Mechanism of the Hydrogenation of Phenylacetylene Catalyzed by [Ir(COD)(η^2-*i*Pr$_2$PCH$_2$CH$_2$OMe)]BF$_4$

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The synthesis of the mononuclear complexes of formulas IrCl(COD)(*i*Pr$_2$PCH$_2$CH$_2$OMe) (**1**) (COD = 1,5-cyclooctadiene), IrCl(COD)(*i*Pr$_2$PCH$_2$CH$_2$NMe$_2$) (**2**), [Ir(diolefin)(η^2-*i*Pr$_2$PCH$_2$CH$_2$OMe)]BF$_4$ (diolefin = COD (**3**), TFB (**5**) (TFB = tetrafluorobenzobarrelene)), [Ir(diolefin)(η^2-*i*Pr$_2$PCH$_2$CH$_2$NMe$_2$)]BF$_4$ (diolefin = COD (**4**), TFB (**6**)), [IrH(C$_2$Ph)(COD)(η^2-*i*Pr$_2$PCH$_2$CH$_2$OMe)]BF$_4$ (**7**), and [IrH$_2$(COD)(η^2-*i*Pr$_2$PCH$_2$CH$_2$OMe)BF$_4$ (**8**) are described. The X-ray crystal structure of **3** has been determined (monoclinic space group $P2_1/n$ (No. 14) with a = 8.466(3) Å, b = 9.004(3) Å, c = 27.052(13) Å, β = 97.71(2)°, and Z = 4). **3** is found to be a very active and highly selective catalyst for the hydrogenation of phenylacetylene to styrene. Although the hydrido–alkynyl–diolefin compound **7** is the main species under catalytic conditions, the reaction proceeds via the dihydrido–diolefin intermediate **8** according to the following set of reactions: **8** + H$_2$ ⇌ [IrH(CH=CHPh)(COD)(η^2-*i*Pr$_2$PCH$_2$CH$_2$OMe)]BF$_4$ (**9**) and **9** + H$_2$ → **8** + PhCH=CH$_2$ where the reaction between **9** and molecular hydrogen is the rate-determining step. The catalytic activity of **3**–**6** in the hydrogenation of olefins is also reported.

Introduction

Shapley, Schrock, and Osborn[1] made the important discovery of the existence of the cationic rhodium and iridium complexes with the general formula [M(diene)L$_a$]$^+$ (a = 2 or 3), which are active catalysts for the hydrogenation of olefins,[2] dienes,[3] internal alkynes,[4] and ketones.[5] In solvents such as acetone, ethanol or acetonitrile, these compounds react with molecular hydrogen to give the dihydrido–metal complexes [MH$_2$S$_x$L$_a$]$^+$ (M = Rh, Ir; S = solvent).[1,3c]

The chemistry of the complex [Rh(NBD)(dppe)]$^+$ (NBD = 2,5-norbornadiene, dppe = 1,2-bis(diphenylphosphino)ethane) differs in some respects from that of complexes containing monodentate ligands L.[6] In methanol solution, it reacts rapidly with hydrogen to give the solvated species [Rh(MeOH)$_x$(dppe)]$^+$, which is an effective catalyst for the hydrogenation of alkene derivatives. Kinetic measurements of the hydrogenation of 1-hexene were consistent with the following mechanism:

$$[Rh(MeOH)_x(dppe)]^+ + \text{1-hexene} \overset{MeOH}{\rightleftharpoons} [Rh(\eta^2\text{-1-hexene})(dppe)]^+ \quad \text{(fast)} \quad \text{(a)}$$

$$[Rh(\eta^2\text{-1-hexene})(dppe)]^+ + H_2 \overset{MeOH}{\rightarrow} [Rh(MeOH)_x(dppe)]^+ + \text{hexane} \quad \text{(slow)} \quad \text{(b)}$$

The cation [Ir(COD)(py)$_2$]$^+$ (COD = 1,5-cyclooctadiene, py = pyridine), in contrast to [Rh(NBD)(dppe)]$^+$, is totally inactive as a catalyst, apparently because it fails to add hydrogen.[7] However, the mixed-ligand complexes [Ir(COD)L(PR$_3$)$_2$]$^+$ (L = nitrogen donor ligand) are active catalysts for the reduction of a variety of substrates, particularly tetrasubstituted alkenes. Thus, in dichloromethane as solvent the complex [Ir(COD)(py)(PCy$_3$)]$^+$, known as Crabtree's catalyst, catalyzes the hydrogenation of 2,3-dimethyl-2-butene;[2d] interestingly, better results are obtained for the benzonitrile derivative [Ir(COD)(NCPh)(L)]$^+$ (L = PCy$_3$ or neomenthyldiphenylphosphine).[8] This benzonitrile catalyst precursor is able to hydrogenate tetrasubstituted alkene moieties of prochiral didehydro amino acid derivatives, although poor enantiomeric excesses are obtained with chiral monodentate phosphine ligands.

The reduction of terminal alkynes catalyzed by the cationic systems mentioned above has been scarcely observed,[2f] due to the formation of nonactive alkynyl derivatives during the hydrogenation. In this article we describe the results obtained from a kinetic and spectro-

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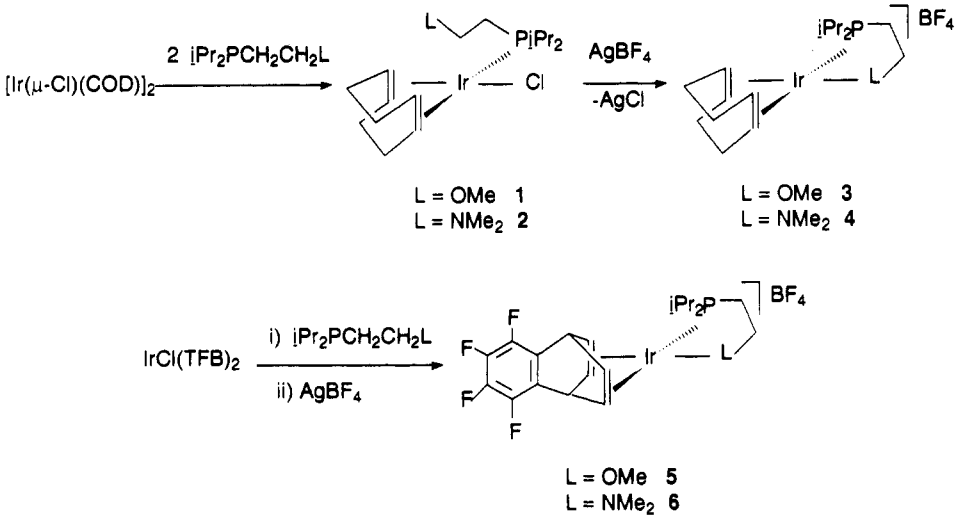
Scheme I



scopic study on the hydrogenation of phenylacetylene catalyzed by a new family of cationic compounds of the type $[Ir(diene)(P\text{-}L)]^+$ (diene = COD, TFB (tetrafluorobenzobarrelene); P-L = $iPr_2PCH_2CH_2OMe$, $iPr_2PCH_2CH_2NMe_2$), as well as the catalytic activity of the new complexes in the hydrogenation of olefins.

Results and Discussion

1. Preparation and Characterization of the Catalysts. The new catalysts were prepared according to the reactions shown in Scheme I. The halide bridges in the dimeric compound $[Ir(\mu\text{-}Cl)(COD)]_2$ are readily split by the ligands $iPr_2PCH_2CH_2OMe$ and $iPr_2PCH_2CH_2NMe_2$ to give the square-planar mononuclear complexes **1** and **2**. The subsequent treatment of these compounds with $AgBF_4$ in acetone leads to the cationic catalysts **3** and **4**. The analogous complexes **5** and **6**, containing tetrafluorobenzobarrelene as diolefin ligand, were obtained in the presence of $AgBF_4$, by addition of the corresponding P-L ligands to suspensions of the monomeric starting material $IrCl(TFB)_2$ in dichloromethane.

Complexes **1–6** were fully characterized by elemental analysis and IR, ^1H NMR, and $^{31}P\{^1H\}$ NMR spectroscopic data. The definitive characterization of **3–6** as mononuclear derivatives came from a single crystal X-ray diffraction investigation of **3**. A view of the molecular geometry of this compound is shown in Figure 1. Selected bond distances and angles are listed in Table I.

Figure 1 reveals that the coordination geometry around the iridium center is almost square-planar. The greatest deviation from the best plane through the Ir, O, and P atoms and the midpoints of the two coordinated C=C double bonds is 0.049(6) Å for the center between C5 and C6. Due to the ring strain in the five membered $IrPC_2O$ chelating system, the angle P—Ir—O is decreased to 81.4(1)°. The iridium to oxygen distance (2.152(3) Å) in **3** is very close to the expected value for an Ir—O single bond (sum of covalent radii 2.03 Å) and indicates a fairly strong interaction between the oxygen atom and the positively charged metal center. A very similar distance is found in the cationic vinylidene complex $[Ir(=C=CHCO_2Me)(\eta^2\text{-}P\text{-}O)(\eta^1\text{-}P\text{-}O)]SbF_6$ (P-O = $iPr_2PCH_2CH_2OMe$) (2.163(5) Å).[9] Due to the different trans influence of the P and O donors, a significant difference

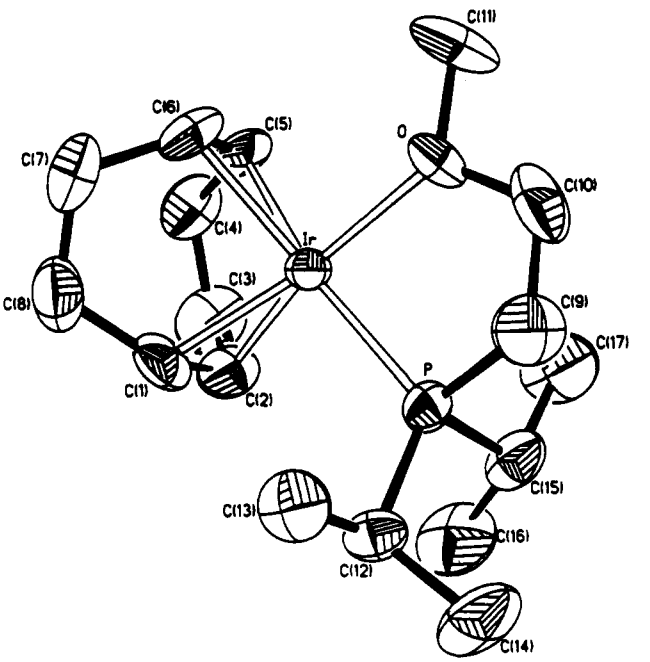


Figure 1. ORTEP drawing of complex **3**.

Table I. Selected Bond Distances (Å) and Angles (deg) with Esd's for 3

Ir–P	2.289(1)	P–Ir–O	81.4(1)
Ir–O	2.152(3)	P–Ir–C1	99.2(2)
Ir–C1	2.119(5)	P–Ir–C2	94.2(1)
Ir–C2	2.100(5)	P–Ir–C5	158.8(1)
Ir–C5	2.204(4)	P–Ir–C6	162.5(2)
Ir–C6	2.198(5)	O–Ir–C1	158.1(2)
O–C10	1.434(7)	O–Ir–C2	162.5(2)
O–C11	1.453(7)	O–Ir–C5	96.6(2)
C1–C2	1.416(8)	O–Ir–C6	92.2(2)
C5–C6	1.411(7)	Ir–O–C10	122.0(3)
		Ir–O–C11	125.5(4)

in the iridium to carbon distances of the coordinated diolefin is observed. Whereas the carbon atoms C1 and C2 (trans to O) were located at a distance of 2.119(5) and 2.100(5) Å from the metal center, the Ir—C bond lengths for C5 and C6 (trans to P) are longer by ca. 0.1 Å. Owing to the coordination to the metal center, the distances between the sp^2-carbon atoms C1, C2 and C5, C6 are increased to 1.416(8) and 1.411(8) Å, respectively. All other bond distances and angles lie in the expected range and deserve no further comment.

(9) Schulz, M. Ph.D. Thesis, University of Würzburg, 1991.

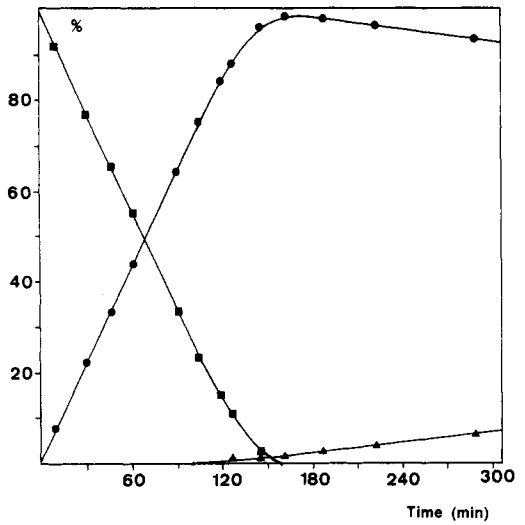


Figure 2. Hydrogenation of phenylacetylene to styrene catalyzed by [Ir(COD)(η^2-*i*Pr$_2$PCH$_2$CH$_2$OMe)]BF$_4$ (**3**) in dichloromethane at 25 °C (1 atm of H_2, 1.6 × 10^{-3} M **3**, 0.2 M PhC≡CH): (■) phenylacetylene; (●) styrene; (▲) ethylbenzene.

2. Hydrogenation of Phenylacetylene. The complexes **3** and **5** efficiently catalyze the sequential hydrogenation of phenylacetylene in dichloromethane solution. At 25 °C and atmospheric pressure, selectivities close to 100% are achieved for the hydrogenation of the alkyne to the alkene, as illustrated in Figure 2. Reduction of the double bond only begins to take place when most of the alkyne has been consumed. In the absence of the alkyne, styrene is hydrogenated to ethylbenzene at slower rates than those observed in the reduction of the acetylene triple bond. Under the same conditions **4** and **6** are fully inactive, while the solutions of **3** catalyze the reduction of the triple bond at rates about twice as fast as those observed for **5**.

In order to obtain information about the mechanism of the hydrogenation of phenylacetylene to styrene, a kinetic and spectroscopic investigation of the reduction catalyzed by **3** was carried out.

Kinetic Studies. Initial hydrogenation rates were obtained from gas uptake experiments at 25 °C, as exemplified in Figure 3.

A simple rate law for a catalytic hydrogenation of phenylacetylene to styrene is

$$-d[PhC_2H]/dt = -d[H_2]/dt = k_1[PhC_2H]^m[cat]^n[H_2]^q \quad (1)$$

At constant temperature and catalyst concentration, this rate law is further simplified to

$$-d[PhC_2H]/dt = -d[H_2]/dt = k_{obs}[PhC_2H]^m(P(H_2))^q \quad (2)$$

where $P(H_2)$ is the hydrogen pressure.

The reactions were followed by measuring the hydrogen consumption as a function of time. The volume of H_2 corrected to 1 atm was converted to the pseudo-zero-order rate constant k_{obs} by using eq 3, where $-dV/dt$ is the initial

$$-(dV/dt)/RTV_{sol} = k_{obs}[PhC_2H]^m(P(H_2))^q \quad (3)$$

rate measured from gas uptake experiments, R is the molar gas constant, T is the temperature (K), and V_{sol} is the total volume (L) of the reacting solution.

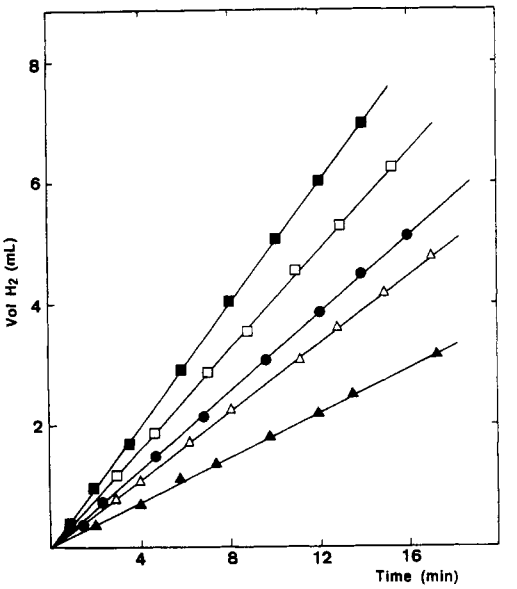


Figure 3. H_2 gas uptake plots for the [Ir(COD)(η^2-*i*Pr$_2$PCH$_2$CH$_2$OMe)]BF$_4$ (**3**) catalyzed hydrogenation of phenylacetylene to styrene in dichloromethane at 25 °C (1 atm of H_2, 0.2 M PhC≡CH). [**3**]: (▲) 0.6 × 10^{-3} M; (△) 0.8 × 10^{-3} M; (●) 1.0 × 10^{-3} M; (□) 1.2 × 10^{-3} M; (■) 1.6 × 10^{-3} M.

Table II. Kinetic Data for the Hydrogenation of Phenylacetylene to Styrene Catalyzed by 3[a]

10^3[**3**], M	$P(H_2)$, atm	[PhC≡CH], M	10^6(−dV/dt), L s^{-1}	10$^5k_{obs}$, M s^{-1} atm^{-2}	10$^2k_4$, s^{-1} atm^{-2}
0.6	1.00	0.2	3.0	1.5	2.5
0.8	1.00	0.2	4.7	2.4	3.0
1.0	1.00	0.2	5.3	2.7	2.7
1.2	1.00	0.2	6.8	3.5	2.9
1.6	1.00	0.2	8.3	4.3	2.7
1.0	1.00	0.1	5.3	2.7	2.7
1.0	1.00	0.3	5.5	2.8	2.8
1.0	1.00	0.4	5.0	2.6	2.6
1.0	0.70	0.2	2.4	2.5	2.5
1.0	0.72	0.2	2.1	2.1	2.1
1.0	0.75	0.2	2.7	2.5	2.5
1.0	0.78	0.2	3.1	2.6	2.6
1.0	0.88	0.2	3.4	2.2	2.2
1.0	0.90	0.2	4.0	2.5	2.5

[a] In dichloromethane at 25 °C.

In order to determine the rate dependence on the various reaction components, hydrogenation runs were performed at different catalyst (**3**) and substrate concentrations and at different hydrogen pressures. The data collected in Table II indicate that the reaction is practically independent of the substrate concentration, while a plot of log(−dV/dt) versus log($P(H_2)$) yields a straight line of slope 2.30, suggesting that the reduction of the alkyne is second-order in hydrogen pressure. The values of k_{obs} collected in Table II were thus obtained from eq 3 for $m = 0$ and $q = 2$. A plot of log(−dV/dt) versus log ([**3**]) yields a straight line of slope 1.0, demonstrating that the reaction is first-order in catalyst concentration ($n = 1$ in eq 1). The catalytic rate law therefore is

$$d[\text{styrene}]/dt = -d[PhC_2H]/dt = k_4[\mathbf{3}](P(H_2))^2 \quad (4)$$

and

$$k_{obs} = k_4[\mathbf{3}] \quad (5)$$

A plot of k_{obs} versus [**3**] (Figure 4) yields a value for k_4 of (2.7 ± 0.1) × 10^{-2} s^{-1} atm^{-2}, at 298 K.

Spectroscopic Studies. The $^{31}P\{^1H\}$ NMR spectra of

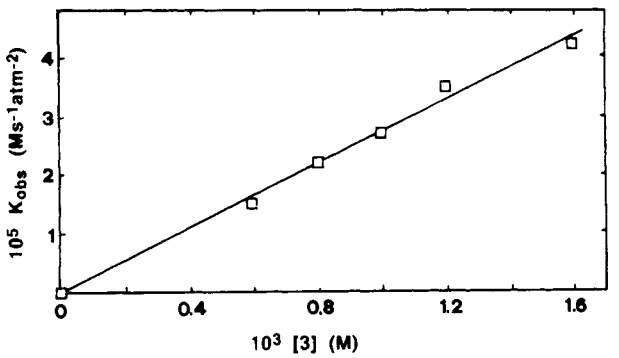
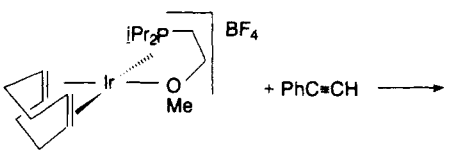


Figure 4. Rate constant for the hydrogenation of phenylacetylene to styrene catalyzed by [Ir(COD)(η^2-*i*$Pr_2PCH_2CH_2$OMe)]BF_4 (**3**) in dichloromethane at 25 °C (1 atm of H_2, 0.2 M PhC≡CH).

the solutions recorded during the catalysis show only one signal at 42.6 ppm. The same spectrum was observed when, under argon atmosphere, to a NMR tube containing a solution of **3** in dichloromethane-d_2 was added an excess of phenylacetylene (ca. 4 equiv). The subsequent addition of diethyl ether to this solution led to the precipitation of an off-white solid. The ^1H NMR spectrum of this solid, in $CDCl_3$ at 20 °C, exhibits four signals due to four chemically inequivalent 1,5-cyclooctadiene vinyl protons at 6.02, 5.04, 4.00, and 3.77 ppm, along with the resonances of *i*$Pr_2PCH_2CH_2OMe$ and C≡CPh, whereas in the hydride region a doublet is observed at −23.24 ppm (J(PH) = 9.6 Hz). These data suggest that the compound obtained by reaction of **3** with phenylacetylene is the hydrido–alkynyl complex **7**, which can be formed according to eq 6.



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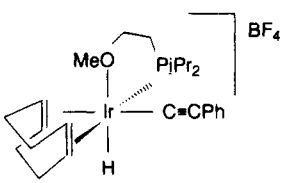


(6)

7

The unambiguous characterization of **7** as a six-coordinate hydrido–alkynyl–diolefin compound came from the IR and $^{13}C\{^1H\}$ NMR spectra of the off-white solid. Thus, the IR spectrum in Nujol shows two bands at 2280 and 2120 cm^{-1}, which can be assigned to the ν(C≡C) and ν(Ir—H) absorptions, respectively. Furthermore, the $^{13}C\{^1H\}$ NMR spectrum in $CDCl_3$ contains in the δ = 105–80 region five signals (Figure 5). The doublets A (J(PH) = 8.5 Hz) and B (J(PH) = 13.6 Hz) can be assigned to the vinyl carbon atoms of the diolefin ligand coordinated trans to the phosphorus atom of the ether–phosphine ligand, while the singlets C and D an be assigned to the vinyl carbon atoms of the diolefin ligand coordinated trans to the oxygen atom of *i*$Pr_2PCH_2CH_2OMe$. The doublet E (J(PH) = 11.1 Hz) assigned to the Ir—C≡ carbon atom strongly supports the presence of the alkynyl ligand in the compound.

The $^{31}P\{^1H\}$ NMR spectrum of the off-white solid in dichloromethane, which shows a singlet at 42.6 ppm, proves

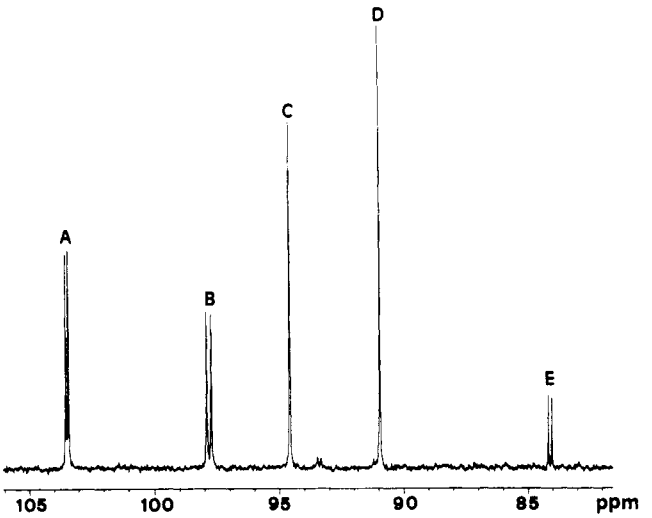
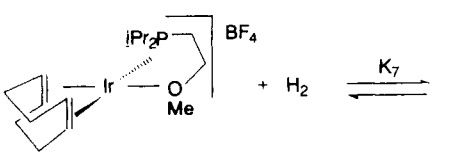


Figure 5. $^{13}C\{^1H\}$ NMR spectra of complex [Ir(COD)(η^2-*i*$Pr_2PCH_2CH_2OMe$)]BF_4 (**3**) in the 105–80 ppm region.

that **7** is the main species under catalytic conditions. Thus, at first glance, it could be proposed that the mechanism of the hydrogenation of phenylacetylene catalyzed by **3** might initially involve the step shown in eq 6. However this is difficult to reconcile with the observed kinetic data (m = 0 in eq 2). Furthermore, it is of interest to note that the hydrogenation of unsaturated organic substrates catalyzed by metal complexes which do not contain a M–H bond implies as the initial step the reaction with molecular hydrogen followed by the reaction of the resulting hydride intermediate with the substrate.[10] It seems to be reasonable, therefore, to assume that **7** is a side product in the catalytic cycle and that the catalysis could proceed via a dihydrido–diolefin metal intermediate formed in no detectable concentration under catalytic conditions. This possibility, which is consistent with the observed kinetic data, prompted us to study the ^1H and $^{31}P\{^1H\}$ NMR spectra of **3** under hydrogen atmosphere in the absence of phenylacetylene. Under these conditions the $^{31}P\{^1H\}$ NMR spectrum shows two singlets, one at 50.26 ppm assigned to **3** and another at 55.5 ppm corresponding to a new intermediate. The ^1H NMR spectrum of the same solution displays at high field two doublet of doublets at −12.21 (J(PH) = 18.99 Hz, J(HH) = 3.5 Hz) and −24.20 (J(PH) = 12.93 Hz, J(HH) = 3.5 Hz). These observations suggest that under the above mentioned conditions the equilibrium shown in eq 7 is reached.



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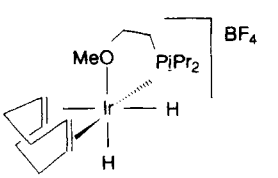
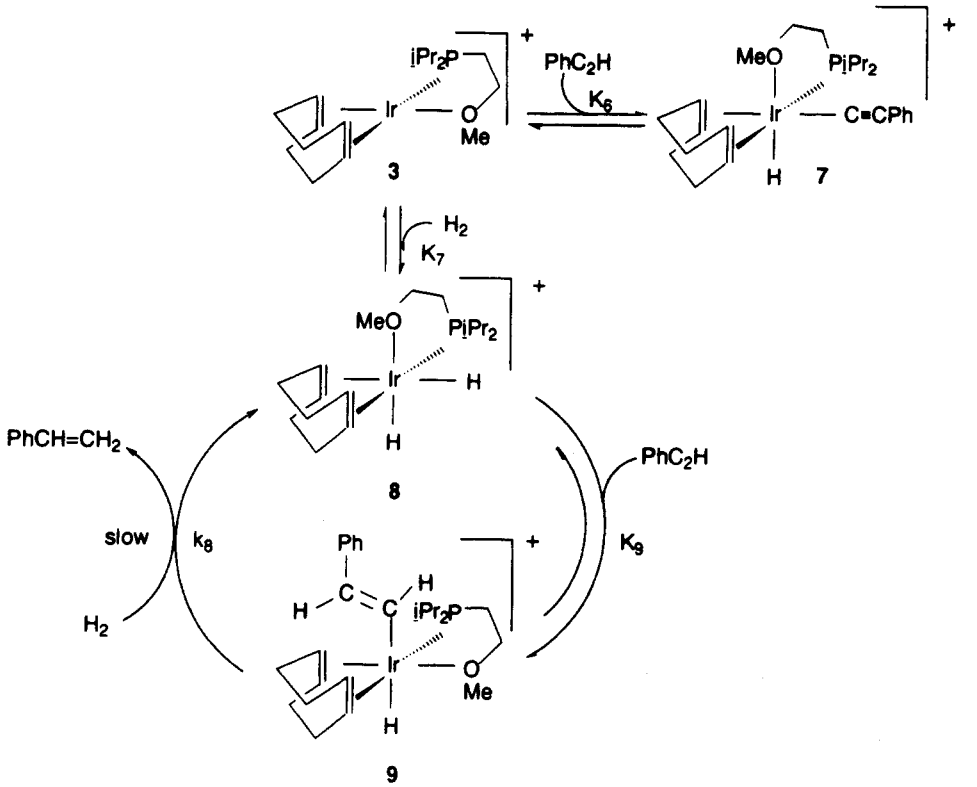


(7)

8

(10) James, B. R. *Homogeneous Hydrogenation*; John Wiley and Sons: New York, 1973.

Scheme II. Catalytic Cycle for the Hydrogenation of Phenylacetylene to Styrene Catalyzed by [Ir(COD)(η^2-*i*Pr$_2$PCH$_2$CH$_2$OMe)]BF$_4$ (3)



The preparation of the cation *cis*-[IrH$_2$(COD)(dppe)]$^+$ (dppe = 1,2-bis(diphenylphosphino)ethane), comparable in structure to **8**, has been reported previously. This compound decomposes in solution by hydrogenation of the coordinated diene (ca. 30% at 20 °C).[3c] In contrast, the complex *cis*-[IrH$_2$(COD)(dppm)]BF$_4$ (dppm = 1,2-bis(diphenylphosphino)methane) is stable at this temperature, neither losing molecular hydrogen nor transferring it to the coordinated 1,5-cyclooctadiene.[11] Similar to the latter compounds, **8** is stable in solution and the hydrogenation of the coordinated diolefin is not observed.

Mechanism. From the results of the spectroscopic studies, we conclude that although the hydrido–alkynyl–diolefin **7** is the main species under catalytic conditions, the dihydrido–diolefin **8** can also be formed in no detectable concentration. Furthermore, the kinetic study suggests that **7** is a side product in the catalytic cycle ($m = 0$ in eq 2) and that **3** is the catalyst precursor, which is in a rapid equilibrium with the active species **8** ($q = 2$ in eq 2). In accordance with this, we propose that the hydrogenation of phenylacetylene to styrene catalyzed by **3** proceeds by the mechanism shown in Scheme II, in which the reaction between **9** and hydrogen is the rate-determining step. Thus, the rate of formation of styrene is

$$\mathrm{d[styrene]}/\mathrm{d}t = k_8[\mathbf{9}]P(\mathrm{H_2}) \qquad (8)$$

The concentration of the key intermediate **9** can be determined as follows:

$$[\mathrm{Ir}]_{\mathrm{Tot}} = [\mathbf{7}] + [\mathbf{3}] + [\mathbf{8}] + [\mathbf{9}] \qquad (9)$$

Since $[\mathbf{8}] = [\mathbf{9}]/K_9[\mathrm{PhC_2H}]$ and $[\mathbf{3}] = [\mathbf{9}]/K_7K_9[\mathrm{PhC_2H}]P(\mathrm{H_2})$, we have $[\mathbf{7}] = K_6[\mathbf{3}][\mathrm{PhC_2H}] = K_6[\mathbf{9}]/K_7K_9P(\mathrm{H_2})$, and finally

$$[\mathbf{9}] = \frac{K_7K_9[\mathrm{Ir}]_{\mathrm{Tot}}[\mathrm{PhC_2H}]P(\mathrm{H_2})}{1 + K_6[\mathrm{PhC_2H}] + K_7P(\mathrm{H_2}) + K_7K_9[\mathrm{PhC_2H}]} \qquad (10)$$

7 is the only spectroscopically detected species in the course of the catalysis under atmospheric pressure of hydrogen, suggesting that $K_6[\mathrm{PhC_2H}] \gg (1 + K_7P(\mathrm{H_2}) + K_7K_9[\mathrm{PhC_2H}])$ when $P(\mathrm{H_2}) \leq 1$. Therefore [**9**] can be written as follows:

$$[\mathbf{9}] = \frac{K_7K_9}{K_6}[\mathrm{Ir}]_{\mathrm{Tot}}P(\mathrm{H_2}) \qquad (11)$$

Combining eqs 8 and 11, we obtain eq 12, where $[\mathrm{Ir}]_{\mathrm{Tot}}$ is the initial concentration of the catalyst precursor.

$$\frac{\mathrm{d[styrene]}}{\mathrm{d}t} = \frac{k_8K_7K_9}{K_6}[\mathrm{Ir}]_{\mathrm{Tot}}(P(\mathrm{H_2}))^2 \qquad (12)$$

Inspection of eq 12 shows that the rate of the catalytic reaction is proportional to the initial concentration of the catalyst precursor, second-order with respect to hydrogen pressure, and independent of substrate concentration, which agrees well with experimental data (see eq 4).

According to the stability of **8**, Scheme II suggests that the diolefin ligand remains coordinated during the catalytic cycle, in contrast with previous observations on [M(diolefin)L$_a$]$^+$ catalyst precursors, where the hydrogenation of the diolefin and the formation of species [MH$_2$S$_x$L$_a$]$^+$ (S = solvent) or [MH$_2$(subs)$_x$L$_a$]$^+$ have been proposed as active catalytic intermediates.

Some more details of the cycle depicted in Scheme II remain to be elucidated, because the reaction of **8** with phenylacetylene is likely to involve a series of elementary steps. One plausible sequence would be the dissociation

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of the OMe group of the ether–phosphine ligand to give a 16 e dihydride intermediate, which by coordination of the alkyne and subsequent migration of one hydride to the carbon–carbon triple bond could yield **9**. If the alkyne enters the coordination sphere of the iridium by displacement of the –OMe group, the alkyne would then be cis to one hydride but trans to the other. So, if the cis hydride migrates to the alkyne and the stereochemistry does not change further, the resulting hydrido–vinyl intermediate would have trans stereochemistry. This trans coordination would not facilitate the reductive elimination of styrene in the next step, suggesting that the reaction of **9** with molecular hydrogen is necessary for the formation of the alkene.

The selectivity observed in the reduction of phenylacetylene may have kinetic reasons. Figure 2 shows that phenylacetylene is hydrogenated at a rate which is much greater than the rate at which styrene is hydrogenated. The same behavior has been observed for the hydrogenation of 2-hexyne to *cis*-2 hexene catalyzed by [Rh(diene)$(PR_3)_2$]$^+$. In this case, it has been argued that the alkyne competes strongly with the olefin for coordination sites at the metal center.[4] Consequently, the higher coordination ability of phenylacetylene, in comparison with styrene, could favor the displacement of the OMe group of the ether–phosphine and therefore the alkyne hydrogenation.

In contrast to these cationic systems, the selectivity observed for the hydrogenation of phenylacetylene catalyzed by $OsHCl(CO)(P\textit{i}Pr_3)_2$ seems to be thermodynamically controlled. The independent study of the reduction of C≡C and C=C bonds indicates that the latter is kinetically favored. However the vinyl complex Os((*E*)-CH=CHPh)Cl(CO)$(P\textit{i}Pr_3)_2$ is the main species under catalytic conditions; this complex represents a thermodynamic sink that causes virtually all the osmium present in solution to be tied up in this form, and consequently, the kinetically unfavorable pathway becomes the only one available in the presence of phenylacetylene.[12]

From a mechanistic point of view, it is finally worth mentioning that the hydrogenation of phenylacetylene catalyzed by the cationic systems described in this article does not involve the hydrogenation of the diolefins of the catalyst precursors, in contrast to the cationic rhodium and iridium systems previously reported, where the reduction of the diene and formation of the species $[MH_2S_xL_a]^+$ or $[MH_2(subs)_xL_a]^+$ has been assumed.

3. Hydrogenation of Olefins. The complexes **3** and **5** are also very effective catalysts for the hydrogenation of olefins. In dichloromethane as solvent, at 25 °C, and under atmospheric pressure of hydrogen, the initial reduction rates for 0.2 M solutions of 1-hexene, cyclohexene, and 2,3-dimethyl-2-butene, with 1.0×10^{-3} M of catalyst, are faster than 6.8×10^{-4} M s^{-1}.

The complexes **4** and **6** catalyze the hydrogenation of 1-hexene and cyclohexene, but they are not active for the reduction of 2,3-dimethyl-2-butene. Under the same conditions as those described for **3** and **5**, the compounds **4** and **6** catalyze the hydrogenation of 1-hexene to hexane at rates as fast as those observed for **3** and **5**, while the reduction of cyclohexene to cyclohexane is about 1 order of magnitude slower than the reduction of 1-hexene. These results seem to indicate that the initial reduction rates of olefins in the presence of **4** and **6** are strongly dependent on their steric requirements. Whereas the reduction of a terminal olefin (1-hexene) is very fast, **4** and **6** are not active catalysts for the hydrogenation of a tetrasubstituted olefin (2,3-dimethyl-2-butene). In contrast, the complexes **3** and **5**, which contain the ether–phosphine ligand, are very efficient catalysts, even for the reduction of 2,3-dimethyl-2-butene, and interestingly, no relationship between the initial reduction rate of the olefin and its steric requirement is observed.

(12) Andriollo, A.; Esteruelas, M. A.; Meyer, U.; Oro, L. A.; Sánchez-Delgado, R. A.; Sola, E.; Valero, C.; Werner, H. *J. Am. Chem. Soc.* **1989**, *111*, 7431.

Concluding Remarks

This study has revealed that the cationic complexes [Ir(diene)(η^2-*i*Pr$_2$PCH$_2$CH$_2$OMe)]BF$_4$ (diene = COD, TFB) catalyze the selective hydrogenation of phenylacetylene to styrene an the hydrogenation of olefins such as 1-hexene, cyclohexene, and 2,3-dimethyl-2-butene to the corresponding alkanes.

The kinetic and spectroscopic investigations carried out on the hydrogenation of phenylacetylene to styrene catalyzed by [Ir(COD)(η^2-*i*Pr$_2$PCH$_2$CH$_2$OMe)]BF$_4$ indicate that the hydrido–alkynyl complex [IrH(C$_2$Ph)(COD)(η^2-*i*Pr$_2$PCH$_2$CH$_2$OMe)]BF$_4$ is the main species udner catalytic conditions. However, it is a side intermediate of the reaction which proceeds via the dihydride [IrH$_2$(COD)(η^2-*i*Pr$_2$PCH$_2$-CH$_2$OMe)]BF$_4$ according to the following set of reactions:

$$[Ir(COD)(\eta^2\text{-}i\text{Pr}_2\text{PCH}_2\text{CH}_2\text{OMe})]BF_4 + H_2 \rightleftharpoons [IrH_2(COD)(\eta^2\text{-}i\text{Pr}_2\text{PCH}_2\text{CH}_2\text{OMe})]BF_4$$

$$[IrH_2(COD)(\eta^2\text{-}i\text{Pr}_2\text{PCH}_2\text{CH}_2\text{OMe})]BF_4 + PhC_2H \rightleftharpoons [IrH(CH{=}CHPh)(COD)(\eta^2\text{-}i\text{Pr}_2\text{PCH}_2\text{CH}_2\text{OMe})]BF_4$$

$$[IrH(CH{=}CHPh)(COD)(\eta^2\text{-}i\text{Pr}_2\text{PCH}_2\text{CH}_2\text{OMe})]BF_4 + H_2 \rightarrow [IrH_2(COD)(\eta^2\text{-}i\text{Pr}_2\text{PCH}_2\text{CH}_2\text{OMe})]BF_4 + CH_2{=}CHPh$$

where the last equation is the rate-determining step. The above mentioned set of reactions implies that the diolefin remains coordinated during the catalytic process, in contrast to previous observations reported for related cationic diolefin iridium complexes

Experimental Section

General Comments. All manipulations were conducted with rigorous exclusion of air. Solvents were dried by known procedures and distilled under argon prior to use. Phenylacetylene (Merck) was purified by distillation and 1-hexene (Merck), cyclohexene (Merck), and 2,3-dimethyl-2-butene (Fluka) by passage through an alumina column.

Physical Measurements. ^{1}H, ^{31}P{^{1}H}, and ^{13}C{^{1}H} NMR spectra were recorded on JEOL FX 90Q and Varian UNYT 300 instruments, at 20 °C. Chemical shifts are expressed in parts per million upfield from Si(CH$_3$)$_4$ (^{1}H and ^{13}C) and 85% H$_3$PO$_4$ (^{31}P), and coupling constants (*J*) are given in hertz. IR spectra were recorded on a Perkin-Elmer 1420 or 783 infrared spectrophotometer. C, H, and N analyses were carried out with a Perkin-Elmer 240 C microanalyzer.

The catalytic reactions were followed, at constnat pressure, by measuring the hydrogen consumption as a function of time on a gas buret (Afora 516256). The analyses of the products of the catalytic reactions were carried out on a Perkin-Elmer 8500 gas chromatograph with a flame ionization detector and ββ′-

oxydipropionitrile on Chromosorb W-HP 80/100-mesh (4 m × $^1/_8$ in.) column at 60 °C for the olefins hydrogenations, and with an FFAP on Chromosorb GHP 80/100-mesh (3.6 m × $^1/_8$ in.) column at 100 °C for the phenylacetylene hydrogenation.

Starting Materials. The complexes $[Ir(\mu\text{-Cl})(COD)]_2$[13] and $IrCl(TFB)_2$[14] and the ligands i-$Pr_2PCH_2CH_2OMe$ and i-$Pr_2PCH_2CH_2NMe_2$[15] were prepared as described previously.

Preparation of IrCl(COD)(η^1-i-$Pr_2PCH_2CH_2OMe$) (1). A solution of $[Ir(\mu\text{-Cl})(COD)]_2$ (100 mg, 0.149 mmol) in 10 mL of benzene was treated at room temperature with i-$Pr_2PCH_2CH_2OMe$ (56 μL, 53 mg, 0.298 mmol). After stirring for 10 min, the solution was concentrated in vacuo. Addition of pentane caused the precipitation of yellow crystals. The solvent was decanted, and the solid was washed with pentane and dried in vacuo. Yield: 116 mg (76%). Anal. Calcd for $C_{17}H_{33}ClIrOP$: C, 39.87; H, 6.50. Found: C, 39.96; H, 6.75. IR (C_6H_6): $\nu(C\text{—}O\text{—}C)_{asym}$ 1114 cm^{-1}. ^1H NMR (C_6D_6, 90 MHz): δ 5.24, 3.12 (both m, =CH–, COD), 3.45 (m, PCH_2CH_2OMe), 3.04 (s, PCH_2CH_2OMe), 2.34 (m, $PCHCH_3$), 2.07–1.43 (m, $-CH_2-$, COD), 1.93 (m, PCH_2CH_2OMe), 1.24 (dd, J(PH) = 15.2, J(HH) = 7.0, $PCHCH_3$), 1.01 (dd, J(PH) = 13.6, J(HH) = 7.2, $PCHCH_3$). $^{31}P\{^1H\}$ NMR (C_6D_6, 36.2 MHz): δ 17.29 (s).

Preparation of IrCl(COD)(η^1-i-$Pr_2PCH_2CH_2NMe_2$) (2). This was prepared as described for 1, starting from $[Ir(\mu\text{-Cl})(COD)]_2$ (122 mg, 0.183 mmol) and i-$Pr_2PCH_2CH_2OMe$ (77 μL, 69 mg, 0.366 mmol). Yield: 137 mg (71%) (orange-yellow crystals). Anal. Calcd for $C_{18}H_{36}ClIrNP$: C, 41.17; H, 6.91; N, 2.67. Found: C, 41.58; H, 7.14; N, 2.85. ^1H NMR (C_6D_6, 90 MHz): δ 5.18, 3.34 (both m, =CH–, COD), 2.47 (m, $PCH_2CH_2NMe_2$), 2.31 (m, $PCHCH_3$), 2.25 (s, $PCH_2CH_2NMe_2$), 2.06–1.51 (m, $-CH_2-$, COD), 1.81 (m, $PCH_2CH_2NMe_2$), 1.27 (dd, J(PH) = 15.1, J(HH) = 7.0, $PCHCH_3$), 1.18 (dd, J(PH) = 15.3, J(HH) = 7.2, $PCHCH_3$). $^{31}P\{^1H\}$ NMR (C_6D_6, 36.2 MHz): δ 17.41 (s).

Preparation of [Ir(COD)(η^2-i-$Pr_2PCH_2CH_2OMe$)]BF_4 (3). A solution of $AgBF_4$ (26 mg, 0.133 mmol) in 2 mL of acetone was added to a solution of complex 1 (68 mg, 0.133 mmol) in 5 mL of acetone. After stirring for 20 min, at room temperature, the solution was filtered and the solvent was removed in vacuo. The residue was dissolved in 2 mL of dichloromethane and slow addition of 10 mL of diethyl ether caused the precipitation of orange-yellow crystals. The solvent was decanted, and the crystals were washed with diethyl ether and dried in vacuo. Yield: 72 mg (96%). Anal. Calcd for $C_{17}H_{33}BF_4IrOP$: C, 36.24; H, 5.90. Found: C, 35.99; H, 5.80. IR (CH_2Cl_2): $\nu(C\text{—}O\text{—}C)_{asym}$ 1061 cm^{-1}. ^1H NMR (CD_2Cl_2, 90 MHz): δ 5.32, 3.76 (both m, =CH–, COD), 4.06 (m, PCH_2CH_2OMe), 3.90 (s, PCH_2CH_2OMe), 2.30 (m, $PCHCH_3$), 2.27–1.74 (m, $-CH_2-$, COD), 1.77 (m, PCH_2CH_2OMe), 1.29 (dd, J(PH) = 16.6, J(HH) = 7.2, $PCHCH_3$), 1.25 (dd, J(PH) = 15.3, J(HH) = 7.0, $PCHCH_3$). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 36.2 MHz): δ 50.26 (s).

Preparation of [Ir(COD)(η^2-i-$Pr_2PCH_2CH_2NMe_2$)]BF_4 (4). The procedure described for 3, but starting from 2 (72 mg, 0.137 mmol) and $AgBF_4$ (27 mg, 0.137 mmol), gave orange-red crystals. Yield: 73 mg (92%). Anal. Calcd for $C_{18}H_{36}BF_4IrNP$: C, 37.50; H, 6.29; N, 2.43. Found: C, 37.37; H, 6.33; N, 2.53. ^1H NMR (CD_2Cl_2, 90 MHz): δ 4.69, 4.00 (both m, =CH–, COD), 2.76 (m, $PCH_2CH_2NMe_2$), 2.67 (s, $PCH_2CH_2NMe_2$), 2.35 (m, $PCHCH_3$), 2.28–1.74 (m, $-CH_2-$, COD), 1.77 (m, $PCH_2CH_2NMe_2$), 1.29 (dd, J(PH) = 16.2, J(HH) = 7.3, $PCHCH_3$), 1.25 (dd, J(PH) = 15.0, J(HH) = 6.8, $PCHCH_3$). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 36.2 MHz): δ 45.65 (s).

Preparation of [Ir(TFB)(η^2-i-$Pr_2PCH_2CH_2OMe$)]BF_4 (5). A suspension of $IrCl(TFB)_2$ (129 mg, 0.19 mmol) in 10 mL of dichloromethane was treated with i-$Pr_2PCH_2CH_2OMe$ (35.5 μL, 33.5 mg, 0.19 mmol). After stirring for 20 min, at room temperature, the resulting yellow solution was evaporated to dryness in vacuo. The oily residue was dissolved in 5 mL of acetone, and the solution was treated with a solution of $AgBF_4$ (37 mg, 0.19 mmol) in 3 mL of acetone. After stirring for 10 min, the solution was filtered to remove AgCl and evaporated to dryness in vacuo. The orange residue was dissolved in 2 mL of dichloromethane, and 10 mL of diethyl ether was slowly added to precipitate 5 as orange crystals. The solvent was decanted, and the crystals were washed with diethyl ether and dried in vacuo. Yield: 98 mg (76%). Anal. Calcd for $C_{21}H_{27}BF_8IrOP$: C, 37.01; H, 3.99. Found: C, 36.89; H, 3.77. IR (CH_2Cl_2): $\nu(C\text{—}O\text{—}C)_{asym}$ 1040 cm^{-1}. ^1H NMR (CD_2Cl_2, 90 MHz): δ 5.77 (m, >CH-, TFB), 4.65 (m, =CH–, TFB), 4.12 (m, PCH_2CH_2OMe), 3.93 (s, PCH_2CH_2OMe), 2.91 (m, =CH–, TFB), 2.17 (m, $PCHCH_3$), 1.91 (m, PCH_2CH_2OMe), 1.26 (dd, J(PH) = 15.6, J(HH) = 7.0, $PCHCH_3$), 1.23 (dd, J(PH) = 16.8, J(HH) = 7.0, $PCHCH_3$). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 36.2 MHz): δ 53.17 (s).

Preparation of [Ir(TFB)(η^2-i-$Pr_2PCH_2CH_2NMe_2$)]BF_4 (6). The procedure described for 5, but starting from $IrCl(TFB)_2$ (124 mg, 0.182 mmol), i-$Pr_2PCH_2CH_2NMe_2$ (38.5 μL, 34.5 mg, 0.182 mmol), and $AgBF_4$ (35.4 mg, 0.182 mmol), gave red crystals. Yield: 90 mg (71%). Anal. Calcd for $C_{22}H_{30}BF_8IrNP$: C, 38.05; H, 4.35; N, 2.02. Found: C, 38.10; H, 4.60; N, 2.19. ^1H NMR (CD_2Cl_2, 90 MHz): δ 5.82 (m, >CH-, TFB), 4.50, 3.28 (both m, =CH–, TFB), 2.88 (m, $PCH_2CH_2NMe_2$), 2.66 (s, $PCH_2CH_2NMe_2$), 2.24 (m, $PCHCH_3$), 1.96 (m, $PCH_2CH_2NMe_2$), 1.25 (dd, J(PH) = 15.3, J(HH) = 7.3, $PCHCH_3$), 1.23 (dd, J(PH) = 15.2, J(HH) = 7.2, $PCHCH_3$). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 36.2 MHz): δ 51.28 (s).

Preparation of [IrH(C≡CPh)(COD)(η^2-i-$Pr_2PCH_2CH_2OMe$)]BF_4 (7). (a) Complex 7 was prepared in situ as follows: Phenylacetylene (12.6 μL, 11.7 mg, 0.115 mmol) was added to a NMR tube containing a solution of complex 3 (15.0 mg, 0.027 mmol) in 0.7 mL of CD_2Cl_2. Immediately, the color of the solution changed from orange to almost colorless.

(b) A solution of complex 3 (102 mg, 0.181 mmol) in 10 mL of dichloromethane was treated with PhC≡CH (25 μL, 23 mg, 0.225 mmol). The resulting almost colorless solution was stirred for 30 min before reducing the volume to ca. 0.5 mL in vacuo. Diethyl ether (10 mL) was slowly added to precipitate the product as an off-white powder. After removal of the supernatant, the solid was washed with diethyl ether and dried in vacuo. Yield: 92.8 mg (77%). Anal. Calcd for $C_{25}H_{39}BF_4IrOP$: C, 45.11; H, 5.90. Found: C, 45.49; H, 6.34. IR (Nujol): ν(C≡C) 2280, ν(IrH) 2120 cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz): δ 7.32–7.20 (m, Ph), 6.02, 5.04, 4.00 and 3.77 (each m, =CH–, COD), 4.90 (m, PCH_2CH_2OMe), 3.93 (s, PCH_2CH_2OMe), 3.20, 3.05, 2.7–2.4 and 2.1 (each m, $-CH_2-$, COD), 2.83 (m, $PCHCH_3$), 2.25 (m, PCH_2CH_2OMe), 1.56 (dd, J(PH) = 14.5, J(HH) = 7.1, $PCHCH_3$), 1.50 (dd, J(PH) = 14.1, J(HH) = 7.3, $PCHCH_3$), 1.39 (dd, J(PH) = 13.9, J(HH) = 7.1, $PCHCH_3$), 1.35 (dd, J(PH) = 16.6, J(HH) = 7.2, $PCHCH_3$), −23.24 (d, J(PH) = 9.6, IrH). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 80.9 MHz): δ 42.60 (s). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75.4 MHz): δ 129.73, 126.86, 125.37 and 124.80 (each s, Ph), 107.31 (s, IrC≡CPh), 103.45 (d, J(PC) = 8.5, =CH–, COD), 97.82 (d, J(PC) = 13.6, =CH–, COD), 94.58 and 90.96 (both s, =CH–, COD), 84.11 (d, J(PC) = 11.1, IrC≡CPh), 74.78 (s, PCH_2CH_2OMe), 61.99 (s, PCH_2CH_2OMe), 35.66, 27.49, 24.78 and 24.35 (each s, $-CH_2-$, COD), 30.66 (d, J(PC) = 4.5, PCH_2CH_2OMe), 23.74 (d, J(PC) = 32.2, $PCHCH_3$), 22.29 (d, J(PC) = 34.2, $PCHCH_3$), 18.54, 18.40, 16.50 and 16.42 (each s, $PCHCH_3$).

Reaction of 3 with H_2. [IrH_2(COD)(η^2-i-$Pr_2PCH_2CH_2OMe$)]BF_4 (8) was prepared in situ as follows: in a NMR tube, at 25 °C, 15.0 mg (0.027 mmol) of 3 were dissolved in 1 mL of CD_2Cl_2, and H_2 was bubbled through the solution for 5 min during which the color of the solution changed from orange to yellow. ^1H NMR (CD_2Cl_2, 300 MHz):[16] δ −12.21 (dd, J(PH) = 18.99, J(HH) = 3.5, $Ir\text{–}H_{trans\ to\ COD}$), −24.20 (dd, J(PH) = 12.93, J(HH) = 3.5, $Ir\text{–}H_{trans\ to\ OMe}$). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 80.9 MHz): δ 55.5 (s, complex 8), 50.26 (s, complex 3).

Catalytic Reactions. In a typical procedure, the substrate dissolved in deaerated dichloromethane (4 mL) was added to a

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(16) In the 6–1 ppm region of the ^1H NMR spectrum, the signals due to complexes 3 and 8 overlap.

Table III. Crystallographic Data for 3

formula	$C_{17}H_{33}BF_4IrOP$
fw	563.45
cryst size, mm	0.25 × 0.40 × 0.45
cryst syst	monoclinic
space group	$P2_1/n$ (No. 14)
cell dimens determn; θ range, deg	23 reflecns; $11 < \theta < 16$
a, Å	8.466(3)
b, Å	9.004(3)
c, Å	27.052(13)
β, deg	97.71(2)
V, Å^3	2044
Z	4
d_{calcd}, g cm^{-3}	1.83
diffractometer	Enraf Nonius CAD 4
radiatn (graphite monochrom); λ, Å	Mo Kα; 0.709 30
temp, °C	20 ± 1
μ, cm^{-1}	66.1
scan method	$\omega/2\theta$
2θ (max), deg	46
total no. of rflns scanned	3305
no. of unique rflns	2827
no. of obsd rflns	2341 ($I > 3\sigma(I)$)
no. of params refined	262
R	0.025
R_w	0.029
rfln/param ratio	8.94
residual electron density, e Å^{-3}	+0.70/−0.76

solution of the catalyst in dichloromethane (4 mL), under argon atmosphere. This solution was syringed through a silicone septum into a 25-mL flask attached to a gas buret, which was in turn connected to a Schlenck manifold and had been previously evacuated and refilled with hydrogen three times. The flask was then immersed in a 25 °C bath and the mixture was vigorously shaken during the run.

Hydrogenation of Phenylacetylene. Reaction conditions: [catalyst] = 1.0×10^{-3} M, [PhC_2H] = 0.2 M, $P(H_2)$ = 1 atm. For the reactions catalyzed by **3** and **5** the initial rates observed ($-dV/dt$) were 5.3×10^{-6} and 2.8×10^{-6} L s^{-1}, respectively. In the presence of **4** or **6**, no consumption of hydrogen was observed. For kinetic data see Table II.

Hydrogenation of Olefins. Reaction conditions: [catalyst] = 1.0×10^{-3} M, [olefin] = 0.2 M, $P(H_2)$ = 1 atm. For the reactions catalyzed by **3** and **5** the rates of consumption of hydrogen were in all cases (1-hexene, cyclohexene, and 2,3-dimethyl-2-butene) higher 1.3×10^{-4} L s^{-1}, which prevented measuring the exact value of the initial rate. For the reactions in the presence of complexes **4** and **6**, the initial rates observed were $>1.3 \times 10^{-3}$ and $\approx 1.6 \times 10^{-5}$ L s^{-1}, for the hydrogenation of 1-hexene and cyclohexene, respectively. No consumption of hydrogen was observed with 2,3-dimethyl-2-butene as the substrate.

X-ray Structural Analysis of 3. Single crystals were grown by solvent diffusion of diethyl ether in a saturated solution of **3** in dichloromethane at 25 °C. Crystal data collection parameters are summarized in Table III. Intensity data were corrected for Lorentz and polarization effects. An empirical absorption correction (ψ-scan method) was applied; the minimal transmission was 81.1%. The structure was solved by the Patterson method (SHELXS-86). Atomic coordinates (see Table IV) and anisotropic thermal parameters of all non-hydrogen atoms were refined using the scattering factors for neutral atoms[17] by full matrix least squares with unit weights. Anomalous dispersion effects were included in the refinement (values for $\Delta f'$ and $\Delta f''$ from ref 18). The positions of all hydrogen atoms were calculated according to ideal geometry (distance C–H 0.95 Å, sp^3 geometry for C1, C2, C5, and C6) and refined by the riding method. The BF_4 counterion shows a 1:1 disordering effect. Independent atomic positions were refined anisotropically with an occupation factor of 0.5. ESD's of bond lengths and angles were derived by analysis of the full covariance matrix. All calculations were performed on a Micro-VAX computer using the program system SDP[19] (Enraf-Nonius). For other details see Table III.

Table IV. Positional Parameters and Their Estimated Standard Deviations[a]

atom	x/a	y/b	z/c	B_{eq}, Å^2
Ir	0.36582(3)	0.13956(3)	0.08244(1)	2.516(5)
P	0.5329(2)	0.1633(2)	0.15580(7)	3.01(4)
F1	0.583(2)	0.103(2)	0.3882(4)	9.0(3)
F1*	0.651(2)	0.075(2)	0.3933(6)	11.0(6)
F2	0.585(2)	0.288(1)	0.3345(4)	6.7(3)
F2*	0.598(2)	0.288(2)	0.3551(7)	10.0(5)
F3	0.585(2)	0.051(1)	0.3082(4)	11.7(5)
F3*	0.462(2)	0.080(2)	0.3297(6)	9.0(4)
F4	0.805(2)	0.128(2)	0.3584(6)	9.1(4)
F4*	0.716(2)	0.117(2)	0.3164(5)	9.2(4)
O	0.3389(7)	−0.0794(6)	0.1118(2)	4.0(1)
C1	0.459(1)	0.3105(9)	0.0410(3)	4.3(2)
C2	0.346(1)	0.369(1)	0.0701(3)	4.8(2)
C3	0.177(1)	0.415(1)	0.0512(4)	6.3(3)
C4	0.085(1)	0.298(1)	0.0174(3)	4.9(2)
C5	0.1421(9)	0.141(1)	0.0304(3)	4.1(2)
C6	0.262(1)	0.072(1)	0.0070(3)	4.4(2)
C7	0.349(1)	0.146(1)	−0.0313(3)	5.2(2)
C8	0.424(1)	0.293(1)	−0.0147(3)	5.7(3)
C9	0.566(1)	−0.030(1)	0.1761(4)	5.3(2)
C10	0.425(1)	−0.127(1)	0.1583(4)	6.9(3)
C11	0.207(1)	−0.179(1)	0.0966(5)	7.5(3)
C12	0.7340(9)	0.240(1)	0.1567(3)	3.6(2)
C13	0.824(1)	0.169(1)	0.1178(3)	4.7(2)
C14	0.829(1)	0.231(2)	0.2091(4)	6.8(3)
C15	0.449(1)	0.253(1)	0.2075(3)	4.7(2)
C16	0.448(1)	0.425(1)	0.2037(4)	7.4(3)
C17	0.281(1)	0.193(2)	0.2116(4)	7.5(3)
B	0.620(2)	0.141(2)	0.3468(4)	6.1(3)

[a] Anisotropically refined atoms (marked by asterisks) are given in the form of the isotropic equivalent displacement parameter defined as $B_{eq} = {}^4/_3[a^2B(1,1) + b^2B(2,2) + c^2B(3,3) + ab(\cos\gamma)B(1,2) + ac(\cos\beta)B(1,3) + bc(\cos\alpha)B(2,3)]$.

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Supplementary Material Available: Tables of bond distances, bond angles, least-squares planes, torsional angles, positional parameters and general displacement parameters (10 pages). Ordering information is given on any current masthead page.

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