# *Notes*

## Reactivity of $[Ir(COE)_2(solvent)_2]PF_6$ Complexes toward Alkylphosphines: Room-Temperature C−H Activation (Cyclometalation) and Isolation of a 14-Electron Alkyl−Iridium(III) Complex

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*Received December 10, 2002*



*Summary: Isolated, cationic bis(cyclooctene)−Ir(I) complexes stabilized by acetonitrile or acetone solvent molecules were obtained and reacted with simple alkylphosphines, leading to selective displacement of the cyclooctene ligand. With the bulky $^tBu_3P$, facile intramolecular C−H activation is observed, giving cyclometalated, solvent-stabilized bis(phosphine)−Ir(III) species and leading to the isolation of the first 14-electron alkyl−Ir(III) complex.*

The synthesis of new coordinatively unsaturated late-transition-metal complexes has been driven by the vital role these complexes play as key intermediates in many stoichiometric and catalytic processes.[1] Cationic iridium complexes have been shown to mediate a range of catalytic transformations[2] and have proved to be advantageous systems for alkane C−H activation.[3] In many cases, unsaturated cationic complexes are stabilized by coordination of solvent molecules and/or by agostic interactions involving C−H bonds,[4] but due to their high reactivity, isolated and characterized examples of such complexes are rare. We have recently isolated Rh(I) and Ir(I) complexes stabilized by the common solvent DMSO as the only dative ligand, leading to compounds which show high reactivity in substitution and oxidative addition reactions.[5] Caulton and Eisenstein have reported detailed experimental and computational investigations on highly unsaturated Ir(III) complexes stabilized by agostic interactions.[6]

We describe here the synthesis of solvent-stabilized, cationic Ir(I)−COE complexes (COE = cyclooctene), whose isolation as analytically pure compounds failed in the past.[7] These Ir(I) complexes undergo selective substitution of cyclooctene by alkylphosphines, and intramolecular C−H activation (cyclometalation) of bulky alkylphosphines (i.e. $^tBu_3P$) is observed at ambient temperature for the first time. The Ir(III) complexes thus obtained are stabilized either by coordination of solvent molecules or by what appears to be an agostic interaction stabilizing the first isolated 14-electron alkyl−iridium(III) complex.[8]

### Results and Discussion

The complex $[Ir(COE)_2\{O{=}C(CH_3)_2\}_2]PF_6$ (**1**) can be isolated as a yellow microcrystalline solid by treating a suspension of $[Ir_2Cl_2(COE)_4]$ in acetone with $AgPF_6$. Subsequent workup gives complex **1** in good yield.[9] It has been characterized by elemental analysis and by NMR spectroscopic techniques, and in analogy to the recently isolated rhodium analogue, the cis arrangement of the acetone ligands seems most likely.[10] When complex **1** is dissolved in $CD_3CN$, the $^1H$ NMR spectrum shows substitution of the acetone molecules, leading to the complex $[Ir(COE)_2(CD_3CN)_2]PF_6$ (**2**) (Scheme 1). The main difference in the $^1H$ NMR spectrum is the significant downfield shift of the olefin signal from 2.61 ppm (complex **1**) to 3.47 ppm (complex **2**). It is also worth noting that the cyclooctene ligands in complex **2** seem to be more labile as compared to **1**.[11] As a result, **2** is less stable than **1**.

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(6) (a) Cooper, A. C.; Streib, W. E.; Eisenstein, O.; Caulton, K. G. *J. Am. Chem. Soc.* **1997**, *119*, 9069. (b) Ujaque, G.; Cooper, A. C.; Maseras, F.; Eisenstein, O.; Caulton, K. G. *J. Am. Chem. Soc.* **1998**, *120*, 361. (c) Cooper, A. C.; Clot, E.; Huffman, J. C.; Streib, W. E.; Maseras, F.; Eisenstein, O.; Caulton, K. G. *J. Am. Chem. Soc.* **1999**, *121*, 97.

(7) (a) Schrock, R. R.; Osborn, J. A. *J. Am. Chem. Soc.* **1971**, *93*, 3089. (b) Bosch, M.; Ilg, K.; Werner, H. *Eur. J. Inorg. Chem.* **2001**, 3181.

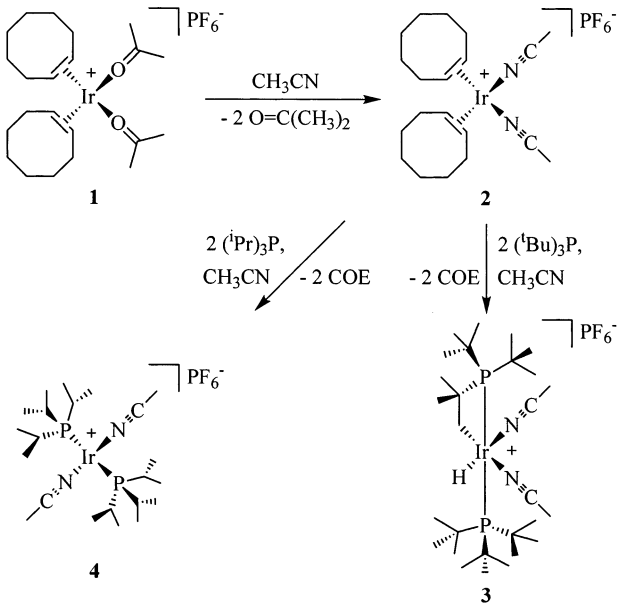
(8) A closely related aryl−iridium complex was reported recently.[6c]

(9) Strictly anhydrous solvents have to be used for the synthesis of compound **1**.

(10) The X-ray crystal structure of the rhodium compound has been determined; see: Werner, H.; Schneider, M. E.; Bosch, M.; Wolf, J.; Teuben, J. H.; Meetsma, A.; Troyanov, S. I. *Chem. Eur. J.* **2000**, *6*, 3052.

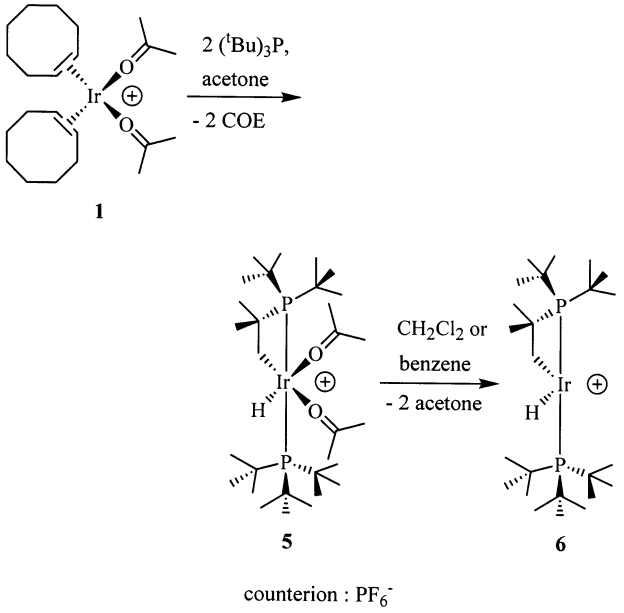
10.1021/om020997+ CCC: $25.00 
Publication on Web 05/29/2003

**Scheme 1. Synthesis and Reactivity of Complex 2 toward Alkylphosphines**




Stirring an acetonitrile solution of $[Ir(COE)_2(CH_3CN)_2]PF_6$ (**2**) with 2 equiv (or excess) of $^tBu_3P$ at room temperature overnight and subsequent precipitation in diethyl ether led to selective substitution of cyclooctene, giving the cyclometalated complex $[IrH(^tBu_3P)\{^tBu_2P[C(CH_3)_2(CH_2)]\}(CH_3CN)_2]PF_6$ (**3**) as an off-white solid in high yield (Scheme 1).[12] Complex **3** was characterized by NMR spectroscopy and by elemental analysis. The $^{31}P\{^1H\}$ NMR spectrum in $CD_3CN$ shows that cyclometalation of one of the phosphine ligands occurred, giving rise to the expected AX pattern for the two phosphines, with a large coupling constant of 307 Hz, characteristic of a mutually trans configuration. The signal of the metalated phosphine appears at low frequency at 2.13 ppm, whereas the signal of the nonmetalated $^tBu_3P$ ligand appears at 49.3 ppm. The $^1H$ NMR spectrum shows the expected hydride peak at −20.23 ppm as a doublet of doublets and several peaks corresponding to the alkyl groups of the ligand between 1.30 and 1.59 ppm. Interestingly, no cyclometalation is observed when $[Ir(COE)_2(CH_3CN)_2]PF_6$ (**2**) is treated with 2 equiv (or excess) of $^iPr_3P$ even when the solution is left stirring for several days at room temperature. Instead, a lemon yellow solid is isolated in high yield which, according to spectroscopic data and elemental analysis, has the formula *trans*-$[Ir(^iPr_3P)_2(CH_3CN)_2]PF_6$ (**4**).[13] This reactivity is somewhat surprising and contrasts with the neutral system alkylphosphine/$[Ir_2Cl_2(COE)_4]$/N-ligand, where the ease of C−H activation follows the trend $^iPr_3P > (^tBu)_2(^nBu)P > ^tBu_3P$.[14,15]

**Scheme 2. Reaction of Complex 1 with $^tBu_3P$ and Isolation of the 14e Alkyl−Ir(III) Complex 6**




The C−H activation of $^tBu_3P$ is even more facile when the more electron-rich acetone complex **1** is used as the starting material. Indeed, addition of 2 equiv of $^tBu_3P$ to an acetone-$d_6$ solution of **1** leads to an immediate fading of the color and quantitative formation of a cyclometalated species after 5 min. To the best of our knowledge, complexes **1** and **2** are the first Ir(I) complexes to undergo cyclometalation of simple alkylphosphines (except for benzyl) at room temperature.[16] Spectroscopic data and elemental analysis of the acetone complex are in agreement with the octahedral formulation $[IrH(^tBu_3P)\{^tBu_2P[C(CH_3)_2(CH_2)]\}\{O{=}C(CH_3)_2\}_2]PF_6$ (**5**) (Scheme 2). The $^1H$ NMR spectrum of **5** (acetone-$d_6$) shows the expected hydride peak at −31.83 ppm, indicating that shielding of the hydride is much more pronounced in this complex as compared to **3**, due to the significantly weaker trans influence of acetone as compared to acetonitrile. In addition, the metalated $CH_2$ group shows two separate resonances at 2.59 and 3.25 ppm. In the $^{31}P\{^1H\}$ NMR spectrum, the two phosphorus nuclei are seen at 33.9 ppm (metalated) and 59.2 ppm (nonmetalated) with a coupling constant of 301 Hz. Again, the different ligands (acetone vs acetonitrile) trans to the metalated $CH_2$ group affects the metalated ring and leads to a clear shift in the phosphorus spectrum of the metalated ligand, which appears at significantly lower field as compared to complex **3**, although the magnitude of the observed chemical shift difference is somewhat unexpected.[17] When complex **5** is dissolved in acetonitrile, substitution of the acetone ligands by acetonitrile is observed, leading to the formation of **3**, which can be isolated in quantitative

(11) Attempts to precipitate **2** were not successful, due to what appeared to be substitution of the COE ligands by the excess acetonitrile present during workup. Unfortunately, weakly coordinating solvents (such as chloroform, dichloromethane, nitromethane, and benzene) reacted with complex **1** and excluded the use of stoichiometric amounts of acetonitrile for the synthesis of complex **2**.

(12) Attempts to observe and isolate intermediates prior to C−H activation did not succeed.

(13) A virtual triplet in the $^{13}C$ spectrum for the $PCH(CH_3)_2$ signal confirms the trans configuration of the phosphines in complex **4**.

(14) (a) Hietkamp, S.; Stufkens, D. J.; Vrieze, K. *J. Organomet. Chem.* **1977**, 139, 189. See also: (b) Schulz, M.; Milstein, D. *J. Chem. Soc., Chem. Commun.* **1993**, 318.

(15) Heating an acetone solution containing **4** did show some cyclometalation, but no clean product was isolated. Treating complex **1** with $^iPr_3P$ was not selective and led to a mixture of products.

(16) See ref 14 and: (a) Dahlenburg, L.; Yardimcioglu, A. *J. Organomet. Chem.* **1985**, *291*, 371. (b) Dahlenburg, L.; Höck, N. *Inorg. Chim. Acta* **1985**, *104*, L29−L30. (c) Dahlenburg, L.; Yardimcioglu, A. *J. Organomet. Chem.* **1986**, *299*, 149.

(17) The most closely related analogue of complexes **3** and **5**, namely the neutral, trigonal-bipyramidal complex $IrH(Cl)(^tBu_3P)\{^tBu_2P[C(CH_3)_2(CH_2)]\}$, shows resonances at $\delta$ 19.6 and 62.2 ppm.[16c]

yield by precipitation in diethyl ether. Interestingly, when **5** is dissolved in the noncoordinating solvent dichloromethane, a color change to red takes place, forming the complex $[IrH(^tBu_3P)\{^tBu_2P[C(CH_3)_2(CH_2)]\}]PF_6$ (**6**), thus confirming the lability of the acetone ligands. More surprisingly, simple washings of the yellow solid **5** with benzene leads to a color change to pink-red and formation of the same complex (**6**) (Scheme 2). This formally 14e Ir(III) complex was characterized by elemental analysis and spectroscopic methods. The $^{31}P\{^1H\}$ NMR spectrum in $CD_2Cl_2$ compares well with the spectra of complexes **3** and **5**, cyclometalation of one of the phosphine ligands giving rise to the expected AX pattern ($J = 277$ Hz) for the two phosphines, appearing at 39.8 ppm (metalated) and 67.3 ppm (nonmetalated). The closely related 14e cationic agostic complex $[IrH(^tBu_2PhP)\{^tBu_2P(C_6H_4)\}]^+$ shows an almost identical $J_{P'P}$ value of 278 Hz.[6c] $^1H$ NMR shows a characteristic set of peaks for the metalated $CH_2$ group, which gives rise to one doublet at 2.91 ppm and to a doublet of doublets signal for the other hydrogen atom at 4.22 ppm. This shows that one of the hydrogen atoms couples with both phosphine nuclei, whereas the other only gives rise to the expected geminal coupling. Several doublet signals for the inequivalent $^t$Bu groups of the phosphine ligands and a doublet of doublets in the far upfield region (−45.97 ppm) for the hydride ligand complete the $^1H$ NMR spectrum. Indeed, such low ppm values for hydride ligands are found only when they are trans to a vacant site.[18] For comparison, the hydride in the 14e complex $[IrH(^tBu_2PhP)\{^tBu_2P(C_6H_4)\}]^+$ resonates at slightly lower field (−41.6 ppm).[6c] In the $^{13}C$ NMR spectrum, the most characteristic peaks arise from the metalated *C*$H_2$ group (upfield doublet at 1.37 ppm) and its neighboring quaternary $(CH_3)_2C(CH_2)$ atom (downfield doublet at 63.16 ppm).

Stabilization of the 14-electron complex **6** by coordination of $CH_2Cl_2$ was not observed. In fact, the $^{31}P\{^1H\}$ and $^1H$ spectra of **6** recorded in $C_6H_5F/C_6D_6$ (4:1) show nearly identical chemical shift values. Furthermore, the anion $^{19}F$ and $^{31}P\{^1H\}$ NMR spectra of **6** showed no interaction between the $PF_6^-$ group and the metal center. Instead, a clear indication of an agostic interaction involving the aliphatic phosphine substituents is seen in its IR spectrum (KBr pellet), which displays one band of medium intensity at 2557 $cm^{-1}$, typical for such an interaction,[4] and recently seen by X-ray crystallography for the closely related complex $[IrH(^tBu_2PhP)\{^tBu_2P(C_6H_4)\}]PPh_4$.[6c] In analogy to this compound, several variable-temperature NMR studies of complex **6** in $CD_2Cl_2$ were not able to show any features consistent with agostic bonding in solution, nor was coordination of solvent molecules observed within the temperature range studied (30 to −90 °C).[19] Finally, a spin saturation transfer experiment involving selective irradiation of the hydride ligand indicated no chemical exchange between the hydride and the methylene and/or methyl protons.

## Conclusions

We have reported here the isolation and characterization of cationic Ir(I)−solvento complexes $[Ir(COE)_2(S)_2]PF_6$ (S = acetone, acetonitrile). Reaction with the bulky $^tBu_3P$ at room temperature resulted in intramolecular C−H activation of one of the methyl groups of the phosphine, yielding octahedral, solvent-stabilized bis(phosphine)−Ir(III) complexes. The acetone-stabilized Ir(III) complex is unusually labile, and simple washings of the solid with benzene lead to acetone loss and to the isolation of the first 14e alkyl−Ir(III) complex. The pronounced lability/unsaturation of the cationic complexes described herein makes them attractive precursors for the intermolecular substrate activation and functionalization.

## Experimental Section

All experiments were carried out under an atmosphere of purified nitrogen in a Vacuum Atmospheres glovebox. NMR spectroscopic experiments were carried out on a Bruker DPX-250 NMR spectrometer or on a Bruker DRX-400 NMR spectrometer. FT-IR spectra were recorded on a Nicolet PROTEGE 460 spectrometer. Elemental analyses were done by H. Kolbe, Mikroanalytisches Laboratorium, 45470 Mühlheim an der Ruhr, Germany.

**$[Ir(COE)_2\{O{=}C(CH_3)_2\}_2]PF_6$ (1).** To a bright orange acetone (30 mL) suspension of $[Ir_2Cl_2(COE)_4]$ (534 mg, 0.590 mmol; COE = cyclooctene) at −30 °C was added dropwise an acetone (3 mL) solution of $AgPF_6$ (301 mg, 1.190 mmol). The solution was allowed to reach room temperature with stirring, and stirring was continued for another 45 min. The resulting orange solution was slowly filtered using cotton/Celite and concentrated to ca. 3 mL in vacuo. Addition of diethyl ether (15 mL) resulted in the formation of a yellow microcrystalline solid, which was filtered off, washed with diethyl ether, and dried in vacuo. Yield: 573 mg, 72%. $^1H$ NMR (acetone-$d_6$): $\delta$ 1.29 (m, 4 H), 1.47 (m, 12 H), 1.66 (m, 4 H), 2.06 (m and s, 4 and 12 H), 2.61 (s, br, 4 H) ppm. $^{13}C\{^1H\}$ NMR (acetone-$d_6$): $\delta$ 27.04 (s), 28.61 (s), 29.92 (s), 30.13 (septet, $J_{DC} = 19.41$ Hz), 63.02 (s), 207.09 (s) ppm. Anal. Calcd for $C_{22}H_{40}F_6IrO_2P$: C, 39.22; H, 5.98. Found: C, 39.14; H, 6.04.

**In Situ Characterization of $[Ir(COE)_2(CD_3CN)_2]PF_6$ (2).** Complex **1** (15 mg, 0.022 mmol) was dissolved in $CD_3CN$ (1 mL). Stirring at room temperature for 2 min led to a color change from orange to orange-yellow. Complex **2** is stable at 0 °C but decomposes slowly when left in an acetonitrile solution at room temperature. $^1H$ NMR ($CD_3CN$): $\delta$ 1.60 (s, br, 16 H), 1.87 (m, br, 8 H), 2.07 (free acetone, 12 H), 3.47 (s, br, 4 H) ppm. $^{13}C\{^1H\}$ NMR ($CD_3CN$, 0 °C): $\delta$ 27.01 (s), 27.19 (s, br), 30.83 (s, free acetone), 31.95 (s, br), 54.93 (s, very br), 207.56 (s, free acetone) ppm.

**$[IrH(^tBu_3P)\{^tBu_2P[C(CH_3)_2(CH_2)]\}(CH_3CN)_2]PF_6$ (3).** Complex **1** (40 mg, 0.059 mmol) was dissolved in $CH_3CN$ (1.5 mL). Tri-*tert*-butylphosphine (49 mg, 0.242 mmol) in $CH_3CN$ (2 mL) was added with stirring, and the solution was left at room temperature overnight, during which time the color faded. The colorless solution was then poured into diethyl ether (40 mL), leading to the precipitation of an off-white solid. The solution was decanted, and the solid was washed with diethyl ether and dried in vacuo. Yield: 40 mg, 83%. Complex **3** can also be readily prepared by dissolving compound **6** in acetonitrile. $^{31}P\{^1H\}$ NMR ($CD_3CN$): $\delta$ −143.7 (septet, 1P, $PF_6^-$), 2.1 (d, 1P, $J_{PP} = 307$ Hz, metalated); 49.3 (d, 1P, $J_{PP} = 307$

(18) For examples of related Ir(III) systems, see: (a) Masters, C. J.; Shaw, B. L. *J. Chem. Soc. A* **1971**, 3679. (b) Masters, C. J.; Shaw, B. L.; Stainbank, R. E. *J. Chem. Soc., Chem. Commun.* **1971**, 209. (c) Cooper, A. C.; Huffman, J. C.; Caulton, K. G. *Organometallics* **1997**, *16*, 1974. (d) Kanzelberger, M.; Singh, B.; Czerw, M.; Krogh-Jespersen, K.; Goldman, A. S. *J. Am. Chem. Soc.* **2000**, *122*, 11017.

(19) Crystals apparently suitable for X-ray crystallography were obtained (from either a $CH_2Cl_2$ or a $C_6H_5F/C_6D_6$ solution), and data from these crystals were measured. The symmetry of the crystals (*I*4/*m* or *R*$\bar{3}$) and the location of the Ir on special positions meant that the structure of **6** could not be refined satisfactorily (cf. ref 6c); however, the absence of coordinated solvent molecules could be clearly seen.

Hz, nonmetalated). $^1$H NMR ($CD_3CN$): $\delta$ −20.23 (dd, 1 H, $J_{PH}$ = 15.6, 12.6 Hz), 1.30−1.59 (m, 53 H) ppm. $^{13}C\{^1H\}$ NMR ($CD_3CN$): $\delta$ −8.15 (dd, $CH_2$-M, $J_{PC}$ = 25.2 and 2.7 Hz), 30.21 (s, br), 31.12 (dd, $J_{PC}$ = 2.6 and 1.4 Hz), 31.91 (dd, $J_{PC}$ = 2.6 and 1.8 Hz), 32.13 (s, br), 32.39 (d, $J_{PC}$ = 2.0 Hz), 33.21 (s, br), 38.15 (dd, $J_{PC}$ = 11.6 and 3.2 Hz), 38.93 (dd, $J_{PC}$ = 6.0 and 4.0 Hz), 41.97 (dd, $J_{PC}$ = 8.8 and 2.8 Hz), 58.90 (dd, $[CH_3]_2CCH_2$, $J_{PC}$ = 24.4 and 1.8 Hz) ppm. Anal. Calcd for $C_{28}H_{60}N_2F_6IrP_3$: C, 40.82; H, 7.34; N, 3.40. Found: C, 40.51; H, 7.29; N, 3.58.

***trans*-[Ir($^i$Pr$_3$P)$_2$(CH$_3$CN)$_2$]PF$_6$ (4).** Complex **1** (40 mg, 0.059 mmol) was dissolved in $CH_3CN$ (2 mL). The resulting orange-yellow solution was left at room temperature for 10 min. Triisopropylphosphine (38 mg, 0.237 mmol) in $CH_3CN$ (0.5 mL) was added, leading to an immediate color change to bright yellow. The solution was stirred at room temperature for 5 h and was then poured into diethyl ether (20 mL), leading to the precipitation of a lemon yellow solid. The solution was decanted, and the solid was washed with diethyl ether and dried in vacuo. Yield: 42 mg, 96%. $^{31}P\{^1H\}$ NMR (acetone-$d_6$): $\delta$ −142.6 (septet, 1P, $PF_6^-$), 35.6 (s, 2P); $^1$H NMR (acetone-$d_6$): $\delta$ 1.34 (q, 36 H), 2.53 (t, 6 H, $J_{PH}$ = 1.4 Hz), 2.55 (m, 6 H). $^{13}C\{^1H\}$ NMR (acetone-$d_6$): $\delta$ 3.96 (s, $CH_3CN$), 19.41 (s, $PCH\{CH_3\}_2$), 23.36 (vt, $J^{vt}$ = 12.7 Hz, $PCH\{CH_3\}_2$), 120.89(s, $CH_3CN$) ppm. Anal. Calcd for $C_{22}H_{48}F_6IrN_2P_3$: C, 35.72; H, 6.54; N, 3.79. Found: C, 35.59; H, 6.63; N, 3.85.

**[IrH($^t$Bu$_3$P){$^t$Bu$_2$P[C(CH$_3$)$_2$(CH$_2$)]}{O=C(CH$_3$)$_2$}$_2$]PF$_6$ (5).** Compound **1** (140 mg, 0.208 mmol) was dissolved in acetone (3 mL). The resulting solution was stirred at room temperature for 10 min. Tri-*tert*-butylphosphine (84 mg, 0.415 mmol) in acetone (3 mL) was added dropwise to the orange-red solution, leading to a color change to yellow-orange. Stirring of the solution was continued for 2 h. Concentration to 4 mL and subsequent precipitation into pentane (30 mL) gave a yellow solid, which was washed with pentane and dried in vacuo. Yield: 135 mg, 76%. Complex **5** can also be prepared by dissolving compound **6** in acetone. $^{31}P\{^1H\}$ NMR (acetone-$d_6$): $\delta$ −142.9 (septet, 1P, $PF_6^-$), 33.9 (d, 1P, $J_{PP}$ = 301 Hz), 59.2 (d, 1P, $J_{PP}$ = 301 Hz). $^1$H NMR (acetone-$d_6$): $\delta$ −31.83 (dd, 1 H, $J_{PH}$ = 13.7 Hz), 1.28−1.67 (several d, 51 H), 2.59 (d, 1 H, $J_{HH}$ = 8.2 Hz), 3.25 (ddd, 1 H, $J$ = 7.6 Hz, 5.1 Hz and 19,7 Hz) ppm. $^{13}C\{^1H\}$ NMR (acetone-$d_6$): $\delta$ −7.25 (dd, $CH_2$-M, $J_{PC}$ = 19.8 Hz), 21.57 (m), 29.89 (s), 30.36 (m), 31.58 (s, br), 32.19 (m), 33.25 (m), 39.22 (dd, $J_{PC}$ = 13.2 and 2.8 Hz), 40.48 (dd, $J_{PC}$ = 5.8 Hz), 42.05 (dd, $J_{PC}$ = 13.6 and 2.0 Hz), 62.67 (d, $[CH_3]_2CCH_2$, $J_{PC}$ = 19.2 Hz) ppm. Anal. Calcd for $C_{30}H_{66}F_6O_2IrP_3$: C, 42.00; H, 7.76. Found: C, 41.79; H, 7.53.

**[IrH($^t$Bu$_3$P){$^t$Bu$_2$P[C(CH$_3$)$_2$(CH$_2$)]}]PF$_6$ (6).** The same procedure as for **5** was employed, but the yellow complex **5** was subsequently washed with benzene and the precipitate turned pink-red. This solid was washed again with pentane and dried in vacuo. Yield: 105 mg, 68%. $^{31}P\{^1H\}$ NMR ($CD_2Cl_2$): $\delta$ −143.1 (septet, 1P, $PF_6^-$), 39.8 (d, 1P, $J_{PP}$ = 277 Hz), 67.3 (d, 1P, $J_{PP}$ = 277 Hz). $^1$H NMR ($CD_2Cl_2$): $\delta$ −45.97 (dd, 1 H, $J_{PH}$ = 12.0 and 9.9 Hz), 1.37−1.67 (several d, 51 H), 2.91 (d, 1 H, $J_{HH}$ = 10.0 Hz), 4.22 (ddd, 1 H, $J_{HH}$ = 10.0 Hz, $J_{PH}$ = 20.8 and 5.1 Hz). $^{13}$C NMR ($CD_2Cl_2$): $\delta$ 1.87 (d, $CH_2$−Ir, $J_{PC}$ = 18.4 Hz), 28.35 (d, $J_{PC}$ = 3.2 Hz), 30.23 (s), 31.71 (dd, $J_{PH}$ = 3.0 Hz and 1.2 Hz), 31.77 (dd, $J_{PH}$ = 2.7 Hz and 1.5 Hz), 32.00 (br s), 32.80 (s), 34.52 (dd, $J_{PH}$ = 3.2 Hz and 1.2 Hz), 37.96 (dd, $J_{PH}$ = 7.1 Hz and 4.9 Hz), 42.15 (dd, $J_{PH}$ = 14.5 Hz and 1.7 Hz), 42.78 (dd, $J_{PH}$ = 11.1 Hz and 1.2 Hz), 64.17 (dd, $[CH_3]_2CCH_2$, $J_{PC}$ = 19.5 Hz and 1.5 Hz) ppm. Anal. Calcd for $C_{24}H_{54}F_6IrP_3$: C, 38.86; H, 7.34. Found: C, 39.01; H, 7.42.

**Acknowledgment.** This work was supported by the Israel Science Foundation, Jerusalem, Israel, by the MINERVA foundation, Munich, Germany, and by the Helen and Martin Kimmel Center for Molecular Design. D.M. is the Israel Matz Professor of Organic Chemistry. We thank Dr H. Rozenberg and Dr. L. J. W. Shimon for their efforts regarding the X-ray structure of **6**.

OM020997+