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Anionic Iridium Monohydrides

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Introduction

Of all the transition metals, iridium forms the largest number of hydrido complexes.[1,2] Hundreds of various neutral and cationic iridium hydrides have been isolated and reliably characterized. At the same time, very little is known about anionic hydrido complexes of iridium.[3] Although a few mononuclear polyhydridoiridates,[4,5] anionic cluster hydrides,[6] and two π-acid-stabilized $[HIrL_5]^{3-}$ (L = CN or $SnCl_3$) trianions[7] have been reported, simplest members of the family, i.e., mononuclear monohydridoiridate monoanions remain unknown. In this note, we report the synthesis of such complexes, the first remarkably electron-rich, yet air-stable mononuclear anionic iridium hydrides, their X-ray structures, and solution behavior.

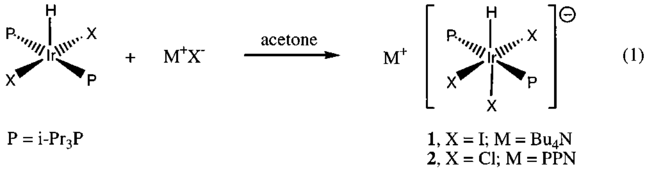
Results and Discussion

Table 1. Selected Crystallographic Data for **1**·Me_2CO and **2**

	1·Me_2CO	**2**
empirical formula	$C_{37}H_{85}I_3IrNOP_2$	$C_{54}H_{73}Cl_3IrNP_4$
fw	1194.94	1158.64
crystal size, mm	0.17 × 0.18 × 0.21	0.22 × 0.35 × 0.37
crystal system	triclinic	triclinic
space group	$P\bar{1}$	$P\bar{1}$
temp, K	173	173
a, Å	12.946(1)	14.164(1)
b, Å	16.178(1)	19.729(1)
c, Å	12.396(1)	9.614(1)
α, deg	106.26(1)	96.93(1)
β, deg	92.12(1)	91.06(1)
γ, deg	96.58(1)	89.26(1)
volume, Å^3	2469.5	2666.3
Z	2	2
calcd density, g cm^{-1}	1.607	1.443
μ(Mo), cm^{-1}	46.37	27.98
diffractometer	Rigaku RU 300	Rigaku RU 300
2θ range, deg	3.2−50.0	3.5−48.2
scan type	ω	ω
abs corr	no	no
no. of reflns collcd	26 136	27 814
no. of unique reflns used in refinement ($I > 3\sigma(I)$)	5603	6098
no. of params refined	410	571
data-to-param ratio	13.54	10.63
R_1, %^{a}	3.5	3.2
R_w, %^{a}	3.9	3.8
goodness of fit	2.05	2.23

[a] $R = \sum(||F_o| - |F_c||)/\sum|F_o|$; $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$.

While the *green* complex $[(i\text{-}Pr_3P)_2Ir(H)I_2]$ is virtually insoluble in pure acetone, it readily dissolves in acetone containing either NaI or Bu_4NI, to produce stable *orange-tan* solutions. When Bu_4NI was the iodide source, brown-red crystals of $[Bu_4N][(i\text{-}Pr_3P)_2Ir(H)I_3]\cdot Me_2CO$ (**1**·Me_2CO) were isolated in 76% yield (eq 1). Similarly, *bright yellow* crystals of $[PPN][(i\text{-}Pr_3P)_2Ir(H)Cl_3]$, **2**, were isolated in 85% yield upon dissolving *deep-purple* $[(i\text{-}Pr_3P)_2Ir(H)Cl_2]$ in an acetone solution of PPN Cl. Given the unique set of electron-rich ligands on the metal, both **1** and **2** are remarkably air-stable in the solid state, showing no sign of decomposition for months. When exposed to air, solutions of **1** or **2** decompose over the course of hours at room temperature.



(1)

Single-crystal X-ray diffraction of **1** and **2** (Table 1) showed *mer-trans* octahedral structures for both anions (Figures 1 and 2). No bonding contacts were observed between **1** and the cocrystallized acetone molecule. The Ir−H bond distances of 1.56(4) Å for **1** and 1.46(4) Å for **2** are close to the average value of 1.6 Å obtained from X-ray and ND studies of neutral hydrido iridium complexes.[8] In comparison with the Ir−X bonds that are mutually trans, the Ir−X bond trans to the hydride is remarkably elongated (by 0.14 and 0.19 Å for X = I and Cl, respectively) due to the strong trans-influence of the H. This

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[†] Contribution No. 7887.

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(2) For recent general reviews of classical and nonclassical transition metal hydrides, see: (a) *Transition Metal Hydrides*; Dedieu, A., Ed.; VCH: New York, 1992. (b) Jessop, P. G.; Morris, R. H. *Coord. Chem. Rev.* **1992**, *121*, 155. (c) Heinekey, D. M.; Oldham, W. J. *Chem. Rev.* **1993**, *93*, 913.

(3) Darensbourg, M. Y.; Ash, C. E. *Adv. Organomet. Chem.* **1987**, *27*, 1.

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(5) (a) Deprotonation of $[Cp^*IrH_4]$, $[Cp^*Ir(PMe_3)H_2]$, and $[Cp^*Ir(SiMe_3)H_3]$ with strong bases produces highly reactive species which have been used as synthons of anionic hydrides. See: Gilbert, T. M.; Bergman, R. G. *J. Am. Chem. Soc.* **1985**, *107*, 3502, 6391. Gilbert, T. M.; Hollander, F. J.; Bergman, R. G. *J. Am. Chem. Soc.* **1985**, *107*, 3508. McGhee, W. D.; Bergman, R. G. *J. Am. Chem. Soc.* **1985**, *107*, 3388. (b) Very recently, it was demonstrated that deprotonation of $[Cp^*Ir(PMe_3)H_2]$ with *t*-BuLi resulted in the formation of $[Cp^*Ir(PMe_3)(H)(Li)]$, from which no lithium decoordination occurred in THF, DME, or benzene, even in the presence of 12-crown-4. See: Peterson, T. H.; Golden, J. T.; Bergman, R. G. *Organometallics* **1999**, *18*, 2005.

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10.1021/ic990068j CCC: $18.00

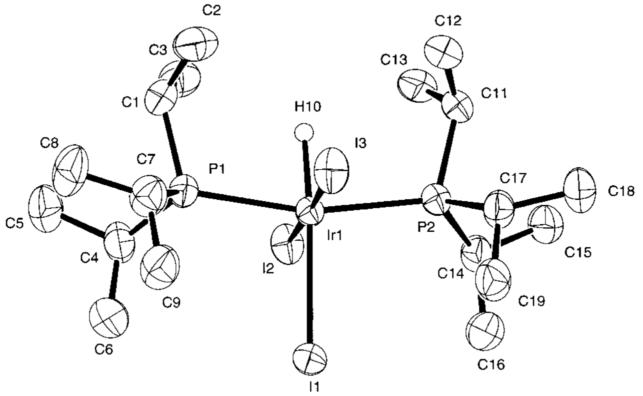


Figure 1. ORTEP drawing for the anion of **1**, $[(i\text{-}Pr_3P)_2Ir(H)I_3]^-$, showing the atom-labeling scheme. Hydrogen atoms, except Ir−H, are omitted for clarity. Selected bond distances (Å) and angles (deg): Ir(1)−H(1), 1.558(42); Ir(1)−I(1), 2.8345(5); Ir(1)−I(2), 2.6946(5); Ir(1)−I(3), 2.6930(5); Ir(1)−P(1), 2.383(1); Ir(1)−P(2), 2.379(1); I(1)−Ir(1)−I(2), 89.43(1); I(1)−Ir(1)−I(3), 93.88(1); I(1)−Ir(1)−P(1), 97.39(1); I(1)−Ir(1)−P(2), 97.58(1); I(2)−Ir(1)−H(10), 85(2); I(3)−Ir(1)−H(10), 91(2); P(1)−Ir(1)−H(10), 80(1); P(2)−Ir(1)−H(10), 86(1).

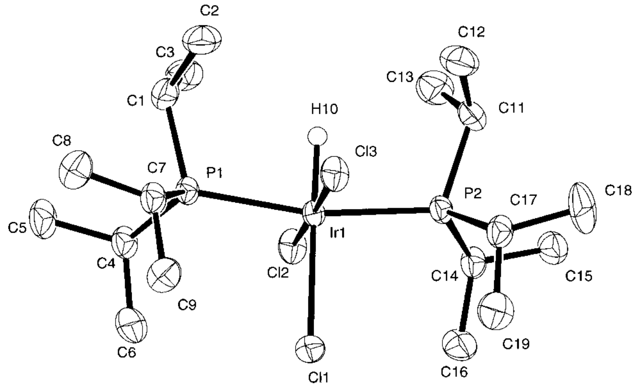
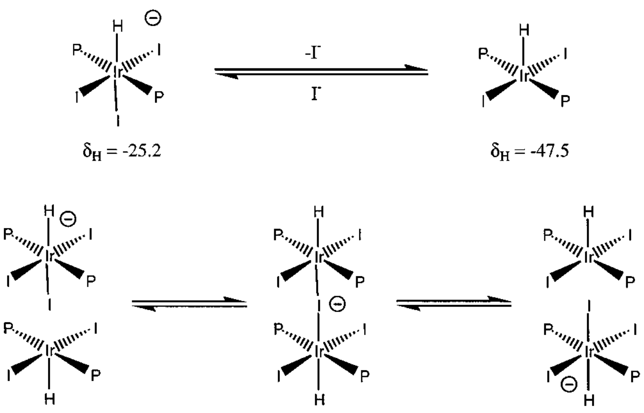


Figure 2. ORTEP drawing for the anion of **2**, $[(i\text{-}Pr_3P)_2Ir(H)Cl_3]^-$, showing the atom-labeling scheme. Hydrogen atoms, except Ir−H, are omitted for clarity. Selected bond distances (Å) and angles (deg): Ir(1)−H(1), 1.459(40); Ir(1)−Cl(1), 2.564(1); Ir(1)−Cl(2), 2.379(1); Ir(1)−Cl(3), 2.373(1); Ir(1)−P(1), 2.348(1); Ir(1)−P(2), 2.348(1); Cl(1)−Ir(1)−Cl(2), 90.97(3); Cl(1)−Ir(1)−Cl(3), 92.14(4); Cl(1)−Ir(1)−P(1), 96.36(4); Cl(1)−Ir(1)−P(2), 95.72(4); Cl(2)−Ir(1)−H(10), 89(1); Cl(3)−Ir(1)−H(10), 87(1); P(1)−Ir(1)−H(10), 85(1); P(2)−Ir(1)−H(10), 83(1).

difference is consistent with the halide trans to the H being labile in solution (see below).

Only one broad ($\Delta\nu_{1/2} \approx 1500$ Hz) line at −27 ppm was observed in the hydride region of room temperature ^{1}H NMR spectra of **1** and its sodium analogue, $Na^+[(i\text{-}Pr_3P)_2Ir(H)I_3]^-$ (generated in situ from NaI and $[(i\text{-}Pr_3P)_2Ir(H)I_2]$ (1:1) in acetone-d_6).[9] Cooling this solution to −20 °C narrowed the signal to $\Delta\nu_{1/2} = 80$ Hz, and at −50 °C, this resonance transformed into a sharp, well-resolved 1:2:1 triplet at −25.2 ppm with $J = 14.5$ Hz, fully consistent with the *mer-trans* octahedral structure determined in the solid state (Figures 1 and 2). A weak broad line at −36 ppm was also observed in the −50 °C spectrum. Further cooling the sample to −80 °C transformed this minor resonance into two broadened singlets at −36.1 ppm (weak; species **A**; $\Delta\nu_{1/2} = 70$ Hz) and −34.0 ppm (very weak; species **B**; $\Delta\nu_{1/2} = 50$ Hz), with the triplet at −25.2 ppm due to **1** remaining unchanged. In accord with this ^{1}H NMR data, the $^{31}P\{^1H\}$ NMR spectrum at −80 °C exhibited three singlet resonances from **1**, **A**, and **B** at −19.9, −1.0, and −5.2 ppm, respectively, the ratio being ca. 60:3:1. Magnetization transfer experiments (^{31}P NMR) demonstrated that at −80 and even at −90 °C, species **A** and **B** were in rapid exchange with one another, whereas neither one exchanged with **1**. At −70 °C, however, **1** was already involved in slow exchange with both **A** and **B**.[10] Importantly, the characteristic hydrido resonance of the pentacoordinate hydride $[(i\text{-}Pr_3P)_2Ir(H)I_2]$ (at −47.5 ppm in the ^{1}H NMR spectrum) was not observed in spectra of $[(i\text{-}Pr_3P)_2Ir(H)I_3]^-$ in acetone-d_6, acquired over the temperature range of +20 to −90 °C. Saturating this solution of **1** with $[(i\text{-}Pr_3P)_2Ir(H)I_2]$ (<1 equiv dissolved) did not lead to the appearance of the resonance at −47.5 ppm but rather increased the population of **A**/**B**.

Scheme 1



Ligand exchange processes in solutions of **1** and **2** slowed considerably in the presence of excess halide. When 8−15 equiv of I$^-$ and Cl$^-$, respectively, was added to solutions of **1** and **2**, the octahedral anions became inert on the NMR time scale at *room* temperature.[11,12] Neither **A**/**B** nor any Ir complexes other than **1** and **2** were detected in these halide-enriched solutions. Scheme 1 provides a rationale for the observed solution behavior of **1**, proposing that the pentacoordinate neutral hydride may catalyze the halide exchange via the formation of a halogen-bridged Ir dimer intermediate. The proposal of two conformers of the dimer (e.g., from hindered rotation around the Ir−P, Ir−(μ-X), and/or C−P bonds) would account for the observation of the two species, **A** and **B**, whose proton resonances average at −50 °C and above. In the presence of excess iodide, the catalytic role of $[(i\text{-}Pr_3P)_2Ir(H)I_2]$ is eliminated as the equilibrium is shifted to $[(i\text{-}Pr_3P)_2Ir(H)I_3]^-$. It is to be stressed that although excess halide favors the formation of **1** and **2** *thermodynamically* (Scheme 1), it should not affect *kinetics* of Ir−Hal ionization that proceeds via the dissociative mechanism.[13]

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[9] Similarly, broad lines were observed in ^{1}H and ^{31}P NMR spectra of **2** in acetone-d_6 or CD_2Cl_2 at room temperature.

[10] Based on consideration of ^{31}P T_1's "rapid" and "slow" exchange designate rates that are on the order of 10 and 1 s^{-1}, respectively. Line broadening of **A** and **B** at −70 °C corresponds to exchange rates of approximately 100 s^{-1}.

[11] (a) Spectral data for $Na^+[(i\text{-}Pr_3P)_2Ir(H)I_3]^-$ in acetone-d_6 containing NaI (8 equiv) at 20 °C. ^{1}H NMR, δ: −25.2 (t, 1H, $J_{P-H} = 14.5$ Hz, Ir−H); 1.4 (dd, 36H, $J = 6.6$ and 13.2 Hz, CH_3); 3.5 (br s, 6H, CH). $^{31}P\{^1H\}$ NMR, δ: −18.4 (s). Similar patterns were obtained for **1** in the presence of extra Bu_4NI. (b) Spectral data for **2** in CD_2Cl_2 containing PPN Cl (15 equiv) at 20 °C. ^{1}H NMR, δ: −27.9 (t, 1H, $J_{P-H} = 14.5$ Hz, Ir−H); 1.3 (dd, 36H, $J = 6.6$ and 13.2 Hz, CH_3); 2.8 (m, 6H, CH). $^{31}P\{^1H\}$ NMR, δ: 1.7 (s, Ir−P); 22.2 (s, PPN).

[12] (a) Under similar conditions, the iodo complex **1** is more inert than its chloro analogue **2**. This difference may be rationalized in terms of $d_\pi - p_\pi$ filled/filled repulsions[12b] that are stronger for Cl than I. (b) Caulton, K. G. *New J. Chem.* **1994**, *18*, 25.

Experimental Section

All reagents and solvents were purchased from Strem, Johnson Matthey, and Aldrich Chemical Companies, and used as received.

[(i-Pr$_3$P)$_2$Ir(H)Cl$_2$].[16] Triisopropylphosphine (3.2 mL; 16.8 mmol) was added to an O$_2$-free mixture of IrCl$_3$·nH$_2$O (53.64% Ir; 2.00 g; 5.6 mmol), concentrated HCl (5.5 mL), and i-PrOH (40 mL), and the resulting suspension was refluxed under N$_2$ for 4 h. After water (10 mL) was added, the mixture was refluxed for 15 more min, left at room temperature overnight, and then worked up in air. The dark-purple crystals were filtered off, thoroughly washed with 2-propanol, and dried under vacuum. The yield was 2.40 g (74%; it may vary from 60 to 87%). ^{1}H NMR (CD$_2$Cl$_2$, 20 °C), δ: -48.9 (t, 1H, $J_{\mathrm{P-H}} = 11.8$ Hz, Ir$-$H); 1.4 (dd, 36H, $J = 7.9$ and 14.5 Hz, CH$_3$); 3.1 (m, 6H, CH). ^{31}P{^{1}H} NMR (CD$_2$Cl$_2$, 20 °C), δ: 33.2 (s).

[(i-Pr$_3$P)$_2$Ir(H)I$_2$]. A solution of [(i-Pr$_3$P)$_2$Ir(H)Cl$_2$] (0.358 g; 0.6 mmol), NaI (3.00 g; 20 mmol), and acetone (12 mL) was kept at room temperature for 5 days. As the exchange occurred,[13] solid NaCl precipitated out of the orange solution. After water (40 mL) was added, the dark green solid was filtered off in air, washed with water, and dried under vacuum. The yield was 0.453 g (96%). Anal. Calcd for C$_{18}$H$_{43}$I$_2$IrP$_2$: C, 28.2; H, 5.6; Cl, 0.0; I, 33.1. Found: C, 27.9; H, 5.3; Cl, 0.01; I, 32.1. ^{1}H NMR (CD$_2$Cl$_2$, 20 °C), δ: -47.5 (t, 1H, $J_{\mathrm{P-H}} = 11.8$ Hz, Ir$-$H); 1.4 (dd, 36H, $J = 6.6$ and 13.2 Hz, CH$_3$); 3.6 (m, 6H, CH). ^{31}P{^{1}H} NMR (CD$_2$Cl$_2$, 20 °C), δ: 30.3 (s).

[Bu$_4$N][(i-Pr$_3$P)$_2$Ir(H)I$_3$]·Me$_2$CO. In air, [(i-Pr$_3$P)$_2$Ir(H)I$_2$] (106 mg; 0.14 mmol) and Bu$_4$N I (66 mg; 0.18 mmol) were dissolved in warm acetone (1.5 mL). The resulting dark brown solution was left at room-temperature overnight and then kept at -10 °C for 6 h. The solution was separated from well-shaped brown-red crystals by a pipet, and the crystals were quickly washed with cold acetone (2 × 0.5 mL) and dried by a nitrogen flow. The yield of the 1:1 acetone solvate was 125 mg (76%). Anal. Calcd for C$_{37}$H$_{85}$I$_3$IrNOP$_2$: C, 37.2; H, 7.2; I, 31.9; N, 1.2. Found: C, 37.1; H, 7.2; I, 31.3; N, 1.1.

[PPN][(i-Pr$_3$P)$_2$Ir(H)Cl$_3$]. In air, [(i-Pr$_3$P)$_2$Ir(H)Cl$_2$] (97 mg; 0.17 mmol) was added to a solution of PPN Cl (100 mg; 0.17 mmol) in acetone (5 mL). As the purple complex dissolved, a bright yellow precipitate began to form. After CH$_2$Cl$_2$ (3 mL) was added to dissolve all solids, the resulting solution was treated with ether (10 mL) and left for 2.5 h. The yellow precipitate was separated, washed with ether (3 × 3 mL), and dried under vacuum. The yield was 163 mg (85%). Anal. Calcd for C$_{54}$H$_{73}$Cl$_3$IrNP$_4$: C, 56.0; H, 6.3; Cl, 9.2. Found: C, 56.4; H, 6.2; Cl, 9.3.

X-ray Diffraction Studies. The structures of **1**·Me$_2$CO and **2** were determined using a Rigaku RU 300 diffractometer and the teXsan structure solution package.[18] Crystal and data parameters for the structure determinations may be found in Table 1. Because no reliable absorption correction programs exist for image plates, data were not corrected for absorption. Absorption was minimized however by selecting crystals with shapes as isotropic as possible and by using a large number of redundant data for averaging. The final refinement was done using the Z-refinement package[19] and converged at $R_1 = 3.5\%$ and $R_w = 3.9\%$ for **1**·Me$_2$CO and $R_1 = 3.2\%$ and $R_w = 3.8\%$ for **2**, where $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$ with w proportional to $[\sigma^2(I) + 0.0009I^2]^{-1/2}$. Atomic scattering factors were taken from the International Tables for X-ray Crystallography, Vol. IV, including anomalous terms for Ir, P, Cl, and I.

Acknowledgment. We thank Drs. David L. Thorn and Nadine de Vries for a stimulating discussion.

Supporting Information Available: Full details of crystallographic studies, ORTEP drawings of **1** and **2**, tables of fractional coordinates and isotropic thermal parameters, anisotropic thermal parameters, interatomic distances, intramolecular angles, intramolecular nonbonding distances, and selected intermolecular distances. This material is available free of charge via the Internet at http://pubs.acs.org.

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(13) Studying the Cl/I exchange between [(i-Pr$_3$P)$_2$Ir(H)Cl$_2$] and NaI in acetone by ^{1}H and ^{31}P NMR revealed that the reaction is *first order* in the Ir complex and *zero order* in NaI ($k = 2.1 \cdot 10^{-5}$ s^{-1} at 25 °C). The displacement of Cl ligands is stepwise, as indicated by the observation of two intermediates, [(i-Pr$_3$P)$_2$Ir(H)Cl$_2$(I)]$^-$ and [(i-Pr$_3$P)$_2$Ir(H)ClI$_2$]$^-$. As the reaction occurs, resonances from [(i-Pr$_3$P)$_2$Ir(H)Cl$_2$(I)]$^-$ (^{1}H NMR, -26.1 ppm, t, $J_{\mathrm{P-H}} = 13.2$ Hz; ^{31}P NMR, -2.2 ppm) and [(i-Pr$_3$P)$_2$Ir(H)ClI$_2$]$^-$ (^{1}H NMR, -25.5 ppm, t, $J_{\mathrm{P-H}} = 14.5$ Hz; ^{31}P NMR, -10.1 ppm) can be observed. These lines gradually disappear, being replaced by the signals from **1**.[11a] The rate-limiting step is the dissociation of an inert Cl$^-$ trans to I or Cl from the 18e octahedral anion. Like the Finkelstein reaction,[14] the Cl/I exchange is driven to completion by the insolubility of NaCl in acetone.[15]

(14) Finkelstein, H. *Chem. Ber.* **1910**, *43*, 1528.

(15) (a) Six ^{31}P NMR singlet resonances of different intensities ($\delta = -1.2$ to -7.3 ppm) were observed for six[15b] possible species [(i-Pr$_3$P)$_2$Ir(H)X$_3$]$^-$ (X = Cl, Br) formed from [(i-Pr$_3$P)$_2$Ir(H)Cl$_2$] and Bu$_4$N Br (1: 10) upon equilibration in acetone after 4 days at room temperature. The incomplete conversion to [(i-Pr$_3$P)$_2$Ir(H)Br$_3$]$^-$ was because unlike NaCl, the acetone-soluble Bu$_4$N Cl stayed in solution, participating in the exchange. (b) [(i-Pr$_3$P)$_2$Ir(H)Cl$_3$]$^-$ (one isomer, **2**), [(i-Pr$_3$P)$_2$Ir(H)Br$_3$]$^-$ (one isomer), [(i-Pr$_3$P)$_2$Ir(H)Cl$_2$Br]$^-$ (two isomers), and [(i-Pr$_3$P)$_2$Ir(H)ClBr$_2$]$^-$ (two isomers).

(16) Over the past decade, this procedure has been used many times by one of us (VVG) and found to be simpler and more efficient than any of the literature methods,[17] affording the hydride which is carbonyl-free.[17c] In the solid state, the complex does not decompose in air for years. In solution, however, this hydride is only moderately air-stable.

(17) (a) Werner, H.; Wolf, J.; Höhn, A. *J. Organomet. Chem.* **1985**, *287*, 395. (b) Grushin, V. V.; Vymenits, A. B.; Vol'pin, M. E. *J. Organomet. Chem.* **1990**, *382*, 185. (c) Capitani, D.; Mura, P. *Inorg. Chim. Acta* **1997**, *258*, 169.

(18) *Crystal Structure Analysis Package*; Molecular Structure Corporation: The Woodlands, TX, 1985 and 1992.

(19) Calabrese, J. C. *Crystal Structure Analysis Package*; E. I. DuPont de Nemours & Co.: Wilmington, DE, 1994.