

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 $[\text{HIrL}_5]^{3-}$ ($\text{L} = \text{CN}$ or SnCl_3) trianions⁷ 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

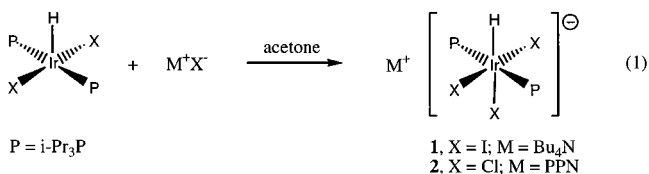
While the *green* complex $[(\text{i-Pr}_3\text{P})_2\text{Ir}(\text{H})\text{I}_2]$ is virtually insoluble in pure acetone, it readily dissolves in acetone

Table 1. Selected Crystallographic Data for **1**·Me₂CO and **2**

	1 ·Me ₂ CO	2
empirical formula	C ₃₇ H ₈₅ I ₃ IrNOP ₂	C ₅₄ H ₇₃ Cl ₃ IrNP 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	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$
temp, K	173	173
<i>a</i> , Å	12.946(1)	14.164(1)
<i>b</i> , Å	16.178(1)	19.729(1)
<i>c</i> , 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
<i>Z</i>	2	2
calcd density, g cm ⁻³	1.607	1.443
$\mu(\text{Mo})$, cm ⁻¹	46.37	27.98
diffractometer	Rigaku RU 300	Rigaku RU 300
2 θ range, deg	3.2–50.0	3.5–48.2
scan type	ω	ω
abs corr	no	no
no. of reflns colld	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
<i>R</i> ₁ , % ^a	3.5	3.2
<i>R</i> _w , % ^a	3.9	3.8
goodness of fit	2.05	2.23

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

containing either NaI or Bu₄NI, to produce stable *orange-tan* solutions. When Bu₄NI was the iodide source, brown-red crystals of $[\text{Bu}_4\text{N}][(\text{i-Pr}_3\text{P})_2\text{Ir}(\text{H})\text{I}_3]\cdot\text{Me}_2\text{CO}$ (**1**·Me₂CO) were isolated in 76% yield (eq 1). Similarly, *bright yellow* crystals



of $[\text{PPN}][(\text{i-Pr}_3\text{P})_2\text{Ir}(\text{H})\text{Cl}_3]$, **2**, were isolated in 85% yield upon dissolving *deep-purple* $[(\text{i-Pr}_3\text{P})_2\text{Ir}(\text{H})\text{Cl}_2]$ 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.

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

(8) Bau, R.; Teller, R. G.; Kirtley, S. W.; Koetzle, T. F. *Acc. Chem. Res.* **1979**, 12, 176. Teller, R. G.; Bau, R. *Struct. Bonding (Berlin)* **1981**, 44, 1. Koetzle, T. F. *Trans. Am. Crystallogr. Assoc.* **1995**, 31, 57. Bau, R.; Drabnis, M. H. *Inorg. Chim. Acta* **1997**, 259, 27.

[†] Contribution No. 7887.

- (1) Geoffroy, G. L.; Lehman, J. R. *Adv. Inorg. Chem. Radiochem.* **1977**, 20, 189.
- (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.
- (4) Bronger, W.; Gehlen, M.; Aufferman, G. *J. Alloys Compd.* **1991**, 176, 255. Kadir, K.; Noreus, D. J. *J. Alloys Compd.* **1994**, 209, 213. Abdur-Rashid, K.; Gusev, D. G.; Landau, S. E.; Lough, A. J.; Morris, R. H. *J. Am. Chem. Soc.* **1998**, 120, 11826.
- (5) (a) Deprotonation of $[\text{Cp}^*\text{IrH}_4]$, $[\text{Cp}^*\text{Ir}(\text{PMe}_3)_2\text{H}_2]$, and $[\text{Cp}^*\text{Ir}(\text{SiMe}_3)_3]$ 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 $[\text{Cp}^*\text{Ir}(\text{PMe}_3)_2\text{H}_2]$ with *t*-BuLi resulted in the formation of $[\text{Cp}^*\text{Ir}(\text{PMe}_3)_2(\text{H})(\text{Li})]$, 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.
- (6) Ciani, G.; Manassero, M.; Albano, V. G.; Canziani, F.; Giordano, G.; Martinengo, S.; Chini, P. *J. Organomet. Chem.* **1978**, 150, C17. Bau, R.; Chiang, M. Y.; Wei, C.-Y.; Garlaschelli, L.; Martinengo, S.; Koetzle, T. F. *Inorg. Chem.* **1984**, 23, 4758. Ceriotti, A.; Pergola, R. D.; Garlaschelli, L.; Laschi, F.; Manassero, M.; Masciocchi, N.; Sansoni, M.; Zanello, P. *Inorg. Chem.* **1991**, 30, 3349. Beringhelli, T.; Ciani, G.; D'Alfonso, G.; Garlaschelli, L.; Moret, M.; Sironi, A. *J. Chem. Soc., Dalton Trans.* **1992**, 1865. Pergola, R. D.; Cea, F.; Garlaschelli, L.; Masciocchi, N.; Sansoni, M. *J. Chem. Soc., Dalton Trans.* **1994**, 1501.
- (7) Krogmann, K.; Binder, W. *Angew. Chem., Int. Ed. Engl.* **1967**, 6, 881. Whitesides, G. M.; Maglio, G. *J. Am. Chem. Soc.* **1969**, 91, 4980. Mockford, M. J.; Griffith, W. P. *J. Chem. Soc., Dalton Trans.* **1985**, 717. Yamakawa, T.; Shinoda, S.; Saito, Y.; Moriyama, H.; Pregosin, P. S. *Magn. Reson. Chem.* **1985**, 23, 202.

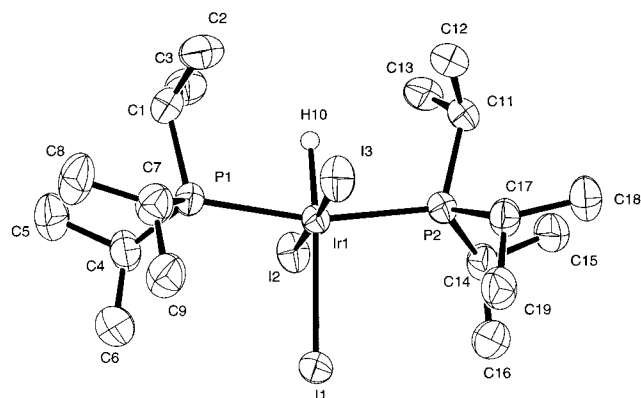


Figure 1. ORTEP drawing for the anion of **1**, $[(i\text{-Pr}_3\text{P})_2\text{Ir}(\text{H})\text{I}_3]^-$, showing the atom-labeling scheme. Hydrogen atoms, except Ir–H, are omitted for clarity. Selected bond distances (Å) and angles (deg): Ir(1)–H(1), 1.558(42); Ir(1)–I(1), 2.8345(5); Ir(1)–I(2), 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).

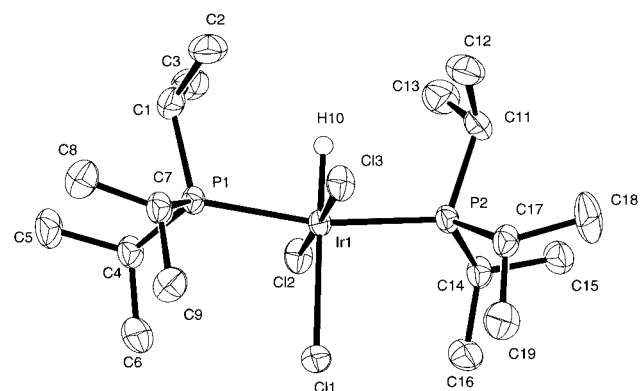
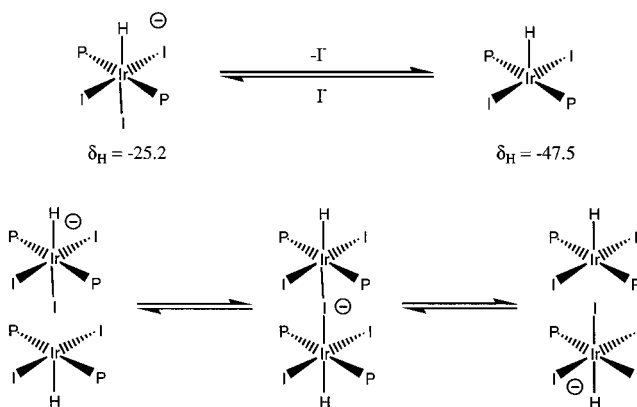


Figure 2. ORTEP drawing for the anion of **2**, $[(i\text{-Pr}_3\text{P})_2\text{Ir}(\text{H})\text{Cl}_3]^-$, showing the atom-labeling scheme. Hydrogen atoms, except Ir–H, are omitted for clarity. Selected bond distances (Å) and angles (deg): Ir(1)–H(1), 1.459(40); Ir(1)–Cl(1), 2.564(1); Ir(1)–Cl(2), 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 ^1H NMR spectra of **1** and its sodium analogue, $\text{Na}^+[(i\text{-Pr}_3\text{P})_2\text{Ir}(\text{H})\text{I}_3]^-$ (generated in situ from NaI and $[(i\text{-Pr}_3\text{P})_2\text{Ir}(\text{H})\text{I}_2]$ (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 ^1H NMR data, the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum at -80 °C exhibited

Scheme 1



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 hydride resonance of the pentacoordinate hydride $[(i\text{-Pr}_3\text{P})_2\text{Ir}(\text{H})\text{I}_2]$ (at -47.5 ppm in the ^1H NMR spectrum) was not observed in spectra of $[(i\text{-Pr}_3\text{P})_2\text{Ir}(\text{H})\text{I}_3]^-$ in acetone- d_6 , acquired over the temperature range of $+20$ to -90 °C. Saturating this solution of **1** with $[(i\text{-Pr}_3\text{P})_2\text{Ir}(\text{H})\text{I}_2]$ (<1 equiv dissolved) did not lead to the appearance of the resonance at -47.5 ppm but rather increased the population of **A/B**.

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 $[(i\text{-Pr}_3\text{P})_2\text{Ir}(\text{H})\text{I}_2]$ is eliminated as the equilibrium is shifted to $[(i\text{-Pr}_3\text{P})_2\text{Ir}(\text{H})\text{I}_3]^-$. 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

- (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 $\text{Na}^+[(i\text{-Pr}_3\text{P})_2\text{Ir}(\text{H})\text{I}_3]^-$ in acetone- d_6 containing NaI (8 equiv) at 20 °C. ^1H NMR, δ : -25.2 (t, 1H, $J_{\text{P-H}} = 14.5$ Hz, Ir–H); 1.4 (dd, 36H, $J = 6.6$ and 13.2 Hz, CH_3); 3.5 (br s, 6H, CH). $^{31}\text{P}\{^1\text{H}\}$ 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. ^1H NMR, δ : -27.9 (t, 1H, $J_{\text{P-H}} = 14.5$ Hz, Ir–H); 1.3 (dd, 36H, $J = 6.6$ and 13.2 Hz, CH_3); 2.8 (m, 6H, CH). $^{31}\text{P}\{^1\text{H}\}$ 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 $d_{\pi\text{-p}}$ filled/filled repulsions^{12b} that are stronger for Cl than I. (b) Caulton, K. G. *New J. Chem.* **1994**, 18, 25.

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

Experimental Section

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

[(i-Pr₃P)₂Ir(H)Cl₂].¹⁶ Triisopropylphosphine (3.2 mL; 16.8 mmol) was added to an O₂-free mixture of IrCl₃·nH₂O (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 N₂ 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%). ¹H NMR (CD₂Cl₂, 20 °C), δ: -48.9 (t, 1H, J_{P-H} = 11.8 Hz, Ir-H); 1.4 (dd, 36H, J = 7.9 and 14.5 Hz, CH₃); 3.1 (m, 6H, CH). ³¹P{¹H} NMR (CD₂Cl₂, 20 °C), δ: 33.2 (s).

[(i-Pr₃P)₂Ir(H)I₂]. A solution of [(i-Pr₃P)₂Ir(H)Cl₂] (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 C₁₈H₄₃I₂IrP₂: 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. ¹H NMR (CD₂Cl₂, 20 °C), δ: -47.5 (t, 1H, J_{P-H} = 11.8 Hz, Ir-H); 1.4 (dd, 36H, J = 6.6 and 13.2 Hz, CH₃); 3.6 (m, 6H, CH). ³¹P{¹H} NMR (CD₂Cl₂, 20 °C), δ: 30.3 (s).

[Bu₄N][(i-Pr₃P)₂Ir(H)I₃]·Me₂CO. In air, [(i-Pr₃P)₂Ir(H)I₂] (106 mg;

0.14 mmol) and Bu₄N 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 C₃₇H₈₅I₃IrNOP₂: 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-Pr₃P)₂Ir(H)Cl₂]. In air, [(i-Pr₃P)₂Ir(H)Cl₂] (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 CH₂Cl₂ (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 C₅₄H₇₃Cl₃IrNP₄: 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**·Me₂CO 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 package¹⁹ and converged at R₁ = 3.5% and R_w = 3.9% for **1**·Me₂CO and R₁ = 3.2% and R_w = 3.8% for **2**, where R_w = [Σw(|F_o| - |F_c|)²/Σw|F_o|²]^{1/2} with w proportional to [σ²(I) + 0.0009I]^{-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.

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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-Pr₃P)₂Ir(H)Cl₂] and NaI in acetone by ¹H and ³¹P NMR revealed that the reaction is *first order* in the Ir complex and *zero order* in NaI (*k* = 2.1·10⁻⁵ s⁻¹ at 25 °C). The displacement of Cl ligands is stepwise, as indicated by the observation of two intermediates, [(i-Pr₃P)₂Ir(H)Cl₂(I)]⁻ and [(i-Pr₃P)₂Ir(H)ClI₂]⁻. As the reaction occurs, resonances from [(i-Pr₃P)₂Ir(H)Cl₂(I)]⁻ (¹H NMR, -26.1 ppm, t, J_{P-H} = 13.2 Hz; ³¹P NMR, -2.2 ppm) and [(i-Pr₃P)₂Ir(H)ClI₂]⁻ (¹H NMR, -25.5 ppm, t, J_{P-H} = 14.5 Hz; ³¹P 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 ³¹P NMR singlet resonances of different intensities (δ = -1.2 to -7.3 ppm) were observed for six^{15b} possible species [(i-Pr₃P)₂Ir(H)X₃]⁻ (X = Cl, Br) formed from [(i-Pr₃P)₂Ir(H)Cl₂] and Bu₄N Br (1: 10) upon equilibration in acetone after 4 days at room temperature. The incomplete conversion to [(i-Pr₃P)₂Ir(H)Br₃]⁻ was because unlike NaCl, the acetone-soluble Bu₄N Cl stayed in solution, participating in the exchange. (b) [(i-Pr₃P)₂Ir(H)Cl₃]⁻ (one isomer, **2**), [(i-Pr₃P)₂Ir(H)Br₃]⁻ (one isomer), [(i-Pr₃P)₂Ir(H)Cl₂Br]⁻ (two isomers), and [(i-Pr₃P)₂Ir(H)ClBr₂]⁻ (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.