ELSEVIER

Inorganica Chimica Acta 240 (1995) 135–143

Inorganica Chimica Acta

# The synthesis and reactivity of electrophilic iridium(III) complexes containing bis(diphenylphosphino)ethane ☆

Brian P. Cleary, Richard Eisenberg *

*Department of Chemistry, University of Rochester, Rochester, NY 14627, USA*

Received 7 January 1995; revised 3 May 1995

## Abstract

The complex $Ir(CH_3)(CO)(CF_3SO_3)_2(dppe)$ (**1**) has been synthesized from the reaction of $Ir(CH_3)I_2(CO)(dppe)$ and silver triflate. Methane and $IrH(CO)(CF_3SO_3)_2(dppe)$ (**2**) are formed when a methylene chloride solution of **1** is placed under 760 torr dihydrogen. Conductivity studies indicate that methylene chloride solutions of complexes **1** and **2** are weak electrolytes and only partially ionized at concentrations above 1 mM. Complex **2** is an effective hydrogenation catalyst for ethylene and 1-hexene while acetone hydrogenation is inhibited by the formation of $[IrH_2(HOCH(CH_3)_2)(CO)(dppe)](OTf)$ (**3**). Linear dimerization and polymerization of styrene occurs via a carbocationic mechanism initiated by triflic acid elimination from **2**. Treatment of an acetonitrile solution of $Ir(CH_3)I_2(CO)(dppe)$ with silver hexafluorophosphate produces the solvent promoted carbonyl insertion product $[Ir(C(O)CH_3)(NCCH_3)_3(dppe)][PF_6]_2$ (**7**) which readily undergoes deinsertion in methylene chloride to form $[Ir(CH_3)(CO)(NCCH_3)_2(dppe)][PF_6]_2$ (**8**) and acetonitrile.

*Keywords:* Catalysis; Hydrogenation; Polymerization; Iridium complexes; Carbonyl complexes; Hydride complexes; Alkyl complexes

## 1. Introduction

Much of the chemistry surrounding organometallic complexes of the platinum group metals has been concerned with reactions involving hydrogenation, hydrosilation and hydroformylation [1,2]. These reactions are well understood and are made possible by the ability of complexes of these metals to undergo oxidative addition and reductive elimination reactions. Recently, interest has been directed toward the preparation of late transition metal electrophilic complexes and investigation of their reaction chemistry. Examples include olefin/CO copolymerization catalyzed by Pd(II) and Rh(I) complexes [3–11], oligomerization of ethylene promoted by Cp* (Cp* = pentamethylcyclopentadienide) and triazanonane complexes of Rh(III), and styrene dimerization and polymerization catalyzed by cationic complexes of Pd(II) [12–18]. These studies have stimulated us to investigate the electrophilic behavior of cationic di(phosphine) iridium(III) complexes having labile ligands. Herein we report the synthesis and characterization of several iridium(III) complexes containing the chelating di(phosphine) ligand dppe (dppe = 1,2-bis(diphenylphosphino)ethane). These complexes, which are found to be weak electrolytes in dichloromethane, activate molecular hydrogen, and one of them serves as a source of strong Brønsted acid that promotes the linear dimerization and polymerization of styrene.

## 2. Results and discussion

### 2.1. Formation of $Ir(CH_3)(CO)(OTf)_2(dppe)$ (1)

The complex $Ir(CH_3)(CO)(OTf)_2(dppe)$ (**1**), (OTf = trifluoromethanesulfonate) is synthesized by the addition of 2.1 equiv. of AgOTf to a methylene chloride solution of $Ir(CH_3)I_2(CO)(dppe)$ [1] [19] under $N_2$ as shown in Eq. (1). After crystallization from methylene chloride/hexanes, the product is isolated in 73% yield as an analytically pure white powder. Spectroscopic characterization of **1** reveals a terminal $\nu(CO)$ of 2100 $cm^{-1}$, IR bands characteristic of coordinated triflate, a $^1H$ resonance at 0.52 ppm (dd, $^3J(H–P) = 6.2, 2.0$ Hz) corresponding to coordinated $CH_3$ and two $^{31}P$ signals at 23.12 and 11.43 ppm (d, $^2J(P–P) = 7.5$ Hz) for inequivalent phosphine donors of the dppe ligand. Based on these results and related spectroscopic char-

---

☆ Dedicated to Professor Fred Basolo for his personal friendship and ageless leadership and support of inorganic chemistry around the world.

* Corresponding author.

[1] Synthesized by the oxidative addition of excess methyl iodide to a methylene chloride solution of IrI(CO)(dppe).

*SSDI* 0020-1693(95)04527-G

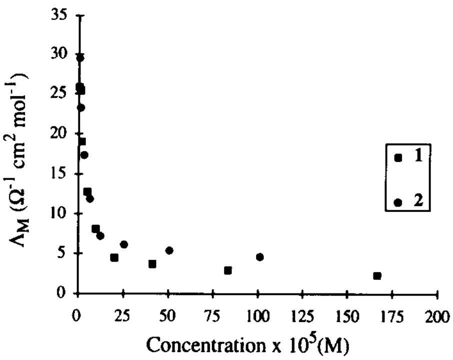
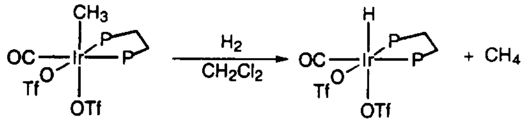


Fig. 1. Plot of molar conductivity ($\Lambda_M$) dependence on concentration (C) of $Ir(CH_3)(CO)(OTf)_2(dppe)$ (**1**) and $IrH(CO)(OTf)_2(dppe)$ (**2**).

acterization of $Ir(CH_3)I_2(CO)(dppe)$, it is possible to assign the coordination geometry unambiguously to that shown in Eq. (1). A similar synthesis has been reported by Atwood and co-workers for the preparation of the related $Ir(CH_3)(CO)(OTf)_2(PPh_3)_2$ complex from the corresponding diiodide precursor [20].



(1)

**1** **2**

As shown in Fig. 1, complex **1** shows a marked dependence of molar conductivity on concentration consistent with the behavior of a weak electrolyte [21]. Through the use of Ostwald's Dilution Law given by Eq. (2) [21], the equilibrium constant $K_{eq}$ for the dissociation equilibrium shown in Eq. (3) has been determined to be $1.51\times10^{-5}$ M in $CH_2Cl_2$ solution at 296 K. For a 1.7 mM solution of **1**, this corresponds to 9.1% ionization [22–24]. Based on the conductivity results, we conclude that whereas very dilute solutions of complex **1** exist in primarily dissociated form as $[Ir(CH_3)(CO)(OTf)(dppe)]^+$ and $OTf^-$, solutions above 1 mM concentration are only partially ionized according to Eq. (3).

$$K_{eq}=\frac{(\Lambda'_M/\Lambda_M)^2}{1-(\Lambda'_M/\Lambda_M)}\times C \qquad (2)$$

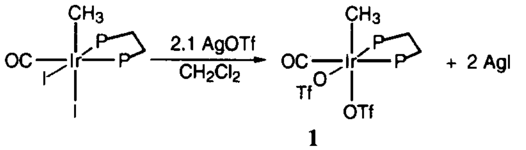
where $\Lambda'_M$ = molar conductivity at infinite dilution, $\Lambda_M$ = observed molar conductivity, C = concentration

$$Ir(R)(CO)(OTf)_2(dppe) \overset{K_{eq}}{\rightleftharpoons} [Ir(R)(CO)(OTf)(dppe)]^+ + (TfO)^- \qquad (3)$$

$R=CH_3$; **1**, H; **2**

### 2.2. Reaction of 1 with dihydrogen; formation of $IrH(CO)(OTf)_2(dppe)$ (2)

A $CH_2Cl_2$ solution of **1** reacts rapidly with dihydrogen (600–760 torr) at room temperature yielding methane and the analytically pure mono-hydride complex **2**, as shown in Eq. (4). Complex **2** is characterized by IR and NMR



(4)

**1**

spectroscopies, and by conductivity measurements. Spectroscopic characterization of **2** indicates a terminal $\nu(CO)$ of 2108 $cm^{-1}$, a $\nu(Ir\text{–}H)$ of 2061 $cm^{-1}$, IR bands characteristic of coordinated triflate, a $^1H$ NMR resonance at $-23.39$ ppm (dd, $^2J(H\text{–}P)=17.0$, 13.6 Hz) corresponding to a terminal hydride ligand and two $^{31}P$ NMR signals at 35.82 and 22.04 ppm (d, $^2J(P\text{–}P)=7.5$ Hz) for inequivalent *cis*-phosphine donors. As shown in Fig. 1, complex **2** is only partially ionized at concentrations above 1 mM.

The mechanism by which **1** generates **2** is of interest since **1** is a $d^6$ Ir(III) system that is formally coordinatively saturated and unlikely to activate $H_2$ by traditional oxidative addition chemistry. Since conductivity results indicate that a facile equilibrium between neutral and ionized forms of **1** in methylene chloride exists, the vacant site required for reaction is generated in this manner, after which reaction with $H_2$ occurs. Similarly, Burger and Bergman have shown that an equilibrium between neutral and ionized $Cp^*Ir(CH_3)(PMe_3)(OTf)$ is responsible for its observed reactivity with silanes and methane [25]. As shown in Fig. 2, we can envision three modes of reaction of $H_2$ with the resultant $[Ir(CH_3)(CO)(OTf)(dppe)]^+$ complex: (i) concerted $H_2$ oxidative addition yielding an Ir(V) intermediate which forms **2** after reductive elimination of methane and coordination of free $TfO^-$; (ii) concerted heterolytic dihydrogen activation via a four-membered transition state, which scissions to produce methane and the hydride complex

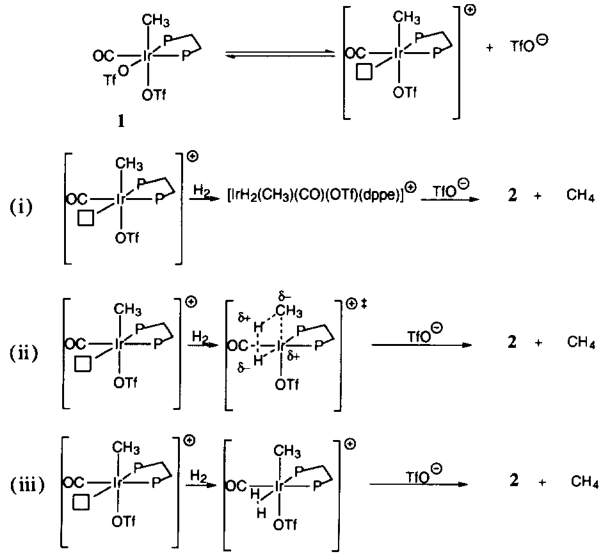


Fig. 2. Possible mechanisms for the formation of **2** from **1** + $H_2$ via oxidative addition (i), σ-bond metathesis (ii) and formation of a cationic molecular hydrogen complex (iii).

[26–33]; and (iii) formation of a cationic molecular hydrogen complex, $[Ir(H_2)(CH_3)(CO)(OTf)(dppe)]^+$, that serves as a source of strong acid to protolyze the Ir–$CH_3$ bond giving $CH_4$ and, upon $TfO^-$ recoordination, the hydride complex **2**. To date, no reaction intermediates have been observed when the reaction is monitored by NMR spectroscopy at temperatures as low as 190 K. While it is not possible at this time to provide experimental evidence for or against the three possible modes of $H_2$ addition, we strongly favor the notion of a cationic dihydrogen intermediate based on the known reaction chemistry of cationic dihydrogen systems that clearly show the dihydrogen ligand to be highly acidic and capable of protolyzing metal–alkyl bonds [34–38].

### 2.3. *Formation of 2-$d_1$ from 2 and $D_2$; evidence for reversible hydrogen/hydride exchange*

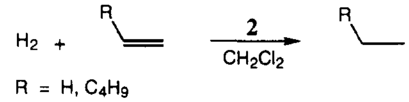
The addition of $D_2$ (700 torr) to a $CD_2Cl_2$ solution of **2** leads to the quantitative formation **2-d₁** after 1 day as evidenced by the disappearance of the hydride signal for **2** and the appearance of a 1:1:1 triplet at 4.57 ppm ($^1J$(H–D) = 42 Hz) for HD in the $^1$H NMR spectrum. Deuterium incorporation into the hydride ligand indicates that **2** reversibly reacts with $H_2$, although under *para*-hydrogen it does not exhibit the PHIP effect [39–43].

Since conductivity results support a facile equilibrium between neutral and ionized forms of **2** in methylene chloride, the same mechanisms used to explain the reaction of **1** with $H_2$ can be employed to rationalize the formation of **2-d₁**. However, in an alternative mechanism, $H^+$ is eliminated from $[IrH(CO)(OTf)(dppe)]^+$ yielding an Ir(I) intermediate that forms $[IrD_2(CO)(OTf)(dppe)]$ after $D_2$ oxidative addition. Complex **2-d₁** and HD then form upon protolysis of one of the Ir–D bonds in $[IrD_2(CO)(OTf)(dppe)]$ by in situ generated triflic acid. Evidence for the generation of strong acid from $IrH(CO)(OTf)_2(dppe)$ is provided by monitoring a THF solution of **2** under 700 torr $H_2$. After 6 h at room temperature, the viscosity of the solvent increases significantly and after 24 h the solvent is completely solidified. These observations indicate that a hydride ligand originating from **2** is acidic enough to catalyze the ring opening polymerization of THF.

The question of how acid is eliminated from **2** is intriguing since hydride ligands of iridium are considered to be weak Brønsted acids. Two possibilities accounting for the generation of acid from **2** are: (i) concerted reductive elimination yielding triflic acid and an Ir(I) intermediate; and (ii) dissociation of $TfO^-$ generating $[IrH(CO)(OTf)(dppe)]^+$ which upon deprotonation results in $H^+$ and Ir(CO)(OTf)(dppe). Since conductivity results indicate a facile equilibrium between neutral and ionized forms of **2**, it is most reasonable to conclude that $H^+$ originates from $[IrH(CO)(OTf)(dppe)]^+$. Although hydride ligands of iridium are generally thought of as weak Brønsted acids, certain ionic hydride species have significantly increased acidities over their neutral analogs. For example, the ionic hydride complex, *cis*-$[(dfepe)_2IrH_2]OTf$ (dfepe = 1,2-bis(dipentafluoroethylphosphino)ethane), is deprotonated to $(dfepe)_2IrH$ by mild bases such as diethyl ether or acetone and is regenerated by the addition of excess triflic acid [44]. Further reactivity trends (vide infra) will establish that the hydride ligand of **2** is best viewed as a strong Brønsted acid.

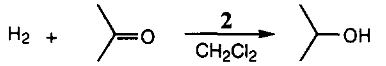
### 2.4. *Hydrogenation reactions with 2; formation of $[IrH_2(HOCH(CH_3)_2)(CO)(dppe)](OTf)$ (3), from acetone hydrogenation*

Complex **2** catalyzes the hydrogenation of olefins in methylene chloride under mild conditions (730 torr $H_2$, 25 °C) (Eq. (5)). Ethylene (200 torr) is quantitatively hydrogenated to ethane at a rate of 120 turnovers/h while 1-hexene is converted to n-hexane at a rate of 52 turnovers/h. These reactions produce no observable iridium containing intermediates as determined by NMR spectroscopies but a small amount of internal olefin is formed during 1-hexene hydrogenation.



(5)

As shown in Eq. (6), the hydrogenation of acetone to 2-propanol is catalyzed by methylene chloride solutions of **2**.



(6)

In two recent reports, organometallic complexes possessing highly acidic hydride ligands promote both hydrogenation and H/D exchange reactions with ketones [45,46]. Here we propose a similar mechanism for acetone hydrogenation, namely protonation of the ketone oxygen by $[IrH(CO)(OTf)(dppe)]^+$ which generates a secondary carbocation that is subsequently reduced to 2-propanol by hydride transfer. The hydrogenation of acetone to 2-propanol initially proceeds at a modest rate of 13 turnovers/h but the reaction ceases after ~20 h. Examination of $^1$H and $^{31}$P{$^1$H} NMR spectra of the reaction solution during hydrogenation indicates that a new iridium complex (**3**) is formed at the same rate as 2-propanol. Plots of 2-propanol and complex **3** formation versus time are shown in Fig. 3.

Complex **3** is assigned as the 2-propanol complex $[IrH_2(HOCH(CH_3)_2)(CO)(dppe)](OTf)$ based on $^1$H and $^{31}$P{$^1$H} NMR spectroscopies. In the $^1$H NMR spectrum, a separate resonance at 7.79 ppm is present for two *ortho*-phenyl protons while the remaining eighteen dppe phenyl protons appear as overlapping multiplets between 7.66 and 7.30 ppm. The four dppe methylene protons are displayed as two 1:1 multiplets at 3.13 and 2.83 ppm while the coordinated 2-propanol ligand displays a broad singlet at 6.45 ppm, a septet ($^3J$(H–H) = 6.2 Hz) at 3.63 ppm and a doublet ($^3J$(H–H) = 6.2 Hz) at 1.08 ppm in a 1:1:6 ratio respectively. Resonances at −9.81 ppm (ddd, $^2J$(H–P) = 107.7, 13.6 Hz, $^2J$(H–H) = 2.1 Hz) and −10.85 ppm (ddd, $^2J$(H–P) = 15.8,

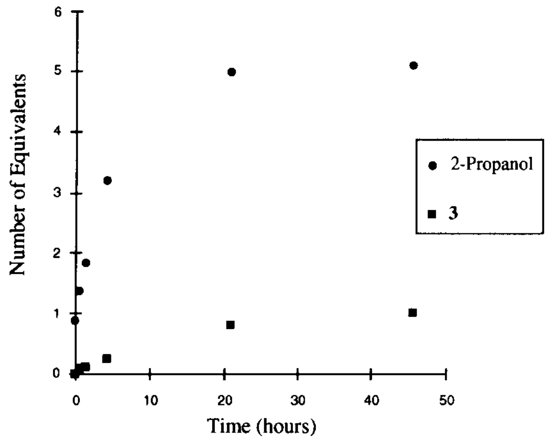
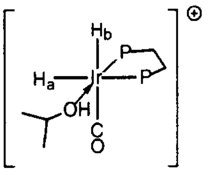


Fig. 3. Plot of the number of equiv. (with respect to **2**) of 2-propanol and **3** produced vs. time during hydrogenation of acetone by **2**.

14.5 Hz, $^2J$(H–H) = 2.1 Hz) are present for the hydride ligands $H_a$ and $H_b$, respectively, where based on $^2J$(H–P), the former is *trans* and *cis* to the two dppe phosphorus nuclei while the latter is *cis* to both phosphorus nuclei. The $^{31}P\{^1H\}$ NMR spectrum of **3** displays two doublets ($^2J$(P–P) = 2.4 Hz) at 28.59 and 23.79 ppm consistent with two inequivalent *cis*-phosphorus nuclei. Based on the spectroscopy, and a comparison of the chemical shift of $H_b$ with other hydride resonances found in known $IrH_nX_{(3-n)}(CO)(dppe)$ ($n$ = 3, 2, 1; X = I, Br, Cl) complexes with *trans* H–Ir–(CO) arrangements [47–50], the stereochemistry of **3** is most consistent with $H_b$ *trans* to CO as illustrated below.

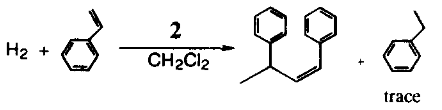


**3**

A reasonable mechanism to account for the formation of **3** is shown in Fig. 4. Elimination of triflic acid from **2** generates the four-coordinate Ir(I)-triflate intermediate (**A**) which undergoes oxidative addition of dihydrogen to yield the dihydride intermediate **B**. Complex **3** is formed from **B** after triflate displacement by 2-propanol.

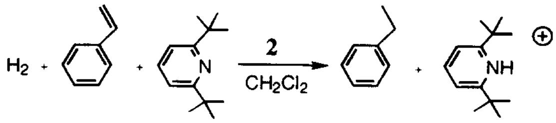
### 2.5. *Acid catalyzed dimerization and polymerization of styrene via triflic acid elimination from 2*

The reaction of a methylene chloride solution of **2**, styrene (10–50 equiv.) and $H_2$ (760 torr) leads to the *cis*-linear dimer, 1,3-diphenyl-1-butene in 80% yield, and surprisingly only a trace of ethylbenzene, Eq. (7).



(7)

The dimerization of styrene to 1,3-diphenyl-1-butene can be envisioned to occur by either of the following two electrophilic mechanisms: attack by a cationic complex of Ir(III) on styrene, or attack by a strong Brønsted acid on styrene. To determine if the strong acid is responsible for the dimerization, the reaction was carried out in the presence of 2,6-di-t-butylpyridine (DTBP) which is recognized as an efficient proton scavenger. During the reaction, a broad triplet at 12.25 ppm ($^2J$(H–N) = 60 Hz) is observed in the $^1H$ NMR spectrum corresponding to $H(DTBP)^+$ and after complete styrene consumption, ethylbenzene is the only organic product generated according to Eq. (8). Two important conclusions result from this experiment. First, since dimerization is halted when DTBP is present, the reaction proceeds via generation of a Brønsted acid, the identity of which is most likely triflic acid eliminated from **2**. Second, the production of ethylbenzene indicates prior coordination of styrene to the iridium(III) center.



8)

While the dimerization of styrene proceeds via protonation and the intermediacy of the styryl cation, the role of the iridium complex subsequent to acid elimination was not apparent. The styryl cation can react with either free styrene or coordinated styrene to generate the dimer product. To further elucidate the role of the metal complex in this reaction, the optically active diphosphine chiraphos (chiraphos = (2*S*, 3*S*)-bis(diphenylphosphino)butane) was substituted for dppe to probe whether the *cis*-1,3-diphenyl-1-butene produced would possess any enantiomeric excess associated with the chirality at C3. If the product exhibited any net chirality, then involvement of coordinated styrene in the dimerization process would be required.

The complexes $Ir(CH_3)I_2(CO)(chiraphos)$ (**4**), $Ir(CH_3)(CO)(OTf)_2(chiraphos)$ (**5**) and $IrH(CO)(OTf)_2(chiraphos)$ (**6**) were synthesized similarly to the dppe analogs. As illustrated in Fig. 5, complexes **4**–**6** exist as diastereomeric pairs (**A** and **B**) resulting from chirality at the iridium center as well as on the chiraphos ligand [51].

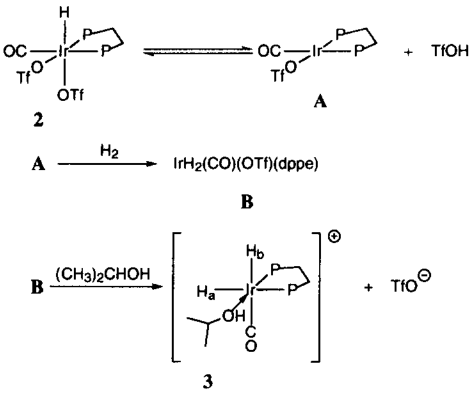
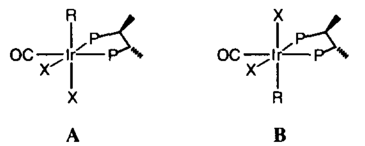


Fig. 4. Proposed mechanism for the formation of **3**.



4, R = $CH_3$, X = I

5, R = $CH_3$, X = TfO

6, R = H, X = TfO

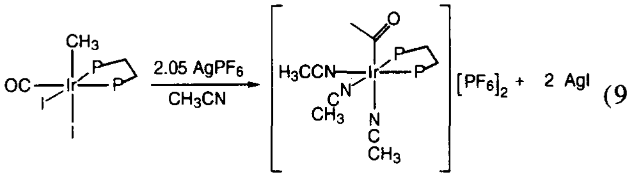
Fig. 5. Diastereomers for complexes **4**–**6**. Assignment of metal centered chirality to give **A** or **B** is arbitrary and does not necessarily correlate with the assignment of resonances described in Section 4.

Although assignment of the metal-centered chirality for the diastereomers is ambiguous at this time, the existence of more than one diastereomer for **6** should not affect the enantioselectivity of the *cis*-1,3-diphenyl-1-butene produced because chirality at C3 is determined by the approach of the styryl cation to the *exo* face of the coordinated olefin. The reaction of **6** with styrene was carried out, after which the catalyst was separated from the dimer. The organic fraction was then examined by polarimetry, but no optical activity was observed. Thus, the role of the metal complex in the dimerization of styrene appears to be solely as a source of strong Brønsted acid.

Further support for a carbonium ion/Brønsted acid mechanism was established by determining reactivity trends of $IrH(CO)(OTf)_2(dppe)$ (**2**), with styrene derivatives and styrene in more polar solvents and comparing the results to those known for reactions catalyzed by $H^+$ [52,53]. The reaction of a methylene chloride solution of $\alpha$-methylstyrene and **2** is less selective than the analogous reaction of styrene, leading to several di- and trimerization products. Furthermore, the rate of reaction is an order of magnitude faster for $\alpha$-methylstyrene which is consistent with previously reported reactivity trends for 3° versus 2° carbocations [52]. In nitromethane solution, **2** promotes the formation of polystyrene from styrene within minutes, once again consistent with a carbocation mechanism in a more polar solvent. Solvent polarity is one of the most important requirements for successful acid catalyzed polymerizations of olefins [52]. In the present case, nitromethane, a more polar solvent than methylene chloride, stabilizes the propagating polymer chain more efficiently resulting in polymer formation. An additional confirmatory result was obtained by the oligomerization of styrene in methylene chloride (0.50 ml) using neat triflic acid (0.5 μl). However, dilution studies to yield triflic acid concentrations on the order of those generated by **2** were not conducted.

### 2.6. *Synthesis of $[Ir(C(O)CH_3)(NCCH_3)_3(dppe)][PF_6]_2$ (7); effect of solvent on CO insertion*

Treatment of an acetonitrile solution of $Ir(CH_3)I_2(CO)(dppe)$ with 2.05 equiv. silver hexafluorophosphate leads to the formation of the acetyl complex **7** and silver iodide after stirring for 3 h in the dark (Eq. (9)). Following separation of silver iodide and crystallization from diethyl ether, **7** is isolated as an analytically pure white powder in 80% yield.

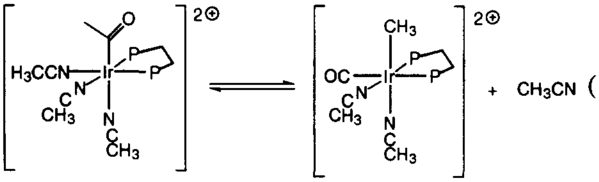


7

(9)

Ambient temperature spectroscopic characterization of **7** in acetonitrile reveals an acyl $\nu(CO)$ at 1656 $cm^{-1}$ in the IR spectrum, a singlet at 2.69 ppm in the $^1H$ NMR spectrum corresponding to the coordinated acetonitrile ligands *trans* to dppe, and a singlet at 2.29 ppm for the acetyl methyl group. Due to rapid exchange with $CD_3CN$, the coordinated acetonitrile *trans* to the acetyl ligand is not observed in the $^1H$ NMR spectrum but is accounted for as 1 equiv. of free acetonitrile at 1.94 ppm. Rapid exchange occurs even when a frozen sample of **7** is thawed in a dry ice/acetonitrile bath and immediately placed into a precooled NMR probe (−40 °C). Furthermore, when the $^1H$ NMR spectrum of **7** is monitored for ~5 min at room temperature, the singlet at 2.29 ppm disappears while the resonance for free acetonitrile increases indicating that the acetonitrile ligands *trans* to dppe also exchange with solvent. The $^{31}P\{^1H\}$ NMR spectrum of **7** shows a singlet for equivalent dppe phosphorus nuclei at 22.79 ppm and a septet at −144.61 ppm for the hexafluorophosphate counterion in a 2:2 ratio. Based on the spectroscopy and elemental microanalysis, the identity of **7** is most consistent with the dicationic octahedral iridium(III) complex, $[Ir(C(O)CH_3)(NCCH_3)_3(dppe)][PF_6]_2$, which possesses three facial acetonitrile ligands and an acetyl group.

An equilibrium between **7** and the decarbonylated complex **8** plus free acetonitrile is established when **7** is placed in $CD_2Cl_2$ as shown in Eq. (10). The methylene chloride solution IR spectrum of the equilibrium mixture displays a new strong absorption band at 2096 $cm^{-1}$ corresponding to the terminal $\nu(CO)$ for **8**. In the $^1H$ NMR spectrum of **8** two doublets of doublets are present for two inequivalent acetonitrile ligands at 2.74 ppm ($^5J(H–P)$ = 1.1, 0.8 Hz) and 2.05 ppm ($^5J(H–P)$ = 1.8, 0.5 Hz) while the terminal methyl group appears as a doublet of doublets ($^3J(H–P)$ = 5.1, 2.0 Hz) at 1.43 ppm. In the $^{31}P\{^1H\}$ NMR spectrum, two doublets ($^2J(P–P)$ = 7.6 Hz) are present for *cis* inequivalent dppe phosphorus nuclei of **8** while the hexafluorophosphate counterion of both species resonates as a septet at −144.61 ppm.



7 8

(10)

Low temperature $^1H$ NMR characterization of the equilibrium solution indicates that coordinated acetonitrile *trans* to the acetyl group in **7** undergoes facile exchange with free acetonitrile. The rate constant for this exchange process at the coalescence temperature of 10 °C is determined to be 345 $s^{-1}$ with a corresponding free energy of activation, $\Delta G^{\neq} = 6.9$ kcal $mol^{-1}$.

Solvent identity and concentration can greatly influence the rate of CO migratory insertion and deinsertion in metal alkyl complexes [54,55]. In a seminal kinetic study on $CH_3Mn(CO)_5$ it was determined that the mechanism of CO migratory insertion follows a two step process schematically shown as Eqs. (11) and (12) [56]. A qualitative understanding of these steps helps to rationalize why **7** is the only product formed in acetonitrile and why **7** and **8** exist in equilibrium

$$[M](CO)R \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} [M](C(O)R) \qquad (11)$$

$$[M](C(O)R) + L \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} [M](C(O)R)L \qquad (12)$$

in methylene chloride. The lability of the acetonitrile ligands (established above by $^1H$ NMR spectroscopy for $CD_3CN$ incorporation into **7**) suggests that $[Ir(C(O)CH_3)(NCCH_3)_2(dppe)]^+$, shown as [M](C(O)R) in Eq. (12), forms from $[Ir(C(O)CH_3)(NCCH_3)_3(dppe)]^{2+}$ shown as [M](C(O)R)L by the $k_{-2}$ pathway. Since no CO deinsertion is observed during solvent exchange, the rate at which acetonitrile traps $[Ir(C(O)CH_3)(NCCH_3)_2(dppe)]^+$ must be considerably faster than the rate of CO deinsertion from $[Ir(C(O)CH_3)(NCCH_3)_2(dppe)]^+$ ($k_2$[acetonitrile] $\gg k_{-1}$). This result is not unexpected since acetonitrile is present as the solvent and its concentration is very large. When the solvent is changed to methylene chloride, the concentration of acetonitrile is greatly reduced, resulting in an equilibrium between **7** and **8**. This observation suggests that when the concentration of acetonitrile is similar to the concentration of the metal complex, $k_{-1}$ becomes competitive with $k_2$[acetonitrile].

## 3. Summary

The preparation of electrophilic organometallic complexes of the platinum group metals has been a recent subject of chemical interest. Here we have described the reactivity of electrophilic complexes of Ir(III) that are easily prepared by treating solutions of $Ir(CH_3)I_2(CO)(dppe)$ with either AgOTf or $AgPF_6$. The unusual reactivity of $Ir(CH_3)(CO)(OTf)_2(dppe)$ (**1**), with hydrogen yielding $IrH(CO)(OTf)_2(dppe)$ (**2**), is facilitated by an equilibrium between neutral and ionized forms of **1** and is likely to occur via the formation of a molecular hydrogen complex which serves to protolyze the Ir–$CH_3$ bond originating from **1**. Complex **2** catalyzes the hydrogenation of olefins and in contrast to many hydride containing compounds of iridium, participates in the hydrogenation of acetone. Methylene chloride solutions of **2** promote the *cis*-linear dimerization of styrene while nitromethane solutions yield polystyrene. Both reactions with styrene are catalyzed by the elimination of strong acid from $[IrH(CO)(OTf)(dppe)]^+$. Since the chemical reactivity of **2** is dominated by facile elimination of $H^+$, the investigation of electrophilic reactions promoted by complexes of iridium(III) containing ligands other than hydride is warranted. Solvent promoted carbonyl migratory insertion accounts for the formation of **7** in acetonitrile but due to the lability of the acetonitrile ligands, **8** is generated in methylene chloride after facile CO deinsertion.

## 4. Experimental

Reactions and sample preparations were performed in a nitrogen filled glove box or under the appropriate gas using a high vacuum line or Schlenk line. All solvents were reagent grade or better and were dried and degassed by accepted methods [57]. Hydrogen (99.99%, Air Products), and carbon monoxide (99.3%, Air Products) were used as received. Methyl iodide (Fisher) was washed with a dilute aqueous solution of sodium thiosulfate, dilute aqueous sodium carbonate, water, and dried over calcium chloride. The iodine-free methyl iodide was distilled from a suspension of calcium hydride and stored under nitrogen in an amber vial over copper wire. Silver triflate (99+%, Aldrich) was used as received. Silver hexafluorophosphate (98%, Aldrich) was recrystallized from acetonitrile immediately prior to use. IrI(CO)(dppe) [49], IrI(CO)(chiraphos) [51] and $Ir(CH_3)I_2(CO)$dppe [19] were prepared according to literature procedures.

Most NMR samples were prepared using resealable NMR tubes fitted with J Young teflon valves (Brunfeldt) and high vacuum line adapters. Otherwise, samples were placed in NMR tubes with high vacuum line adapters and flame sealed after solvent transfer. Stoichiometric amounts of gases were delivered to NMR samples by measuring the volume of the NMR tubes and calculating the corresponding pressure using the ideal gas law. $^1H$, $^{13}C$ and $^{31}P$ NMR spectra were recorded at 400.13, 100.62 and 161.98 MHz, respectively, on a Bruker AMX 400 NMR spectrometer. Temperature control was achieved using a B-VT 1000 variable temperature unit with a Cu-Constantan temperature sensor and was calibrated for high and low temperatures using ethylene glycol and methanol standards, respectively. $^1H$ NMR chemical shifts are reported in ppm downfield of tetramethylsilane but measured from residual $^1H$ signal in the deuterated solvents. $^{13}C$ NMR spectra are reported in ppm downfield of tetramethylsilane and referenced to a known carbon signal in the solvent. $^{31}P$ NMR spectra are reported in ppm downfield of an external 85% solution of phosphoric acid. Methylene chloride-$d_2$ (Cambridge) was dried and distilled from a calcium hydride suspension. Acetonitrile-$d_3$ (Cambridge) was dried over $P_2O_5$ and distilled prior to use. Solution infrared spectra were recorded on a Matteson 6020 Galaxy FT-infrared spectrometer. Molar conductivities were obtained using a YSI model 31 conductivity bridge with a FisherBrand dip type conductivity cell and were calibrated relative to 0.1 M aqueous KCl. Elemental analyses were performed by Desert Analytics Laboratory, Tucson, Az.

### *4.1. $Ir(CH_3)(CO)(OTf)_2(dppe)$ (1)*

To a methylene chloride (30 ml) solution of $Ir(CH_3)I_2(CO)(dppe)$ (0.10 g, 0.113 mmol) was added a methylene chloride suspension (10 ml) of 2.1 equiv. of silver triflate (0.061 g, 0.237 mmol). The mixture immediately turned bright yellow as silver iodide precipitated from solution. After 15 min of stirring, the reaction mixture was decanted, the residue washed with methylene chloride (3 × 5 ml), and the combined filtrates were passed through a glass wool column (0.6 cm diameter x 4 cm long) to remove any remaining silver iodide. The volume of the solvent was reduced to 5 ml and the product was precipitated after the addition of 50 ml hexanes. Recrystallization from methylene chloride/hexanes afforded **1** in 73% yield.

Spectroscopic data for **1**: IR ($CH_2Cl_2$, $cm^{-1}$): 2100 ($\nu$(CO)); $^1$H NMR ($CD_2Cl_2$): $\delta$7.88 (dd, 2H, *o*-Ph), 7.70–7.38 (overlapping m, 18H, Ph), 3.22–2.85 (m, 3H, $-PCH_2CHHP-$), 2.76 (m, 1H, $-PCH_2CHHP-$), 0.52 (dd, $^3J$(H–P) = 6.2, 2.0 Hz, 3H, $-CH_3$); $^{31}P\{^1H\}$ NMR ($CD_2Cl_2$): $\delta$ 23.12 (d, $^2J$(P–P) = 7.5 Hz), 11.43 (d, $^2J$(P–P) = 7.5 Hz); $^{13}C\{^1H\}$ NMR ($CD_2Cl_2$): $\delta$169.29 (dd, $^2J$(C–P) = 137, 8 Hz, CO), −20.51 (t, $^2J$(C–P) = 4 Hz, $CH_3$). Conductivity: $\Lambda_{M\infty}$ ($CH_2Cl_2$) = 25.7 $\Omega^{-1}$ cm$^2$ mol$^{-1}$. *Anal.* Calc. for $C_{30}H_{27}F_6IrO_7P_2S_2$: C, 38.67; H, 2.90. Found: C, 38.26; H, 2.91%.

### *4.2. $IrH(CO)(OTf)_2(dppe)$ (2)*

To a degassed methylene chloride (10 ml) solution of **1** (0.05 g, 0.0537 mmol) was added 760 torr dihydrogen. The solution was stirred for 5 min followed by the addition of 50 ml hexanes under hydrogen. The volume of the solution was reduced under a stream of hydrogen and the product was isolated on a Schlenk frit. Complex **2** was recrystallized from methylene chloride/hexanes under hydrogen and isolated as a white solid in 60% yield. Contact of **2** with oxygen containing solvents should be avoided as they are readily protonated.

Spectroscopic data for **2**: IR ($CH_2Cl_2$, $cm^{-1}$): 2108 (CO), 2061 (Ir–H); $^1$H NMR ($CD_2Cl_2$): $\delta$ 7.74 (dd, 2H, *o*-Ph), 7.68–7.46 (overlapping m, 18H, Ph), 3.22 (m, 1H, $-PCHHCH_2P-$), 2.98 (m, 1H, $-PCHHCH_2P-$), 2.50 (overlapping m, 2H, $-PCH_2CH_2P-$), −23.39 (dd, $^2J$(H–P) = 17.0, 13.6 Hz, 1H, Ir–H); $^{31}P\{^1H\}$ NMR ($CD_2Cl_2$): $\delta$ 35.82 (d, $^2J$(P–P) = 6.0 Hz), 22.04 (d, $^2J$(P–P) = 6.0 Hz); $^{13}C\{^1H\}$ NMR ($CD_2Cl_2$): $\delta$ 169.21 (dd, $^2J$(C–P) = 127, 8 Hz, CO). Conductivity: $\Lambda_{M\infty}$ ($CH_2Cl_2$) = 29.5 $\Omega^{-1}$ cm$^2$ mol$^{-1}$. *Anal.* Calc. for $C_{29}H_{25}F_6IrO_7P_2S_2$: C, 37.95; H, 2.73. Found: C, 38.15; H, 2.99%.

### *4.3. Hydrogenation reactions with 2*

Typical experiments employed a 5 mM $CD_2Cl_2$ degassed solution of the precatalyst **1** in a resealable NMR tube to which was added 10–100 fold molar equiv. of substrate and 730 torr hydrogen. Fresh hydrogen was periodically placed over those reactions not involving ethylene. Reaction progress was monitored by $^1$H NMR spectroscopy. Identity of hydrogenation products was confirmed by comparison of the $^1$H NMR spectra to authentic samples, and by GC/MS. For experiments involving ethylene, the $CD_2Cl_2$ solution of **1** was put through 3 freeze/pump/thaw cycles on a high vacuum line prior to the addition of 500 torr of ethylene. The solution was frozen in a liquid $N_2$ bath immediately prior to the addition of 730 torr hydrogen.

### *4.4. Spectroscopic data for $[IrH_2(HOCH(CH_3)_2)(CO)(dppe)](OTf)$ (3)*

$^1$H NMR ($CD_2Cl_2$): $\delta$ 7.79 (dd, 14.1, 7.1 Hz, 2H, *o*-Ph), 7.66–7.30 (m, 18H, Ph), 6.45 (broad s, 1H, $-OH$), 3.63 (sept, 6.2 Hz, 1H, $(CH_3)_2CH-$), 3.13 (m, 2H, $-PCH_2$-$CH_2P-$), 2.83 (m, 2H, $-PCH_2CH_2P-$), 1.08 (d, 6.2 Hz, 6H, $(CH_3)_2CH-$), −9.81 (ddd, 107.7, 13.6, 2.5 Hz, 1H, Ir–H), −10.85 (ddd, 15.8, 14.5, 2.1 Hz, 1H, Ir–H); $^{31}P\{^1H\}$ NMR ($CD_2Cl_2$): $\delta$ 28.59 (d, $^2J$(P–P) = 2.4 Hz), 23.79 (d, $^2J$(P–P) = 2.4 Hz).

### *4.5. $Ir(CH_3)I_2(CO)(chiraphos)$ (4A), (4B)*

To a 50 ml round bottom flask containing a stirbar, 0.45 g (0.582 mmol) of IrI(CO)(chiraphos) and 20 ml of methylene chloride was added 10 equiv. of methyl iodide (0.37 ml, 5.820 mmol) The color immediately lightened from dark orange to yellow–orange and after 1 h of stirring a yellow solution was present. The volume of the solvent was reduced to 10 ml followed by the addition of 10 ml of hexanes. Complexes **4A** and **4B** were isolated in a 1:0.7 ratio, respectively as a cream colored powder in 89% combined yield after washing with hexanes (3 × 2 ml) and being dried in vacuo.

Spectroscopic data for **4A**: $^1$H NMR ($CD_2Cl_2$): $\delta$ 8.26 (m, 2H, *o*-Ph), 7.62 (m, overlapping Ph), 7.35 (m, overlapping Ph), 3.12 (m, 1H, $-PC(CH_3)HC(CH_3)HP-$), 3.02 (m, 1H, $-PC(CH_3)HC(CH_3)HP-$), 1.31 (dd, $^3J$(H–P) = 12.2, $^4J$(H–P) = 6.8 Hz, 3H, $-PC(CH_3)HC(CH_3)HP-$), 1.00 (dd, $^3J$(H–P) = 13.0, $^4J$(H–P) = 5.4 Hz, 3H, $-PC(CH_3)$-$HC(CH_3)HP-$), 0.76 (dd, $^3J$(H–P) = 4.8, 4.2 Hz, 3H, $-CH_3$); $^{31}P\{^1H\}$ NMR ($CD_2Cl_2$): $\delta$ 21.52 (d, $^2J$(P–P) = 13.3 Hz), 3.34 (d, $^2J$(P–P) = 13.3 Hz).

Spectroscopic data for **4B**: $^1$H NMR ($CD_2Cl_2$): $\delta$ 8.18 (m, 2H, *o*-Ph), 7.87 (dd, 2H, *o*-Ph), 7.62 (m, overlapping Ph), 7.35 (m, overlapping Ph), 7.25 (dd, 2H, *o*-Ph), 6.95 (dd, 2H, *o*-Ph), 3.93 (m, 1H, $-PC(CH_3)HC(CH_3)HP-$), 2.65

(m, 1H, -PC($CH_3$)HC($CH_3$)*H*P–), 1.25 (dd, $^3J$(H–P) = 12.7, $^4J$(H–P) = 6.8 Hz, 3H, -PC(C*H*$_3$)HC($CH_3$)HP–), 1.16 (dd, $^3J$(H–P) = 4.8, 2.8 Hz, 3H, –C*H*$_3$), 0.99 (dd, $^3J$(H–P) = 13.8, $^4J$(H–P) = 6.8 Hz, 3H, –PC($CH_3$)-HC(C*H*$_3$)HP–); $^{31}P\{^1H\}$ NMR ($CD_2Cl_2$): $\delta$ 20.54 (d, $^2J$(P–P) = 13.3 Hz), 2.63 (d, $^2J$(P–P) = 13.3 Hz).

### 4.6. *Ir($CH_3$)(CO)(OTf)$_2$(chiraphos) (5A), (5B)*

To a 50 ml round bottom flask containing a stirbar, 0.45 g (0.492 mmol) Ir($CH_3$)$I_2$(CO)(chiraphos) (**4A**) and (**4B**), and 20 ml methylene chloride was added a methylene chloride suspension (10 ml) of 2.1 equiv. silver triflate (0.266 g, 1.033 mmol). The mixture immediately turned bright yellow as silver iodide precipitated from solution. After 15 min of stirring, the reaction mixture was decanted, the residue washed with methylene chloride (3×5 ml), and the combined filtrates were passed through a glass wool column (0.6 cm diameter x 4 cm long) to remove any remaining silver iodide. An oil was produced following volume reduction to 10 ml and the addition of 10 ml hexanes. After trituration with hexanes, a white solid was obtained which upon recrystallization from methylene chloride/hexanes afforded complexes **5A** and **5B** in 60% combined yield in a 1:0.8 ratio respectively.

Spectroscopic data for **5A**: $^1H$ NMR ($CD_2Cl_2$): $\delta$ 7.89 (dd, 2H, *o*-Ph), 7.83–7.16 (m, overlapping Ph), 3.11 (m, 1H, –PC($CH_3$)*H*C($CH_3$)HP–), 3.01 (m, 1H, –PC-($CH_3$)HC($CH_3$)*H*P–), 1.24 (dd, $^3J$(H–P) = 15.3, $^4J$(H–P) = 6.8 Hz, 3H, –PC(C*H*$_3$)HC($CH_3$)HP–), 1.13 (dd, $^3J$-(H–P) = 13.0, $^4J$(H–P) = 6.2 Hz, 3H, –PC($CH_3$)HC-(C*H*$_3$)HP–), 0.71 (dd, $^3J$(H–P) = 6.1, 1.0 Hz, 3H, –C*H*$_3$); $^{31}P\{^1H\}$ NMR ($CD_2Cl_2$): $\delta$ 28.98 (d, $^2J$(P–P) = 14.4 Hz), 14.59 (d, $^2J$(P–P) = 14.4 Hz).

Spectroscopic data for **5B**: $^1H$ NMR ($CD_2Cl_2$): $\delta$ 7.98 (dd, 2H, *o*-Ph), 7.83–7.16 (m, overlapping Ph), 3.26 (m, 1H, –PC($CH_3$)*H*C($CH_3$)HP–), 2.76 (m, 1H, –PC-($CH_3$)HC($CH_3$)*H*P–), 1.49 (dd, $^3J$(H–P) = 13.0, $^4J$(H–P) = 6.8 Hz, 3H, –PC(C*H*$_3$)HC($CH_3$)HP–), 0.97 (dd, $^3J$(H–P) = 15.3, $^4J$(H–P) = 6.2 Hz, 3H, –PC($CH_3$)-HC(C*H*$_3$)HP–), 0.77 (dd, $^3J$(H–P) = 4.9, 2.0 Hz, 3H, –C*H*$_3$); $^{31}P\{^1H\}$ NMR ($CD_2Cl_2$): $\delta$ 24.72 (d, $^2J$(P–P) = 16.2 Hz), 14.65 (d, $^2J$(P–P) = 16.2 Hz).

### 4.7. *IrH(CO)(OTf)$_2$(chiraphos) (6A), (6B)*

To a resealable NMR tube charged with ~5 mg of **5A** and **5B** was vacuum transfered 0.5 ml $CD_2Cl_2$ and 550 torr of hydrogen. Examination of the solution by NMR spectroscopy indicated the formation of the mono-hydride complexes **6A** and **6B** in a 1:0.3 ratio respectively.

Spectroscopic data for **6A**: $^1H$ NMR ($CD_2Cl_2$): $\delta$ 8.15–7.03 (m, overlapping Ph), 3.70–0.81 (overlapping multiplets, chiraphos), −24.01 (dd, $^2J$(H–P) = 20.1, 12.4 Hz, Ir–H); $^{31}P\{^1H\}$ NMR ($CD_2Cl_2$): $\delta$ 39.92 (d, $^2J$(P–P) = 15.3 Hz), 15.40 (d, $^2J$(P–P) = 15.3 Hz).

Spectroscopic data for **6B**: $^1H$ NMR ($CD_2Cl_2$): $\delta$ 8.15–7.03 (m, overlapping Ph), 3.70–0.81 (overlapping multiplets, chiraphos), −23.72 (t, $^2J$(H–P) = 15.3 Hz, Ir–H); $^{31}P\{^1H\}$ NMR ($CD_2Cl_2$): $\delta$ 31.77 (d, $^2J$(P–P) = 15.3 Hz), 27.70 (d, $^2J$(P–P) = 15.3 Hz).

### 4.8. *[Ir(C(O)$CH_3$)($NCCH_3$)$_3$(dppe)]($PF_6$)$_2$ (7)*

To an acetonitrile (10 ml) solution of Ir($CH_3$)-$I_2$(CO)(dppe) (0.10 g, 0.113 mmol) was added 2.05 equiv. freshly recrystallized silver hexafluorophosphate (0.059 g, 0.232 mmol) in 5 ml acetonitrile. After 3 h stirring in the dark, the reaction solution was decanted from the silver iodide residue and passed through a glass wool column (0.6 cm diameter×4 cm long). The filtrate was concentrated to 1 ml and the crude product was precipitated by the addition of 10 ml diethyl ether. Complex **7** was isolated in 80% yield as a white solid after recrystallization from acetonitrile/diethyl ether.

Spectroscopic data for **7**: IR ($CH_3CN$, $cm^{-1}$): 1656 (acetyl); $^1H$ NMR ($CH_3CN$): $\delta$ 7.69–7.37 (overlapping m, 20H, Ph), 3.33 (m, 2H, –PCH*H*CH*H*P–), 3.10 (m, 2H, –PC*H*HC*H*HP–), 2.69 (s, 6H, NCC*H*$_3$), 2.29 (s, 3H, –C*H*$_3$); $^{31}P\{^1H\}$ NMR ($CD_3CN$): $\delta$ 27.31 (s), −139.55 (sept, $^1J$(P–F) = 706.8 Hz); $^1H$ NMR ($CD_2Cl_2$, −50°C): $\delta$ 7.75–7.33 (overlapping m, Ph), 3.41 (m, –PCH*H*CH*H*P–), 2.99 (–PC*H*HC*H*HP–), 2.73 (s, equatorial NCC*H*$_3$), 2.23 (s, 3H, –C*H*$_3$), 1.74 (s, 3H, axial NCC*H*$_3$); $^{31}P\{^1H\}$ NMR ($CD_3CN$): $\delta$ 22.79 (s), −144.61 (sept, $^1J$(P–F) = 710.6 Hz). *Anal.* Calc. for $C_{34}H_{36}F_{12}IrOP_4$: C, 40.64; H, 3.61. Found: C, 40.46; H, 3.58%.

### 4.9. *[Ir($CH_3$)(CO)($NCCH_3$)$_2$(dppe)]($PF_6$)$_2$ (8)*

A 10 mM $CD_2Cl_2$ (0.5 ml) solution of **7** (5 mg, $5.0\times10^{-3}$ mmol) was added to a resealable NMR tube. Analysis of the solution by NMR and IR spectroscopies revealed an equilibrium between **7**, the CO deinserted product (**8**) and free acetonitrile in a 1.3:1.0:1.0 ratio, respectively.

Spectroscopic data for **8**: IR ($CH_2Cl_2$, $cm^{-1}$): 2096 (CO); $^1H$ NMR ($CD_2Cl_2$): $\delta$ 7.75–7.33 (overlapping m, Ph), 3.41 (m, –PCH*H*CH*H*P–), 2.99 (–PC*H*HC*H*HP–), 2.74 (dd, $^5J$(H–P) = 1.1, 0.8 Hz, 3H, NCC*H*$_3$), 2.05 (dd, $^5J$(H–P) = 1.8, 0.5 Hz, 3H, NCC*H*$_3$), 1.43 (dd, $^3J$(H–P) = 5.1, 2.0 Hz, 3H, –C*H*$_3$); $^{31}P\{^1H\}$ NMR ($CD_2Cl_2$): $\delta$ 20.21 (d, $^2J$(P–P) = 7.6 Hz), 7.75 (d, $^2J$(P–P) = 7.6 Hz), −144.61 (sept, $^1J$(P–F) = 710.6 Hz).

## Acknowledgements

We wish to thank the National Science Foundation (Grants CHE 89-09060 and CHE 94-04991) for support of this work, the Johnson Matthey Co. Inc., for a generous loan of iridium trichloride, and Drs Faisal Shafiq and Paul Deutsch for helpful discussions. B.P.C. gratefully acknowledges Sherman Clarke, Bristol Myers-Squibb and Arnold Weissberger fellowships.

## References

[1] F.A. Cotton and G. Wilkinson, *Advanced Inorganic Chemistry*, 5th ed., Wiley, New York, 1988, p. 1455.

[2] J.P. Collman, L.S. Hegedus, J.R. Norton and R.G. Finke, *Principles and Applications of Organotransition Metal Chemistry*, University Science Books, Mill Valley, CA, 1987.

[3] E. Drent, J.A.M. van Broekhoven and M.J. Doyle, *J. Organomet. Chem., 417* (1991) 235–251.

[4] M. Brookhart, F.C. Rix, J.M. DeSimone and J.C. Barborak, *J. Am. Chem. Soc., 114* (1992) 5894–5895.

[5] A. Sen and J.S. Brumbaugh, *J. Organomet. Chem., 279* (1985) C5–C10.

[6] A. Sen, J.S. Brumbaugh and M. Lin, *J. Mol. Catal., 73* (1992) 297–323.

[7] A. Sen, *Acc. Chem. Res., 26* (1993) 303–310.

[8] A. Sen and T.-W. Lai, *J. Am. Chem. Soc., 104* (1982) 3520–3522.

[9] T.-W. Lai and A. Sen, *Organometallics, 3* (1984) 866–870.

[10] G.G. Consiglio, B. Studer, F. Oldani and P. Pino, *J. Mol. Catal., 58* (1990) L9–L12.

[11] U. Klabunde, T.H. Tulip, D.C. Roe and S.D. Ittel, *J. Organomet. Chem., 334* (1987) 141–156.

[12] M. Brookhart and D.M. Lincoln, *J. Am. Chem. Soc., 110* (1988) 8719–8720.

[13] L. Wang and T.C. Flood, *J. Am. Chem. Soc., 114* (1992) 3169–3170.

[14] G.F. Schmidt and M. Brookhart, *J. Am. Chem. Soc., 107* (1985) 1443–1444.

[15] R. Cramer, *J. Am. Chem. Soc., 98* (1965) 4717–4727.

[16] Z. Jiang and A. Sen, *J. Am. Chem. Soc., 112* (1990) 9655–9657.

[17] A. Sen, T.-W. Lai and R.R. Thomas, *J. Organomet. Chem., 358* (1988) 567–588.

[18] A. Sen, *Acc. Chem. Res., 21* (1988) 421–428.

[19] P.P. Deutsch, B.P. Cleary and R. Eisenberg, manuscript in preparation.

[20] M.R. Churchill, J.C. Fettinger, T.S. Janik, W.M. Rees, J.S. Thompson, S. Tomaszewski and J.D. Atwood, *J. Organomet. Chem., 323* (1987) 233–246.

[21] P.W. Atkins, *Physical Chemistry*, W.H. Freeman, San Francisco, CA, 1978.

[22] W.J. Geary, *Coord. Chem. Rev., 7* (1971) 81–122.

[23] P. Uguagliati, G. Deganello, L. Busetto and U. Belluco, *Inorg. Chem., 8* (1969) 1625–1630.

[24] M.R. Rosenthal and R.S. Drago, *Inorg. Chem., 4* (1965) 840–844.

[25] P. Burger and R.G. Bergman, *J. Am. Chem. Soc., 115* (1993) 10462–10463.

[26] P.J. Fagan, J.M. Manriquez, E.A. Maatta, A.M. Seyam and T.J. Marks, *J. Am. Chem. Soc., 103* (1981) 6650–6667.

[27] P.J. Fagan, J.M. Manriquez, T.J. Marks, C.S. Day, S.H. Vollmer and V.W. Day, *Organometetallics, 1* (1982) 170–180.

[28] K.I. Gell and J. Schwartz, *J. Am. Chem. Soc., 100* (1978) 3246–3248.

[29] K.I. Gell, B. Posin, J. Schwartz and G.M. Williams, *J. Am. Chem. Soc., 104* (1982) 1846–1855.

[30] G.G. Hlatky and R.H. Crabtree, *Coord. Chem. Rev., 65* (1985) 1–48.

[31] J.M. Mayer and J.E. Bercaw, *J. Am. Chem. Soc., 104* (1982) 2157–2165.

[32] D.R. McAlister, D.K. Erwin and J.E. Bercaw, *J. Am. Chem. Soc., 100* (1978) 5966–5968.

[33] M.L. Steigerwald and W.A. Goddard III, *J. Am. Chem. Soc., 106* (1984) 308–311.

[34] M.S. Chinn and D.M. Heinekey, *J. Am. Chem. Soc., 109* (1987) 5865–5967.

[35] M.S. Chinn, D.M. Heinekey, N.G. Payne and C.D. Sofield, *Organometallics, 8* (1989) 1824–1826.

[36] C. Bianchini, C. Mealli, A. Meli, M. Peruzini and F. Zanobini, *J. Am. Chem. Soc., 110* (1988) 8725–8726.

[37] C. Bianchini, K. Linn, D. Masi, M. Peruzzini, A. Polo, A. Vacca and F. Zanobini, *Inorg. Chem., 32* (1993) 2366–2376.

[38] M. Schlaf, A.J. Lough and R.H. Morris, *Organometallics, 12* (1993) 3808–3809.

[39] S.B. Duckett, C.L. Newell and R. Eisenberg, *J. Am. Chem. Soc., 115* (1993) 1156–1157.

[40] R. Eisenberg, *Acc. Chem. Res., 24* (1991) 110–116.

[41] R. Eisenberg, T.C. Eisenschmid, M.S. Chinn and R.U. Kirss, *Adv. Chem. Ser., 230* (1992) 47–74.

[42] T.C. Eisenschmid, R.U. Kirss, P.P. Deutsch, S.I. Hommeltoft, R. Eisenberg, J. Bargon, R.G. Lawler and A.L. Balch, *J. Am. Chem. Soc., 109* (1987) 8089–8091.

[43] T.C. Eisenschmid, J. McDonald and R. Eisenberg, *J. Am. Chem. Soc., 111* (1989) 7267–7269.

[44] R.C. Schnabel and D.M. Roddick, *Organometallics, 12* (1993) 704–711.

[45] F. Shafiq and R. Eisenberg, *J. Organomet. Chem., 472* (1994) 337–345.

[46] C. Bianchini, E. Farnetti, M. Graziani, M. Peruzzini and A. Polo, *Organometallics, 12* (1993) 3753–3761.

[47] B.P. Cleary and R. Eisenberg, *Organometallics, 11* (1992) 2335–2337.

[48] M.K. Hays and R. Eisenberg, *Inorg. Chem., 30* (1991) 2623–2630.

[49] C.E. Johnson, B.J. Fisher and R. Eisenberg, *J. Am. Chem. Soc., 105* (1983) 7772–7774.

[50] C.E. Johnson and R. Eisenberg, *J. Am. Chem. Soc., 107* (1985) 3148–3160.

[51] A.J. Kunin, R. Farid, C.E. Johnson and R. Eisenberg, *J. Am. Chem. Soc., 107* (1985) 5315–5317.

[52] J.P. Kennedy and E. Marèchal, *Carbocationic Polymerization*, Wiley, New York, 1982.

[53] J.P. Kennedy, *Cationic Polymerization of Olefins: a Critical Inventory*, Wiley, New York, 1975.

[54] F. Calderazzo and F.A. Cotton, *Inorg. Chem., 1* (1962) 30–36.

[55] M.J. Wax and R.G. Bergman, *J. Am. Chem. Soc., 103* (1981) 7028–7030.

[56] I.S. Butler, F. Basolo and R.G. Pearson, *Inorg. Chem., 6* (1967) 2074–2079.

[57] D.D. Perrin and W.L.F. Armarego, *Purification of Laboratory Chemicals*, 3rd ed., Pergamon, Oxford, UK, 1988, p. 391.