Hemilabile Pincer-Type Hydride Complexes of Iridium

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Received June 5, 2007

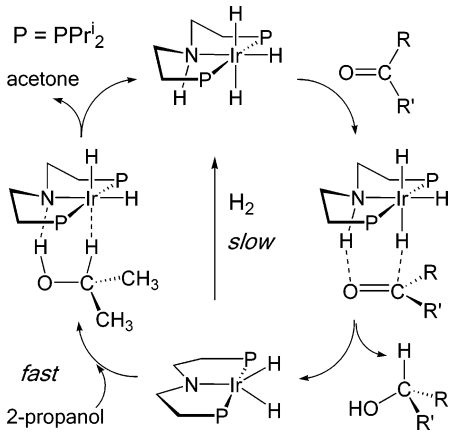
The ligand ^{t}Bu$_2$PC$_2$H$_4$NHC$_2$H$_4$NEt$_2$ (PNHN) was synthesized starting from 2-(diethylamino)ethyl chloride hydrochloride and ethanolamine. Reaction of PNHN with [IrCl(COE)$_2$]$_2$ under H_2 afforded the dihydride *cis*-IrH$_2$Cl(κ^3-PNHN) (**1**) in excellent yield. Treatment of **1** with ^{t}BuOK led to clean formation of the 16-electron amido complex IrH$_2$(κ^3-PNN) (**2**). Hydrogenation of **2** in toluene or ethyl acetate produced the trihydride *mer*-IrH$_3$(κ^3-PNHN) (**3**). This complex was unstable and dimerized to give [IrH$_2$(κ^2-PNHN)]$_2$(μ-H)$_2$ (**4**) with uncoordinated NEt$_2$ groups. The structures of **1** and **4** were established by X-ray crystallography. Complex **2** demonstrated good catalytic activity for transfer hydrogenation of acetophenone, cyclohexanone, and butanone.

Introduction

A good number of competent transition metal catalysts are now available for homogeneous hydrogenation of ketones.[1] One example prepared in our laboratory is the pincer-type complex *mer*-IrH$_3$(PNHP) (PNHP = HN(C$_2$H$_4$P^{i}Pr$_2$)$_2$), which catalyzes transfer hydrogenation of a typical substrate, acetophenone, with S/C ratios of up to 10^5 and conversions exceeding 90% in 2-propanol at 80 °C.[2] Interestingly, IrH$_3$(PNHP) is not active for hydrogenation under hydrogen because of a relatively slow rate of H_2 addition to the intermediate IrH$_2$(PNP) (Scheme 1) and slow regeneration of the catalyst, IrH$_3$(PNHP). This behavior is not exceptional; in fact, Noyori and co-workers recently noted that most of the existing ketone hydrogenation catalysts are effective for only one of the two reactions, i.e., for either transfer hydrogenation or hydrogenation under H_2.[1h] Exact reasons for such selectivity are not clear since both types of ketone hydrogenation are linked mechanistically and are believed to involve formation of amido intermediates under catalytic conditions. Perhaps only one catalyst, the Ru triflate complex Ru(OTf){(*S*,*S*)-Ts-dpen}(*p*-cymene), is known to operate as a transfer hydrogenation catalyst under basic conditions in 2-propanol and is also active for H_2 hydrogenation under acidic conditions in methanol.[1h]

Transfer hydrogenation is a convenient method for preparation of gram quantities of alcohols in laboratory settings, yet hydrogenation of neat ketons under H_2, when possible, is an attractive alternative for large-scale industrial applications. Therefore, development of versatile ketone hydrogenation catalysts is an important fundamental and practical challenge.

Scheme 1



In this project, we decided to explore the effect of a modification of IrH$_3$(PNHP) aimed at enabling partial dissociation of the coordinated pincer ligand in order to facilitate H_2 addition to Ir under catalytic conditions. To this end, we thought of modifying the original PNHP ligand by substituting a NEt$_2$ group for a P^{i}Pr$_2$ group; the product, PNHN = R$_2$PC$_2$H$_4$NHC$_2$H$_4$NEt$_2$, was expected to give rise to a hemilabile complex, IrH$_3$(PNHN), containing a weakly coordinated NEt$_2$ group.

It may be instructive to consider calculated structures of the model systems IrH$_3$[HN(C$_2$H$_4$PMe$_2$)$_2$] and IrH$_3$[Me$_2$PC$_2$H$_4$NHC$_2$H$_4$NMe$_2$], presented in Figure 1 along with atomic charges on the hydrides calculated according to three different definitions. The Ir−N2 bond is longer than the Ir−P bond (2.220 vs 2.187 Å, respectively) in IrH$_3$[Me$_2$PC$_2$H$_4$NHC$_2$H$_4$NMe$_2$], in agreement with the expected hemilabile nature of the system. In both complexes in Figure 1, the *trans*-hydrides H2 and H3 form long polarized bonds to Ir, whereas Ir−H4 is a nonpolar covalent bond. Atoms H2 and H3 are more hydridic in IrH$_3$[Me$_2$PC$_2$H$_4$NHC$_2$H$_4$NMe$_2$] compared to IrH$_3$[HN(C$_2$H$_4$PMe$_2$)$_2$], and it appears that the Ir center in the former complex is more "electron-rich".[3] An exact relationship between the catalyst's hydricity and the rate of transfer hydrogenation is not known;

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(1) (a) Noyori, R. *Angew. Chem., Int. Ed.* **2002**, *41*, 2008. (b) Backvall, J.-E. *J. Organomet. Chem.* **2002**, *652*, 105. (c) Genet, J.-P. *Acc. Chem. Res.* **2003**, *36*, 908. (d) Blaser, H.-U.; Malan, C.; Pugin, B.; Spindler, F.; Steiner, H.; Studer, M. *Adv. Synth. Catal.* **2003**, *345*, 103. (e) Clapham, S. E.; Hadzovic, A.; Morris, R. H. *Coord. Chem. Rev.* **2004**, *248*, 2201. (f) Bullock, R. M. *Chem.−Eur. J.* **2004**, *10*, 2366. (g) Ikariya, T.; Murata, K.; Noyori, R. *Org. Biomol. Chem.* **2006**, *4*, 393. (h) Sandoval, C. A.; Ohkuma, T.; Utsumi, N.; Tsutsumi, K.; Murata, K.; Noyori, R. *Chem. Asian J.* **2006**, 1−2, 102. (i) Lundgren, R. J.; Rankin, M. A.; McDonald, R.; Schatte, G.; Stradiotto, M. *Angew. Chem., Int. Ed.* **2007**, *46*, 4732.

(2) Clarke, Z. E.; Maragh, P. T.; Dasgupta, T. P.; Gusev, D. G.; Lough, A. J.; Abdur-Rashid, K. *Organometallics* **2006**, *25*, 4113.

(3) In agreement with this, our calculations on model iridium carbonyl complexes show that the ν_{CO} = 2019.0 cm^{-1} in IrCp(CO)(NMe$_3$) is lower than ν_{CO} = 2028.3 cm^{-1} in IrCp(CO)(P^{t}Bu$_3$).

10.1021/om700550x CCC: $37.00
Publication on Web 09/13/2007

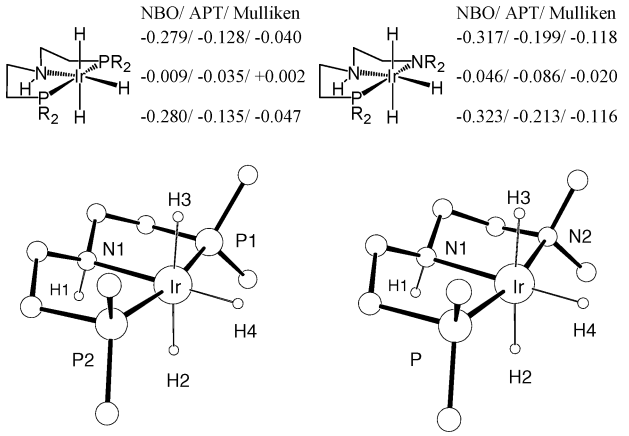
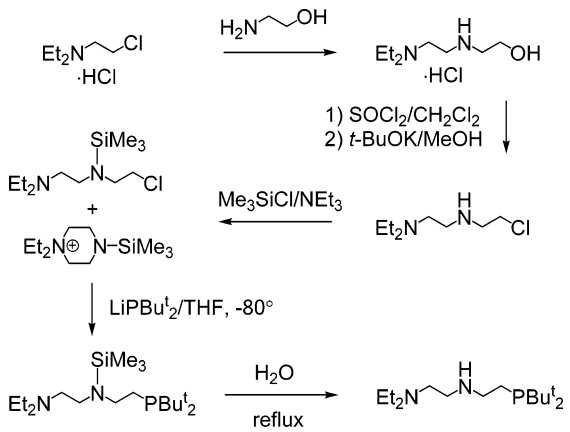


Figure 1. Calculated structures of *mer*-$IrH_3[HN(C_2H_4PMe_2)_2]$ and *mer*-$IrH_3[Me_2PC_2H_4NHC_2H_4NMe_2]$. Most of the hydrogen atoms are not shown for clarity. Selected distances (Å) and angles (deg): (left) Ir−H2 1.673, Ir−H3 1.673, Ir−H4 1.582, Ir−N1 2.248, Ir−P 2.258, H2−Ir−H3 175.0, N1−Ir−H4 179.6; (right) Ir−H2 1.680, Ir−H3 1.677, Ir−H4 1.586, Ir−N1 2.217, Ir−P 2.187, Ir−N2 2.220, H2−Ir−H3 176.1, N1−Ir−H4 178.5.

Scheme 2



however, it is commonly assumed that the outer-sphere (also called "bifunctional") hydrogenation mechanism requires a properly polarized catalyst incorporating a protic and a hydridic hydrogen atom.[1]

Results and Discussion

The new PNHN ligand $^tBu_2PC_2H_4NHC_2H_4NEt_2$ was synthesized employing conventional organic reactions diagramed in Scheme 2. One complication encountered in this part of the project was the relatively fast self-alkylation of $ClC_2H_4N(SiMe_3)C_2H_4NEt_2$, which produced 1-diethyl-4-(trimethylsilyl)-piperazinium chloride. Both compounds apparently reacted with LiP^tBu_2 to give $^tBu_2PC_2H_4N(SiMe_3)C_2H_4NEt_2$. This, after hydrolysis, afforded the PNHN ligand as a colorless oil.

Dissolving equivalent amounts of the PNHN ligand and $[IrCl(COE)_2]_2$ in toluene under argon resulted in displacement of cyclooctene and formation of a new complex containing coordinated PNHN (^{31}P NMR: δ 38.5 vs 23.2 for free PNHN). Continued stirring of this solution under 1 atm of H_2 finally afforded the dihydride *cis*-$IrH_2Cl(\kappa^3$-PNHN) (**1**) (Scheme 3) in excellent yield. The NEt_2 group is weakly coordinated in **1**, and we noted that when the PNHN ligand was used in excess, a *trans*-diphosphine species formed along with **1**, characterized by a large $^2J_{PP}$ = 319 Hz. The $^{31}P\{^1H\}$ NMR spectrum of **1** showed a singlet at δ 53.3, while the ^1H NMR spectrum

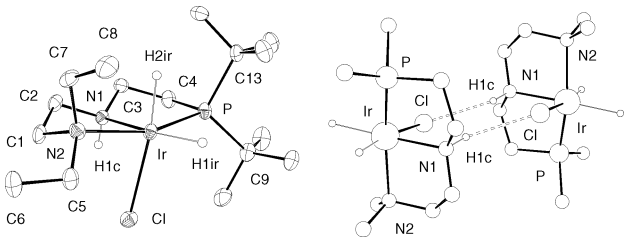
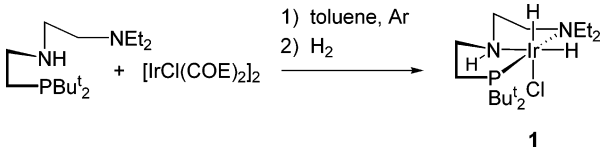


Figure 2. ORTEP and atom-labeling scheme for **1** with the ellipsoids at 30%. Most of the hydrogen atoms are omitted for clarity. Selected bond distances (Å) and angles (deg): Ir−P 2.2108(18), Ir−N1 2.155(5), Ir−N2 2.235(5), Ir−Cl 2.5453(17), P−Ir−N2 161.32(14), N1−Ir−N2 82.41(19), N1−Ir−Cl 83.06(15), N2−Ir−Cl 86.07(15), N1−Ir−P 85.63(14), P−Ir−Cl 106.70(6).

Scheme 3



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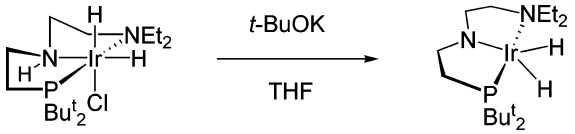
Scheme 4



1 **2**

exhibited the hydride resonances at δ −19.34 and −26.66 as doublets of doublets. The observation of two CH_3 resonances of the NEt_2 group (δ 1.05, 0.77) confirmed Ir−NEt_2 bonding in solution. The symmetry of **1** is C_1; thus, the ^{t}Bu groups on phosphorus and all CH_2 protons of the NEt_2 group are magnetically inequivalent in this complex. The IR spectrum of **1** showed a strong band at 3195 cm^{-1} due to the N−H stretch and two strong bands at 2290 and 2084 cm^{-1} for the Ir−H vibrations.

The X-ray diffraction structure of **1** (Figure 2) exhibits a distorted octahedral geometry for the most part similar to those of the crystallographically characterized complexes $IrH_2Cl[HN(C_2H_4P^iPr_2)_2]$[2] and $IrH_2Cl[HN(SiMe_2CH_2PPh_2)_2]$.[4a] The molecules of **1** form hydrogen-bonded pairs in the solid state where the intermolecular and intramolecular Cl···H1c distances are similar: ca. 2.6 and 2.7 Å, respectively. The chloride of **1** is noticeably bent toward N2, away from the bulky phosphorus group: ∠P−Ir−Cl = 106.7°, ∠N2−Ir−Cl = 86.1°. The PNHN ligand of **1** is coordinated in a pincer-type *mer* fashion. The P^tBu_2 and NEt_2 groups are *trans* and are slightly bent toward the NH. The Ir−N2 bond must be weak since it is very long, 2.235(5) Å, compared to the Ir−P (2.2108(18) Å) and Ir−N1 (2.155(5) Å) distances.

Dehydrochlorination of **1** with potassium *tert*-butoxide in THF cleanly afforded the amido complex $IrH_2(\kappa^3$-PNN) (**2**) (Scheme 4), which was isolated as a viscous oil. The product was well soluble in hexane, and we were unable to obtain crystalline samples for X-ray and elemental analyses. NMR spectra of **2** are provided with the Supporting Information. The ^1H NMR and $^{13}C\{^1H\}$ NMR spectra indicate an effective C_s symmetrical structure in solution where the PNN atoms define the mirror

(4) (a) Fryzuk, M. D.; MacNeil, P. A.; Rettig, S. J. *J. Am. Chem. Soc.* **1987**, *109*, 2803. (b) Fryzuk, M. D.; MacNeil, P. A. *Organometallics* **1983**, *2*, 682.

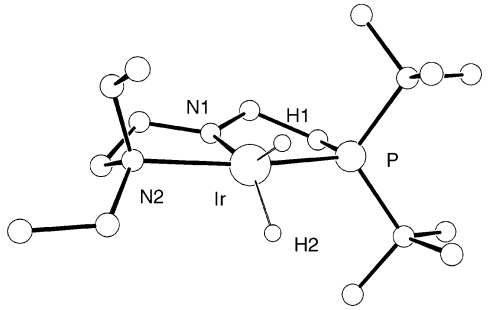
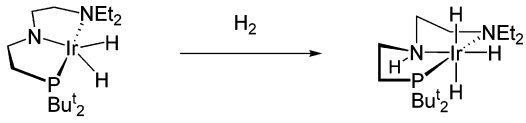


Figure 3. Calculated structure of **2**. Most of the hydrogen atoms are omitted for clarity. Selected bond distances (Å) and angles (deg): Ir−P 2.231, Ir−N1 1.994, Ir−N2 2.224, Ir−H1 1.581, Ir−H2 1.595, H1···H2 1.697, P−Ir−N1 84.6, P−Ir−N2 165.4, N1−Ir−N2 80.9, N1−Ir−H1 147.2, N1−Ir−H2 148.1.

Scheme 5



2 **3**

plane. Thus, the two hydrides, two ^{t}Bu, and two Et groups are pairwise equivalent in the NMR spectra of **2**, as well as the hydrogens of the CH_2 groups of the PNN ligand backbone. The IrH_2 resonance is seen at δ −22.14 as a doublet of quintets ($^2J_{HP}$ = 12.9, $^4J_{HH}$ = 3.1 Hz) exhibiting unusual long-range coupling to two CH_2 groups of the PNN ligand. Similar ^{1}H chemical shifts, −22.35 and −24.86 ppm, were reported for the related dihydrides $IrH_2Cl[HN(C_2H_4P^iPr_2)_2]$[2] and $IrH_2Cl[HN(SiMe_2CH_2PPh_2)_2]$, respectively.[4b] The $^{31}P\{^1H\}$ NMR spectrum of **2** shows a singlet at 85.3 ppm, representing a downfield shift of about 30 ppm relative to **1**.

The molecular geometry of **2** could not be established experimentally; therefore, we determined the structure of this complex with the help of DFT calculations. The optimized geometry of **2** is presented in Figure 3 and shows a distorted trigonal-bipyramidal structure. The molecule of **2** is Y-shaped in the equatorial part, where ∠H−Ir−H = 64.6° is strongly reduced compared to the 120° angle expected in the ideal trigonal-bipyramidal geometry. This type of distortion works to strengthen π-bonding between the nitrogen and iridium, resulting in a short Ir−N bond, 1.99 Å. The electronic factors have been discussed in detail for a related iridium dihydride, $IrH_2Cl(PPh^tBu_2)_2$, which has ∠H−Ir−H = 72.7° in the structure determined by neutron diffraction.[5] The smaller H−Ir−H angle in **2** can be attributed to a stronger π-donor ability of the amido nitrogen compared to that of chloride.

Stirring solutions of **2** under 1 atm of H_2 afforded the expected trihydride *mer*-$IrH_3(\kappa^3$-PNHN) (**3**) (Scheme 5). Formation of **3** was monitored by ^{31}P NMR and appeared to be relatively slow in benzene and toluene, where a small amount of **2** was observable 15 min after the preparation of the samples. In ethyl acetate, the spectrum recorded 10 min after the sample preparation showed quantitative hydrogenation of **2** and clean formation of **3**. Complex **3** proved to be unstable in all solvents and dimerized within hours to give a new species **4**, which will be discussed below. Among the salient spectroscopic features of **3** are three 1:1:1 ^{1}H NMR resonances at δ −20.08, −9.44, and −8.17. The latter two can be assigned to the *trans*-hydrides in **3** on the basis of the characteristically large $^2J_{HH}$ = 12.0 Hz.[6] The observation of two triplets at δ 1.06 and 0.99 for inequivalent methyl groups of NEt_2 proves retention of Ir−NEt_2 bonding in solution. The $^{31}P\{^1H\}$ NMR spectrum of **3** exhibits a singlet at 70.8 ppm.

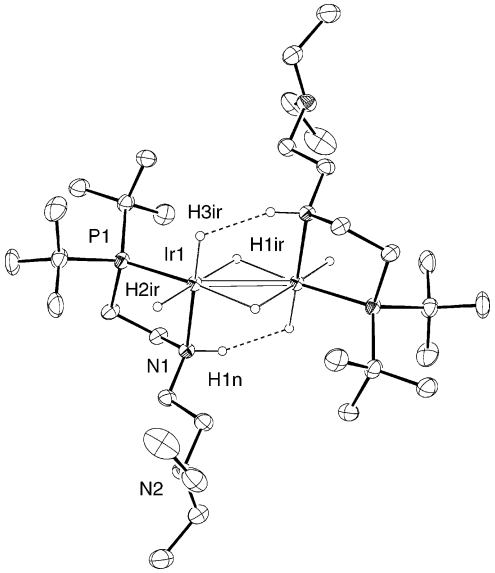


Figure 4. ORTEP and atom-labeling scheme for **4a** with the ellipsoids at 30%. Most of the hydrogen atoms are omitted for clarity. The positional and isotropic displacement parameters of the three unique hydride ligands have been refined. Selected bond distances (Å) and angles (deg): Ir1−N1 2.231(4), Ir1−P1 2.2431(14), Ir−Ir 2.7325(7), N1−Ir1−P1 83.76(11).

Formation of **4** from **3** proceeded slowly in benzene and ethyl acetate; however it was fast when **1** was treated with ^{t}BuOK in 2-propanol, where **3** presumably was formed but apparently dimerized too rapidly to be detected by NMR. Spectroscopic characterization of **4** was complicated by isomerization of the complex in solution. The $^{31}P\{^1H\}$ NMR spectra showed single resonances of **4a** and **4b** at 82.6 and 81.7 ppm, respectively. In nonpolar benzene, the ratio **4a**/**4b** was 3:1; this changed to 12:1 in the more polar dichloromethane, and only a trace of **4b** was observed in 2-propanol. The structure of **4a** was eventually established by X-ray diffraction.

The X-ray study revealed the dimeric bioctahedral structure $[IrH_2(\kappa^2$-PNHN)$]_2(\mu$-H)$_2$ (Figure 4), in which the halves of the molecule are related by an inversion center and the PNHN ligand is bidentate. Ir−Ir dimers bridged solely by hydrides are uncommon.[7] The Ir−Ir separation of 2.73 Å is consistent with Ir−Ir bonding;[8] furthermore, in related 32-electron complexes of Ir(III) the Ir−Ir distances of 2.71−2.72 Å were interpreted as Ir═Ir double bonds.[9] An interesting feature of **4a** is two very short IrH···HN contacts of only 1.90 Å, consistent with the presence of "dihydrogen" bonding.[10]

(5) Albinati, A.; Bakhmutov, V. I.; Caulton, K. G.; Clot, E.; Eckert, J.; Eisenstein, O.; Gusev, D. G.; Grushin, V. V.; Hauger, B. E.; Klooster, W. T.; Koetzle, T. F.; McMullan, R. K.; O'Loughlin, T. J.; Pélissier, M.; Ricci, J. S.; Sigalas, M. P.; Vymenits, A. B. *J. Am. Chem. Soc.* **1993**, *115*, 7300.

(6) (a) Laporte, C.; Büttner, T.; Rüegger, H.; Geier, J.; Schönberg, H.; Grützmacher, H. *Inorg. Chim. Acta* **2004**, *357*, 1931. (b) Choualeb, A.; Lough, A. J.; Gusev, D. G. *Organometallics* **2007**, *26*, 3509.

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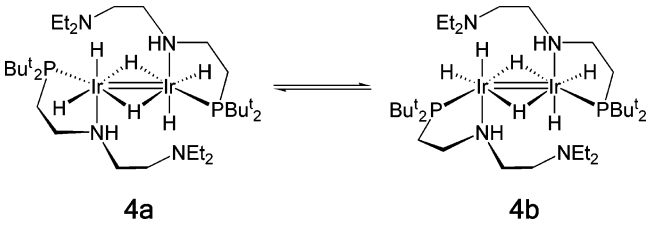
(9) (a) Hanasaka, F.; Fujita, K.; Yamaguchi, R. *Organometallics* **2005**, *24*, 3422. (b) Fujita, K.; Nakaguma, H.; Hanasaka, F; Yamaguchi, R. *Organometallics* **2002**, *21*, 3749.

Scheme 6



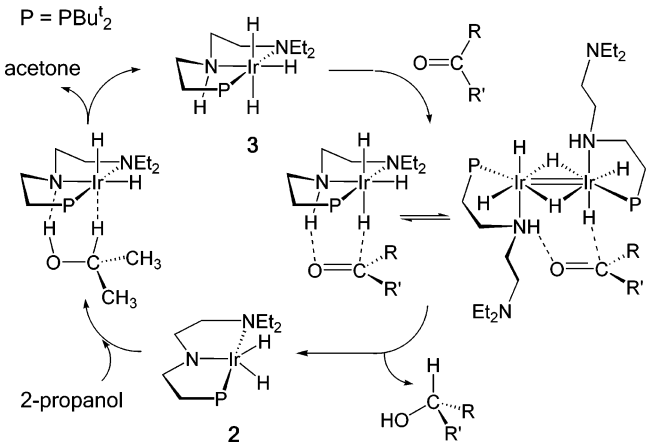
Knowing the structure of **4a** facilitated interpretation of the NMR spectra of the molecule. The C_i symmetry of **4a** is responsible for the observation of single chemical shifts for H1ir, H2ir, H3ir, and P1 atoms. Assignment of the hydride resonances in **4a** was done with the help of an NOE experiment where the NH resonance was irradiated at 4.88 ppm (CD_2Cl_2). This produced a 3.7% NOE at δ −9.75, a 15.5% NOE at δ −21.68, and no NOE at δ −22.94, assigned to H1ir, H3ir, and H2ir, respectively, on the basis of the H···H distances in **4a**. The chemically equivalent hydride and phosphorus spins are magnetically nonequivalent in each pair and comprise a non-first-order system AA′MM′NN′XX′ (A = H1ir, M = H3ir, N = H2ir, X = P). This explains why the ^{1}H NMR spectra of **4a** feature complicated patterns for H2ir and H3ir; only the bridging hydrides H1ir appear as a doublet due to large *trans* coupling to phosphorus ($^2J_{HP}$ = 79.2 Hz).

To get insights into the structure of the second isomer, **4b**, we studied this complex in C_6D_6. In the hydride region, **4b** shows four resonances in a 1:1:2:2 ratio. The bridging hydrides are inequivalent at δ −8.68 and −9.27, and the latter resonance is a triplet with a large $^2J_{HP}$ = 72.4 Hz. Pairwise chemical equivalence of the terminal hydrides (δ −20.56 and −20.95) and the phosphorus groups in **4b** is consistent with an overall C_2 symmetrical structure diagramed in Scheme 6.

It is interesting to note that **3** dimerizes to give **4**, whereas **1** is stable in solution, although dimers analogous to **4** with bridging chlorides are a conceivable and reasonable structural alternative. It is clear that the instability of **3** is only partly due to the hemilabile nature of the PNHN ligand. The other reason behind formation of **4** might be the destabilization caused by the *trans* disposition of two hydrides in **3**.

The new complexes **2**−**4** were tested for hydrogenation of representative ketones using ^{1}H NMR to monitor the reactions. Complex **2** reacted with neat ketones to give a mixture of unidentified iridium species, and no hydrogenation was observed under 1 atm of H_2 even upon heating. Also, when complex **3** was prepared from **2** and H_2 in ethyl acetate, it did not catalyze hydrogenation of either acetophenone or the solvent under 1 atm of H_2. Complex **2** efficiently catalyzed transfer hydrogenation in 2-propanol at 85 °C. With S:C = 1000 for acetophenone and butanone and with S:C = 1200 for cyclohexanone, the turnover frequencies at 50% conversion to the corresponding alcohols were TOF = 1500, 1850, and 1600 mol/h, respectively.[11] These reactions apparently involved mixtures of iridium complexes since **2** reacts with 2-propanol to give **4** (via **3**) and with ketones to give unidentified species. Complex **4** itself showed moderate catalytic activity in 2-propanol, where a TOF = 360 mol/h at 50% conversion was observed for hydrogenation

Scheme 7



of cyclohexanone at 85 °C. Several species implicated in the transfer hydrogenation reactions are included in the catalytic cycle in Scheme 7. It cannot be excluded that complex **4** dissociates at 85 °C to produce some IrH_3(PNHN) in solution. It is also conceivable that **4** can directly hydrogenate 2 equiv of a ketone and dissociate to give **2**.

Concluding Remarks. This study looked into the effects of hemilability on catalytic hydrogenation of ketones. Apparently, hemilability is relatively unimportant for ketone hydrogenation, and successful bifunctional hydrogenation catalysts can be thermally robust species, such as IrH_3(PNHP), which is stable in 2-propanol/acetone. This is different from the conventional homogeneous catalysts, where availability of a vacant coordination site is crucial and hemilability can often be an advantageous property.

Experimental Section

General Considerations. All preparations and manipulations were carried out under hydrogen, nitrogen, or argon atmospheres with the use of standard Schlenk, vacuum line, and glovebox techniques in dry, oxygen-free solvents. Deuterated solvents were degassed and dried before use. Potassium *tert*-butoxide, di-*tert*-butylchlorophosphine, ethanolamine, chlorotrimethylsilane, and ketones were supplied by Aldrich. 2-Diethylaminoethyl chloride hydrochloride was supplied by Alfa. NMR spectra were recorded on a Varian Unity Inova 300 MHz spectrometer. All ^{31}P chemical shifts are reported relative to 85% H_3PO_4. ^{1}H and ^{13}C chemical shifts were measured relative to the solvent peaks but are reported relative to TMS. The infrared spectra were obtained on a Perkin-Elmer Spectrum BXII FT IR spectrometer. The elemental analyses were performed by Midwest Microlab, LLC (Indianapolis, IN).

$Et_2NC_2H_4NHC_2H_4OH$·HCl. A solution of 2-diethylaminoethyl chloride hydrochloride (40 g, 0.232 mol) in ethanolamine (102 g, 1.664 mol) was stirred for 2 h, and then excess ethanolamine was removed by vacuum distillation. The viscous residue was triturated with 140 mL of CH_2Cl_2 to precipitate ethanolamine hydrochloride; the solid was filtered and extracted with 4 × 20 mL of CH_2Cl_2. The solution was evaporated to give $Et_2NC_2H_4NHC_2H_4OH$·HCl (40 g, 0.203 mol, 88%) as a pale yellow solid containing at least 90% of the product, and it was used without further purification. ^{1}H NMR (methanol-d_4): δ 3.68 (t, $^3J_{HH}$ = 5.6, 2H, CH_2O), 3.06 (t, $^3J_{HH}$ = 5.6, 2H, CH_2NH), 2.97 (m, 4H, NCH_2CH_2N), 2.84 (q, $^3J_{HH}$ = 7.3, 4H, NCH_2), 1.11 (t, $^3J_{HH}$ = 7.3, 6H, CH_3). ^{13}C{^{1}H} NMR (methanol-d_4): δ 59.3 (s, *C*H_2O), 51.2 (s, *C*H_2N), 50.5 (s, *C*H_2N), 48.3 (s, *C*H_2N), 45.0 (s, *C*H_2N), 10.6 (s, *C*H_3).

$Et_2NC_2H_4NHC_2H_4Cl$·2HCl. A solution of $SOCl_2$ (16.93 g, 0.142 mol) in 20 mL of CH_2Cl_2 was added dropwise to a vigorously stirred suspension of $Et_2NC_2H_4NHC_2H_4OH$·HCl (20 g, 0.102 mol) in 120

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(11) Complex **2** was added to solutions of the ketones in 2-propanol, and the hydrogenation was monitored by ^{1}H NMR.

mL of CH_2Cl_2 cooled at 0 °C. The ice bath was removed and stirring continued for 1 h. Then the mixture was refluxed for 1 h. After cooling, the suspension was filtered and the product was washed with 2 × 20 mL of CH_2Cl_2 to give a colorless solid of $Et_2NC_2H_4NHC_2H_4Cl\cdot 2HCl$ (20 g, 79.48 mmol, 78%). ^{1}H NMR (methanol-d_4): δ 4.03 (t, $^3J_{HH}$ = 6.1, 2H, CH_2Cl), 3.68 (br s, 4H, CH_2NH), 3.61 (t, $^3J_{HH}$ = 5.7, 2H, Et_2NCH_2), 3.38 (q, $^3J_{HH}$ = 7.3, 4H, CH_3CH_2), 1.43 (t, $^3J_{HH}$ = 7.3, 6H, CH_3). ^{13}C{^{1}H} NMR (methanol-d_4): δ 50.8 (s, NCH$_2$), 49.3 (s, NCH$_2$), 48.5 (s, NCH$_2$), 43.2 (s, NCH$_2$), 40.2 (s, CH$_2$Cl), 9.4 (s, CH$_3$).

^{t}Bu$_2$PC$_2$H$_4$NHC$_2$H$_4$NEt$_2$. The following reactions were carried out under an inert atmosphere. ^{t}BuOK (17.7 g, 158.5 mmol) was added in portions to a solution of $Et_2NC_2H_4NHC_2H_4Cl\cdot 2HCl$ (18.45 g, 73.32 mmol) in 30 mL of methanol cooled at 0 °C. The mixture was stirred at 0 °C for 25 min, then evaporated under vacuum, and $Et_2NC_2H_4NHC_2H_4Cl$ was extracted with 20 mL of toluene and was immediately used in the following step. ^{1}H NMR (benzene-d_6): δ 3.22 (t, $^3J_{HH}$ = 5.9, 2H, CH_2Cl), 2.60 (t, $^3J_{HH}$ = 5.9, 2H, NCH_2), 2.40 (m, 2H, NCH_2), 2.34 (m, 2H, NCH_2), 2.31 (q, $^3J_{HH}$ = 7.2, 4H, NCH_2), 1.73 (br, 1H, NH), 0.87 (t, $^3J_{HH}$ = 7.2, 6H, CH_3). ^{13}C{^{1}H} NMR (benzene-d_6): δ 53.7 (s, NCH$_2$), 51.8 (s, NCH$_2$), 47.8 (s, NCH$_2$), 47.1 (s, NCH$_2$), 45.2 (s, CH$_2$Cl), 12.8 (s, CH$_3$).

Triethylamine (7.38 g, 73.18 mmol) was added to the toluene solution of $Et_2NC_2H_4NHC_2H_4Cl$. The mixture was cooled to 0 °C, and chlorotrimethylsilane (6.82 g, 66.85 mmol) was added dropwise. The mixture was stirred at 0 °C for 1.5 h, then filtered and evaporated under vacuum to give $Et_2NC_2H_4N(SiMe_3)C_2H_4Cl$ (7.64 g, 30.59 mmol) as a colorless oil. ^{1}H NMR (benzene-d_6): δ 3.24 (t, $^3J_{HH}$ = 7.3, 2H, CH_2Cl), 2.98 (t, $^3J_{HH}$ = 7.3, 2H, NCH_2), 2.71 (t, $^3J_{HH}$ = 7.3, 2H, NCH_2), 2.31 (q, $^3J_{HH}$ = 7.2, 4H, NCH_2), 2.26 (t, $^3J_{HH}$ = 7.3, 2H, NCH_2), 0.92 (t, $^3J_{HH}$ = 7.2, 6H, CH_3), 0.02 (s, 9H, CH_3). ^{13}C{^{1}H} NMR (benzene-d_6): δ 55.3 (s, NCH$_2$), 51.0 (s, NCH$_2$), 48.3 (s, NCH$_2$), 47.2 (s, NCH$_2$), 43.7 (s, CH$_2$Cl), 12.3 (s, CH$_3$), 0.4 (s, CH$_3$).

A solution of ^{t}Bu$_2$PLi (9.54 g, 62.88 mmol) in 50 mL of THF was added dropwise to a stirred solution of the freshly prepared $Et_2NC_2H_4N(SiMe_3)C_2H_4Cl$ in 40 mL of THF at −70 °C. The cooling bath was removed, and the mixture was stirred for 2 h at room temperature to give $Et_2NC_2H_4N(SiMe_3)C_2H_4P^tBu_2$ ^{1}H NMR (benzene-d_6): δ 3.07 (m, 2H, NCH_2), 2.96 (t, $^3J_{HH}$ = 7.0, 2H, NCH_2), 2.45 (m, 2H, NCH_2), 2.40 (q, $^3J_{HH}$ = 6.7, 4H, NCH_2), 1.51 (m, 2H, PCH_2), 1.07 (d, $^3J_{HP}$ = 11.0, 18 H, CH$_3$), 0.96 (t, $^3J_{HH}$ = 6.8, 6H, CH_3), 0.20 (s, 9H, CH$_3$). ^{31}P{^{1}H} NMR (benzene-d_6): δ 24.1. ^{13}C{^{1}H} NMR (benzene-d_6): δ 54.8 (s, NCH$_2$), 49.8 (d, $^2J_{CP}$ = 40.8, NCH$_2$), 48.6 (s, NCH$_2$), 46.6 (s, NCH$_2$), 31.4 (d, $^1J_{CP}$ = 22.7, PC), 30.2 (d, $^2J_{CP}$ = 14.1, CH$_3$), 24.1 (d, $^1J_{CP}$ = 24.9, PCH$_2$), 13.1 (s, CH$_3$), 0.8 (s, CH$_3$).

Water (20 mL) was added to the THF solution of $Et_2NC_2H_4N(SiMe_3)C_2H_4P^tBu_2$, and the mixture was stirred at room temperature for 1 h. The organic phase was separated and washed with 15 mL of water, a fresh portion of water (15 mL) was added, and the resulting biphasic mixture was stirred and refluxed for 3 h. After cooling to room temperature the organic phase was separated and washed with 15 mL of water and evaporated. The obtained yellow oil was diluted with 2 mL of hexane and passed through a short column with alumina (2 × 2 cm) and eluted with 20 mL of hexane. The volatiles were removed under vacuum to give the PNHN ligand as light yellow oil (3.0 g, 10.4 mmol, 34% based on $Et_2NC_2H_4N(SiMe_3)C_2H_4Cl$). The product contained about 91% of the PNHN ligand and was used without further purification. The main impurity (ca. 5%) was identified as the dimer ^{t}Bu$_2$P−P^{t}Bu$_2$ (δ ^{31}P 40.8).[12] ^{1}H NMR (benzene-d_6): δ 2.85 (m, 2H, NCH_2), 2.63 (m, NCH_2), 2.47 (t, $^3J_{HH}$ = 6.0, 2H, NCH_2), 2.36 (q, $^3J_{HH}$ = 7.4, 4H, NCH_2), 1.51 (m, 2H, PCH_2), 1.05 (d, $^3J_{HP}$ = 10.7, 18 H, CH$_3$), 0.92 (t, $^3J_{HH}$ = 7.4, 6H, CH_3). ^{31}P{^{1}H} NMR (benzene-d_6): δ 23.1. ^{13}C{^{1}H} NMR (benzene-d_6): δ 53.9 (s, NCH$_2$), 51.8 (d, $^2J_{CP}$ = 31.2, NCH$_2$), 48.8 (s, NCH$_2$), 47.9 (s, NCH$_2$), 31.5 (d, $^1J_{CP}$ = 22.5, PC), 30.2 (d, $^2J_{CP}$ = 14.1, CH$_3$), 23.4 (d, $^1J_{CP}$ = 21.9, PCH$_2$), 12.9 (s, CH$_3$).

IrH$_2$Cl(κ^3-PNHN) (1). A mixture of $[IrCl(COE)_2]_2$ (0.5 g, 0.54 mmol) and $^tBu_2PC_2H_4NHC_2H_4NEt_2$ (0.311 g, 1.08 mmol) was stirred in 15 mL of toluene for 15 min, under argon. Then, the flask was frozen, evacuated, and refilled with H_2, and the orange solution was stirred for 2 h. After evaporation, the residue was washed with 3 × 4 mL of hexane to give a beige solid (0.44 g, 0.85 mmol, 78%). Light yellow crystals were obtained at room temperature from a saturated toluene solution. Anal. Calcd for $C_{16}H_{39}ClIrN_2P\cdot 1/7\ C_7H_8$: C, 38.43; H, 7.62; N, 5.27. Found: C, 38.32; H, 7.69; N, 5.53. IR (KBr, cm^{-1}): ν_{NH} = 3195 (s), ν_{IrH} = 2290 (s), 2084 (vs). ^{1}H NMR (C_6D_6): δ 4.26 (br, 1H, NH), 3.82 (m, 1H, NEt$_2$), 3.26 (td, J_{HH} = 3.4, J_{HH} = 13.3, 1H), 3.04 (overlapped m, 2H, NEt$_2$), 2.92 (m, 2H), 2.64 (m, 1H, NEt$_2$), 2.36 (d, J_{HH} = 12.6, 1H), 2.17 (m, 1H), 1.68 (m, 3H), 1.41 (d, $^3J_{HP}$ = 12.9, 9H, CH_3), 1.14 (d, $^3J_{HP}$ = 12.9, 9H, CH_3), 1.05 (t, $^3J_{HH}$ = 7.6, 3H, CH_3), 0.77 (t, $^3J_{HH}$ = 7.6, 3H, CH_3), −19.34 (dd, $^2J_{HP}$ = 18.1, $^2J_{HH}$ = 7.4, 1H, IrH), −26.66 (dd, $^2J_{HP}$ = 23.4, $^2J_{HH}$ = 7.4, 1H, IrH). ^{31}P{^{1}H} NMR (C_6D_6): δ 53.3. ^{13}C{^{1}H} NMR (C_6D_6): δ 60.4 (d, J_{CP} = 2.2, CH$_2$), 55.7 (s, CH$_2$), 53.8 (s, CH$_2$), 52.2 (s, CH$_2$), 49.6 (d, J_{CP} = 1.7, CH$_2$), 35.5 (d, J_{CP} = 19.1, PC), 31.5 (d, $^2J_{CP}$ = 4.2, CH$_3$), 30.2 (d, $^2J_{CP}$ = 2.6, CH$_3$), 29.6 (d, $^1J_{CP}$ = 23.3, PCH$_2$), 11.8 (s, CH$_3$), 10.6 (s, CH$_3$).

IrH$_2$(κ^3-PNN) (2). KO^{t}Bu (0.083 g, 0.74 mmol) was added to a solution of **1** (0.32 g, 0.617 mmol) in 5 mL of THF. The mixture was stirred for 1 h, then filtered and evaporated under vacuum. Extraction of the residue with 3 mL of hexane afforded **2** as a viscous, dark orange oil (0.25 g, 0.519 mmol, 84%). Due to the nature of **2**, no sample was submitted for elemental analysis. IR (Nujol, cm^{-1}): ν_{IrH} = 2144, 2087 (m). ^{1}H{^{31}P} NMR (C_6D_6): δ 3.34 (m, 2H, NCH_2), 3.26 (m, 2H, NCH_2), 2.90 (dq, $^2J_{HH}$ = 13.1, $^3J_{HH}$ = 7.2, 2H, NEt$_2$), 2.67 (dq, $^2J_{HH}$ = 13.1, $^3J_{HH}$ = 7.2, 2H, NEt$_2$), 2.59 (t, $^3J_{HH}$ = 5.6, 2H, CH_2NEt$_2$), 1.90 (t, $^3J_{HH}$ = 6.3, 2H, CH_2P), 1.28 (s, 18H, CH_3), 0.99 (t, $^3J_{HH}$ = 7.2, 6H, NEt$_2$), −22.14 (quintet, $^4J_{HH}$ = 3.1, 2H, IrH$_2$). ^{31}P{^{1}H} NMR (C_6D_6): δ 85.3 (s). ^{13}C{^{1}H} NMR (C_6D_6): δ 63.7 (d, J_{CP} = 2.6, CH$_2$), 61.9 (d, J_{CP} = 2.1, CH$_2$), 60.2 (s, CH$_2$), 54.2 (d, $^3J_{CP}$ = 2.2, NEt$_2$), 34.5 (d, $^1J_{CP}$ = 25.4, PC), 29.8 (d, $^2J_{CP}$ = 4.4, CH$_3$), 28.9 (d, $^1J_{CP}$ = 24.7, PCH$_2$), 12.5 (s, CH$_3$).

IrH$_3$(κ^3-PNN) (3). ^{1}H NMR (C_6D_6): δ 2.0−3.5 (overlapped m, CH_2 of the PNHN ligand), 1.45 (d, $^3J_{HP}$ = 12.6, 9H, CH_3), 1.40 (d, $^3J_{HP}$ = 12.6, 9H, CH_3), 1.06 (t, $^3J_{HH}$ = 7.2, 3H, CH_3), 0.99 (t, $^3J_{HH}$ = 7.2, 3H, CH_3), −8.19 (ddd, $^2J_{HH}$ = 5.5, 12.0, $^2J_{HP}$ = 11.1, 1H, IrH), −9.44 (ddd, $^2J_{HH}$ = 4.8, 12.0, $^2J_{HP}$ = 16.2, 1H, IrH), −20.08 (apparent dt, $^2J_{HH}$ ≈ 5.0, $^2J_{HP}$ = 18.0, 1H, IrH). ^{31}P{^{1}H} NMR (C_6D_6): δ 70.8.

[IrH$_2$(κ^2-PNHN)]$_2$(μ-H)$_2$ (4). Complex **2** (0.19 g, 0.394 mmol) was stirred in 3 mL of 2-propanol for 6 h. The solvent was evaporated and the residue was washed with 2 mL of hexane to give a yellow powder of **4**. The hexane solution was concentrated and an additional amount of **4** crystallized. Combined yield: 77 mg (0.159 mmol, 40%). Anal. Calcd for $C_{32}H_{80}Ir_2N_4P_2$ (967.4): C, 39.73; H, 8.34; N, 5.79. Found: C, 39.95; H, 9.15; N, 5.63. IR (KBr, cm^{-1}): ν_{NH} = 3216 (m), ν_{IrH} = 2166 (shoulder), 2085 (s). ^{1}H NMR (CD_2Cl_2): δ 4.88 (br, 1H, NH), 3.12 (m, 1H), 2.93 (m, 1H), 2.82 (m, 2H), 2.60 (m, 1H), 2.50 (m, 4H, CH_2, NEt$_2$), 2.30 (m, 1H), 1.77 (m, 2H, PCH_2) 1.33 (d, $^3J_{HP}$ = 12.3, 9H, CH_3), 1.27 (d, $^3J_{HP}$ = 12.6, 9H, CH_3), 0.96 (t, $^3J_{HH}$ = 6.9, 6H, CH_3), −9.75 (d, $^2J_{HP}$ = 79.2, 1H, μ-H), −21.68 (m, 1H, IrH), −22.93 (m, 1H, IrH). ^{31}P{^{1}H} NMR (CD_2Cl_2): δ 81.3. ^{13}C{^{1}H} NMR (CD_2Cl_2): δ 56.2 (s, CH$_2$), 54.7 (d, J_{CP} = 3.8, CH$_2$), 53.4 (s, CH$_2$), 47.6 (s, CH$_2$, NEt$_2$), 34.1 (d, $^1J_{CP}$ = 25.4, PC), 31.7 (d, $^1J_{CP}$ = 20.7, PC), 30.5 (d, $^2J_{CP}$ = 4.7, CH$_3$), 30.1 (d, $^2J_{CP}$ = 4.7, CH$_3$), 24.1 (d, $^1J_{CP}$ = 20.1, PCH$_2$), 12.1 (s, CH$_3$).

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Computational Details. The DFT calculations were carried out using Gaussian 03.[13] All geometries were fully optimized without symmetry or internal coordinate constraints using the MPW1PW91 functional, which included the modified Perdew−Wang exchange and the Perdew−Wang 91 correlation.[14] The basis sets employed in this work included SDD (associated with ECP) for Ir, 6-311+G-(d,p) for the P, Cl, and NH atoms and the hydrides, and 6-31G-(d,p) for the rest of the atoms.[15] The nature of the stationary points was verified by frequency calculations.

Acknowledgment. We gratefully acknowledge the Natural Sciences and Engineering Research Council of Canada (NSERC) and the Ontario Government for funding.

Supporting Information Available: ^{1}H, ^{13}C, and ^{31}P NMR spectra of the PNHN ligand and complex **2**. CIF files for complexes **1** and **4**. This material is available free of charge via the Internet at http://pubs.acs.org.

OM700550X

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