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Addition of carbanions to tris(trimethylphosphine)(cyclooctadiene)-iridium(I) chloride: three different modes of reaction depending on the nature of the carbanion

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Abstract

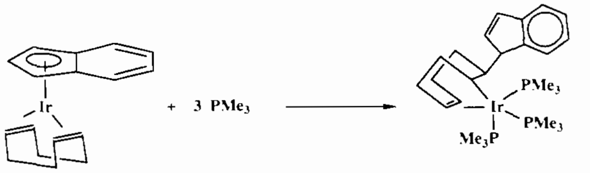
Reaction between carbanions and the cationic cyclooctadiene iridium complex, $[Ir(COD)(PMe_3)_3]Cl$, gives rise to one of three different products depending on the nature of the carbanion. For resonance stabilized carbanions (indenyl, allyl, benzyl), the products are (2-substituted cyclooct-5-en-1-yl)tris(trimethylphosphine)iridium complexes derived from nucleophilic attack of the carbanion on one of the double bonds of the coordinated cyclooctadiene. One such complex, (2-benzylcyclooct-5-en-1-yl)tris(trimethylphosphine)iridium was characterized by single crystal X-ray diffraction and crystallizes in the orthorhombic space group $P2_12_12_1$ with $a = 9.179(2)$, $b = 15.210(3)$, $c = 19.474(4)$ Å, $V = 2718.8$ Å^3 and $Z = 4$. For non-stabilized anions such as methyl, ethyl and vinyl, the products are bis(trimethylphosphine)(cyclooctadiene)iridium alkyl (or vinyl) complexes derived from the displacement of PMe_3 from iridium by the carbanion. For non-stabilized secondary or tertiary carbanions, the product is an unsubstituted (cyclooct-5-en-1-yl)tris(methylphosphine)iridium complex derived from the addition of hydride to coordinated cyclooctadiene. Some information and discussion concerning the mechanisms of these reactions are provided.

Key words: Crystal structures; Iridium complexes; Diene complexes; Carbanion complexes

Introduction

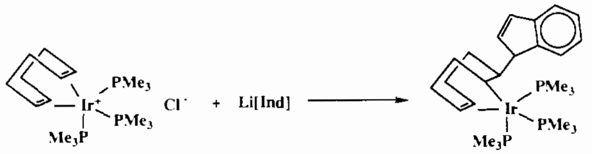
The attack of nucleophiles on olefins coordinated to a metal center provides the basis for an important commercial reaction, the Wacker process, as well as the foundation for a number of other interesting reactions [1]. While instances of nucleophilic attack on coordinated olefins have been reported for a number of metal systems, the bulk of the studies have involved palladium, platinum and iron [2]. To the best of our knowledge, there are very few descriptions of nucleophiles reacting with olefins coordinated to iridium [3].

Previously, while investigating the chemistry of indenyliridium complexes, we uncovered an interesting reaction involving the migration of indenyl (Ind) to coordinated cyclooctadiene (COD) upon treatment of η^5-IndIrCOD with trimethylphosphine (PMe_3) (eqn. (1)) [3].



(1)

We were able to show that a key step in this transformation is the nucleophilic attack of indenide on the coordinated COD in $[Ir(COD)(PMe_3)_3]^+$. Support for this step in the reaction came from independent synthesis of this cation as $[Ir(COD)(PMe_3)_3]Cl$ and demonstration that lithium indenide (and other substituted indenides) will indeed attack the coordinated COD to form a complex with a new C–C bond (eqn. (2)).



(2)

With $[Ir(COD)(PMe_3)_3]Cl$ in hand [4], we wished to investigate the chemistry of this complex further. We have already published numerous reports on the use

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of $[Ir(COD)(PMe_3)_3]Cl$ as a convenient source of iridium(I) for a variety of oxidative addition reactions including the oxidative addition of H–H bonds [5], B–H bonds [6], C–H bonds [7], N–H bonds [8], O–H bonds [9] and C–S bonds [10]. We were interested in uncovering whether or not the addition of carbanions to the COD in $[Ir(COD)(PMe_3)_3]Cl$ was a general reaction. If it were, this reaction may have interesting synthetic possibilities or at least serve as a model system for the study of nucleophilic attack on olefins. In this paper we wish to present our findings on the chemistry of $[Ir(COD)(PMe_3)_3]Cl$ with a broad range of carbon nucleophiles.

Experimental

General

All reactions were carried out under an atmosphere of prepurified nitrogen. All organic solvents were dried by the appropriate procedure and distilled prior to use. $IrCl_3 \cdot 3H_2O$ was purchased from Johnson Matthey and $[Ir(COD)Cl]_2$ was synthesized using a literature procedure [11]. $[Ir(COD)(PMe_3)_3]Cl$ was synthesized as reported previously [4]. ^1H, ^{13}C and ^{31}P NMR spectra were all recorded on a Bruker WP-200SY spectrometer operating at 200 MHz for proton and referenced to the residual protons in the deuterated solvent. Microanalyses were performed by Atlantic Microlab, Inc. Norcross, GA.

Reaction between [Ir(COD)(PMe₃)₃]Cl and indenyllithium

$[Ir(COD)(PMe_3)_3]Cl$, 0.5 g (0.9 mmol), was slurried in 50 ml THF. Indenyllithium, 0.12 g (1 mmol), was added and the mixture became a homogeneous solution which was stirred at room temperature for 1 h. THF was removed under reduced pressure and the residue was extracted with pentane. The pentane was slowly evaporated with cooling to deposit 0.46 g (79% yield) of **1a**. Complete analytical and spectroscopic data for **1a** were reported in an earlier paper [3a].

Reaction between [Ir(COD)(PMe₃)₃]Cl and 1-trimethylsilylindenyllithium

$[Ir(COD)(PMe_3)_3]Cl$, 0.5 g (0.9 mmol), was slurried in 100 ml THF. 1-Trimethylsilylindenyllithium, 0.20 g (1 mmol), was added and the mixture became a homogeneous solution which was stirred at room temperature for 3 h. THF was removed under reduced pressure and the residue was extracted with pentane. The pentane was slowly evaporated with cooling to deposit 0.61 g (0.85 mmol, 94% yield) of **1b**. Complete analytical and spectroscopic data for **1b** were reported in an earlier paper [3a].

Reaction between [Ir(COD)(PMe₃)₃[Cl and benzylmagnesium chloride

$[Ir(COD)(PMe_3)_3]Cl$, 1.02 g (1.8 mmol), was slurried in 50 ml THF. Benzylmagnesium chloride, 2.0 ml of a 2 M solution (4 mmol), was added and the mixture became a homogeneous solution which was stirred at room temperature overnight. THF was removed under reduced pressure and the residue was extracted with pentane. The pentane was slowly evaporated with cooling to deposit 1.02 g (1.65 mmol, 91% yield) of **1c** identified on the basis of the following information: *Anal.* Calc. for $C_{24}H_{46}IrP_3$: C, 46.51; H, 7.48. Found: C, 46.63; H, 7.52%. NMR spectra: ^1H NMR (200 MHz, $CDCl_3$): δ 0.57 (d, $J(^{31}P\text{–}^1H)=6.4$ Hz, 9H, $P(CH_3)_3$), 0.89 (d, $J(^{31}P\text{–}^1H)=6.3$ Hz, 9H, $P(CH_3)_3$), 0.93 (d, $J(^{31}P\text{–}^1H)=5.9$ Hz, 9H, $P(CH_3)_3$) 1.3–2.3 (series of complex multiplets not fully assigned but due to cyclooctenyl aliphatic and olefinic protons), 2.47 (AB pattern, 2H, benzylic CH_2), 2.92 (br m, 1H, H1), 6.8–7.0 (m, aryl) ppm; $^{13}C\{^1H\}$ NMR (50 MHz, $CDCl_3$): δ 18.0 (complex m, $P(CH_3)_3$), 22.0 (complex m, $P(CH_3)_3$), 26.0–45.0 (a series of complex resonances not assigned but due to cyclooctenyl carbons and the benzylic carbon), 125.0–145.0 (aryl) ppm; $^{31}P\{^1H\}$ NMR (81 MHz, C_6D_6): an ABC pattern which appears as an apparent triplet at δ −56.88 and an apparent doublet at −57.5 ppm.

Reaction between [Ir(COD)(PMe₃)₃]Cl and allylmagnesium chloride

$[Ir(COD)(PMe_3)_3]Cl$, 0.5 g (0.9 mmol), was slurried in 50 ml THF. Allylmagnesium chloride, 0.5 ml of a 2M solution in THF (1 mmol), was added and the mixture became a homogeneous solution which was stirred at room temperature for 1 h. THF was removed under reduced pressure and the residue was extracted with pentane. The pentane was slowly evaporated with cooling to deposit 0.46 g (0.8 mmol, 89% yield) of **1d** identified on the basis of the following information: *Anal.* Calc. for $C_{20}H_{44}IrP_3$: C, 42.17; H, 7.78. Found: C, 42.00; H, 8.12%. NMR spectra: ^1H NMR (200 MHz, $CDCl_3$): δ 0.89 (d, $J(^{31}P\text{–}^1H)=6.4$ Hz, 9H, $P(CH_3)_3$), 1.24 (d, $J(^{31}P\text{–}^1H)=6.0$ Hz, 9H, $P(CH_3)_3$), 1.31 (d, $J(^{31}P\text{–}^1H)=5.7$ Hz, 9H, $P(CH_3)_3$), 1.4–2.0 (series of complex multiplets not fully assigned but due to cyclooctenyl aliphatic protons), 2.27 (apparent t, 2H, allylic CH_2), 2.4–3.2 (br m, cyclooctenyl olefinic), 5.0–6.0 (ABX pattern for allylic $CH{=}CH_2$) ppm; $^{13}C\{^1H\}$ NMR (50 MHz, $CDCl_3$): δ 18.0 (complex m, $P(CH_3)_3$), 22.0 (complex m, $P(CH_3)_3$), 26.0–45.0 (a series of complex resonances not assigned but due to cyclooctenyl), 65.6, 87.9 (allylic $CH{=}CH_2$ carbons) ppm.

Reaction between [Ir(COD)(PMe$_3$)$_3$]Cl and lithium triethylborohydride

[Ir(COD)(PMe$_3$)$_3$]Cl, 1.0 g (1.8 mmol), was slurried in 100 ml THF. Lithium triethylborohydride, 0.2 g (1.9 mmol), was added and the mixture became a homogeneous solution which was stirred at room temperature for 1 h. THF was removed under reduced pressure and the residue was extracted with pentane. The pentane was slowly evaporated with cooling the deposit 0.82 g (1.55 mmol, 86% yield) of **1e** identified on the basis of the following information: *Anal.* Calc. for $C_{17}H_{40}IrP_3$: C, 38.55; H, 7.61; Ir, 36.29; P, 17.54. Found: C, 38.36; H, 7.57; Ir, 36.58; P, 17.31%. NMR spectra: ^{1}H NMR (200 MHz, C_6D_6): δ 0.60 (d, $J(^{31}P\text{–}^1H) = 6.4$ Hz, 9H, $P(CH_3)_3$), 0.94 (d, $J(^{31}P\text{–}^1H) = 5.8$ Hz, 9H, $P(CH_3)_3$), 1.01 (d, $J(^{31}P\text{–}^1H) = 6.3$ Hz, 9H, $P(CH_3)_3$), 1.25–3.0 (series of complex multiplets not fully assigned but due to COD aliphatic and olefinic protons) ppm; $^{13}C\{^1H\}$ NMR (50 MHz, C_6D_6): δ 18.8 (complex m, $P(CH_3)_3$), 21.9 (complex m, $P(CH_3)_3$), 27.0–45.0 (a series of resonances not assigned but due to cyclooctenyl carbons) ppm.

Reaction between [Ir(COD)(PMe$_3$)$_3$]Cl and lithium triethylborodeuteride

Using the same conditions employed in the reaction above, [Ir(COD)(PMe$_3$)$_3$]Cl was allowed to react with lithium triethylborodeuteride. The ^{1}H and ^{13}C NMR spectra of the deuterated material were essentially identical to those of the completely protiated compound. There was insufficient resolution of peaks in the aliphatic C–H region to determine the position of the D atom. A ^{2}H NMR spectrum was recorded, and we were surprised to discover multiple resonances for deuterium in the 1.5–3.0 ppm region of the spectrum preventing us from making an assignment of the stereochemistry of the hydride addition.

Reaction between [Ir(COD)(PMe$_3$)$_3$]Cl and methylmagnesium chloride

[Ir(COD)(PMe$_3$)$_3$]Cl, 1.0 g (1.8 mmol), was slurried in 100 ml THF. Methylmagnesium chloride, 0.55 ml of a 4 M solution (2.2 mmol), was added and the mixture became a homogeneous solution which was stirred at room temperature overnight. THF was removed under reduced pressure and the residue was extracted with pentane. The pentane was slowly evaporated with cooling to deposit 0.75 g (1.60 mmol, 89% yield) of **2a** identified on the basis of the following information. *Anal.* Calc. for $C_{15}H_{33}IrP_2$: C, 38.53; H, 7.11. Found: C, 36.97; H, 6.84%. NMR spectra: ^{1}H NMR (200 MHz, C_6D_6): δ 0.13 (t, $J(^{13}P\text{–}^1H) = 11$ Hz, 3H, Ir–CH_3), 1.13 (m, 18H, $P(CH_3)_3$), 2.1–2.7 (broad series of multiplets not fully assigned but due to COD aliphatic protons), 3.4 (br m, 4H, COD olefinic protons) ppm; $^{13}C\{^1H\}$ NMR (50 MHz, C_6D_6): δ −19.4 (t, $J(^{31}P\text{–}^{13}C) = 10$ Hz, Ir–CH_3), 18.7 (complex m, $P(CH_3)_3$), 35.2 (br m, COD aliphatic C), 66 (br m, COD olefinic C) ppm.

Reaction between [Ir(COD)(PMe$_3$)$_3$]Cl and ethylmagnesium chloride

[Ir(COD)(PMe$_3$)$_3$]Cl, 1.0 g (1.8 mmol), was slurried in 100 ml THF. Ethylmagnesium chloride, 1.2 ml of a 2 M solution (2.4 mmol), was added and the mixture became a homogeneous solution which was stirred at room temperature overnight. The THF was removed under reduced pressure and the residue was extracted with pentane. The pentane was slowly evaporated with cooling to deposit 0.70 g (1.60 mmol, 89% yield) of **2b** identified on the basis of the following information. *Anal.* Calc. for $C_{16}H_{35}IrP_2$: C, 39.90; H, 7.33. Found: C, 37.17; H, 6.88%. NMR spectra: ^{1}H NMR (200 MHz, C_6D_6): δ 1.10 (m, 18H, $P(CH_3)_3$), 1.34 (t, $J(^1H\text{–}^1H) = 7.7$ Hz, 3H, CH_2CH_3), 2.3 (br m, COD aliphatic protons), 3.0 (br m, 4H, COD olefinic protons) ppm, ethyl CH_2 resonances apparently buried under $P(CH_3)_3$ resonances; $^{13}C\{^1H\}$ NMR (50 MHz, C_6D_6): δ −10.6 (t, $J(^{31}P\text{–}^{13}C) = 8$ Hz, Ir–CH_2CH_3), 17.9 (t, $J(^{31}P\text{–}^{13}C) = 9$ Hz, Ir–CH_2CH_3), 18.7 (complex m, $P(CH_3)_3$), 35.2 (br m, COD aliphatic C) ppm, COD olefinic C not observed.

Reaction between [Ir(COD)(PMe$_3$)$_3$]Cl and trimethylsilylmethylmagnesium chloride

[Ir(COD)(PMe$_3$)$_3$]Cl, 1.0 g (1.8 mmol), was slurried in 100 ml THF. Trimethylsilylmethylmagnesium chloride, 1.2 ml of a 2 M solution (2.4 mmol), was added and the mixture became a homogeneous solution which was stirred at room temperature overnight. THF was removed under reduced pressure and the residue was extracted with pentane. The pentane was slowly evaporated with cooling to deposit 0.70 g (1.60 mmol, 89% yield) of **2c** identified on the basis of the following information. *Anal.* Calc. for $C_{18}H_{41}IrP_2Si$: C, 40.05; H, 7.66. Found: C, 39.44; H, 7.21%. NMR spectra: ^{1}H NMR (200 MHz, C_6D_6): δ −0.21 (t, $J(^{31}P\text{–}^1H) = 12$ Hz, 2H, Ir–$CH_2Si(CH_3)_3$), 0.36 (s, 9H, $Si(CH_3)_3$), 1.10 (m, 18H, $P(CH_3)_3$), 2.0–2.5 (br m, COD aliphatic protons), 3.0 (br m, 4H, COD olefinic protons) ppm; $^{13}C\{^1H\}$ NMR (50 MHz, C_6D_6): δ −21.3 (t, $J(^{31}P\text{–}^{13}C) = 8$ Hz, Ir–$CH_2Si(CH_3)_3$), 4.7 (s, $Si(CH_3)_3$), 18.4 (m, $P(CH_3)_3$), 35.0 (br m, COD aliphatic C) ppm, COD olefinic C not observed.

Reaction between [Ir(COD)(PMe$_3$)$_3$]Cl and vinylmagnesium chloride

[Ir(COD)(PMe$_3$)$_3$]Cl, 0.5 g (0.9 mmol), was slurried in 50 ml THF. Vinylmagnesium chloride, 1.2 ml of a 1 M solution (1.2 mmol), was added and the mixture became a homogeneous solution which was stirred at room temperature overnight. THF was removed under reduced pressure and the residue was extracted with pentane. The pentane was slowly evaporated with cooling to deposit 0.40 g (0.83 mmol, 92% yield) of **2d** identified on the basis of the following information. *Anal.* Calc. for $C_{16}H_{38}IrP_2$: C, 39.65; H, 7.90. Found: C, 41.00; H, 8.11%. NMR spectra: ^1H NMR (200 MHz, C_6D_6): δ 1.39 (m, 18H, $P(CH_3)_3$), 2.0–2.5 (br m, COD aliphatic protons), 3.3 (br m, 4H, COD olefinic protons), 4.8, 5.7, 7.5 (each complex m, 1H, $Ir-CH=CH_2$, an ABX pattern not fully analyzed) ppm; $^{13}C\{^1H\}$ NMR (50 MHz, C_6D_6, r.t.): δ 18.9 (m, $P(CH_3)_3$), 35.0 (br m, COD aliphatic C), 116.7 (t, $J(^{31}P-^{13}C) = 8$ Hz, $Ir-CH=CH_2$), 138.6 (t, $J(^{31}P-^{13}C) = 14$ Hz, $Ir-CH=CH_2$) ppm, COD olefinic C not observed. The assignment of the vinylic CH versus CH_2 carbon was confirmed by an INEPT experiment. Low-temperature ^1H and ^{13}C NMR spectra were also recorded: ^1H NMR (200 MHz, toluene-d_8, 243 K): δ 1.4 (m, 18H, $P(CH_3)_3$), 2.1 (br s, 4H, COD aliphatic H), 2.6 (br s, 4H, COD aliphatic H), 2.9 (br s, 2H, COD olefinic H), 3.1 (br s, 2H, COD olefinic H), the vinyl resonances appear at the same chemical shifts as in the r.t. spectrum, but they are considerably broadened. $^{13}C\{^1H\}$ NMR (50 MHz, toluene-d_8, 243 K): δ 18.5 (m, $P(CH_3)_3$), 34.1 (s, COD aliphatic C), 36.3 (s, COD aliphatic C), 52.4 (br m, COD olefinic C), 73.8 (s, COD olefinic C), 116.1 (br s, $Ir-CH=CH_2$), 138.9 (br s, $Ir-CH=CH_2$) ppm.

Reaction between $[Ir(COD)(PMe_3)_3]Cl$ and t-butylmagnesium chloride

$[Ir(COD)(PMe_3)_3]Cl$, 1.0 g (1.8 mmol), was slurried in 100 ml THF. t-Butylmagnesium chloride, 1.0 ml of a 1.9 M solution in THF (1.9 mmol), was added and the mixture became a homogeneous solution which was stirred at room temperature overnight. The THF was removed under reduced pressure and the residue was extracted with pentane. The pentane was slowly evaporated with cooling to deposit 0.70 g (1.32 mmol, 73% yield) of **1e** whose spectral properties were identical to those of the product formed in the reaction between $[Ir(COD)(PMe_3)_3]Cl$ and $LiEt_3BH$.

Reaction between $[Ir(COD)(PMe_3)_3]Cl$ and cyclohexylmagnesium chloride

$[Ir(COD)(PMe_3)_3]Cl$, 0.54 g (0.9 mmol), was slurried in 50 ml THF. Cyclohexylmagnesium chloride, 0.8 ml of a 1.2 M solution in THF (0.96 mmol), was added and the mixture became a homogeneous solution which was stirred at room temperature overnight. THF was removed under reduced pressure by trapping THF and other volatiles in a liquid N_2 trap and the residue was extracted with pentane. The pentane was slowly evaporated with cooling to deposit 0.4 g (0.76 mmol, 84% yield) of **1e** whose spectral properties were identical to those of the product formed in the reaction between $[Ir(COD)(PMe_3)_3]Cl$ and $LiEt_3BH$. The volatiles trapped in the liquid N_2 trap were analyzed by gas chromatography indicating the presence of cyclohexane.

Synthesis of $PhCH_2Ir(COD)(PMe_3)_2$

$[Ir(COD)Cl]_2$, 2.0 g (2.98 mmol), was dissolved in 200 ml THF. To this solution, PMe_3 (0.9 g, 5.8 mmol) in 10 ml THF was added slowly with vigorous stirring. To the resulting yellow–orange solution benzylmagnesium chloride, 3.0 ml of a 2 M solution in THF (6.0 mmol), was added slowly. The reaction mixture was stirred at room temperature for 30 min, THF was removed under reduced pressure and the residue was extracted with pentane. The pentane was slowly evaporated with cooling to deposit 2.5 g (4.6 mmol, 77% yield) of a pale yellow waxy solid identified as **2e** on the basis of the following information. *Anal.* Calc. for $C_{21}H_{37}IrP_2$: C, 46.39; H, 6.86; Ir, 35.5; P, 11.39. Found: C, 44.17; H, 6.73; Ir, 34.74; P, 11.20%. NMR spectra: ^1H NMR (200 MHz, $CDCl_3$): δ 1.21 (m, 18H, $P(CH_3)_3$), 2.2–2.5 (br m, 8H, COD aliphatic protons), 2.59 (t, $J(^{31}P-^1H) = 10.5$ Hz, 2H, $Ir-CH_2Ph$), 2.9 (br m, 4H, COD olefinic protons), 7.0–7.5 (m, 5H, phenyl) ppm.

Synthesis of $HIr(COD)(PMe_3)_2$

$[Ir(COD)Cl]_2$, 1.0 g (1.49 mmol), was dissolved in 100 ml THF. To this solution, PMe_3 (0.44 g, 5.8 mmol) in 25 ml THF was added slowly with vigorous stirring. The resulting yellow–orange solution was cooled to −78 °C using a dry ice/acetone bath. t-Butylmagnesium chloride, 1.7 ml of a 1.9 M solution in THF (3.2 mmol), was added while maintaining the temperature at −78 °C. The reaction mixture was stirred at −78 °C for 30 min and then the reaction mixture was allowed to warm very slowly to room temperature. After the reaction reached room temperature, THF was removed under reduced pressure and the residue was extracted with pentane. The pentane was slowly evaporated with cooling to deposit 1.1 g (2.43 mmol, 82% yield) of a pale yellow waxy solid identified as **2f** on the basis of the following information. NMR spectra: ^1H NMR (200 MHz, C_6D_6): δ −13.8 (t, $J(^{31}P-^1H) = 24$ Hz, 1H, $Ir-H$), 1.32 (m, 18H, $P(CH_3)_3$), 2.0–2.5 (br m, COD aliphatic protons), 3.5 (br m, 4H, COD olefinic protons) ppm.

Attempted reactions of $PhCH_2Ir(COD)(PMe_3)_2$

Several attempts were made to induce migration of the benzyl group from iridium to COD. In all cases, the reactions were monitored by ^1H NMR spectroscopy. In separate experiments, $Ph_2CH_2Ir(COD)(PMe_3)_2$ was allowed to react with 1 equiv. of PMe_3 at room temperature and at 100 °C. In both cases, there was no evidence for migration of the benzyl group. In addition, $Ph_2CH_2Ir(COD)(PMe_3)_2$ was allowed to react with a large excess (> 10 equiv. of PMe_3, again both at room temperature and at 100 °C with no evidence for benzyl migration. Both C_6D_6 and THF-d_8 were employed as NMR solvents for these reactions in the event that the solvent plays a role. No differences were found in reactions in the two solvents. Finally, several experiments were performed with $MgCl_2$ added to determine if this effects the course of the reaction. Again, the results were the same: no migration of the benzyl group from iridium to COD.

Reactions of HIr(COD)(PMe$_3$)$_2$

HIr(COD)$(PMe_3)_2$, 40 mg (0.8 mmol), was dissolved in 0.3 ml of C_6D_6 in a 5 mm NMR tube and sealed with a septum cap. An initial ^{1}H NMR spectrum of HIr(COD)$(PMe_3)_2$ was recorded. PMe_3, 7 μl (0.8 mmol), was added to the tube via syringe and the tube was shaken to mix the contents. A second ^{1}H NMR spectrum was recorded immediately after addition of PMe_3 which showed that migration of H from iridium to COD had occurred to the extent of about 30%. A third ^{1}H NMR spectrum was recorded 30 min after addition of PMe_3 and the reaction was complete. The NMR spectrum recorded was identical to that of **1c** synthesized as described above.

Reaction between [Ir(COD)(PMe$_3$)$_3$]Cl and indenyllithium in the presence of excess PMe$_3$

[Ir(COD)$(PMe_3)_3$]Cl, 0.5 g (0.9 mmol), was slurried in 100 ml THF. PMe_3, 0.33 g (4.3 mmol), was added to the slurry followed by indenyllithium, 0.12 g (1 mmol), and the mixture became a homogeneous solution which was stirred at room temperature for 1 h. THF was removed under reduced pressure and the residue was extracted with pentane. The pentane was slowly evaporated with cooling to deposit 0.46 g (79% yield) of **1a** identical in all respects to that formed in the absence of added PMe_3.

Reaction between [Ir(COD)(PMe$_3$)$_3$]Cl and methylmagnesium chloride in the presence of excess PMe$_3$

[Ir(COD)$(PMe_3)_3$]Cl, 0.5 g (0.9 mmol), was slurried in 100 ml THF. PMe_3, 0.33 g (4.3 mmol), was added to the slurry followed by 0.3 ml of methylmagnesium chloride and the mixture was stirred at room temperature overnight. THF was removed under reduced pressure and the residue was extracted with pentane. The pentane was slowly evaporated with cooling to deposit 0.13 g (0.28 mmol, 31% yield) of **2a**. MeIr(COD)$(PMe_3)_2$. ^{1}H NMR analysis of the pentane insolubles showed that much of the [Ir(COD)$(PMe_3)_3$]Cl remained unreacted.

Crystal structure determination of 1c

Data collection was performed on a Siemens R3mV single crystal diffractometer with data reduction performed using SHELXTL-Plus software for PC [12]. Pertinent experimental details for the structure determination of **1c** are summarized in Table 1. Table 2 is a listing of the fractional atomic coordinates for **1c** and Table 3 is a listing of important bond lengths and angles. Figure 1 is a thermal ellipsoid plot of **1c** showing the atom labeling scheme.

TABLE 1. Crystallographic data for **1c**

Empirical formula	$C_{24}H_{46}Ir_1P_3$
Color; habit	colorless; rectangular prism
Crystal size (mm)	0.3×0.3×0.5
Crystal system	orthorhombic
Space group	$P2_12_12_1$
Unit cell dimensions	
a (Å)	9.179(2)
b (Å)	15.210(3)
c (Å)	19.474(4)
Volume (Å^3)	2718.850(0)
Z	4
Formula weight	619.7
Density (calc.) (g/cm^3)	1.514
Absorption coefficient (mm^{-1})	5.095
Diffractometer used	Siemens R3m/V
Radiation, λ (Å)	Mo Kα, 0.71073
Temperature (K)	298
Monochromator	highly oriented graphite crystal
2θ Range (°)	3.5–50.0
Scan type	Wyckoff
Scan speed (°/min in ω)	variable; 5.00–30.00
Scan range (ω) (°)	1.00
Standard reflections	3 measured every 400 reflections
Index ranges	$0 \leq h \leq 10$, $0 \leq k \leq 18$, $0 \leq l \leq 23$
Reflections collected	2698
Independent reflections	2698 ($R_{int}=0.00\%$)
Observed reflections	2072 ($F>2.0\sigma(F)$)
Absorption correction	semi-empirical
Transmission, min./max.	0.7265/1.0000
System used	Siemens SHELXTL PLUS (PC Version)
Solution	direct methods
Refinement method	full-matrix least-squares
Quantity minimized	$\Sigma w(F_o-F_c)^2$
Absolute structure, η	0.96(4)
Extinction correction, χ	−0.000032(6), where $F^*=F[1+0.002\chi F^2/\sin(2\theta)^{-1/4}$
Hydrogen atoms	riding model, fixed isotropic U
Weighting scheme	$w^{-1}=\sigma^2(F)+0.0000F^2$
No. parameters refined	255
Final R indices (obs. data) (%)	
R	3.63
R_w	2.47
R indices (all data) (%)	
R	5.38
R_w	2.61
Goodness-of-fit	0.74

Results and discussion

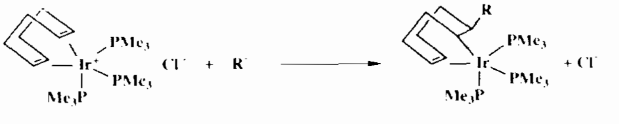
Initial results from the reactions of some carbanions with [Ir(COD)$(PMe_3)_3$]Cl seemed to indicate that the attack of carbon nucleophiles on a coordinated double

TABLE 2. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement coefficients ($Å^2 \times 10^3$) for **1c**

	x	y	z	U_{eq}[a]
Ir(1)	−2179(1)	−1460(1)	−1698(1)	31(1)
P(1)	−2986(5)	−2906(2)	−1661(3)	53(1)
P(2)	256(3)	−1827(2)	−1716(2)	42(1)
P(3)	−2589(4)	−1188(2)	−2845(2)	42(1)
C(1)	−4159(14)	−973(10)	−1193(8)	62(6)
C(2)	−3130(15)	−1351(11)	−661(6)	53(6)
C(3)	−2419(20)	−858(9)	−103(7)	73(7)
C(4)	−1732(15)	73(10)	−230(7)	51(6)
C(5)	−830(14)	136(9)	−872(6)	41(5)
C(6)	−1657(13)	−86(8)	−1547(6)	34(5)
C(7)	−3000(15)	474(7)	−1617(8)	44(5)
C(8)	−4313(18)	3(10)	−1297(9)	67(7)
C(9)	−32(15)	1025(7)	−922(6)	48(5)
C(10)	972(17)	1241(9)	−326(7)	52(6)
C(11)	2217(22)	739(11)	−233(8)	75(7)
C(12)	3158(27)	983(14)	331(12)	114(12)
C(13)	2718(32)	1633(19)	779(11)	121(14)
C(14)	1554(29)	2103(14)	654(11)	121(13)
C(15)	597(18)	1926(10)	115(8)	63(7)
C(1A)	−4878(15)	−3102(10)	−1457(9)	99(9)
C(1B)	−2797(18)	−3695(8)	−2366(7)	84(7)
C(1C)	−2162(22)	−3549(11)	−967(7)	100(7)
C(2A)	1524(14)	−999(9)	−2024(7)	58(6)
C(2B)	874(13)	−2775(9)	−2230(7)	62(6)
C(2C)	1149(14)	−2066(10)	−892(7)	76(7)
C(3A)	−2234(18)	−1991(8)	−3511(5)	77(6)
C(3B)	−1659(15)	−260(9)	−3257(9)	80(7)
C(3C)	−4481(14)	−935(10)	−3070(7)	92(8)

[a] Equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor.

bond of COD was a general reaction (eqn. (3)). The reaction shown in eqn. (3) was successful for indenyl (and substituted indenyl), benzyl and allyl. In all



1a: R = indenyl
1b: R = 3-TMS-indenyl
1c: R = benzyl
1d: R = allyl

(3)

cases, the structures of complexes **1a**–**d** as cyclooctenyl iridium compounds could be deduced from ^{1}H NMR spectroscopy. In general, three doublets arising from the methyl protons of the three inequivalent PMe_3 ligands are observed in the 0.5–1.5 ppm region of the spectrum. The aliphatic protons of the cyclooctenyl ligand give rise to a complex series of resonances in the 2–3 ppm region and the olefinic protons are observed at around 3–4 ppm. Resonances due to the protons on the added R group are easily assigned. Other spectroscopic data (^{13}C, ^{31}P) are also consistent with the structure shown in eqn. (3).

TABLE 3. Important bond lengths (Å) and angles (°) for **1c**

Bond lengths			
Ir(1)–P(1)	2.322(3)	C(2)–C(3)	1.472(20)
Ir(1)–P(2)	2.304(3)	C(3)–C(4)	1.570(21)
Ir(1)–P(3)	2.303(3)	C(4)–C(5)	1.503(18)
Ir(1)–C(1)	2.194(14)	C(5)–C(6)	1.555(17)
Ir(1)–C(2)	2.206(12)	C(5)–C(9)	1.541(18)
Ir(1)–C(6)	2.163(12)	C(6)–C(7)	1.505(18)
C(1)–C(2)	1.515(20)	C(7)–C(8)	1.535(21)
C(1)–C(8)	1.505(21)	C(9)–C(10)	1.518(19)
Bond angles (°)			
P(1)–Ir(1)–P(2)	94.6(1)	Ir(1)–P(3)–C(3B)	119.1(5)
P(1)–Ir(1)–P(3)	98.5(2)	Ir(1)–P(3)–C(3C)	115.1(5)
P(2)–Ir(1)–P(3)	100.8(2)	Ir(1)–C(1)–C(2)	70.3(7)
P(1)–Ir(1)–C(1)	92.4(4)	Ir(1)–C(1)–C(8)	110.5(10)
P(2)–Ir(1)–C(1)	153.1(4)	C(2)–C(1)–C(8)	121.7(13)
P(3)–Ir(1)–C(1)	103.8(4)	Ir(1)–C(2)–C(1)	69.5(7)
P(1)–Ir(1)–C(2)	85.2(5)	Ir(1)–C(2)–C(3)	122.6(10)
P(2)–Ir(1)–C(2)	114.6(4)	C(1)–C(2)–C(3)	126.0(14)
P(3)–Ir(1)–C(2)	144.1(4)	C(2)–C(3)–C(4)	121.5(12)
C(1)–Ir(1)–C(2)	40.3(5)	C(3)–C(4)–C(5)	114.2(12)
P(1)–Ir(1)–C(6)	168.9(3)	C(4)–C(5)–C(6)	114.9(11)
P(2)–Ir(1)–C(6)	91.2(3)	C(4)–C(5)–C(9)	111.8(11)
P(3)–Ir(1)–C(6)	89.7(3)	C(6)–C(5)–C(9)	111.7(10)
C(1)–Ir(1)–C(6)	78.3(5)	Ir(1)–C(6)–C(5)	115.7(8)
C(2)–Ir(1)–C(6)	83.7(5)	Ir(1)–C(6)–C(7)	110.6(8)
Ir(1)–P(1)–C(1A)	118.0(5)	C(5)–C(6)–C(7)	110.7(11)
Ir(1)–P(1)–C(1B)	124.6(5)	C(6)–C(7)–C(8)	110.0(11)
Ir(1)–P(1)–C(1C)	113.4(6)	C(1)–C(8)–C(7)	116.2(12)
Ir(1)–P(2)–C(2A)	117.3(4)	C(5)–C(9)–C(10)	115.4(10)
Ir(1)–P(2)–C(2B)	119.8(4)	C(9)–C(10)–C(11)	118.7(13)
Ir(1)–P(2)–C(2C)	117.9(5)	C(9)–C(10)–C(15)	118.9(13)
Ir(1)–P(3)–C(3A)	123.0(4)	C(11)–C(10)–C(15)	122.3(14)

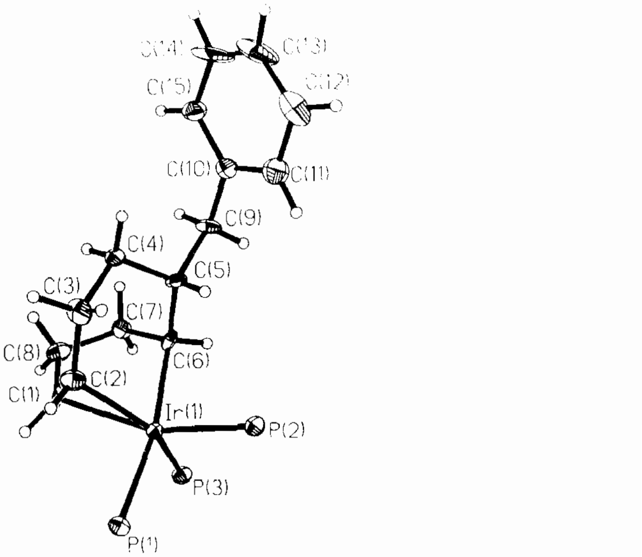
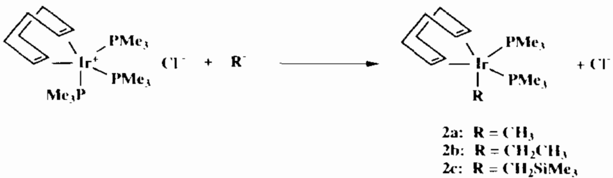


Fig. 1. Thermal ellipsoid plot of **1c** showing atom labeling scheme.

Final confirmation of this structure type came from a single crystal X-ray structure determination of the product from addition of the benzyl anion (Fig. 1). This structure is similar to that we reported previously for the product from the addition of indenyl anion to [Ir(COD)(PMe$_3$)$_3$]Cl [3]. The stereochemistry at C5 with the benzyl group being *exo* with respect to the iridium indicates that the product is formed by an external attack of the anion on the coordinated double bond of the COD.

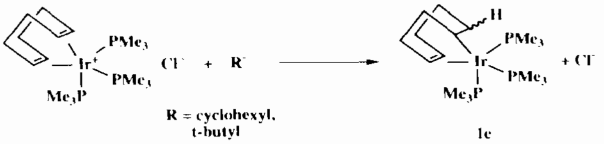
Further studies with a wider variety of carbanions, however, showed that nucleophilic attack on the coordinated olefin did *not* occur in all cases. Rather, with certain carbanions attack occurred at the iridium center with displacement of PMe$_3$ (eqn. (4)). The reaction shown in eqn. (4) was followed for R = methyl, ethyl, trimethylsilylmethyl and vinyl. The NMR spectral data for complexes **2a–d** are strikingly different from those found for compounds **1a–d**. In general, the ^{1}H NMR spectra for compounds of type **2** show a multiplet ('filled in doublet') at around 1 ppm arising from the methyl protons on the PMe$_3$ ligands. A very broad resonance attributable to the COD aliphatic protons is found from 2 to 2.5 ppm. In most cases, the resonances due to the olefinic protons are so broad as to be barely detectable above the baseline. The protons on the various R groups are readily apparent and any protons on carbon directly bonded to iridium experience a distinct upfield shift. These features are all indicative of a fluxional, five-coordinate iridium complex of the structure type shown in eqn. (4).



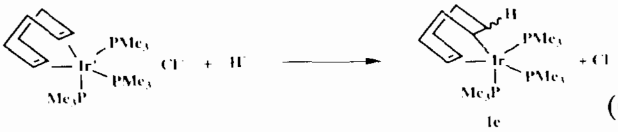
(4)

Compounds **2a** and **b** are analogous to the R-Ir(COD)(PR$_3$)$_2$ complexes studied by Shapley and Osborn [13] (and crystallographically by Churchill *et al.* [14]). They found that R-Ir(COD)(PX$_3$)$_2$ compounds where PX$_3$ = PPh$_3$, MePPh$_2$ and Me$_2$PPh, are fluxional in solution at room temperature with a ground state structure based on a trigonal bipyramid with the R group occupying one axial position, the two PMe$_3$ groups in equatorial positions and the COD spanning equatorial and axial sites. While no crystallographic studies were carried out on any of the R-Ir(COD)(PMe$_3$)$_2$ compounds reported here, the fluxional behavior and ground state structure of one of them, H$_2$C=CH-Ir(COD)(PMe$_3$)$_2$ (**2d**) was probed by variable temperature ^{1}H and ^{13}C NMR spectroscopy. In the ^{1}H NMR spectrum of **2d** at room temperature, the COD aliphatic protons give rise to a very broad, featureless resonance at around δ 2.2 ppm. The olefinic COD protons give rise to signals that are extremely broad and are barely discernible from the baseline at around 3 ppm. On cooling to 243 K, the broad multiplet at δ 2.2 resolves into two broad signals of equal intensity. The olefinic protons are clearly observable at 243 K with two separate signals at δ 2.8 and 3.3 ppm. Consistent results were found in the variable temperature ^{13}C NMR experiment: at room temperature, a single, broad resonance was observed for the aliphatic COD carbons with the olefinic carbons not observed. On cooling to 243 K, two singlets are observed for the aliphatic COD carbons and two signals are observed for the olefinic COD carbons. For the latter, one of the olefins gives rise to a singlet while the signal due to the other olefin shows phosphorus coupling. All of this is consistent with the previous reports by Shapley and Osborn [13]. Compounds **2a–d** then would appear to be fluxional in solution at room temperature and have a ground state trigonal bipyramidal structure with the R group in an axial position, the PMe$_3$ ligands in equatorial positions and the COD ligands spanning an equatorial and axial position.

Surprisingly, yet a third reaction path was observed for the reaction between [Ir(COD)(PMe$_3$)$_3$]Cl and secondary or tertiary carbanions. In this case, a product is obtained that is the formal result of hydride addition to coordinated COD (eqn. (5)). In addition to the spectral data which are consistent with this formulation, further support of this product is that the same complex is formed when [Ir(COD)(PMe$_3$)$_3$]Cl is allowed to react with a hydride reagent such as Li[Et$_3$BH] (eqn. (6)).



(5)



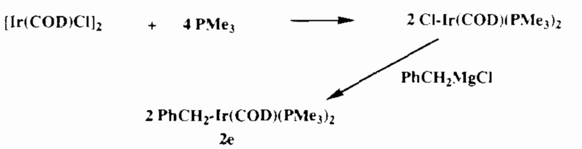
(6)

In the reactions shown in eqns. (5) and (6), the stereochemistry of the added hydride is not known. An attempt was made to use deuterium labeling to determine the stereochemistry of the addition using lithium triethylborodeuteride. However, the results from this experiment were inconclusive and no stereochemical information could be obtained.

The results discussed above point to the existence of at least three different pathways for the reaction of carbanions with [Ir(COD)(PMe$_3$)$_3$]Cl. We were interested in probing these reactions a little more deeply to determine if there was a common pathway leading to all three types of products or if all three reactions have totally independent paths. One possibility is that all carbanions initially attack the iridium forming

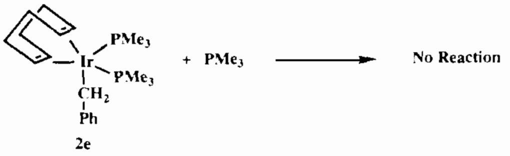
$RIr(COD)(PMe_3)_2$ compounds. Then, indenyl, benzyl and allyl will migrate to the COD while alkyl and vinyl groups will not. The stereochemistry of the final product as evidenced by the crystal structure of the benzyl addition product would suggest that this is *not* the case, but several experiments were performed to address this question further.

In order to determine if benzyl (or any of the groups that attacked the coordinated double bond of COD) would migrate from iridium to COD, we had need to prepare $PhCH_2Ir(COD)(PMe_3)_2$ (**2e**). We found that we could easily prepare **2e** by the sequence of reactions depicted in eqn. (7).



(7)

With **2e** in hand, we could explore if there were any conditions under which the benzyl ligand may be induced to migrate from iridium to COD. Treatment of **2e** with PMe_3 at room temperature does *not* result in the migration of the benzyl groups (eqn. (8)). The basic reaction shown in eqn. (8) was attempted with one equivalent of PMe_3, with a large excess of PMe_3, at room temperature, at elevated temperatures, in different solvents, and in the presence of $MgCl_2$ (as would be present in the Grignard solutions). In no case were we able to observe the migration of the benzyl group from iridium to COD.

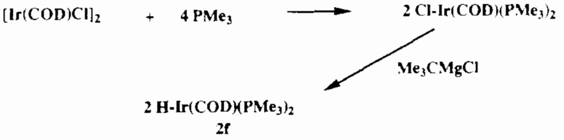


(8)

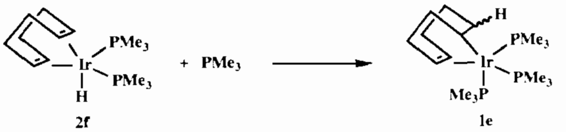
In addition, carrying out the reaction between MeMgCl and $[Ir(COD)(PMe_3)_3]Cl$ in the presence of a large excess of PMe_3 resulted in the reaction slowing down considerably. While careful kinetic measurements were not made, the difference in yield of the product obtained after the same reaction time was striking (30 versus 90%). Moreover, the only other iridium material isolated from this reaction mixture was unreacted $[Ir(COD)(PMe_3)_3]Cl$. So, slowing down the attack on iridium in this case does not open up the attack on the COD ligand. On the other hand, reaction between lithium indenide and $[Ir(COD)(PMe_3)_3]Cl$ in the presence of a large excess of PMe_3 does not effect the reaction in all: the same, high yield of product derived from addition to a COD double bond is found both in the presence and absence of excess PMe_3.

These results, along with the stereochemistry of the addition products, would suggest that, once the iridium–carbon bond is formed in this system, migration does not take place and that attack of the carbanion on iridium is not a common path in these two reactions. They also indicate that there is not a simple kinetic discrimination between two different pathways.

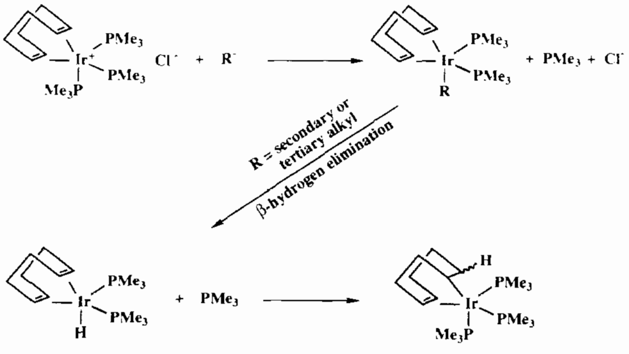
Some reactions were performed in an attempt to uncover the nature of the reactions between $[Ir(COD)(PMe_3)_3]Cl$ and secondary and tertiary carbanions. Again, the question is: do these carbanions first attack the iridium in the same manner as the other alkyl anions which result in stable iridium alkyl products? One can envision that the secondary and tertiary alkyl iridium compounds would be unstable with respcct to β-hydride elimination yielding an iridium hydride which could then migrate to the COD. In order to test this, it was necessary to synthesize $H-Ir(COD)(PMe_3)_2$ (**2f**), which could be made via the sequence shown in eqn. (9). Note here that the use of t-butylmagnesium chloride to yield the iridium hydride **2f** gives support to the hypothesis that these iridium alkyls are unstable with respect to β-hydride elimination. Treatment of **2f** with PMe_3 results in the clean migration of H from iridium to COD (eqn. (10)). These results lead to a view of the reaction of $[Ir(COD)(PMe_3)_3]Cl$ with certain simple carbanions as shown in Scheme 1. While a true migratory insertion reaction must give the product with the migrated H *endo* with respect to the metal, we do not have any hard evidence that this is the case.



(9)



(10)



Scheme 1.

It is not unreasonable to conclude that reaction between alkyl carbanions do have a common path in that they all initially attack the metal with loss of PMe_3. The primary alkyl iridium compounds appear to be stable while the secondary and tertiary alkyl iridium compounds undergo β-hydride elimination forming a hydridoiridium compound. GC analysis of the reaction mixture from the addition of cyclohexylmagnesium chloride and $[Ir(COD)(PMe_3)_3]Cl$ unambiguously showed the presence of cyclohexene. The alkyliridium compounds once formed do not undergo alkyl migration reactions and so are the final products. The hydridoiridium complex, however, reacts with PMe_3 that was liberated in the first step of the reaction to form the product derived from migration of H from iridium to COD.

This study leaves one very crucial question unanswered: why do some carbanions attack the COD double bond while others attack the metal? Examination of the two types of anions shows an important difference between them: those that attack the metal are simple, unstabilized carbanions such as methyl, ethyl and vinyl. On the other hand, those that attack the coordinated COD are resonance stabilized carbanions: benzyl, indenyl and allyl. A similar behaviour had previously been reported for the attack of nucleophiles on allylpalladium complexes [15].

At this point, unfortunately, we can only offer speculation. Several theoretical studies have been done on the reaction of nucleophiles with coordinated olefins [16], but there is little available from those studies to explain the effect of the nucleophile. Some of the observations made in this study are reminiscent of discussions of the role of electron transfer in the reactions of Grignard reagents and lithium reagents with ketones. Clearly, more experimental work must be done in order to fully understand the effect of the nucleophile on these reactions.

Conclusions

Due to the stoichiometric nature of the reaction of carbanions with $[Ir(COD)(PMe_3)_3]Cl$ as well as the complexity of the reaction, there is little prospect of turning this system into one that has some synthetic utility. Nevertheless, this system has provided some intriguing information on the nature of the reaction of nucleophiles with coordinated double bonds. Future studies are planned that will delve into the mechanisms involved in the reactions discussed above.

Supplementary material

Complete details of the X-ray structural determination of **1c** including complete listings of bond lengths and angles, anisotropic thermal parameters, and structure factor tables are available from the corresponding author.

Acknowledgements

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