 37.85; H, 6.23; N, 1.91.

[(PNP)Ir(CO)]PF$_6$ (4). In a resealable Teflon-valve NMR tube, deep red [(PNP)Ir(COE)]PF_6 (8.4 mg, 0.010 mmol) was dissolved in acetone-d_6 (0.30 mL). Carbon monoxide (300 Torr) was admitted to the tube. On shaking, the color of the solution immediately changed from deep red to bright yellow. The solvent was removed under vacuum, and the bright yellow residue washed with pentane (2 × 5 mL) and dried under vacuum to yield 6.8 mg (90%). The product was recrystallized by slow diffusion of pentane into a concentrated acetone solution at −35 °C. ^{1}H NMR (acetone-d_6, 300 MHz): δ 8.13 (t, 1H, $J = 7.5$ Hz, Py), 7.83 (d, 2H, $J = 7.8$ Hz, Py), 4.28 (vt, 4H, $J = 3.9$ Hz, CH_2), 1.48 (vt, 36H, $J = 7.5$ Hz, C(CH_3)$_3$). ^{31}P{^{1}H} NMR (acetone-d_6): δ 75.37 (s, Ir-*P*), −142.67 (h, $^1J_{F-P} = 709$ Hz, *P*F_6). IR (thin film): $\nu_{CO} = 1962$ cm^{-1}. Anal. Calcd for $C_{24}H_{43}F_6IrNOP_3$: C, 37.89; H, 5.70; N, 1.84. Found: C, 38.33; H, 5.86; N, 1.82.

***cis*-[(PNP)Ir(CO)H$_2$]PF$_6$ (*cis*-2).** A resealable Teflon-valve NMR tube was charged with [(PNP)Ir(H)$_2$]PF_6 (5.4 mg, 0.0073 mmol), and CD_2Cl_2 (0.25 mL) was added by vacuum transfer, forming a golden yellow solution. Acetone (0.39 μmol) was added as an internal standard. Carbon monoxide (300 Torr) was admitted to the tube. On shaking, the solution instantly turned a greenish-yellow color. The reaction mixture was immediately frozen, the CO atmosphere removed under vacuum, and hydrogen (700 Torr) admitted to the tube. Upon thawing, examination of the reaction mixture by ^{1}H NMR revealed quantitative conversion to ***cis*-2** (integration against the internal standard). Left at room temperature, the color of the solution gradually turned bright yellow. After 4.5 h, examination of the reaction mixture revealed complete conversion to **4**. ***cis*-2**: ^{1}H NMR (CD_2Cl_2, 300 MHz): δ 7.86 (t, 1H, $J = 8.1$ Hz, Py), 7.57 (d, 2H, $J = 7.8$ Hz, Py), 3.90 (m, 4H, CH_2), 1.43 (vt, 18H, $J = 7.0$ Hz, C(CH_3)$_3$), 1.27 (vt, 18H, $J = 7.0$ Hz, C(CH_3)$_3$), −8.87 (dt, 1H, $^2J_{P-H} = 16.8$ Hz, $^2J_{H-H} = 3.0$ Hz, Ir-*H*), −17.75 (dt, 1H, $^2J_{P-H} = 11.7$ Hz, $^2J_{H-H} = 3.0$ Hz, Ir-*H*). ^{31}P{^{1}H} NMR (CD_2Cl_2): 63.14 (s, Ir-*P*), −143.86 (h, $^1J_{F-P} = 709$ Hz, *P*F_6). IR (thin film): $\nu_{Ir-H} = 2133$ cm^{-1}, $\nu_{CO} = 2000$ cm^{-1}, $\nu_{Ir-H} = 1969$ cm^{-1}.

Thermolysis of 1 in CH$_3$OD. Complex **1** (3.0 mg, 0.0037 mmol) and CH_3OD (0.35 mL) were added to a resealable Teflon-valve NMR tube under nitrogen. The tube was heated at 80 °C for 20 h. Upon reaction completion, examination of the ^{1}H NMR spectrum revealed the formation of ***trans*-2-*h*$_2$**. The volatiles were removed under vacuum and analyzed by GC-MS. Examination of the iridium product by ^{2}H NMR spectroscopy confirmed the formation of ***trans*-2-*h*$_2$**.

Reaction of 1 with Triethylamine. In a resealable Teflon-valve NMR tube, complex **1** (4.6 mg, 0.0057 mmol) was dissolved in CD_3OD (0.25 mL). Under nitrogen, triethylamine (0.8 μL, 0.0058 mmol) was added. After 15 min, examination of the reaction mixture by ^{1}H and ^{2}H NMR spectroscopy revealed complete deuterium incorporation into the hydride position on **1**. A similar experiment conducted in CH_3OD also showed complete deuterium incorporation into the hydride position of **1**.

Reaction of 3-*d*$_2$ with Paraformaldehyde. Complex **3-*d*$_2$** (3.5 mg, 0.0048 mmol), paraformaldehyde (0.8 mg, 0.0262 mmol), and CD_3OD (0.30 mL) were added to a resealable Teflon-valve NMR tube under nitrogen. The tube was heated to 80 °C, and the reaction monitored by ^{1}H NMR spectroscopy. After 3 h, complete conversion to ***trans*-2-*h*$_2$** had occurred.

X-ray Crystal Structure of *trans*-2. Crystals of **2** were grown from a concentrated methanol solution at room temperature. X-ray data were collected on a Nonius Kappa CCD X-ray defractometer with φ-scans with the details given in Table 1.

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Supporting Information Available: A CIF file containing X-ray crystallographic data for ***trans*-2**. This material is available free of charge via the Internet at http://pubs.acs.org.

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