

Synthesis of Trimethylphosphine-Substituted (Pentamethylcyclopentadienyl)iridium Hydride Complexes; Protonation and Deprotonation of $(C_5(CH_3)_5)Ir(P(CH_3)_3)H_2$

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Abstract: Trimethylphosphine reacts with $[(C_5(CH_3)_5)Ir]_2(\mu-H)_3A$ (**1**, $A = PF_6, BF_4$) to yield the monohydride-bridged dimer $[(C_5(CH_3)_5)Ir(P(CH_3)_3)(H)]_2(\mu-H)A$ (**2**). Reaction of **2**· BF_4 with a third equivalent of $P(CH_3)_3$ at elevated temperature gives the monomeric species $(C_5(CH_3)_5)Ir(P(CH_3)_3)H_2$ (**4**) and $(C_5(CH_3)_5)Ir(P(CH_3)_3)_2HBF_4$. Reduction of dimer **2** with $LiEt_3BH$ yields 2 equiv of **4**. Protonation of dihydride **4** occurs with $HBF_4 \cdot OEt_2$ to give $(C_5(CH_3)_5)Ir(P(CH_3)_3)_2H_3BF_4$, the first example of a cationic iridium(V) complex. Low-temperature 1H NMR studies reveal an anomalously large H-H coupling constant, suggesting potentially interesting structural features. Deprotonation of dihydride **4** with *t*-BuLi/pmdeta leads to $(C_5(CH_3)_5)Ir(P(CH_3)_3)H[Li(pmdeta)_x]$, which reacts with alkylating agents to yield complexes of the type $(C_5(CH_3)_5)Ir(P(CH_3)_3)(R)(H)$. This route provides a method of synthesizing hydrido(alkyl)iridium complexes in good yield.

Strongly electron donating ligands promote a large range of interesting chemical transformations at transition-metal centers.¹ Two donating ligands which have been prominent in recent efforts of this type are trimethylphosphine,²⁻⁴ characterized by relatively small steric bulk,⁵ and the much more sterically demanding pentamethylcyclopentadienyl group.⁶⁻⁸ Both ligands have allowed the development of chemistry not accessible to complexes containing more commonly used ligands such as triphenylphosphine or the cyclopentadienyl (C_5H_5) group. Maitlis and co-workers, in particular, have extensively developed the chemistry of (pentamethylcyclopentadienyl)rhodium and iridium compounds, aspects of which may be found in recent reviews.^{9,10}

In 1982, workers from our laboratory reported¹¹ the insertion of a photogenerated (trimethylphosphine)(pentamethylcyclopentadienyl)iridium(I) intermediate into the carbon-hydrogen bonds of various organic compounds, including the simple alkanes cyclohexane and neopentane, yielding thermally stable iridium(III) hydridoalkyls. Motivated by this series of results, we attempted to synthesize new (trimethylphosphine)(pentamethylcyclopentadienyl)iridium hydride species, with an eye toward preparing complexes of varied formal oxidation state of iridium. We report here the synthesis of a number of such compounds, including the interesting salts $(C_5(CH_3)_5)Ir(P(CH_3)_3)_2H_3BF_4$, (**5**), the first example of a cation containing iridium in the formal +5 oxidation state, and $(C_5(CH_3)_5)Ir(P(CH_3)_3)H[Li(pmdeta)_x]$ [**6**·(pmdeta)_x], which allows the high yield preparation of a number of iridium(III) hydridoalkyls.

Experimental Section

General. Unless otherwise noted, all reactions and manipulations were performed in dried glassware under inert atmosphere with either standard Schlenk techniques or a nitrogen-filled Vacuum Atmospheres 553-2 drybox equipped with a MO-40-1 inert gas purifier. Reagent THF,

benzene, toluene, and diethyl ether were distilled from Na/benzophenone under nitrogen. Acetone was distilled from anhydrous $CaSO_4/4 \text{ \AA}$ molecular sieves. Spectral grade hexane and pentane were distilled from $LiAlH_4$; dichloromethane was distilled from CaH_2 . Chloroform was distilled from Na/Pb alloy (Dri-Na) onto 4 \AA molecular sieves and purged with nitrogen before use. Methanol was vacuum distilled from $Mg(OMe)_2$. $LiEt_3BH$ (Super-Hydride, 1 M in THF), $HBF_4 \cdot OEt_2$, and *t*-BuLi (1.7-1.9 M in pentane) were obtained from Aldrich and stored in the drybox at appropriate temperatures. $P(CH_3)_3$ (Strem Chemical) was vacuum transferred from sodium and handled by using known volume bulb techniques. *N,N,N',N'',N''*-Pentamethyldiethylenetriamine (pmdeta, Alfa) was distilled in vacuo from sodium and stored on 4 \AA molecular sieves in the drybox. Alkyl trifluoromethylsulfonates (triflates) were prepared by methods described in a review,¹² distilled under vacuum, and confirmed as pure by 1H and $^{13}C\{^1H\}$ NMR. All other reagents were purified in an appropriate fashion or were used as received from suppliers.

1H , ^{13}C , ^{19}F , and ^{31}P NMR were recorded on the 180, 200, 250, 300, and 500 MHz instruments at the UCB NMR facility and are reported as ppm downfield of Me_4Si (1H , ^{13}C), CFC_3 in $CDCl_3$ (^{19}F), or 85% H_3PO_4 (^{31}P). Elemental analyses were performed by V. Tashinian at the UCB Microanalysis Facility. IR spectra were recorded on a Perkin-Elmer 283 spectrometer. Mass spectra were recorded at the UCB Mass Spectrometry Facility under the conditions noted. Melting points and decomposition ranges were determined in sealed nitrogen-filled capillaries on a Thomas UniMelt apparatus and are uncorrected.

$[(C_5(CH_3)_5)Ir]_2(\mu-H)_3PF_6$ (**1**· PF_6). The method of Maitlis¹³ was used with slight modification. A slurry of $[(C_5(CH_3)_5)IrCl_2]_2$ (10.38 g, 13.0 mmol) in 2:2:1 isopropyl alcohol/acetone/water (750 mL) was warmed to 40 °C as H_2 bubbled through the solution. The orange slurry became a black, homogeneous solution over 3 to 5 h; fresh solvent was added periodically to replace evaporation losses. After 24 h, the solution was cooled to room temperature and approximately half the solvent removed on a rotary evaporator. Addition of an aqueous solution of NH_4PF_6 (5.0 g, 27 mmol) resulted in the immediate precipitation of air-stable yellow powder, which was filtered, washed with water, recrystallized from $CHCl_3$ /octane, and dried in a vacuum desiccator to give 8.44 g (80%) of bright yellow **1**· PF_6 . The 1H NMR of this material agrees with that reported by Maitlis; we have collected the following additional data on this compound: $^{13}C\{^1H\}$ NMR (CD_2Cl_2) δ 94.4 (s, C_5Me_5), 11.2 (s, C_5Me_5).

1· BF_4 was prepared in the same manner with $NaBF_4$ in 80% yield. Anal. Calcd for $C_{20}H_{33}IrBF_4$: C, 32.25; H, 4.47; Cl, 0. Found: C, 32.48; H, 4.53; Cl, 0.55.

$[(C_5(CH_3)_5)Ir(P(CH_3)_3)(H)]_2(\mu-H)PF_6$ (**2**· PF_6). $P(CH_3)_3$ (0.700 mmol) was expanded into a known volume bulb at room temperature and condensed into a degassed acetonitrile solution of **1**· PF_6 (245 mg, 0.305 mmol) at liquid nitrogen temperature. The solution was warmed to room

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24 h, then added dropwise to neat $\text{Me}_3\text{SiO}_3\text{SCF}_3$ (0.575 g, 2.59 mmol) at -40°C . After 3 h at this temperature, the solvent and excess triflate were evaporated to give a white solid. The solid was extracted with pentane, and the extracts were filtered through celite. Evaporation of solvent gave white, air-sensitive iridium silyl hydride (95 mg, 75%), which was dried under high vacuum overnight. This method gave material sufficiently pure for elemental analysis and further study; the complex may be recrystallized from pentane/ $(\text{Me}_3\text{Si})_2\text{O}$, but recovery of material is low. $^1\text{H NMR}$ (C_6D_6) δ 1.89 (d, $J_{\text{PH}} = 1.1$ Hz, 15 H, C_5Me_5); 1.29 (d, $J_{\text{PH}} = 9.6$ Hz, 9 H, PMe_3); 0.67 (s, 9 H, SiMe_3); -18.50 (d, $J_{\text{PH}} = 28.4$ Hz, 1 H, Ir-H). $^{13}\text{C}\{^1\text{H}\}$ NMR (C_6D_6) δ 94.3 (s, C_5Me_5); 23.2 (d, $J_{\text{PC}} = 39.3$ Hz, PMe_3); 11.2 (s, C_5Me_5); 9.6 (s, SiMe_3). $^{31}\text{P}\{^1\text{H}\}$ NMR (C_6D_6) δ -50.3 (s). IR (C_6H_6) $\nu_{\text{Ir-H}}$ 2115 cm^{-1} . Exact ion MS, calcd 478.1796 and 476.1779, found 478.1803 and 476.1762. Anal. Calcd for $\text{C}_{16}\text{H}_{34}\text{IrPSi}$: C, 40.23; H, 7.17. Found: C, 40.04; H, 7.44.

$(\text{C}_5(\text{CH}_3)_5\text{Ir}(\text{P}(\text{CH}_3)_3)\text{H})_2[\text{Li}(\text{pmdeta})_x][6\cdot(\text{pmdeta})_x]$. A pentane solution of dihydride **4** (379 mg, 0.935 mmol) and pmdeta (200 mg, 1.15 mmol) was cooled to -40°C , then treated dropwise with *t*-BuLi (1.4 mmol) while warming slowly to ambient temperature. A yellow precipitate was observed to form as the solution was stirred for 16 h. After the solution was cooled to -40°C , the pale yellow solid was filtered and washed with pentane to give air-sensitive powder as the product (338 mg). Elemental analyses of the product demonstrated the amount of pmdeta present to vary from run to run, with values of *x* between 0.5 and 0.05. The product in all cases proved insoluble in inert solvents, and in general it was characterized by further reaction, as described below. IR (silicone oil) $\nu_{\text{Ir-H}}$ 1950 (br) cm^{-1} .

In order to chemically characterize this material, a pentane slurry of $[6\cdot(\text{pmdeta})_x]$ (9.3 mg, *x* \sim 0.5 by elemental analysis) was treated with excess MeOD (ca. 50 μL). Immediate evaporation of solvent gave pmdeta and $(\text{C}_5(\text{CH}_3)_5\text{Ir}(\text{P}(\text{CH}_3)_3)\text{H})(\text{D})$, the monodeuterated analogue of **4** (0.0134 mmol by integration vs. internal $(\text{Me}_3\text{Si})_2\text{O}$, 56% based on **4**). $^1\text{H NMR}$ (C_6D_6) δ 2.11 (d, $J_{\text{PH}} = 1.6$ Hz, 15 H, C_5Me_5); 1.32 (d, $J_{\text{PH}} = 9.8$ Hz, 9 H, PMe_3); -17.43 (d, $J_{\text{PH}} = 32.1$ Hz, 1 H, Ir-H). $^2\text{H NMR}$ (C_6H_6) δ -17.22 (d, $J_{\text{PD}} = 5.4$ Hz, Ir-D).

$(\text{C}_5(\text{CH}_3)_5\text{Ir}(\text{P}(\text{CH}_3)_3)_2\text{ClPF}_6$ (**7**). Trimethylphosphine (10.0 g, 0.132 mol) was added dropwise to a chloroform solution (ca. 350 mL) of $[(\text{C}_5(\text{CH}_3)_5\text{IrCl}_2)_2]$ (30.0 g, 0.0377 mol) in the drybox. After the solution was stirred for 2 h, volatile materials were evaporated until approximately 10 mL of solution remained. Ether was added, and the precipitated yellow solid filtered (35.25 g). This material, presumably $[(\text{C}_5(\text{CH}_3)_5\text{Ir}(\text{P}(\text{CH}_3)_3)_2\text{Cl})\text{Cl}]$, could not be obtained in analytical purity. $^1\text{H NMR}$ (CDCl_3) δ 1.85 (t, $J_{\text{PH}} = 2.2$ Hz, C_5Me_5); 1.86 (virtual t, $J = 10.9$ Hz, PMe_3).

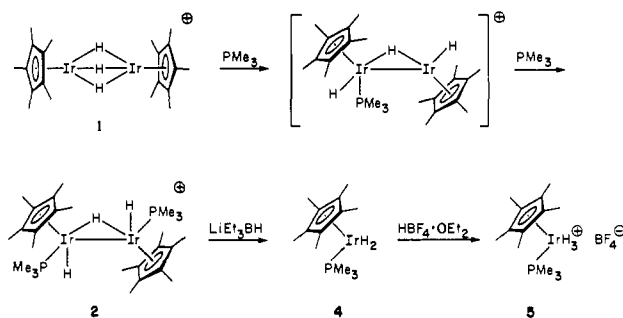
A sample of this material (550 mg) was slurried in isopropyl alcohol in air with KPF_6 (200 mg, 1.09 mmol). The solution was warmed to 45°C and stirred vigorously for 12 h. Removal of solvent gave yellow-white solid, which was taken up in CH_2Cl_2 . The solution was filtered through a frit to remove insoluble material and then treated with an equal volume of toluene. Slow evaporation of CH_2Cl_2 on a rotary evaporator precipitated yellow, air-stable microcrystals of $(\text{C}_5(\text{CH}_3)_5\text{Ir}(\text{P}(\text{CH}_3)_3)_2\text{ClPF}_6$ in analytically pure form (654 mg, 0.991 mmol, 84% based on $[(\text{C}_5(\text{CH}_3)_5\text{IrCl}_2)_2]$). $^1\text{H NMR}$ (CDCl_3) δ 1.80 (t, $J_{\text{PH}} = 2.1$ Hz, 15 H, C_5Me_5); 1.72 (virtual t, $J = 10.7$ Hz, 18 H, PMe_3). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3) δ 98.9 (s, C_5Me_5); 16.9 (complex, PMe_3); 9.5 (s, C_5Me_5). $^{31}\text{P}\{^1\text{H}\}$ NMR (CDCl_3) δ -36.4 (s, PMe_3); -143.8 (septet, $J_{\text{PF}} = 712$ Hz, PF_6). FAB MS (thioglycerol), *m/e* 515/513 ($\text{M}^+ - \text{PF}_6$). Anal. Calcd for $\text{C}_{16}\text{H}_{33}\text{P}_2\text{ClIrPF}_6$: C, 29.12; H, 5.04; Cl, 5.37; P, 14.08. Found: C, 29.23; H, 5.04; Cl, 5.41; P, 13.97.

$(\text{C}_5(\text{CH}_3)_5\text{Ir}(\text{P}(\text{CH}_3)_3)_3(\text{BF}_4)_2$ (**8**). $(\text{C}_5(\text{CH}_3)_5\text{Ir}(\text{acetone})_3(\text{BF}_4)_2$ was prepared in situ from $[(\text{C}_5(\text{CH}_3)_5\text{IrCl}_2)_2]$ (2.00 g, 2.51 mmol) by the method of Maitlis.¹⁶ $\text{P}(\text{CH}_3)_3$ (16 mmol) was expanded into a known volume bulb at room temperature and then added to this solution at liquid nitrogen temperature. Warming to room temperature and stirring for 10 h resulted in the precipitation of white solid. Removal of solvent and recrystallization from water/THF gave 2.39 g (65%) of white, air-stable product. $^1\text{H NMR}$ (D_2O) δ 1.87 (q, $J_{\text{PH}} = 2.0$ Hz, 15 H, C_5Me_5); 1.74 (virtual quartet, $J = 9.6$ Hz, 27 H, PMe_3). $^{13}\text{C}\{^1\text{H}\}$ NMR (D_2O) δ 104.6 (s, C_5Me_5); 18.04 (complex pattern, PMe_3); 9.39 (s, C_5Me_5). $^{31}\text{P}\{^1\text{H}\}$ NMR (D_2O) δ -49.6 (s). Anal. Calcd for $\text{C}_{19}\text{H}_{42}\text{P}_3\text{IrB}_2\text{F}_8$: C, 31.29; H, 5.81. Found: C, 31.28; H, 5.73.

Results and Discussion

Synthesis and Characterization of $[(\text{C}_5(\text{CH}_3)_5\text{Ir}(\text{P}(\text{CH}_3)_3)(\text{H}))_2(\mu\text{-H})\text{A}]$. Treatment of an acetone solution of trihydride $[(\text{C}_5(\text{CH}_3)_5\text{Ir})_2(\mu\text{-H})_3\text{A}]$ ($\text{A} = \text{PF}_6$ or BF_4 , **1**) with $\text{P}(\text{CH}_3)_3$ rapidly yields the bisphosphine dimer $[(\text{C}_5(\text{CH}_3)_5\text{Ir}(\text{P}(\text{CH}_3)_3)(\text{H}))_2(\mu\text{-H})\text{A}]$ (**2**) (Scheme I). The yellow salt crystallizes in analytical purity from acetone/ether or, in the case of **2-PF**₆,

Scheme I



from hot THF. Isolated yields are typically 85%, and air has no effect on solutions of the pure compound. Interestingly, use of less than 2 equiv of phosphine yields a mixture of **2** and unchanged **1**; no complex containing only one phosphine ligand proved isolable. We suspect that the monophosphine complex reacts more quickly with $\text{P}(\text{CH}_3)_3$ than **1** does, and thus this intermediate never builds up during the reaction.

While the alkyl region of the $^1\text{H NMR}$ spectrum of **2** varies little with temperature, the hydride region shows dynamic behavior over a fairly large temperature range. At 60°C , the hydride signal (δ -20.5) appears as an apparent binomial triplet, with $J_{\text{PH}} = 18.3$ Hz, a somewhat low value compared to $J_{\text{PH}} = 32$ Hz observed for $(\text{C}_5(\text{CH}_3)_5\text{Ir}(\text{P}(\text{CH}_3)_3)\text{H}_2$.^{11b} The coupling constant represents an average of three static $^{31}\text{P}\text{-}^1\text{H}$ coupling constants (see below).

At room temperature (23°C), the resonance broadens to a structureless lump just above the base line. Upon cooling the sample to -80°C , two well-resolved patterns are observed, a downfield doublet of doublets (δ -19.2) integrating as two equivalent hydrogens and an upfield triplet of triplets (δ -23.0) integrating as one hydrogen. A $^1\text{H}\{^{31}\text{P}\}$ NMR experiment demonstrated the largest coupling in each case to be due to the phosphorus in the phosphine ligand, with a larger $^{31}\text{P}\text{-}^1\text{H}$ coupling (33.2 Hz) observed for the downfield peak and a smaller coupling (20.9 Hz) for the upfield peak. The three-bond $^{31}\text{P}\text{-}^1\text{H}$ coupling of a terminal hydrogen attached to one iridium center to the phosphorus attached to the other iridium center could not be resolved, and we therefore assume the value of this $J_{\text{PH}} = 0$ Hz. The $^1\text{H}\{^{31}\text{P}\}$ NMR experiment plus the data from the uncoupled $^1\text{H NMR}$ spectrum showed that the smallest coupling (5.4 Hz) is due to the two sets of hydrogens coupling to each other.

In total, the spectrometric evidence suggests a static structure for **2** with two terminal iridium-bound hydrides and one hydride bridging the metals, with one phosphine datively bound to each center. Line shape analysis based on the variable temperature $^1\text{H NMR}$ data (see Appendix), assuming, (a) that exchange occurs through a terminal-bridge-terminal mode, (b) that no more than one hydrogen is terminally bound to a particular iridium at any time, and (c) that no more than two hydrogens occupy sites bridging the metal centers at any moment (two exchange permutations total), yields the activation parameters $\Delta H^\ddagger = 9.1$ (3) kcal, $\Delta S^\ddagger = -6.4$ (1.2) eu, $k_{298}(\text{extrapolated}) = 3.0$ (2) $\times 10^4$ s^{-1} , and $\Delta G^\ddagger_{298} = 10.96$ (4) kcal for the "exchange" of the hydride ligands.

In order to conclusively determine the static structure of dimer **2**, a single-crystal X-ray diffraction study was performed. The details of the study will be reported;¹⁴ Figure 1 shows the ORTEP of the determined structure and gives some important bond lengths and angles. Of note is the rather long Ir-Ir distance (2.981 (1) Å), suggestive of a somewhat weak metal-metal interaction.

The formation of **2** without detection of an intermediate monophosphine complex allows us to suggest an answer to a reported result. Maitlis et al.¹³ noted that trihydride dimer **1** underwent H/D exchange with deuterium gas only in the presence of NEt_3 . We propose that this result is due to the formation of a weakly bound monoamine adduct analogous to our unisolable monophosphine adduct, which then oxidatively adds D_2 and reductively eliminates HD. This proposal obviates the need to

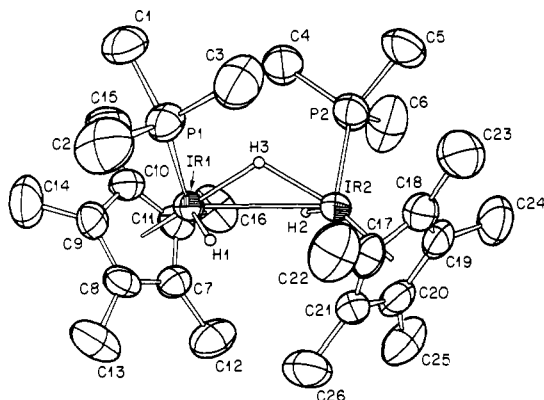
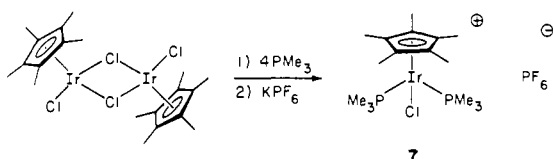


Figure 1. ORTEP drawing of the cation $[(C_5(CH_3)_5)Ir(P(CH_3)_3)(H)]_2-(\mu-H)^+$ (**2**) (PF_6^- anion not shown). Selected bond distances (Å) and angles (deg): Ir(1)–Ir(2) = 2.983 (1); Ir(1)–P(1) = 2.248 (1); Ir(2)–P(2) = 2.246 (1); Ir(1)–Cp*(1) centroid = 1.896 (1); Ir(2)–Cp*(2) centroid = 1.891 (1); Ir(1)–H(1) = 1.47 (5); Ir(2)–H(2) = 1.52 (6); Ir(1)–H(3) = 1.69 (4); Ir(2)–H(3) = 1.80 (4); Ir(2)–Ir(1)–H(1) = 73.4 (17); Ir(1)–Ir(2)–H(2) = 70.9 (19); Ir(2)–Ir(1)–P(1) = 101.51 (3); Ir(2)–Ir(1)–P(2) = 101.28 (3).

Scheme II



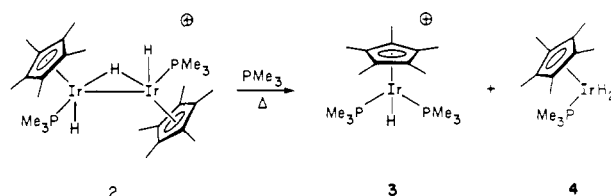
suggest either binuclear reductive elimination or oxidative addition across the metal–metal bond.

Dimer **2** reacts with 1 equiv of $LiEt_3BH$ in ether at room temperature to give $(C_5(CH_3)_5)Ir(P(CH_3)_3)H_2$ in 80% isolated yield (Scheme I). The reaction requires approximately 18 h to go to completion, curiously slow given our experience^{11b} with such reductions. Solubility effects may cause this; the sparing solubility of **2**· PF_6^- in THF probably limits the reaction rate to a value smaller than a reduction run under purely homogeneous conditions.

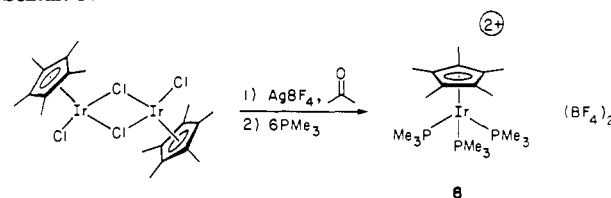
Preparation of Polyphosphine Monomers. During the preparation of $(C_5(CH_3)_5)Ir(P(CH_3)_3)Cl_2$ from $[(C_5(CH_3)_5)IrCl_2]_2$,¹¹ we often noted the presence of a persistent impurity when excess $P(CH_3)_3$ was used. Theorizing this impurity to be the salt $[(C_5(CH_3)_5)Ir(P(CH_3)_3)_2Cl]PF_6$, we treated a sample of the dichloroiridium dimer with excess $P(CH_3)_3$, followed by KPF_6 , allowing the isolation of $(C_5(CH_3)_5)Ir(P(CH_3)_3)_2ClPF_6$ (**7**) as yellow microcrystals in analytical purity (Scheme II). The air-stable material was characterized analytically and spectroscopically; the most interesting features of its NMR spectra involve the resonances due to the $P(CH_3)_3$ ligands. In the 1H NMR, a virtual triplet¹⁷ appears (δ 1.72), with a separation between the tallest side peaks of 10.9 Hz; a complex pattern, somewhat like a quintet with the outermost peaks pushed nearer the center, obtains for the phosphine methyl carbon resonance (δ 16.9) in the $^{13}C\{^1H\}$ NMR. However, only one line is seen in the $^{31}P\{^1H\}$ NMR (δ –36.4); thus the spectra are examples of virtually coupled $X_nAA'X'_n$ systems. In agreement with this view, the virtual triplet in the 1H NMR collapses to a singlet in the $^1H\{^{31}P\}$ NMR spectrum.

The isolation of this bisphosphine monomer suggested that other, similar complexes might be isolable. Indeed, the nucleophilic addition of $P(CH_3)_3$ at elevated temperature splits **2** into interesting monomeric species. The reaction cleanly forms the new complex $(C_5(CH_3)_5)Ir(P(CH_3)_3)_2HBF_4$ (**3**) along with 1 equiv of dihydride **4** to account for all the iridium (Scheme III). The product is a crystalline, colorless salt stable to air for short periods in the solid state; acetone solutions of **3** decompose in air over days. In general, the compound exhibits spectral properties similar to those of $(C_5(CH_3)_5)Ir(P(CH_3)_3)_2ClPF_6$: virtual triplets are observed in both the 1H and $^{13}C\{^1H\}$ NMR spectra for the $P(CH_3)_3$ fragment, while the $C_5(CH_3)_5$ and Ir–H resonances in the 1H

Scheme III



Scheme IV



NMR appear as binomial triplets with ^{31}P – 1H couplings within the normal range.

Maitlis et al. reported the synthesis of the unstable solvent complex $(C_5(CH_3)_5)Ir(acetone)_3^{2+}$, prepared by the silver-induced loss of chloride from $[(C_5(CH_3)_5)IrCl_2]_2$.¹⁶ We have found that replacement of the solvent ligands with $P(CH_3)_3$ occurs at room temperature, yielding the very stable trisphosphine salt $(C_5(CH_3)_5)Ir(P(CH_3)_3)_3(BF_4)_2$ (**8**) (Scheme IV). The dicationic salt does not decompose in water or air (in fact, water is by far the best solvent for the complex) and may be heated to 280 °C in the solid state without noticeable decomposition. Presumably, the cation adopts a “three-legged piano stool” structure, with the anions well-separated in aqueous solution; the $^{31}P\{^1H\}$ NMR spectrum shows a single resonance, implying that the phosphine ligands are equivalent. Solubility problems and the complexity of the room temperature 1H and $^{13}C\{^1H\}$ NMR spectra due to virtual coupling of the phosphorus atoms to the phosphine methyl hydrogen and carbon atoms discouraged us from attempting low-temperature NMR experiments.

Protonation of $(C_5(CH_3)_5)Ir(P(CH_3)_3)H_2$. Several workers have protonated metal hydride complexes in order to prepare either monomeric salts of high oxidation state metals,^{18a–f} or in at least one instance a hydride bridged dimer analogous to **2**.^{18g} Prompted by the latter result, we attempted to prepare **2** by treating dihydride **4** with $HBF_4 \cdot OEt_2$, both at low and ambient temperature using normal and reverse addition techniques. In all cases, the interesting Ir(V) monomer $(C_5(CH_3)_5)Ir(P(CH_3)_3)H_3BF_4$ (**5**) precipitated and proved to be stable toward the hydrogen loss necessary to generate **2** (Scheme I). Spectral and analytical data agree completely with this formulation.

The most interesting aspect of the characterization of **5** stems from the dynamic behavior of the 1H NMR hydride resonance. At room temperature and above, a simple first-order doublet (δ –13.5) with $J_{PH} = 10$ Hz is observed. As has been noted previously for cationic trihydride complexes,^{18b,d} the resonance shifts strongly downfield from that in dihydride **4** (δ –17.4), indicating a significant deshielding of the hydride ligands upon protonation. The remarkably small ^{31}P – 1H coupling, as compared with dihydride **4** ($J_{PH} = 32.1$ Hz), results from the fact that the static couplings of the phosphorus to the two different types of iridium-bound hydrogens (see below) are of opposite sign. Verification of this hypothesis resulted from line shape analysis of the variable temperature 1H NMR data (Figure 2), assuming the smaller J_{PH} to be negative, which mimicked the “fast limit” result accurately. An Eyring plot of the data (see Appendix), assuming exchange only between the sets of hydrogens and not between members of a set (two exchange permutations total), yielded the activation parameters $\Delta H^\ddagger = 12.0$ (4) kcal, $\Delta S^\ddagger = 3.7$ (1.6) eu, k_{298} (extrapolated) = 3.7 (6) $\times 10^4$ s^{–1}, and $\Delta G^\ddagger_{298} = 10.84$ (8) kcal for the hydride ligand exchange process.

Decoalescence of the hydride signal into two different resonances occurs at –30 °C. At –90 °C and a field strength of 300 MHz, a second-order pattern appears, seemingly a downfield

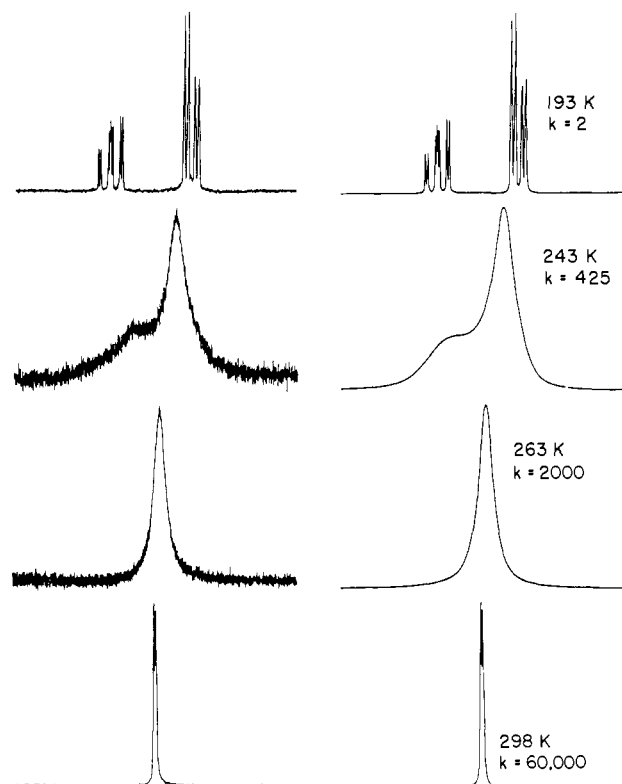


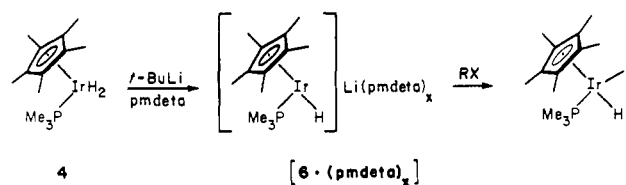
Figure 2. Experimental and calculated ^1H NMR spectra (300 MHz) for **5** at various temperatures. The region shown is that between δ -11 and -16.

doublet of doublets (δ -12.7) integrating as one hydrogen and an upfield doublet of doublets (δ -14.1) integrating as two equivalent hydrogens. However, at -90°C with a field strength of 500 MHz, a first-order pattern obtains, consisting of a downfield triplet of doublets (δ -12.7), integrating as one hydrogen, and an upfield doublet of doublets (δ -14.1), integrating as two hydrogens. Surprisingly, a $^1\text{H}\{^31\text{P}\}$ NMR experiment demonstrated the smallest coupling to each set of hydrides to be due to ^31P - ^1H splitting, with the larger value (21.5 Hz) representing the coupling to the two equivalent hydrogens and the smaller value (12.6 Hz) representing the coupling to the unique hydrogen. This left the larger coupling to be due to the different hydrogen atoms coupling to each other, with the remarkably large value of $J_{\text{HH}} = 56.3$ Hz! We found this value difficult to accept in view of data for similar complexes,^{19,20} but accurate computer simulations of both the first- and second-order spectra with use of the Bruker simulation program PANIC each yielded this value. Given that the HH coupling in free H_2 is approximately 280 Hz,²¹ and that for $(\text{C}_5(\text{CH}_3)_5)\text{IrH}_3\text{L}$ complexes²⁰ typical values of $J_{\text{HH}} = 5$ -8 Hz obtain, the hydrogen atoms in **5** must either sit quite near each other or occupy sites different from those of the "four-legged piano stool".

Deprotonation and Alkylation of $(\text{C}_5(\text{CH}_3)_5)\text{Ir}(\text{P}(\text{CH}_3)_3)_2\text{H}_2$. Deprotonation of $(\text{C}_5(\text{CH}_3)_5)\text{Ir}(\text{P}(\text{CH}_3)_3)_2\text{H}_2$ (**4**) with *t*-BuLi leads to a solution containing some form of " $(\text{C}_5(\text{CH}_3)_5)\text{Ir}(\text{P}(\text{CH}_3)_3)_2\text{H}^-$ " (**6**) as confirmed by further reaction with alkylating agents (Scheme V).^{22a} Interpretation of the ^1H NMR of a solution of this material proved difficult as two products are seen, possibly an equilibrium mixture of oligomers. The only resonance in the upfield hydride region is a structureless lump. At long reaction times in concentrated solution, some precipitation is seen; unfortunately, the precipitated material has proved difficult to characterize properly. Removal of the solvent from the reaction mixture seems to regenerate dihydride **4** in low, impure yield.

A pentane solution/slurry of the salt **6** reacts with $\text{CH}_3\text{O}_3\text{SCF}_3$ (methyl triflate) to generate the photosensitive alkyl hydride $(\text{C}_5(\text{CH}_3)_5)\text{Ir}(\text{P}(\text{CH}_3)_3)(\text{CH}_3)(\text{H})$,¹⁵ in good yield on a large scale, although slightly contaminated with dihydride **4** and $(\text{C}_5(\text{C}-\text{H}_3)_5)\text{Ir}(\text{P}(\text{CH}_3)_3)(\text{CH}_3)_2$. This complex was previously isolated

Scheme V



from the reaction of $(\text{C}_5(\text{CH}_3)_5)\text{Ir}(\text{P}(\text{CH}_3)_3)(\text{CH}_3)\text{Cl}$ with LiBH_4 and, more importantly, by the thermal C-H activation of methane by the proposed intermediate " $(\text{C}_5(\text{CH}_3)_5)\text{Ir}(\text{P}(\text{CH}_3)_3)$ ".

Synthesis of alkyl hydride complexes through this method (Scheme V) has proved useful in determining components of photolytic C-H activation reaction mixtures.¹¹ Products obtained so far include $(\text{C}_5(\text{CH}_3)_5)\text{Ir}(\text{P}(\text{CH}_3)_3)(n\text{-Pr})(\text{H})$ and $(\text{C}_5(\text{CH}_3)_5)\text{Ir}(\text{P}(\text{CH}_3)_3)(n\text{-Bu})(\text{H})$, both on NMR tube scale, and $(\text{C}_5(\text{CH}_3)_5)\text{Ir}(\text{P}(\text{CH}_3)_3)(\text{neopentyl})(\text{H})$, $(\text{C}_5(\text{CH}_3)_5)\text{Ir}(\text{P}(\text{CH}_3)_3)(n\text{-pentyl})(\text{H})$ (see Experimental), and $(\text{C}_5(\text{CH}_3)_5)\text{Ir}(\text{P}(\text{CH}_3)_3)(\eta^1\text{-allyl})(\text{H})$,^{22b} all on preparative scale. Until recently, only primary alkylating agents reacted to give alkyl hydrides in general; secondary and tertiary agents usually resulted in production of dihydride **4** by an undetermined (although probably elimination-based) mechanism. Recently, however, the synthesis of $(\text{C}_5(\text{CH}_3)_5)\text{Ir}(\text{P}(\text{CH}_3)_3)(\text{sec-Bu})(\text{H})$ from a solution of **6** and *sec*-butyl chloride^{22c} has renewed our hope of making this a general synthetic method.

Another interesting complex synthesized by the reaction of a solution of **6** with $\text{Me}_3\text{SiO}_3\text{SCF}_3$ is the silyl hydride $(\text{C}_5(\text{CH}_3)_5)\text{Ir}(\text{P}(\text{CH}_3)_3)(\text{SiMe}_3)(\text{H})$. Further chemistry of this surprisingly air-sensitive material is currently being explored.

When the sequestering agent pentamethyldiethylenetriamine, pmdeta, is added to the *t*-BuLi deprotonation reaction, precipitation of yellow solid is significant and rapid; the isolated material has been characterized as the salt $(\text{C}_5(\text{CH}_3)_5)\text{Ir}(\text{P}(\text{CH}_3)_3)\text{H}^-[\text{Li}(\text{pmdeta})_x]$ [**6** · (pmdeta)_x] (Scheme V). Unfortunately, the amount of pmdeta present in the isolated product varies between 0.5 and 0.05, as determined by elemental analysis. The effect of adding the sequestering agent is clearly a significant acceleration in reaction rate; quantitative deprotonation of dihydride **4** requires minutes when pmdeta is used, while approximately 12 h are necessary for similar results when no pmdeta is present. We do not understand why pmdeta does not sequester the lithium atom in this complex, especially in light of the reproducible preparation of $(\text{C}_5(\text{CH}_3)_5)\text{IrH}_3[\text{Li}(\text{pmdeta})]$,²⁰ a reasonable hypothesis might be that the molecule adopts a structure (possibly oligomeric) in which steric constraints dictate that certain lithium atoms be in positions where stable sequestering is impossible. A single-crystal X-ray diffraction study might answer this question.

Regardless of the amount of pmdeta present in isolated [**6** · (pmdeta)_x], the salt proved completely insoluble in inert solvents at ambient temperature, thus limiting spectral characterization. Upon attempted dissolution in nonhydrocarbon solvents, [**6** · (pmdeta)_x] often scavenges a proton to regenerate dihydride **4**. Surprisingly, solid [**6** · (pmdeta)_x] decomposes relatively slowly in air compared to $(\text{C}_5(\text{CH}_3)_5)\text{IrH}_3\text{Li}$ and $(\text{C}_5(\text{CH}_3)_5)\text{IrH}_3[\text{Li}(\text{pmdeta})]$, requiring minutes rather than seconds to darken completely; possibly this result indicates a closer iridium-lithium contact in [**6** · (pmdeta)_x], or a different degree of oligomerization in the solid state. Of interest is the significant low-frequency shift of the iridium-terminal hydrogen stretching mode in the IR spectrum of [**6** · (pmdeta)_x]; for dihydride **4**, the band appears at 2099 cm^{-1} (C_6H_{12}), while for monohydride [**6** · (pmdeta)_x] the band appears at 1950 cm^{-1} (silicone oil). Unfortunately, not enough data exist to indicate the significance of this result, especially in light of the fact that the stretch for trihydride cation **5** occurs at essentially the same frequency (2090 cm^{-1} , KBr) as for **4**; however, the direction of the shift agrees with previous data.^{23,24}

(23) $\text{Cp}_2\text{MoH}_2/(\text{Cp}_2\text{MoHLi})_x$; D'Aniello, M. J.; Barefield, E. K. *J. Organomet. Chem.* **1974**, *76*, C50. Francis, B. R.; Green, M. L. H.; Luong-Thi, T.; Moser, G. A. *J. Chem. Soc., Dalton Trans.* **1976**, 1339.

Possibly due to the insolubility of this material, or because the sequestering agent presents another substrate with which the anion can react, significant amounts of side products are formed upon attempted alkylation (Scheme V). Foremost among these side products is dihydride **4**, usually comprising the major proportion of material isolated from the reaction. Normally the desired iridium alkyl hydride constitutes the second most abundant product; minor unidentified iridium hydride species account for the balance of the organometallic material. Therefore we commonly generate the anionic reagent in situ without the addition of pmdeta, in spite of the additional time required.

Conclusion

We have shown that a number of trimethylphosphine-substituted (pentamethylcyclopentadienyl)iridium complexes may be prepared, with the metal centers in varied formal oxidation states. Of note is the presumably significant electron density forced on the iridium center by the strongly donating ligands. One would predict that at some point the metal center would become too electron rich to support all the ligands; clearly this point is not reached in any of the complexes described. The fact that the iridium center(s) is formally cationic certainly contributes to the stability of these species; however, comparison with the related complexes $(C_5(CH_3)_5)Co(P(CH_3)_3)_2$,^{25a} $(C_5(CH_3)_5)Rh(P(CH_3)_3)_2$,^{25b} and $(C_5(CH_3)_5)Ir(P(CH_3)_3)_2$,^{22b} as well as $Co(P(CH_3)_3)_4$ ²⁶ and the $M(P(CH_3)_3)_4Cl$ series ($M = Rh$,²⁷ Ir), indicates a remarkable ability of cobalt family metals to accept electron density.

As expected for polyhydride complexes, those described here show fluxional behavior. Line shape analysis has allowed the determination of the activation parameters for the hydride ligand site exchange process; as more data become available, these values should provide insight into the nature of such exchange.^{20,28,29}

The most synthetically useful reaction is that of the deprotonation of dihydride **4** followed by alkylation. Few examples of stable organometallic alkyl hydride complexes exist; in our group, the use of this method to prepare independently products observed in photolysis reactions of **4**¹¹ has proved a boon to further research. At this point, the scope of the reaction is somewhat limited, but recent work suggests that variation of the leaving group may allow considerable range in the type of products accessible.

Trisphosphine dication $(C_5(CH_3)_5)Ir(P(CH_3)_3)_3(BF_4)_2$ represents the final member of an isoelectronic series of (pentamethylcyclopentadienyl)iridium compounds, substituting hydride anions (H^-) for trimethylphosphine, with the other members being $(C_5(CH_3)_5)Ir(P(CH_3)_3)_2HBF_4$, $(C_5(CH_3)_5)Ir(P(CH_3)_3)_2H_2$, and $(C_5(CH_3)_5)IrH_3Li$.²⁰ We point this out to preface our idea that the hydride anion and trimethylphosphine, being sterically undemanding strong σ donor ligands, may be formally, if not necessarily chemically, substituted for each other in certain cases. Such formal substitution of H^- for $P(CH_3)_3$ in organometallic complexes has led us to new chemistry, which is discussed in the following paper.²⁰ Along these lines, we note that, in total, Scheme I may be thought of as describing a step-by-step mechanism for

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the oxidation of dimer cation **1** to 2 equiv of a monomeric iridium(V) complex.

Note Added in Proof. An example of a cationic iridium(V) complex has been reported recently; however, this complex was not isolated.³²

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Appendix

Line shape simulations were performed at the UCB Computer Center, using the program DYNAMAR, a locally modified version of a program described by Meakin and Jesson.²⁹ 1H NMR chemical shifts were assumed to vary linearly with temperature, while coupling constants were maintained at values derived from experimental spectra taken at or near the low-temperature static limit. The number and type of permutations required to define exchange were derived from consideration of possible simplified exchange modes, as described in the text. All permutations were assumed to occur at the same rate at a given temperature. A line-broadening parameter (typically 4–6 Hz) was included on the basis of the static limit experimental spectra and was not varied with temperature.

Values of the exchange rate constant k were determined by comparison of calculated spectra with experimental spectra collected at various temperatures; k values used were estimated to be accurate to $\pm 25\%$ or better. The data were plotted to the form of the Eyring³⁰ equation $\ln(nhk/k_bT) = -\Delta H^\ddagger/RT + \Delta S^\ddagger/R$, where n is the number of permutations, h is Planck's constant, k_b is Boltzmann's constant, and the transmission coefficient has been set equal to 1. From a weighted least-squares fit using a locally modified version of the program ACTPAR,³¹ the values of ΔH^\ddagger , ΔS^\ddagger , $\sigma(\Delta H^\ddagger)$, and $\sigma(\Delta S^\ddagger)$ were determined and used to calculate ΔG^\ddagger_{298} and $\sigma(\Delta G^\ddagger_{298})$.³¹ Correlation coefficients for the least-squares line were typically 0.99 or better.

Registry No. **1**-PF₆, 39385-15-4; **1**-BF₄, 96096-80-9; **2**-PF₆, 96096-82-1; **2**-BF₄, 96096-83-2; **3**, 96096-85-4; **4**, 80146-01-6; **5**, 96096-87-6; **6**, 96096-88-7; **7**, 96096-90-1; **8**, 96096-92-3; $[(C_5(CH_3)_5)Ir(P(CH_3)_3)_2Cl]Cl$, 96096-93-4; $(C_5(CH_3)_5)Ir(P(CH_3)_3)(CH_3)(H)$, 88548-54-3; $(C_5(CH_3)_5)Ir(P(CH_3)_3)(CH_3)_2$, 88548-57-6; $(C_5(CH_3)_5)Ir(P(CH_3)_3)(C_6H_5CH_2CH_2CH_2CH_3)(H)$, 85453-02-7; $(C_5(CH_3)_5)Ir(P(CH_3)_3)(CH_2C(CH_3)_3)(H)$, 80145-84-2; $(C_5(CH_3)_5)Ir(P(CH_3)_3)(Si(CH_3)_3)(H)$, 96096-94-5; $(C_5(CH_3)_5)Ir(P(CH_3)_3)(H)(D)$, 96096-95-6; $(C_5(CH_3)_5)Ir(P(CH_3)_3)(n-Pr)(H)$, 96096-96-7; $(C_5(CH_3)_5)Ir(P(CH_3)_3)(n-Bu)(H)$, 96096-97-8; $(C_5(CH_3)_5)Ir(P(CH_3)_3)(\eta^1\text{-allyl})(H)$, 96096-98-9; $(C_5(CH_3)_5)Ir(P(CH_3)_3)(sec-Bu)(H)$, 96096-99-0; $[(C_5(CH_3)_5)IrCl_2]_2$, 96097-00-6; $(C_5(CH_3)_5)Ir(acetone)_3(BF_4)_2$, 96097-01-7; $(C_5(CH_3)_5)Ir(P(CH_3)_3)(CH_3)(I)$, 96097-02-8; $Me_3SiO_3SCF_3$, 27607-77-8; n -pentyl triflate, 41029-43-0; neopentyl triflate, 66687-89-6; sec -butyl chloride, 78-86-4.

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