Synthesis, Molecular Structure, and Reactivity of Iridium(I) and Iridium(III) Complexes Formed by Coordination and C−H Activation of the Substituted Arenes $C_6H_5CH_2CH_2PiPr_2$ and $C_6H_5OCH_2CH_2PtBu_2$

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The dimer $[Ir(\mu\text{-}Cl)(C_8H_{14})_2]_2$ (**1**) reacts with $AgPF_6$ in acetone to give the bis(acetone) adduct *cis*-$[Ir(acetone)_2(C_8H_{14})_2]PF_6$ (**2**), which upon treatment with $iPr_2PCH_2CH_2C_6H_5$ (L^1) affords the half-sandwich-type complex $[(\eta^6\text{-}L^1\text{-}\kappa\text{-}P)Ir(C_8H_{14})]PF_6$ (**3**). The methoxy-bridged dimer $[Ir(\mu\text{-}OMe)(C_8H_{12})]_2$ (**4**) gives upon treatment with the phosphonium salt $L^1{\cdot}HBF_4$ the compound $[Ir(C_8H_{12})(acetone)(L^1\text{-}\kappa\text{-}P)]BF_4$ (**5**), whereas with $L^2{\cdot}HBF_4$ ($L^2 = tBu_2PCH_2CH_2OC_6H_5$) the bis(chelate) complex $[Ir(C_8H_{12})(L^2\text{-}\kappa^2\text{-}O,P)]BF_4$ (**6**) is generated. Both **5** and **6** react with hydrogen in acetone to yield the dihydridoiridium(III) derivatives $[(\eta^6\text{-}L^1\text{-}\kappa\text{-}P)IrH_2]BF_4$ (**7**) and $[(\eta^6\text{-}L^2\text{-}\kappa\text{-}P)IrH_2]BF_4$ (**8**), respectively. Compounds **7** and **8** react with excess ethene or propene to give the iridium(I) olefin complexes $[(\eta^6\text{-}L^1\text{-}\kappa\text{-}P)Ir(CH_2{=}CHR)]BF_4$ [R = H (**9**), Me (**11**)] and $[(\eta^6\text{-}L^2\text{-}\kappa\text{-}P)Ir(CH_2{=}CHR)]BF_4$ [R = H (**10**), Me (**12**)], which in the presence of H_2 regenerate the dihydrido precursors. The reaction of **7** with 2 equiv of PhC≡CPh affords the π-alkyne complex $[(\eta^6\text{-}L^1\text{-}\kappa\text{-}P)Ir(PhC{\equiv}CPh]BF_4$ (**14**) via the stilbene derivative $[(\eta^6\text{-}L^1\text{-}\kappa\text{-}P)Ir(Z\text{-}PhCH{=}CHPh)]BF_4$ (**13**) as an intermediate. Compound **13** can be isolated upon treatment of **11** with *Z*-stilbene and has been characterized crystallographically. The reactions of **7** and **11** with acetonitrile lead to the cleavage of the arene−metal bond and afford the octahedral iridium(III) complexes $[IrH_2(NCCH_3)_3(L^1\text{-}\kappa\text{-}P)]BF_4$ (**15**) and $[IrH(C_6H_4\text{-}CH_2CH_2PiPr_2\text{-}\kappa^2\text{-}C,P)(NCCH_3)_3]BF_4$ (**16**), respectively. Treatment of the C−H activation product **16** with H_2 yields **15**. The X-ray crystal structure analysis of **16** reveals that the $Ir(NCCH_3)_3$ fragment possesses the *fac* configuration.

Introduction

Recently, we reported the preparation of bulky functionalized phosphine ligands of the general composition $R_2P(CH_2)_nXC_6H_5$ (R = *i*Pr, *t*Bu; X = CH_2, O) which not only are able to coordinate to rhodium(I) in a chelating fashion but, in the coordination sphere of rhodium, also undergo a C−H activation of the six-membered ring under unusually mild conditions.[1,2] In contrast, the structurally related half-sandwich-type compounds $[(\eta^6\text{-arene})Rh(C_8H_{14})(PiPr_3)]PF_6$, in which the arene and the phosphine are not linked by a $(CH_2)_n$ unit, do not react by ring metalation and, in the presence of $PiPr_3$ or H_2, smoothly decompose.[1,3]

Since some of us showed, however, that η^6-arene-(hydrido) complexes of iridium such as $[(\eta^6\text{-arene})IrH_2(PiPr_3)]BF_4$ are stable and catalyze the hydrogenation of various unsaturated substrates, including imines,[4] we were prompted to find out whether also iridium derivatives of the functionalized phosphines are accessible and what their reactivity is. With regard to catalysis, the challenging aspect seemed to be whether the phosphine chelate effect would lead to more robust compounds while maintaining the desirable lability of the arene moiety.

This work describes the preparation and characterization of a series of iridium(I) and iridium(III) compounds in which the chosen phosphines $iPr_2PCH_2CH_2C_6H_5$ (L^1) and $tBu_2PCH_2CH_2OC_6H_5$ (L^2) are coordinated either as two-electron donors or, more frequently, as chelating (6+2)-electron donor ligands. Moreover, it illustrates that in contrast to rhodium chemistry also half-sandwich-type iridium complexes with L^1 as the functionalized arene react by ring metalation and that this process is strictly reversible.

Results and Discussion

1. Preparation of Olefinic Iridium(I) and Dihydridoiridium(III) Complexes with L^1 and L^2 as

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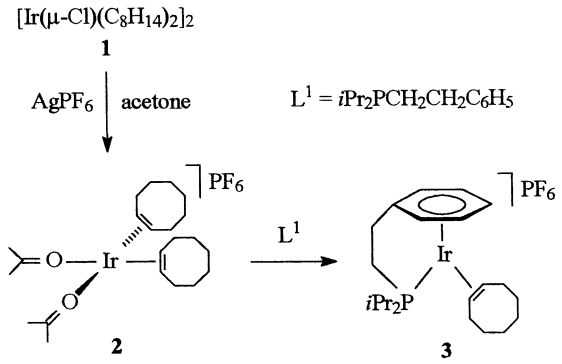
Scheme 1



Ligands. In two recent papers we reported that the highly reactive bis(acetone)rhodium(I) compound *cis*-$[Rh(acetone)_2(C_8H_{14})_2]PF_6$ is an appropriate starting material not only for the synthesis of (η^6-arene)rhodium(I) complexes with chelating diphosphines such as $iPr_2PCH_2CH_2PCy_2$[5] but also for that of cyclooctene derivatives with L^1 and L^2 as supporting ligand.[1] A related methodology has now been applied for the preparation of the new cationic iridium(I) complex **3** (Scheme 1). The first step consists of the reaction of the dimer **1** with $AgPF_6$ in acetone at room temperature, which affords, after separation of AgCl, the bis(acetone) adduct **2** as an orange air-sensitive solid in 89% isolated yield. In the second step, a solution of L^1 in acetone is added to a solution of **2** in the same solvent, which leads to a smooth change of color from orange-red to yellow. After concentrating the solution to about 2 mL, subsequent addition of diethyl ether led to the precipitation of a light yellow solid, the elemental analysis and the spectroscopic data of which correspond to the half-sandwich-type complex **3**. Conductivity measurements confirm the presence of a 1:1 electrolyte. As in the case of the analogous rhodium compound $[Rh(C_8H_{14})(\eta^6\text{-}L^1\text{-}\kappa\text{-}P)]PF_6$,[1] in both the ^1H and $^{13}C\{^1H\}$ NMR spectra of **3** the signals for the protons and carbon atoms of the six-membered ring are significantly shifted to higher field compared to the free arene.

The reaction of **3** with ethene does not lead to a complete replacement of cyclooctene. Even at 333 K under an atmosphere of C_2H_4, the corresponding ethene complex **9** (Scheme 3, see below) is generated only to a maximum amount of ca. 30%. This is in contrast to the related rhodium system where the ethene derivative $[Rh(C_2H_4)(\eta^6\text{-}L^1\text{-}\kappa\text{-}P)]PF_6$ could be isolated as a yellow solid in 92% yield.[1] In the presence of H_2, compound **3** is inert. At room temperature, no reaction takes place, while at 323 K after 20 h only traces of the dihydride **7** (Scheme 2, see below) are formed. The general conclusion is that the cyclooctene ligand of **3** is somewhat more firmly bond to the metal center than in the rhodium counterpart.

The preparation of square-planar iridium(I) complexes with L^1 and L^2 as ligands is possible by using the methoxy-bridged compound **4** as the precursor. The same starting material has already been employed for the synthesis of dihydridoiridium(III) derivatives with benzene as the arene ring.[4] However, while treatment of **4** with the phosphonium salt $L^1{\cdot}HBF_4$ in acetone gives the acetone-containing cation **5** (Scheme 2), the analogous reaction of **4** with $L^2{\cdot}HBF_4$ furnishes the chelate complex **6** in 92% yield. Compound **5** is isolated as an orange oil containing small amounts of impurities, which could not be separated by various techniques. Therefore, the cationic species was characterized by spectroscopic means and by a FAB mass spectrum. The IR spectrum of **5** displays a ν(C=O) stretching mode at 1652 cm^{-1}, whereas the $^{13}C\{^1H\}$ NMR spectrum shows the resonances for the carbon atoms of the coordinated ketone at δ 204.4 (C=O) and 30.2 (CH_3).

The chelate complex **6** was isolated in analytically pure form as an orange solid that is air-stable and readily soluble in polar organic solvents. The value for the conductivity in acetone is practically the same as for the half-sandwich-type compound **3**. Regarding the spectroscopic data of **6**, it is interesting to note that while the room temperature $^{31}P\{^1H\}$ NMR spectrum in $CDCl_3$ shows a sharp singlet at δ 58.9, the spectrum in acetone-d_6 displays a significantly broadened signal, suggesting the facile opening of the *O*,*P*-bonded chelate ring in this solvent. The broadened resonance becomes sharp at 323 K, but it is also quite broad at lower temperatures. Moreover, the spectrum at 173 K exhibits, besides the broadened singlet at δ 59.4, two other resonances at δ 32.0 and 30.8, which could be tentatively attributed to the stabilization of acetone adducts $[Ir(C_8H_{12})(acetone)_n(L^2\text{-}\kappa\text{-}P)]BF_4$ (n = 1 and 2) at low temperature.

Both compounds **5** and **6** react at room temperature in acetone under H_2 atmosphere quite smoothly to give the dihydridoiridium(III) complexes **7** and **8** in 79−87% yield. The reactions have to be stopped if the solutions (which are initially orange-red) become brownish-yellow, since if stirring is continued, decomposition products are formed. After repeated recrystallization from acetone/diethyl ether, white solids are isolated that are air-stable and readily soluble in acetone and dichloromethane. Typical spectroscopic features of **7** and **8** are the two metal−hydride stretching modes at 2241 and 2200 cm^{-1} (for **7**) and 2244 and 2201 cm^{-1} (for **8**) in the IR as well as the high-field signal at δ −14.99 (**7**) and −15.31 (**8**) in the ^1H NMR spectra. The hydride resonance is split into a doublet due to $^1H-^{31}P$ coupling.

2. Reactions of the Dihydridoiridium(III) Complexes 7 and 8 with Olefins and Diphenylacetylene. Since we anticipated that the dihydrido compounds **7** and **8** might be good hydrogenation catalysts, we first had to find out what the reactivity of **7** and **8** toward simple olefins is. When solutions of **7** and **8** in acetone-d_6 were stirred under an ethene or propene atmosphere and the reactions monitored by ^1H NMR spectroscopy, the formation of the corresponding alkanes and the olefin complexes **9**−**12** was observed (Scheme 3). Compared with **7** the rate for the reactions of **8** is rather low at room temperature, and for quantitative hydrogenation, a temperature of ca. 323 K has to be employed. The iridium(I) complexes **9**−**12** are then formed almost quantitatively and can be isolated as light yellow or yellow, only moderately air-sensitive solids in good to excellent yields. The NMR spectra of **9**−**12** are similar to those of their rhodium counterparts[1] and thus deserve no further comment. It should be

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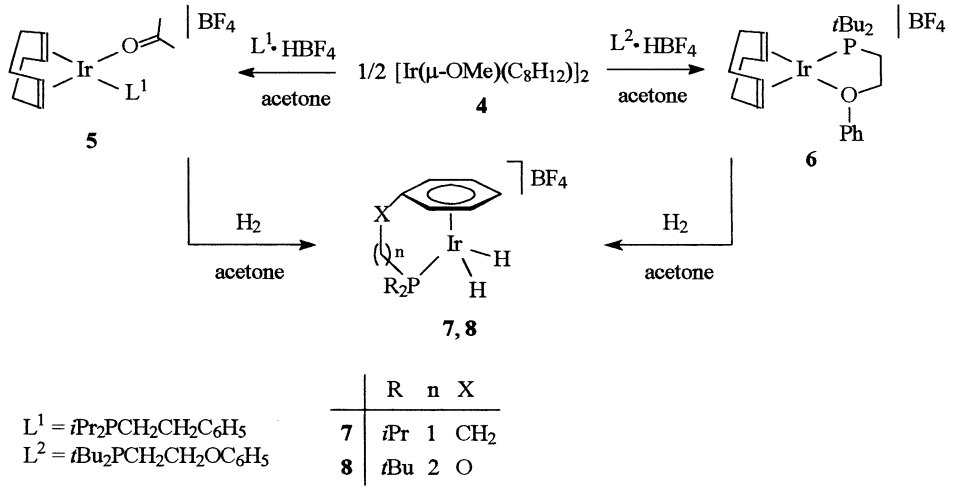
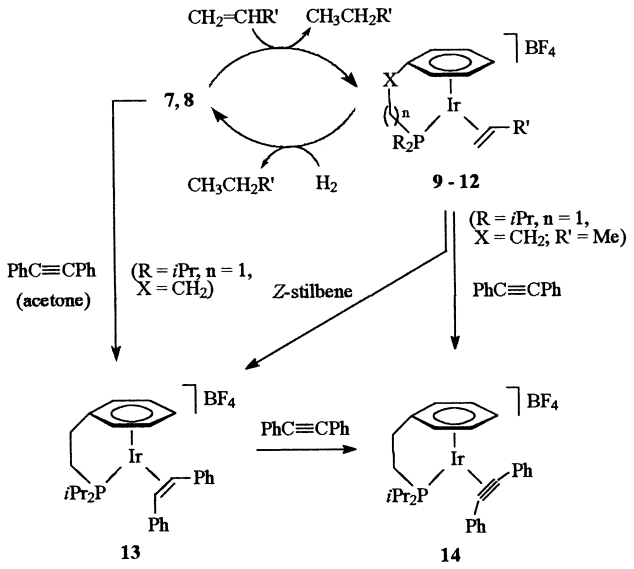
Scheme 2



$L^1 = i\text{Pr}_2\text{PCH}_2\text{CH}_2\text{C}_6\text{H}_5$
$L^2 = t\text{Bu}_2\text{PCH}_2\text{CH}_2\text{OC}_6\text{H}_5$

	R	n	X
7	*i*Pr	1	CH_2
8	*t*Bu	2	O

Scheme 3



	R	n	X	R'
9	*i*Pr	1	CH_2	H
10	*t*Bu	2	O	H
11	*i*Pr	1	CH_2	Me
12	*t*Bu	2	O	Me

noted, however, that the ^{31}P NMR resonances of **9**−**12** are shifted by 22−38 ppm to higher fields compared with **7** and **8**, which indicates a higher electron density at the metal center of the olefin complexes than of the iridium dihydrides.

The feasibility of a reconversion of the olefin to the dihydrido complexes was proven by the reaction of **9** with H_2. At room temperature in acetone-d_6 the dihydride **7** was formed after 20 h in more than 90% yield. Small quantities of byproducts, also containing hydrido ligands, were equally generated, but all attempts to characterize them more precisely failed.

The reaction of **7** with diphenylacetylene in the molar ratio of 1:1 in acetone leads to a mixture of two products, that with a signal at δ 60.2 in the $^{31}P\{^1H\}$ NMR spectrum dominating. Part of the starting material is still present. The second product resonates in the $^{31}P\{^1H\}$ NMR spectrum at δ 47.9. If the reaction mixture is treated with an excess of PhC≡CPh, the signal at higher field disappears, and from the orange solution, after removal of the solvent and recrystallization from acetone/diethyl ether, a yellow solid can be isolated. The spectroscopic data suggest that it is the π-alkyne complex **14** (see Scheme 3). Typical features are the ν(C≡C) stretch at 1824 cm^{-1} in the IR and the signal for the carbon atoms of the C≡C triple bond at δ 93.8. The latter is split into a doublet due to $^{13}C-^{31}P$ coupling. Compound **14** can also be prepared from the propene analogue, **11**, by replacing the olefin for the alkyne; in this case the time for the reaction is 12 h instead of 10 min. However, on both routes, the yield of **14** is excellent.

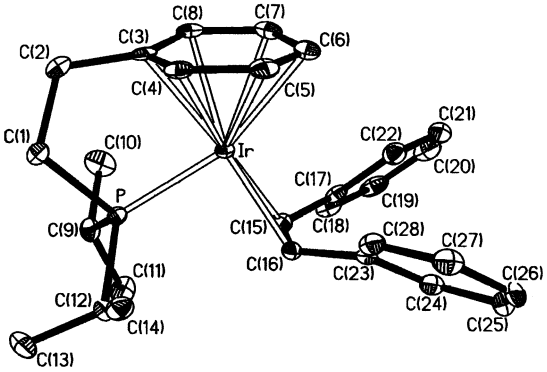


Figure 1. Molecular representation of the cationic complex of **13**.

The second product formed in the reaction of **7** with an equimolar amount of diphenylacetylene is the *Z*-stilbene complex **13**. While it cannot be conveniently prepared from **7** and *Z*-PhCH=CHPh, it is obtained in 80% yield by ligand substitution from **11** and an excess of the Z-stilbene. Even on prolonged heating, no isomerization of the *Z* to the *E* isomer of the stilbene occurs.

The molecular structure of **13** is shown in Figure 1. Similarly to the cyclooctenerhodium compound [Rh(C_8H_{14})(η^6-L^1-κ-*P*)]PF_6, the arene ring possesses a slightly inverse boat conformation, the characteristic feature being that the *ipso*-carbon atom C(3) and, to a smaller extent, the carbon atom C(6) in *para* position are bent toward the metal center. The consequence is that the distance Ir−C(3) (Table 1) is ca. 0.09 Å shorter than the distances Ir−C(4) and Ir−C(8). The bond lengths Ir−

Table 1. Selected Bond Lengths (Å) and Angles (deg) for 13

Ir−P	2.2594(9)	Ir−M(1)[a]	2.000(2)
Ir−C(3)	2.216(3)	P−C(1)	1.850(3)
Ir−C(4)	2.296(3)	P−C(9)	1.852(3)
Ir−C(5)	2.339(3)	P−C(12)	1.845(3)
Ir−C(6)	2.326(4)	C(1)−C(2)	1.540(5)
Ir−C(7)	2.342(3)	C(2)−C(3)	1.510(5)
Ir−C(8)	2.309(3)	C(15)−C(16)	1.452(5)
Ir−G(1)[a]	1.8195(15)	C(15)−C(17)	1.482(5)
Ir−C(15)	2.139(3)	C(16)−C(23)	1.496(4)
Ir−C(16)	2.118(3)		
P−Ir−G(1)[a]	122.26(5)	Ir−P−C(12)	117.51(11)
P−Ir−C(15)	91.57(10)	P−C(1)−C(2)	112.8(2)
P−Ir−C(16)	92.50(9)	C(1)−C(2)−C(3)	111.2(3)
P−Ir−M(1)[a]	92.17(7)	Ir−C(15)−C(16)	69.28(18)
G(1)−Ir−C(15)[a]	142.06(10)	Ir−C(15)−C(17)	119.6(2)
G(1)−Ir−C(16)[a]	139.58(10)	C(16)−C(15)−C(17)	127.6(3)
G(1)−Ir−M(1)[a]	145.54(8)	Ir−C(16)−C(15)	70.82(18)
Ir−P−C(1)	104.29(12)	Ir−C(16)−C(23)	120.9(2)
Ir−P−C(9)	119.68(12)	C(15)−C(16)−C(23)	126.7(3)

[a] G(1) represents the centroid of the arene ring C(3)−C(8). M(1) represents the midpoint of the olefinic bond C(15)−C(16).

C(15), Ir−C(16), and C(15)−C(16) lie in the expected range and are quite similar to those found in other (η^6-arene)iridium complexes containing olefinic ligands.[4,6] The bond angles P−Ir−C(15) and P−Ir−C(16) deviate only slightly from the 90° value and are in good agreement with the proposed piano-stool configuration of the molecule.

3. Dihydrido- and Monohydridoiridium(III) Complexes Formed by Arene Dissociation and C−H Metalation. Treatment of **7** with excess CH_3CN leads to a partial opening of the chelate bond and, even if the ratio of acetone to acetonitrile is 8:1, affords the six-coordinate iridium(III) complex **15** in 87% isolated yield (Scheme 4). Both the elemental analysis and the mass spectrum (FAB) are consistent with the expected composition. The resonance of the hydrido ligands is observed in the ^{1}H NMR spectrum of **15** at δ −22.64 as a doublet, the chemical shift being in agreement with the data of $[IrH_2(NCCH_3)_3(PiPr_3)]BF_4$.[7] Due to the stereochemical inequivalence of the acetonitriles, two signals for the CH_3 protons appear at δ 2.42 and 2.32 with an intensity ratio of 2:1. Only the resonance of the CH_3CN ligand *trans* to the phosphine is split into a doublet with an ^{1}H−^{31}P coupling constant of 0.9 Hz. The splitting pattern for the signals of the acetonitrile carbon atoms in the ^{13}C{^{1}H} NMR spectrum of **15** is quite similar to that for the protons. Although neither the ^{1}H nor the ^{13}C NMR data of **15** reveal whether the *fac* or the *mer* isomer is formed, we assume that in analogy with $[IrH_2(NCCH_3)_3(PiPr_3)]BF_4$[7] the *fac* configuration is preferred.

To get some more insight into the mechanism of the ring displacement leading to **15**, a kinetic study of the reaction of **7** with acetonitrile-d_3 was carried out. For this purpose, solutions of **7** in CD_2Cl_2 were treated at 195 K with different amounts of CD_3CN (30- to 250-fold excess), and, after warming to 253 K, the decrease in intensity of the hydride signal of **7** was measured. Under these conditions, the rate law was of pseudo-first-order, $-d[\mathbf{7}]/dt = k_{obs}[Ir]$, with the observed rate constant corresponding to $k_{obs} = k[CD_3CN]^n$. Owing to this equation, the values of k_{obs} depend on the concentration of CD_3CN and are listed in Table 2. The corresponding plot (see Figure 2) of log(k_{obs}) versus log([CD_3CN]) with a slope of 1.05 illustrates that there is a first-order dependence on the concentration of CD_3CN, which means that the reaction of **7** with acetonitrile-d_3 follows second-order kinetics.

Table 2. Dependence of k_{obs} on the Concentration of CD_3CN for the Reaction of 7 with CD_3CN in Acetone at 298 K

	[CD_3CN] (mol/L)			
	6.38	3.09	1.03	0.28
$10^4 \cdot k_{obs}$ (s^{-1})	30.2	11.4	5.45	1.00

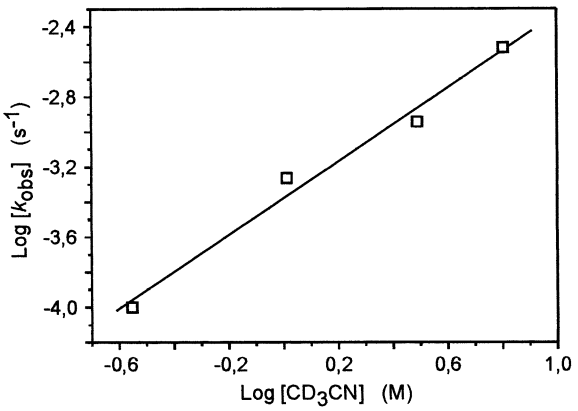


Figure 2. Plot of log(k_{obs}) vs log([CD_3CN]) for the reaction of **7** with CD_3CN in acetone at 253 K.

The mechanistic scheme derived from the kinetic data is depicted in Scheme 5. Although the rate law suggests that the primary and rate-determining step probably consists of the attack of the nitrile ligand to the metal center, the possibility of an equilibrium between **7** and the coordinatively unsaturated intermediate **A** cannot be excluded. If this equilibrium is fast and the subsequent addition of acetonitrile to the free coordination site is slow, a second-order rate law would equally result. We note that a η^6-to-η^4 ring slippage has been discussed for the ligand exchange reactions of (η^6-arene)-chromiumtricarbonyls with different arenes[8] and has been proved for the formation of $[(\eta^5\text{-}C_5Me_5)Ir(\eta^4\text{-}C_6Me_6)]$ from $[(\eta^5\text{-}C_5Me_5)Ir(\eta^6\text{-}C_6Me_6)]^{2+}$ as the precursor.[9]

In contrast to **7**, the half-sandwich-type iridium(I) complex **11** reacts with acetonitrile not only by displacement of the arene ring but also by insertion of the metal into one of the C−H bonds of the C_6H_5 unit. Treating a solution of **11** in acetone with an excess of CH_3CN leads to a stepwise change of color from light yellow to orange-red and then again to light yellow. After removal of the solvent, a solid is isolated, the analytical composition of which corresponds to that of $[Ir(L^1)(NCCH_3)_3]BF_4$. Although the existence of a compound like this is

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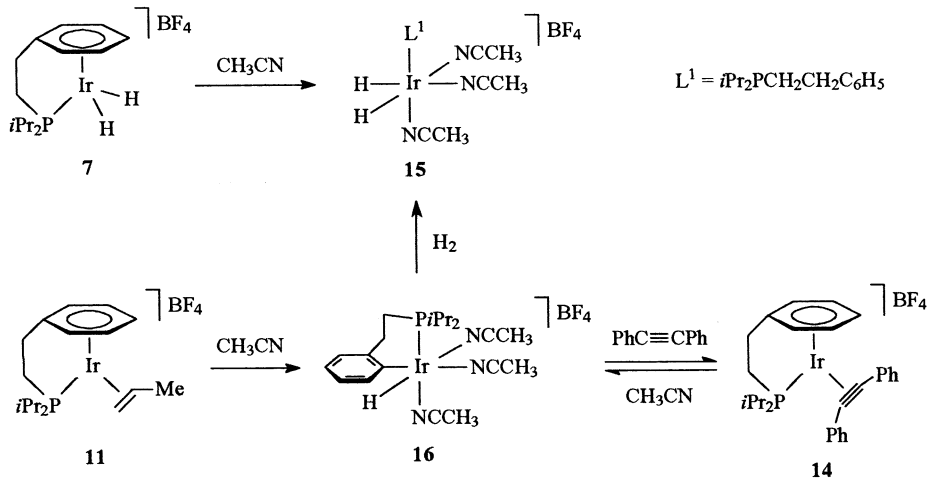
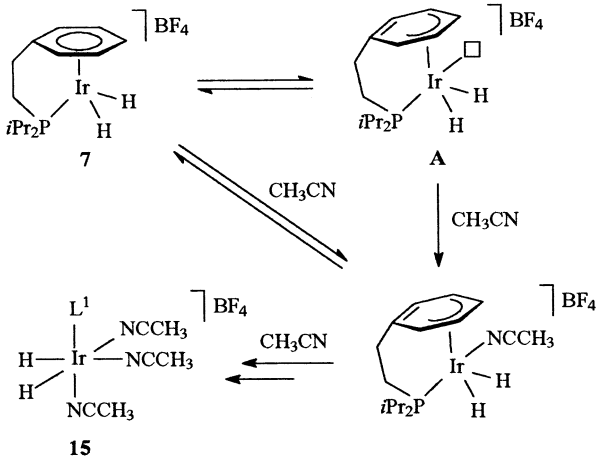
Scheme 4



Scheme 5



$L^1 = i\text{Pr}_2\text{PCH}_2\text{CH}_2\text{C}_6\text{H}_5$

conceivable (it possibly is the short-lived orange-red intermediate), the ^{1}H and ^{13}C{^{1}H} NMR spectra reveal that the isolated product does not contain an intact ligand L^1; the arylhydrido complex **16** is formed instead (see Scheme 4). Typical spectroscopic features are the high-field signal at δ −22.33 (with J(PH) = 19.8 Hz) for the hydride in the ^{1}H NMR and the doublet resonance at δ 125.5 (with J(PC) = 8.3 Hz) for the metalated carbon atom of the six-membered ring in the ^{13}C{^{1}H} NMR spectrum. Moreover, in both the ^{1}H and ^{13}C{^{1}H} NMR spectra three sets of signals for the protons and carbon atoms of the acetonitriles are observed, indicating that they are stereochemically different and thus arranged in a *fac* configuration.

The result of the X-ray crystal structure analysis of **16** is shown in Figure 3. It confirms that an intramolecular C−H metalation has taken place and an isomer of the above-mentioned species $[Ir(L^1)(NCCH_3)_3]BF_4$ has been generated. The coordination geometry around the iridium center corresponds to a distorted octahedron, the *cis* bond angles C(4)−Ir−P, C(4)−Ir−N, P−Ir−N, and N−Ir−N lying between 84.34(12)° and 100.38(9)°, respectively. The Ir−N−C axes are not exactly linear and deviate by ca. 4−10° from the ideal 180° value. The bond lengths Ir−N(1) and Ir−N(3) are nearly identical (see Table 3), while compared with Ir−N(1) and Ir−N(3) the distance Ir−N(2) is somewhat elongated. This could

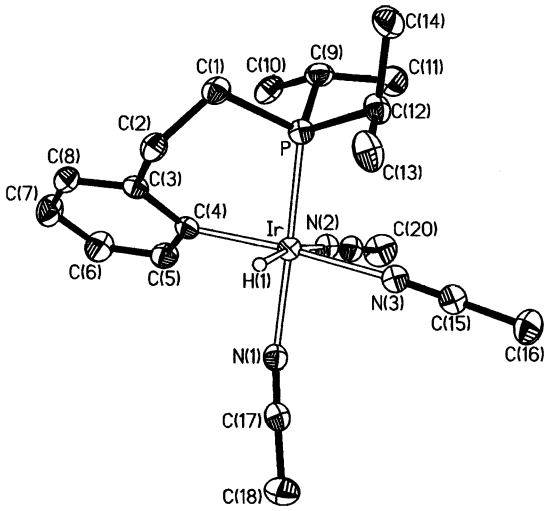


Figure 3. Molecular view of the metal complex of **16**.

Table 3. Selected Bond Lengths (Å) and Angles (deg) for 16

Ir−P	2.2302(10)	P−C(9)	1.840(4)
Ir−N(1)	2.090(3)	P−C(12)	1.843(4)
Ir−N(2)	2.150(3)	N(1)−C(17)	1.134(5)
Ir−N(3)	2.098(3)	N(2)−C(19)	1.129(5)
Ir−C(4)	2.038(4)	N(3)−C(15)	1.134(5)
Ir−H(1)	1.51(4)	C(1)−C(2)	1.515(5)
P−C(1)	1.837(4)	C(2)−C(3)	1.512(5)
P−Ir−N(1)	173.76(9)	N(3)−Ir−H(1)	91.5(15)
P−Ir−N(2)	100.38(9)	C(4)−Ir−H(1)	85.9(15)
P−Ir−N(3)	95.16(9)	Ir−P−C(1)	112.19(14)
P−Ir−C(4)	88.27(10)	Ir−P−C(9)	117.05(14)
P−Ir−H(1)	89.0(15)	Ir−P−C(12)	114.07(14)
N(1)−Ir−N(2)	85.81(12)	P−C(1)−C(2)	114.3(3)
N(1)−Ir−N(3)	84.34(12)	C(1)−C(2)−C(3)	112.5(3)
N(1)−Ir−C(4)	91.96(13)	Ir−N(1)−C(17)	170.6(3)
N(1)−Ir−H(1)	84.8(15)	Ir−N(2)−C(19)	172.2(3)
N(2)−Ir−N(3)	86.57(12)	Ir−N(3)−C(15)	176.2(3)
N(2)−Ir−C(4)	95.44(13)	N(1)−C(17)−C(18)	178.0(5)
N(2)−Ir−H(1)	170.5(15)	N(2)−C(19−C(20)	178.8(5)
N(3)−Ir−C(4)	175.66(13)	N(3)−C(15)−C(16)	179.0(5)

reflect the strong *trans* influence of the hydrido ligand, which in a difference Fourier analysis has been located. The distance Ir−H of 1.51(4) Å corresponds to that of other hydridoiridium complexes.[10] Analogously to the

(10) Typical Ir−H bond lengths are 1.48−1.63 Å. See: Allen, F. H.; Kennard, O. *Chem. Des. Automat. News* **1993**, *8*, 31.

five-coordinate cyclometalated rhodium(III) compound [RhHCl($C_6H_5CH_2CH_2PtBu_2$-κ-*P*)($C_6H_4CH_2CH_2PtBu_2$-κ-*C*,*P*)] (**17**),[2] the six-membered chelate ring of **16** built up by Ir, P, and C(1)−C(4) possesses a boat conformation with the atoms Ir and C(2) representing the top and the end of the boat. The Ir−C(4) bond length of 2.038(4) Å is slightly shorter than in the phenyl(hydrido) derivative [IrH(C_6H_5)Cl($PiPr_3$)$_2$] (2.010(5) Å), the latter being prepared from *trans*-[IrCl(C_8H_{14})($PiPr_3$)$_2$] and benzene by C−H activation.[11]

The cyclometalated complex **16** is formed not only from **11** but also from **14** upon treatment with excess acetonitrile in acetone. If this reaction is monitored by $^{31}P\{^1H\}$ NMR spectroscopy, the yield of **16** is practically 100%. However, if the solvent and other volatile substrates are removed in vacuo, a change of color from light yellow to orange occurs and the π-alkyne compound **14** is partly regenerated. Addition of a 10-fold excess of diphenylacetylene to the solution of the oily residue in acetone affords the half-sandwich-type complex **14** quantitatively.

This result convincingly illustrates that the insertion of the metal into one of the arene C−H bonds is completely reversible. It is in good agreement with the recent observations that, after passing a slow stream of CO or H_2 through a solution of the cyclometalated rhodium complex **17**, the compounds *trans*-[RhCl(CO)($C_6H_5CH_2CH_2PtBu_2$-κ-*P*)$_2$] and [$RhH_2Cl(C_6H_5CH_2CH_2PtBu_2$-$\kappa$-*P*)$_2$], respectively, are formed.[2] Quite similarly, the reaction of **16** with hydrogen in acetone gives after 12 h at room temperature the dihydridoiridium(III) derivative **15**. In this case, the isolated yield of the product is 72%. If instead of H_2 deuterium D_2 is used, owing to the ^1H NMR spectrum the bis(deuteride) [IrD_2($NCCH_3$)$_3$(L^1)]BF_4 (**15-*d*$_2$**) is generated up to at least 95%. Only traces of deuterium might be incorporated into the arene ligand. A plausible interpretation of these observations suggests that not only the reaction of **16** with PhC≡CPh but also the hydrogenation could take place via the postulated 16-electron species [Ir(L^1)($NCCH_3$)$_3$]$^+$, which would be not the thermodynamically but the kinetically favored isomer of **16**.

Conclusions

The results presented in this paper illustrate that the phosphines L^1 and L^2, having a phenyl group in the alkyl side chain, coordinate not only to rhodium but also to iridium in both the oxidation state +I and +III as 2-electron or (6+2)-electron donor ligands. The chelating bonding mode allows the isolation of dihydrido complexes of the formal composition [$IrH_2(L^1)$]BF_4 and [$IrH_2(L^2)$]BF_4, which are suitable precursors for the preparation of various olefin and alkyne iridium(I) compounds of the half-sandwich-type. In the presence of hydrogen, these complexes regenerate the dihydridoiridium(III) derivatives. This behavior is probably important for catalytic purposes, which we are currently studying in our laboratories.

However, the capabilities of the functionalized phosphines used in these studies go beyond the η^6-L^n-κ-*P* and L^n-κ-*P* coordination modes. As it has been shown by the isolation of the six-coordinate complex **16**, the metal can easily insert into one of the C−H bonds of the phenyl group of L^1 to give a new six-membered chelate ring system. This orthometalation reaction not only has a low energy of activation but is also reversible, which is illustrated by the formation of **15-*d*$_2$** from **16** and D_2 and of **14** from **16** and diphenylacetylene. It could well be that compound **16** represents the resting state for hydride transfer reactions of the dihydrido complex **15** with unsaturated substrates, but this has to be proved by further investigations.

Experimental Section

All experiments were carried out under an atmosphere of argon by Schlenk techniques. Solvents were dried by known procedures and distilled before used. The starting materials **1**,[12] **4**,[13] and the phosphines L^1 and L^2 were prepared as described in the literature.[1] D_2 was a product from Aldrich. IR spectra were recorded on a Nicolet 550 spectrometer; NMR spectra (at room temperature or at the temperature mentioned in the appropriate procedure), on a Varian Gemini 2000 instrument. Abbreviations used: s, singlet; d, doublet; t, triplet; sept, septet; m, multiplet; br, broadened signal. The conductivity Λ(M) was measured in acetone with a Philips PW 9501/01 conductometer. Mass spectra were recorded on a VG Autospec instrument.

Preparation of [HP*i*Pr$_2$($CH_2CH_2C_6H_5$)]BF_4 (L^1·HBF_4). To a solution of L^1 (1.37 g, 6.16 mmol) in 20 mL of diethyl ether was added dropwise a 1.6 M solution of HBF_4 (850 μL, 6.17 mmol) in diethyl ether at room temperature. A white solid precipitated. After the suspension was stirred for 12 h, the mother liquor was decanted, and the remaining solid was washed twice with 15 mL portions of diethyl ether and dried. Yield: 1.76 g (92%). Mp: 329 K. ^1H NMR (300 MHz, $CDCl_3$): δ 7.24 (m, 5 H, C_6H_5), 5.81 (br d, J(PH) = 472.9 Hz, 1 H, PH), 3.01 (m, 2 H, PCH_2CH_2), 2.70 (m, 2 H, $PCHCH_3$), 2.50 (m, 2 H, PCH_2), 1.32 (dd, J(PH) = 18.6, J(HH) = 6.9 Hz, 12 H, $PCHCH_3$). $^{13}C\{^1H\}$ NMR (75.5 MHz, $CDCl_3$): δ 138.5 (d, J(PC) = 11.6 Hz, *ipso*-C of C_6H_5), 129.1, 128.4, 127.4 (all s, C_6H_5), 29.4 (d, J(PC) = 4.6 Hz, PCH_2CH_2), 19.2 (d, J(PC) = 42.3 Hz, $PCHCH_3$), 17.1 (d, J(PC) = 2.3 Hz, $PCHCH_3$), 16.5 (d, J(PC) = 2.7 Hz, $PCHCH_3$), 15.5 (d, J(PC) = 41.9 Hz, PCH_2). $^{31}P\{^1H\}$ NMR (121.5 MHz, $CDCl_3$): δ 32.7 (s). Anal. Calcd for $C_{14}H_{24}BF_4P$ (310.1): C, 54.22; H, 7.80. Found: C, 53.94; H, 7.72.

Preparation of [HP*t*Bu$_2$($CH_2CH_2OC_6H_5$)]BF_4 (L^2·HBF_4). The preparation was analogous with that described for L^1·HBF_4, from L^2 (3.78 g, 14.2 mmol) and a 1.6 M solution of HBF_4 (1.95 mL, 14.2 mmol) in diethyl ether. White solid: yield 4.60 g (91%); mp 367 K. ^1H NMR (300 MHz, $CDCl_3$): δ 7.26, 6.97, 6.91 (all m, 5 H, C_6H_5), 5.89 (br d, J(PH) = 468.7 Hz, 1 H, PH), 4.37 (dt, J(PH = 17.1, J(HH) = 6.9 Hz, 2 H, PCH_2CH_2), 2.82 (dt, J(PH) = 14.7, J(HH) = 6.9 Hz, 2 H, PCH_2), 1.50 (d, J(PH) = 16.8 Hz, 18 H, $PCCH_3$). $^{13}C\{^1H\}$ NMR (75.5 MHz, $CDCl_3$): δ 157.2 (s, *ipso*-C of C_6H_5), 129.8, 122.1, 114.6 (all s, C_6H_5), 62.2 (d, J(PC) = 6.9 Hz, PCH_2CH_2), 32.8 (d, J(PC) = 34.9 Hz, $PCCH_3$), 27.1 (s, $PCCH_3$), 16.0 (d, J(PC) = 42.9 Hz, PCH_2). $^{31}P\{^1H\}$ NMR (121.5 MHz, $CDCl_3$): δ 40.3 (s). Anal. Calcd for $C_{16}H_{28}BF_4OP$ (354.2): C, 54.26; H, 7.97. Found: C, 54.00; H, 7.94.

Preparation of *cis*-[Ir(acetone)$_2$(C_8H_{14})$_2$]PF_6 (2). A suspension of **1** (1.05 g, 1.17 mmol) in 15 mL of acetone was treated dropwise with a solution of $AgPF_6$ (593 mg, 2.34 mmol) in 5 mL of acetone at room temperature. A white solid rapidly precipitated and was filtered. The filtrate was concentrated

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to ca. 3 mL in vacuo, and 40 mL of diethyl ether was added. An orange precipitate was formed, which was filtered, washed three times with 10 mL portions of diethyl ether, and dried. Yield: 1.41 g (89%). ^{1}H NMR (300 MHz, acetone-d_6): δ 2.75 (m, 4 H, =CH of C_8H_{14}), 2.21 (s, 12 H, O=C(CH_3)$_2$), 1.75, 1.58, 1.38 (all m, 24 H, CH_2 of C_8H_{14}). ^{13}C{^{1}H} NMR (75.5 MHz, acetone-d_6): δ 28.1 (s, =CH of C_8H_{14}), 27.3, 26.1, 24.3 (all s, CH_2 of C_8H_{14}). The signals for coordinated acetone could not be detected. Even though the NMR data did not reveal the presence of impurities, a correct elemental analysis could not be obtained, probably as a consequence of the high air-sensitivity of the compound.

Preparation of [(η^6-$C_6H_5CH_2CH_2Pi Pr_2$-κ-*P*)Ir(C_8H_{14})]PF_6 (3). A solution of **2** (124 mg, 0.18 mmol) in 3 mL of acetone was treated dropwise over 5 min with a solution of L^1 (41 mg, 0.18 mmol) in 5 mL of acetone at room temperature. A smooth change of color from orange-red to yellow occurred. After the solution was concentrated to ca. 2 mL in vacuo, 10 mL of diethyl ether was added. A light yellow solid precipitated, which was filtered, washed twice with 3 mL portions of diethyl ether, and dried. Yield: 109 mg (90%). Λ(M) = 100 cm^2 Ω^{-1} mol^{-1}. ^{1}H NMR (300 MHz, acetone-d_6): δ 7.15, 6.99, 6.10 (all m, 5 H, C_6H_5), 3.06 (m, 2 H, =CH of C_8H_{14}), 3.04 (dt, J(PH) = 9.3, J(HH) = 7.5 Hz, 2 H, PCH_2), 2.55 (dt, J(PH) = 18.6, J(HH) = 7.5 Hz, 2 H, PCH_2CH_2), 2.42−2.24 (br m, 4 H, CH_2 of C_8H_{14} and P*C*HCH$_3$), 1.71−1.26 (br m, 10 H, CH_2 of C_8H_{14}), 1.24 (dd, J(PH) = 15.6, J(HH) = 6.9 Hz, 6 H, PCHC*H*$_3$), 1.23 (dd, J(PH) = 16.5, J(HH) = 7.2 Hz, 6 H, PCHC*H*$_3$). ^{13}C{^{1}H} NMR (75.5 MHz, acetone-d_6): δ 114.9 (d, J(PC) = 6.4 Hz, *ipso*-C of C_6H_5), 104.3, 93.9 (both s, C_6H_5), 87.3 (d, J(PC) = 10.1 Hz, *para*-C of C_6H_5), 46.8 (s, =CH of C_8H_{14}), 41.8 (d, J(PC) = 35.9 Hz, PCH_2), 34.3, 33.3, 26.1 (all s, CH_2 of C_8H_{14}), 29.8 (s, PCH_2CH_2), 23.6 (d, J(PC) = 32.2 Hz, P*C*HCH$_3$), 18.6, 17.3 (both s, PCH*C*H$_3$). ^{31}P{^{1}H} NMR (121.5 MHz, acetone-d_6): δ 52.6 (s, PiPr$_2$), −139.7 (sept, J(FP) = 712.1 Hz, PF_6). Anal. Calcd for $C_{22}H_{37}F_6P_2Ir$ (669.7): C, 39.46; H, 5.57. Found: C, 39.45; H, 5.48.

Preparation of [Ir(C_8H_{12})(O=CMe_2)($C_6H_5CH_2CH_2Pi Pr_2$-κ-*P*)]BF_4 (5). A suspension of **4** (121 mg, 0.18 mmol) in 2 mL of acetone was treated with a solution of L^1·HBF_4 (113 mg, 0.37 mmol) in 6 mL of acetone at room temperature. A light orange-colored solution was formed, which after removal of the solvent afforded an oily orange-yellow residue. The residue was dissolved in 5 mL of acetone, and the solution was evaporated in vacuo. The NMR spectra of the remaining orange oil indicated that besides **5** some impurities were still present. Repeated recrystallization from acetone could not completely remove the impurities. Data for **5**. IR (CH_2Cl_2): ν(C=O) 1652 cm^{-1}. ^{1}H NMR (300 MHz, acetone-d_6): δ 7.35−7.17 (m, 5 H, C_6H_5), 4.63 (br m, 2 H, =CH of C_8H_{12}), 3.79 (br s, 2 H, =CH of C_8H_{12}), 2.94 (dt, J(PH) = 9.0, J(HH) = 4.5 Hz, 2 H, PCH_2CH_2), 2.42 (m, 2 H, P*C*HCH$_3$), 2.29 (m, 4 H, CH_2 of C_8H_{12}), 2.08 (s, 6 H, O=C(CH_3)$_2$), 2.05 (m, 2 H, PCH_2), 1.78 (m, 4 H, CH_2 of C_8H_{12}), 1.41 (dd, J(PH) = 13.8, J(HH) = 6.9 Hz, 6 H, PCHC*H*$_3$), 1.38 (dd, J(PH) = 15.6, J(HH) = 7.2 Hz, 6 H, PCHC*H*$_3$). ^{13}C{^{1}H} NMR (75.5 MHz, acetone-d_6): δ 204.4 (s, C=O), 142.4 (d, J(PC) = 11.6 Hz, *ipso*-C of C_6H_5), 129.2, 128.6, 127.0 (all s, C_6H_5), 92.4 (d, J(PC) = 11.6 Hz, =CH of C_8H_{12}), 54.1 (s, =CH of C_8H_{12}), 33.7 (d, J(PC) = 3.2 Hz, CH_2 of C_8H_{12}), 30.7 (d, J(PC) = 4.2 Hz, PCH_2CH_2), 30.2 (s, O=C(*C*H$_3$)$_2$), 28.1 (s, CH_2 of C_8H_{12}), 23.9 (d, J(PC) = 27.6 Hz, P*C*HCH$_3$), 18.9 (d, J(PC) = 1.8 Hz, PCH*C*H$_3$), 18.8 (s, PCH*C*H$_3$), 18.5 (d, J(PC) = 22.6 Hz, PCH_2). ^{31}P{^{1}H} NMR (121.5 MHz, acetone-d_6): δ 25.4 (s). MS (FAB): m/z 651 [M$^+$], 564 [M$^+$ − BF_4].

Preparation of [Ir(C_8H_{12})($C_6H_5OCH_2CH_2Pt Bu_2$-κ^2-*O*,*P*)]BF_4 (6). A suspension of **4** (307 mg, 0.46 mmol) in 2 mL of acetone was treated with a solution of L^2·HBF_4 (328 mg, 0.93 mmol) in 8 mL of acetone at room temperature. After the reaction mixture was stirred for 5 min, a clear orange solution was formed. The solvent was evaporated in vacuo, the remaining orange solid was washed twice with 5 mL portions of diethyl ether and dried. Yield: 562 mg (92%). Λ(M) = 97 cm^2 Ω^{-1} mol^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$, 293 K): δ 7.41, 7.25 (both m, 5 H, C_6H_5), 4.63 (dt, J(PH) = 13.8, J(HH) = 6.9 Hz, 2 H, PCH_2CH_2), 4.24, 4.13 (both m, 2 H each, =CH of C_8H_{12}), 2.21 (dt, J(PH) = 8.7, J(HH) = 6.9 Hz, 2 H, PCH_2), 2.20, 2.06, 1.64, 1.51 (all m, 2 H each, CH_2 of C_8H_{12}), 1.43 (d, J(PH) = 13.8 Hz, 18 H, PCCH_3). ^{13}C{^{1}H} NMR (75.5 MHz, $CDCl_3$): δ 157.5 (s, *ipso*-C of C_6H_5), 130.5, 128.0, 121.3 (all m, C_6H_5), 92.2 (d, J(PC) = 10.6 Hz, =CH of C_8H_{12}), 88.1 (br s, PCH_2CH_2), 51.4 (s, =CH of C_8H_{12}), 37.1 (d, J(PC) = 19.9 Hz, P*C*CH$_3$), 33.4 (d, J(PC) = 2.7 Hz, CH_2 of C_8H_{12}), 29.9 (d, J(PC) = 3.6 Hz, PC*C*H$_3$), 27.1 (s, CH_2 of C_8H_{12}), 21.3 (d, J(PC) = 22.6 Hz, PCH_2). ^{31}P{^{1}H} NMR (121.5 MHz, $CDCl_3$, 293 K): δ 58.9 (s). ^{31}P{^{1}H} NMR (121.5 MHz, acetone-d_6, 293 K): δ 58.1 (br s). ^{31}P{^{1}H} NMR (121.5 MHz, acetone-d_6, 323 K): δ 58.6 (s). ^{31}P{^{1}H} NMR (121.5 MHz, acetone-d_6, 173 K): δ 59.4 (br s). Anal. Calcd for $C_{24}H_{39}BF_4OPIr$ (653.6): C, 44.11; H, 6.01. Found: C, 44.09; H, 5.86.

Preparation of [(η^6-$C_6H_5CH_2CH_2Pi Pr_2$-κ-*P*)IrH_2]BF_4 (7). A suspension of **4** (756 mg, 1.14 mmol) in 12 mL of acetone was treated with a solution of L^1·HBF_4 (707 mg, 2.28 mmol) in 40 mL of acetone at room temperature. After stirring for 5 min, an orange solution was formed, which was brought to dryness in vacuo. The oily residue was dissolved in 40 mL of acetone, and the solution was stirred for 50−60 min under a H_2 atmosphere. As soon as the solution began to darken, the solvent was evaporated. The brownish-yellow residue was dissolved in 7 mL of acetone, and 30 mL of diethyl ether was added to the solution. A yellow solid precipitated, which was separated from the mother liquor, washed with 10 mL of diethyl ether, and dried. After repeated recrystallization from acetone/diethyl ether (1:7) a white solid was obtained. Yield: 901 mg (79%). Λ(M) = 112 cm^2 Ω^{-1} mol^{-1}. IR (KBr): ν(IrH) 2241 and 2200 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ 6.86, 6.80, 6.23 (all m, 5 H, C_6H_5), 3.24 (dt, J(PH) = 9.0, J(HH) = 7.5 Hz, 2 H, PCH_2), 2.76 (dt, J(PH) = 19.2, J(HH) = 7.5 Hz, 2 H, PCH_2CH_2), 2.01 (m, 2 H, P*C*HCH$_3$), 1.10 (dd, J(PH) = 16.8, J(HH) = 6.6 Hz, 6 H, PCHC*H*$_3$), 1.07 (dd, J(PH) = 18.0, J(HH) = 7.5 Hz, 6 H, PCHC*H*$_3$), −14.99 (d, J(PH) = 22.8 Hz, 2 H, IrH). ^{13}C{^{1}H} NMR (75.5 MHz, $CDCl_3$): δ 124.5 (d, J(PC) = 7.8 Hz, *ipso*-C of C_6H_5), 98.0 (d, J(PC) = 2.9 Hz, C_6H_5), 90.86 (s, C_6H_5), 81.49 (d, J(PC) = 7.5 Hz, *para*-C of C_6H_5), 38.84 (d, J(PC) = 32.9 Hz, PCH_2), 25.86 (d, J(PC) = 2.0 Hz, PCH_2CH_2), 21.5 (d, J(PC) = 35.8 Hz, P*C*HCH$_3$), 14.2 (s, PCH*C*H$_3$), 13.4 (d, J(PC) = 1.7 Hz, PCH*C*H$_3$). ^{31}P{^{1}H} NMR (121.5 MHz, $CDCl_3$): δ 71.7 (s). Anal. Calcd for $C_{14}H_{25}BF_4PIr$ (503.4): C, 33.41; H, 5.01. Found: C, 33.27; H, 4.74.

Preparation of [(η^6-$C_6H_5OCH_2CH_2Pt Bu_2$-κ-*P*)IrH_2]BF_4 (8). The preparation was analogous with that described for **7**, from **6** (137 mg, 0.21 mmol) and H_2. The product already precipitated upon concentrating the solution in vacuo. After recrystallization from acetone/diethyl ether (1:6) a white solid was obtained. Yield: 100 mg (87%). Λ(M) = 110 cm^2 Ω^{-1} mol^{-1}. IR (KBr): ν(IrH) 2244 and 2201 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ 6.85, 6.61, 6.15 (all m, 5 H, C_6H_5), 4.58 (m, 2 H, PCH_2CH_2), 1.69 (m, 2 H, PCH_2), 1.26 (d, J(PH) = 15.0 Hz, 18 H, PCCH_3), −15.31 (d, J(PH) = 23.7 Hz, 2 H, IrH). ^{13}C{^{1}H} NMR (75.5 MHz, CD_2Cl_2): δ 134.6 (s, *ipso*-C of C_6H_5), 103.8 (d, J(PC) = 2.1 Hz, C_6H_5), 89.8 (s, C_6H_5), 82.3 (d, J(PC) = 7.8 Hz, *para*-C of C_6H_5), 74.9 (d, J(PC) = 2.9 Hz, PCH_2CH_2), 36.1 (d, J(PC) = 31.6 Hz, P*C*CH$_3$), 28.5 (d, J(PC) = 2.4 Hz, PC*C*H$_3$), 9.9 (d, J(PC) = 30.7 Hz, PCH_2). ^{31}P{^{1}H} NMR (121.5 MHz, $CDCl_3$): δ 43.6 (s). Anal. Calcd for $C_{16}H_{29}BF_4OPIr$ (547.4): C, 35.11; H, 5.34. Found: C, 35.00; H, 5.31.

Preparation of [(η^6-$C_6H_5CH_2CH_2Pi Pr_2$-κ-*P*)Ir(C_2H_4)]BF_4 (9). A solution of **7** (125 mg, 0.25 mmol) in 10 mL of acetone was stirred under an ethene atmosphere for 2 h at room temperature. After the solution was concentrated to ca. 2 mL in vacuo, 12 mL of diethyl ether was added. This led to the precipitation of a light yellow solid, which was filtered,

washed twice with 5 mL portions of diethyl ether, and dried. Yield: 123 mg (93%). Λ(M) = 101 cm^2 Ω^{-1} mol^{-1}. ^{1}H NMR (300 MHz, acetone-d_6): δ 7.37−7.18 (m, 4 H, C_6H_5), 5.68 (m, 1 H, C_6H_5), 3.06 (dt, J(PH) = 9.0, J(HH) = 7.5 Hz, 2 H, PCH_2), 2.91 (m, 2 H, *exo*-H of C_2H_4), 2.63 (dt, J(PH) = 18.9, J(HH) = 7.5 Hz, 2 H, PCH_2CH_2), 2.25 (m, 2 H, $PCHCH_3$), 2.07 (m, 2 H, *endo*-H of C_2H_4), 1.21 (dd, J(PH) = 15.9, J(HH) = 7.2 Hz, 6 H, $PCHCH_3$), 1.16 (dd, J(PH) = 16.2, J(HH) = 7.2 Hz, 6 H, $PCHCH_3$). ^{13}C{^{1}H} NMR (75.5 MHz, acetone-d_6): δ 116.9 (d, J(PC) = 6.5 Hz, *ipso*-C of C_6H_5), 101.7 (d, J(PC) = 3.7 Hz, C_6H_5), 95.1 (d, J(PC) = 1.4 Hz, C_6H_5), 86.5 (d, J(PC) = 10.2 Hz, *para*-C of C_6H_5), 42.1 (d, J(PC) = 35.5 Hz, PCH_2), 30.0 (s, PCH_2CH_2), 23.4 (d, J(PC) = 32.2 Hz, $PCHCH_3$), 18.4, 17.2 (both d, J(PC) = 1.8 Hz, $PCHCH_3$), 18.3 (s, C_2H_4). ^{31}P{^{1}H} NMR (121.5 MHz, acetone-d_6): δ 53.4 (s). Anal. Calcd for $C_{16}H_{27}BF_4PIr$ (529.4): C, 36.30; H, 5.14. Found: C, 36.27; H, 5.01.

Reaction of Compound 9 with H_2. A solution of **9** (23 mg, 0.04 mmol) in 0.4 mL of acetone-d_6 was stirred under a hydrogen atmosphere at room temperature. The reaction was monitored by ^{1}H NMR spectroscopy. After 20 h, the signals of **9** had disappeared, while those of **7** dominated. In addition, some signals of low intensity were observed in the high-field region which could not be assigned.

Preparation of [(η^6-$C_6H_5OCH_2CH_2Pt$Bu$_2$-κ-*P*)Ir(C_2H_4)]BF$_4$ (10). A solution of **8** (152 mg, 0.28 mmol) in 5 mL of acetone was stirred under an ethene atmosphere for 12 h at 323 K. After cooling to room temperature, the solvent was evaporated in vacuo, the residue was dissolved in 3 mL of acetone, and the solution was filtered. Addition of 10 mL of diethyl ether to the filtrate led to the precipitation of a light yellow solid, which was filtered, washed twice with 4 mL portions of diethyl ether, and dried. Yield: 116 mg (72%). Λ(M) = 99 cm^2 Ω^{-1} mol^{-1}. ^{1}H NMR (300 MHz, acetone-d_6): δ 7.29−7.17 (m, 4 H, C_6H_5), 5.32 (m, 1 H, C_6H_5), 4.57 (m, 2 H, PCH_2CH_2), 3.16 (m, 2 H, *exo*-H of C_2H_4), 2.49 (m, 2 H, *endo*-H of C_2H_4), 1.83 (m, 2 H, PCH_2), 1.32 (d, J(PH) = 14.1 Hz, 18 H, $PCCH_3$). ^{13}C NMR (75.5 MHz, acetone-d_6): δ 126.6 (s, *ipso*-C of C_6H_5), 102.3 (d, J(PC) = 2.7 Hz, C_6H_5), 92.2 (s, C_6H_5), 84.4 (d, J(PC) = 9.7 Hz, *para*-C of C_6H_5), 71.9 (d, J(PC) = 2.8 Hz, PCH_2CH_2), 37.2 (d, J(PC) = 24.8 Hz, $PCCH_3$), 30.5 (d, J(PC) = 2.8 Hz, $PCCH_3$), 18.3 (d, J(PC) = 2.3 Hz, C_2H_4), 12.9 (d, J(PC) = 31.3 Hz, PCH_2). ^{31}P{^{1}H} NMR (121.5 MHz, acetone-d_6): δ 12.1 (s). Anal. Calcd for $C_{18}H_{31}BF_4OPIr$ (573.4): C, 37.70; H, 5.45. Found: C, 37.36; H, 5.40.

Preparation of [(η^6-$C_6H_5CH_2CH_2Pi$Pr$_2$-κ-*P*)Ir(CH_2=CHCH$_3$)]BF$_4$ (11). A solution of **7** (134 mg, 0.27 mmol) in 10 mL of acetone was stirred under a propene atmosphere for 15 min at room temperature. A gradual change of color from off-white to light yellow occurred. After the solution was concentrated to ca. 2 mL in vacuo, 10 mL of diethyl ether were added. A light yellow solid precipitated, which was filtered, washed twice with 4 mL portions of diethyl ether, and dried. Yield: 132 mg (91%). Λ_M = 112 cm^2 Ω^{-1} mol^{-1}. ^{1}H NMR (300 MHz, acetone-d_6): δ 7.31, 7.26, 7.19, 6.95, 5.95 (all m, 1 H each, C_6H_5), 3.19−2.85 (br m, PCH_2, and =C*H*CH$_3$), 2.72 (dd, J(HH) = 10.2, 1.5 Hz, 1 H, =CH_2], 2.61 (m, 2 H, PCH_2CH_2), 2.41−2.18 (br m, 3 H, =CH_2 and $PCHCH_3$), 1.89 (d, J(HH) = 6.0 Hz, 3 H, =$CHCH_3$), 1.29 (dd, J(PH) = 16.8, J(HH) = 7.2 Hz, 3 H, $PCHCH_3$), 1.25 (dd, J(PH) = 15.6, J(HH) = 6.9 Hz, 3 H, $PCHCH_3$), 1.20 (dd, J(PH) = 16.2, J(HH) = 6.9 Hz, 3 H, $PCHCH_3$), 1.11 (dd, J(PH) = 16.2, J(HH) = 7.2 Hz, 3 H, $PCHCH_3$). ^{13}C{^{1}H} NMR (75.5 MHz, acetone-d_6): δ 115.7 (d, J(PC) = 6.9 Hz, *ipso*-C of C_6H_5), 105.5. 101.2 (both d, J(PC) = 3.2 Hz, C_6H_5), 94.6 (s, C_6H_5), 86.8 (d, J(PC) = 9.7 Hz, C_6H_5), 41.9 (d, J(PC) = 36.4 Hz, PCH_2), 39.1 (d, J(PC) = 1.9 Hz, =*C*HCH$_3$), 29.9 (s, PCH_2CH_2), 26.1 (s, =CH*C*H$_3$), 23.9 (br s, =CH_2), 23.7 (d, J(PC) = 32.3 Hz, $PCHCH_3$), 23.2 (d, J(PC) = 32.2 Hz, $PCHCH_3$), 19.0, 17.8, 17.7 (all s, $PCHCH_3$), 16.7 (d, J(PC) = 2.3 Hz, $PCHCH_3$). ^{31}P{^{1}H} NMR (121.5 MHz, acetone-d_6): δ 47.7 (s). Anal. Calcd for $C_{17}H_{29}BF_4PIr$ (543.4): C, 37.58; H, 5.38. Found: C, 37.54; H, 5.28.

Preparation of [(η^6-$C_6H_5OCH_2CH_2Pt$Bu$_2$-κ-*P*)Ir(CH_2=CHCH$_3$)]BF$_4$ (12). The preparation was analogous to that described for **11**, from **8** (190 mg, 0.35 mmol) and propene. However, the reaction time was 4 days and the reaction temperature 323 K. Yellow solid: yield 145 mg (71%). Λ(M) = 103 cm^2 Ω^{-1} mol^{-1}. ^{1}H NMR (300 MHz, acetone-d_6): δ 7.26, 7.21, 7.18, 7.05, 5.69 (all m, 1 H each, C_6H_5), 4.62−4.47 (m, 2 H, PCH_2CH_2), 3.43 (dddq, J(PH) = 5.7, J(HH) = 11.1, 8.1, 6.0 Hz, 1 H, =C*H*CH$_3$), 2.95 (dd, J(HH) = 11.1, 1.8 Hz, 1 H, =CH_2), 2.74 (ddd, J(PH) = 3.3, J(HH) = 8.1, 1.8 Hz, 1 H, =CH_2,), 2.02, 1.74 (both m, 1 H each, PCH_2), 1.92 (d, J(HH) = 6.0 Hz, 3 H, =$CHCH_3$), 1.43, 1.26 (both d, J(PH) = 13.8 Hz, 9 H each, $PCCH_3$). ^{13}C{^{1}H} NMR (75.5 MHz, acetone-d_6): δ 126.1 (s, *ipso*-C of C_6H_5), 105.6 (d, J(PC) = 1.4 Hz, C_6H_5), 101.7 (d, J(PC) = 3.2 Hz, C_6H_5), 91.1, 90.6 (both s, C_6H_5), 84.2 (d, J(PC) = 9.7 Hz, *para*-C of C_6H_5), 71.5 (d, J(PC) = 2.3 Hz, PCH_2CH_2), 37.8 (d, J(PC) = 24.9 Hz, $PCCH_3$), 37.3 (s, =*C*HCH$_3$), 37.2 (d, J(PC) = 23.9 Hz, $PCCH_3$), 31.6, 29.9 (both d, J(PC) = 2.8 Hz, $PCCH_3$), 25.0 (s, =CH*C*H$_3$), 24.7 (s, =CH_2), 13.5 (d, J(PC) = 31.3 Hz, PCH_2). ^{31}P{^{1}H} NMR (121.5 MHz, acetone-d_6): δ 11.1 (s). Anal. Calcd for $C_{19}H_{33}BF_4OPIr$ (587.5): C, 38.85; H, 5.66. Found: C, 38.54; H, 5.62.

Preparation of [(η^6-$C_6H_5CH_2CH_2Pi$Pr$_2$-κ-*P*)Ir(*Z*-PhCH=CHPh)]BF$_4$ (13). A solution of **11** (100 mg, 0.18 mmol) in 6 mL of acetone was treated with *Z*-stilbene (103 μL, 0.55 mmol) and stirred for 2 h under reflux. After the solution was cooled to room temperature, the solvent was evaporated in vacuo, and the residue was dissolved in 2 mL of CH_2Cl_2. Dropwise addition of 10 mL of diethyl ether led to the precipitation of a yellow solid, which was filtered, washed with 10 mL of diethyl ether, and dried. Yield: 100 mg (80%). IR (KBr): ν(C=C) 1598 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.16 (m, 12 H, $CH_2C_6H_5$ and =CHC_6H_5), 6.18 (m, 2 H, =CHC_6H_5), 5.05 (m, 1 H, $CH_2C_6H_5$), 4.45 (d, J(PH) = 4.9 Hz, 2 H, =C*H*C_6H_5), 3.08 (dt, J(PH) = 9.0, J(HH) = 7.6 Hz, 2 H, PCH_2), 2.61 (dt, J(PH) = 19.5, J(HH) = 7.6 Hz, 2 H, PCH_2CH_2), 2.24 (m, 2 H, $PCHCH_3$), 1.34 (dd, J(PH) = 16.2, J(HH) = 7.1 Hz, 12 H, $PCHCH_3$). ^{13}C{^{1}H} NMR (75.5 MHz, $CDCl_3$): δ 143.0 (s, *ipso*-C of =CHC_6H_5), 129.9, 128.2, 126.6 (all s, =CHC_6H_5), 115.7 (d, J(PC) = 6.9 Hz, *ipso*-C of $CH_2C_6H_5$), 108.1 (d, J(PC) = 2.9 Hz, $CH_2C_6H_5$), 93.4 (s, $CH_2C_6H_5$), 91.8 (d, J(PC) = 9.8 Hz, $CH_2C_6H_5$), 43.0 (d, J(PC) = 1.5 Hz, =*C*HC_6H_5), 41.5 (d, J(PC) = 36.3 Hz, PCH_2), 30.2 (s, PCH_2CH_2), 23.6 (d, J(PC) = 31.2 Hz, $PCHCH_3$), 19.1, 17.7 (both s, $PCHCH_3$). ^{31}P{^{1}H} NMR (121.5 MHz, $CDCl_3$): δ 47.9 (s). Anal. Calcd for $C_{28}H_{35}BF_4PIr$ (681.6): C, 49.34; H, 5.18. Found: C, 49.23; H, 4.88.

Preparation of [(η^6-$C_6H_5CH_2CH_2Pi$Pr$_2$-κ-*P*)Ir(PhC≡CPh)]BF$_4$ (14). (a) A solution of **7** (109 mg, 0.22 mmol) in 8 mL of acetone was treated with a 10-fold excess of diphenylacetylene (392 mg, 2.20 mmol) and stirred for 5 min at room temperature. A change of color from off-white to orange-red occurred. After the solvent and volatile materials were removed in vacuo, the residue was washed with diethyl ether and then dissolved in 3 mL of acetone. Addition of 12 mL of diethyl ether led to the precipitation of a brownish-yellow solid, which was filtered, washed twice with 5 mL portions of diethyl ether, and dried. Yield: 132 mg (90%). (b) A solution of **9** (75 mg, 0.14 mmol) in 6 mL of acetone was treated with a 10-fold excess of diphenylacetylene and stirred for 12 h at room temperature. The reaction mixture was then worked up as described for procedure a). Yield: 80 mg (84%). Λ(M) = 110 cm^2 Ω^{-1} mol^{-1}. IR (KBr): ν(C≡C) 1824 cm^{-1}. ^{1}H NMR (300 MHz, acetone-d_6): δ 7.95 (m, 2 H, $CH_2C_6H_5$), 7.86 (m, 4 H, ≡CC_6H_5), 7.51 (m, 2 H, $CH_2C_6H_5$), 7.47 (m, 4 H, ≡CC_6H_5), 7.34 (m, 2 H, ≡CC_6H_5), 6.08 (m, 1 H, $CH_2C_6H_5$), 3.14 (dt, J(PH) = 9.0, J(HH) = 7.5 Hz, 2 H, PCH_2), 2.90 (dt, J(PH) = 18.0, J(HH) = 7.5 Hz, 2 H, PCH_2CH_2), 1.92 (m, 2 H, $PCHCH_3$), 1.07, (dd, J(PH) = 16.1, J(HH) = 7.1 Hz, 6 H, $PCHCH_3$), 0.91 (dd, J(PH) = 16.7, J(HH) = 7.1 Hz, 6 H, $PCHCH_3$). ^{13}C{^{1}H} NMR (75.5 MHz, acetone-d_6): δ 131.2, 129.2, 128.3, 128.1 (all s, ≡C_6H_5), 119.6 (d, J(PC) = 6.4 Hz, *ipso*-C of $CH_2C_6H_5$), 105.6 (d, J(PC)

= 4.2 Hz, $CH_2C_6H_5$), 93.8 (d, *J*(PC) = 12.0 Hz, C≡C), 93.2 (s, $CH_2C_6H_5$), 82.5 (d, *J*(PC) = 4.6 Hz, *para*-C of $CH_2C_6H_5$), 40.9 (d, *J*(PC) = 35.9 Hz, PCH_2), 30.7 (s, PCH_2CH_2), 24.1 (d, *J*(PC) = 32.7 Hz, P*C*HCH$_3$), 17.2 (s, PCH*C*H$_3$), 16.8 (d, *J*(PC) = 1.8 Hz, PCH*C*H$_3$). $^{31}P\{^1H\}$ NMR (121.5 MHz, acetone-d_6): δ 60.2 (s). Anal. Calcd for $C_{28}H_{33}BF_4PIr$ (679.6): C, 49.49; H, 4.89. Found: C, 49.70; H, 5.13.

Preparation of [IrH$_2$(NCCH$_3$)$_3$(C$_6$H$_5$CH$_2$CH$_2$P*i*Pr$_2$-*η*-*P*)]BF$_4$ (15). (a) A solution of **7** (95 mg, 0.19 mmol) in 4 mL of acetone was treated with excess acetonitrile (0.5 mL, 9.53 mmol) and stirred for 3 h at room temperature. The solution was concentrated to ca. 0.5 mL in vacuo, and 6 mL of diethyl ether was added. A yellow oily product precipitated. After it was washed six times with 10 mL portions of diethyl ether (273 K), a white solid was obtained and dried. Yield: 104 mg (87%). (b) Analogously as described for (a) from **16** (62 mg, 0.10 mmol) and H_2 as starting materials. The reaction time was 12 h. White solid: yield 45 mg (72%). Λ(M) = 97 cm^2 Ω^{-1} mol^{-1}. IR (KBr): ν(IrH) 2227 cm^{-1}. ^{1}H NMR (300 MHz, CD_2Cl_2): δ 7.31 (m, 2 H, C_6H_5), 7.21 (m, 3 H, C_6H_5), 2.79 (dt, *J*(PH) = 12.6, *J*(HH) = 5.1 Hz, 2 H, PCH_2CH_2), 2.42 (d, *J*(PH) = 0.9 Hz, 3 H, CH_3CN), 2.32 (s, 6 H, CH_3CN), 2.12−1.84 (m, 4 H, PCH_2 and PC*H*CH$_3$), 1.12 (dd, *J*(PH) = 15.0, *J*(HH) = 6.9 Hz, 6 H, PCHC*H*$_3$), 1.10 (dd, *J*(PH) = 14.4, *J*(HH) = 6.9 Hz, 6 H, PCHC*H*$_3$), −22.64 (d, *J*(PH) = 21.6 Hz, 2 H, IrH). $^{13}C\{^1H\}$ NMR (75.5 MHz, CD_2Cl_2): δ 142.4 (d, *J*(PC) = 13.4 Hz, *ipso*-C of C_6H_5), 129.0, 128.1, 126.6 (all s, C_6H_5), 119.4 (d, *J*(PC) = 7.8 Hz, CH_3CN), 119.3 (s, CH_3CN), 31.3 (s, PCH_2CH_2), 26.8 (d, *J*(PC) = 32.2 Hz, PCH_2), 25.2 (d, *J*(PC) = 37.8 Hz, P*C*HCH$_3$), 18.2, 18.0 (both s, PCH*C*H$_3$), 3.4 (d, *J*(PC) = 1.4 Hz, *C*H$_3$CN), 3.2 (s, *C*H$_3$CN). $^{31}P\{^1H\}$ NMR (121.5 MHz, CD_2Cl_2): δ 22.2 (s). MS (FAB): *m*/*z* 538 [M$^+$ − H − BF$_4$], 417 [M$^+$ + H − (3·CH$_3$CN) − BF$_4$]. Anal. Calcd for $C_{20}H_{34}BF_4N_3PIr$ (626.5): C, 38.34; H, 5.47; N, 6.71. Found: C, 37.70; H, 5.27; N, 6.46.

Preparation of [Ir(H)(C$_6$H$_4$CH$_2$CH$_2$P*i*Pr$_2$-*κ*^{2}-*C*,*P*)(NCCH$_3$)$_3$]BF$_4$ (16). A solution of **11** (103 mg, 0.19 mmol) in 5 mL of acetone was treated with excess acetonitrile (0.5 mL, 9.53 mmol) and stirred for 12 h at room temperature. A stepwise change of color from light yellow to orange-red and again to light yellow occurred. The solvent and other volatile substances were removed in vacuo, and the oily residue was washed six times with 10 mL portions of diethyl ether (273 K). A light yellow solid was obtained and dried. Yield: 99 mg (83%). Λ(M) = 116 cm^2 Ω^{-1} mol^{-1}. IR (KBr): ν(IrH) 2242 cm^{-1}. ^{1}H NMR (300 MHz, CD_2Cl_2): δ 7.55 (m, 1 H, C_6H_4), 6.82−6.55 (m, 3 H, C_6H_4), 2.83−2.57 (m, 2 H, PCH_2CH_2), 2.46, 2.45, 2.41 (all s, 3 H each, CH_3CN), 2.16, 1.98 (both m, 1 H each, PC*H*CH$_3$), 1.60, 1.25 (both m, 1 H each, PCH_2), 1.20 (dd, *J*(PH) = 15.8, *J*(HH) = 7.1 Hz, 3 H, PCHC*H*$_3$), 1.06 (dd, *J*(PH) = 13.8, *J*(HH) = 6.9 Hz, 3 H, PCHC*H*$_3$), 0.96 (dd, *J*(PH) = 15.6, *J*(HH) = 7.2 Hz, 3 H, PCHC*H*$_3$), 0.66 (dd, *J*(PH) = 14.7, *J*(HH) = 7.2 Hz, 3 H, PCHC*H*$_3$), −22.33 (d, *J*(PH) = 19.8 Hz, 1 H, IrH). $^{13}C\{^1H\}$ NMR (75.5 MHz, acetone-d_6): δ 145.4 (d, *J*(PC) = 6.0 Hz, *ipso*-C of C_6H_4), 139.7 (d, *J*(PC) = 3.6 Hz, CH of C_6H_4), 125.9, 124.9, 122.6 (all s, CH of C_6H_4), 125.5 (d, *J*(PC) = 8.3 Hz, IrC), 121.1 (s, CH_3CN), 120.2 (br s, CH_3CN), 118.2 (d, *J*(PC) = 15.7 Hz, CH_3CN), 40.8 (s, PCH_2CH_2), 24.3 (d, *J*(PC) = 38.6 Hz, PCHCH$_3$), 23.8 (d, *J*(PC) = 35.0 Hz, P*C*HCH$_3$), 17.7, 16.2, 16.1, 16.0 (all s, PCH*C*H$_3$), 15.3 (d, *J*(PC) = 43.2 Hz, PCH_2), 2.3, 2.2, 2.1 (all s, *C*H$_3$CN). $^{31}P\{^1H\}$ NMR (121.5 MHz, CD_2Cl_2): δ 26.6 (s). MS (FAB): *m*/*z* 538 [M$^+$ + H − BF$_4$], 523 [M$^+$ − CH$_3$ − BF$_4$]. Anal. Calcd for $C_{20}H_{32}BF_4N_3PIr$ (624.5): C, 38.47; H, 5.16; N, 6.73. Found: C, 37.78; H, 5.36; N, 6.50.

Reaction of Compound 14 with Acetonitrile. A solution of **14** (20 mg, 0.03 mmol) in 2 mL of acetone was treated with acetonitrile (15 μL, 0.30 mmol) and stirred for 12 h at room temperature. A smooth change of color from orange-red to light yellow occurred. The ^{31}P NMR spectrum revealed that the hydrido complex **16** was exclusively formed. When removing the solvent and other volatile substances in vacuo, again a change of color from light yellow to orange-red took place. The NMR spectra of the oily residue confirmed that compound **14** was partly regenerated. If the residue was dissolved in 2 mL of acetone and an excess of diphenylacetylene was added, the reaction afforded the alkyne complex **14** quantitatively.

Table 4. Crystal Data and Data Collection and Refinement for Complexes 13 and 16

	13	**16**
chem formula	$C_{28}H_{35}BF_4IrP$	$C_{20}H_{32}BF_4IrN_3P$
fw	681.54	624.47
cryst size,mm	0.28 × 0.27 × 0.17	0.237 × 0.171 × 0.136
cryst syst	monoclinic	triclinic
space group	$P2_1/c$	$P\bar{1}$
a, Å	8.4249(5)	11.3293(7)
b, Å	19.1858(11)	11.3608(7)
c, Å	15.9442(9)	11.8529(8)
α, deg	90.0(0)	113.8270(10)
β, deg	93.0220(10)	117.5450(10)
γ, deg	90.0(0)	91.5830(10)
V, Å^3	2573.6(3)	1193.34(13)
Z	4	2
D_{calcd}, gcm^{-3}	1.759	1.738
μ, mm^{-1}	5.295	5.704
no. of measd reflns	16 658	14 641
no. of unique reflns	5976 (R_{int} = 0.0294)	5550 (R_{int} = 0.0326)
min., max. transm factor	0.265, 0.407	0.321, 0.460
no. of data/ restraints/ params	5976/0/454	5550/0/399
$R(F)$ ($F^2 \geq 2\sigma(F^2)$)[a]	0.0255	0.0274
$wR(F^2)$ (all data)[b]	0.0554	0.0502

[a] $R(F) = \sum||F_o| - |F_c||/\sum|F_o|$ for 5348(13) and 4951(16) observed reflections. [b] $wR(F^2) = (\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2])^{1/2}$.

Reaction of Compound 16 with D$_2$. A solution of **16** (25 mg, 0.14 mmol) in 0.5 mL of acetone-d_6 was stirred under a D_2 atmosphere for 3 days at room temperature. The NMR spectra revealed that almost exclusively (>95%) the complex [IrD$_2$(NCCH$_3$)$_3$(C$_6$H$_5$CH$_2$CH$_2$P*i*Pr$_2$-*κ*-*P*)]BF$_4$ (**15-*d*$_2$**) was formed. ^{1}H NMR (300 MHz, acetone-d_6): δ 7.37−7.18 (m, 5 H, C_6H_5), 2.86 (dt, *J*(PH) = 12.3, *J*(HH) = 5.3 Hz, 2 H, PCH_2CH_2), 2.56 (s, 3 H, CH_3CN), 2.49 (s, 6 H, CH_3CN), 2.20−2.03 (m, 4 H, PCH_2 and PC*H*CH$_3$), 1.16 (dd, *J*(PH) = 15.0, *J*(HH) = 7.2 Hz, 6 H, PCHC*H*$_3$), 1.13 (dd, *J*(PH) = 14.7, *J*(HH) = 6.8 Hz, 6 H, PCHC*H*$_3$). $^{13}C\{^1H\}$ NMR (75.5 MHz, acetone-d_6): δ 142.8 (d, *J*(PC) = 12.9 Hz, *ipso*-C of C_6H_5), 129.0, 128.4, 126.5 (all s, C_6H_5), 120.2 (br s, CH_3CN), 31.4 (s, PCH_2CH_2), 26.4 (d, *J*(PC) = 31.3 Hz, PCH_2), 25.1 (d, *J*(PC) = 38.3 Hz, P*C*HCH$_3$), 18.1, 17.9 (both s, PCH*C*H$_3$), 2.2 (d, *J*(PC) = 0.9 Hz, *C*H$_3$CN), 2.1 (s, *C*H$_3$CN). $^{31}P\{^1H\}$ NMR (121.5 MHz, acetone-d_6): δ 27.2 (s).

Kinetic Data for the Reaction of 7 with CD$_3$CN. The kinetics of this reaction were studied by ^{1}H NMR in samples of 0.01−0.03 M solutions of **7** in CD_2Cl_2. The samples were treated at 195 K with different quantities of CD_3CN (30- to 250-fold excess) and, after warming to 253 K, the reaction was followed by measuring the decrease of intensity of the hydride signal of **7**. The pseudo-first-order rate constants (k_{obs}) were obtained by fitting the data to an exponential decay function with the routine programs of the spectrometer.

Crystal Structure Determination of Complexes 13 and 16. A summary of crystal data collection and refinement parameters for the two structural analyses is reported in Table 4. A yellow (**13**) or a pale yellow (**16**) crystals were glued to glass fibers and mounted on a Bruker SMART APEX CCD area detector diffractometer equipped with graphite-monochromated Mo Kα radiation (λ = 0.71073 Å) and low-temperature equipment (100(1) K). Cell constants were refined from the observed setting angles and detector positions of strong reflections (6655 ref, 4.84° ≤ 2θ ≤ 56.40° for **13**, and 6125 ref, 4.36° ≤ 2θ ≤ 53.61° for **16**). During data collection instrument and crystal stability was evaluated from measurement of

equivalent reflections at different measuring times; no important variations were observed. Intensities were integrated from several series of exposure frames covering almost a complete sphere of reciprocal space.[14] Data were corrected for Lorentz and polarization effects, and a semiempiricial absorption correction based on the repeated and symmetry-equivalent reflections was also applied.[15]

The structure was solved by the Patterson method and completed by successive difference Fourier syntheses. Anisotropic thermal parameters were included for all non-hydrogen atoms, with the exception of the disordered fluorine atoms of **13**. In this complex, a model for the disorder of the tetrafluoroborato anion (two moieties, 0.524 and 0.476(10) occupancies) was necessary to be included. Hydrogen atoms were found in the difference maps and were refined with free positional and isotropic displacement parameters. Refinements were carried out by full-matrix least-squares on F^2 for all data.[16] Final agreement factors are collected in Table 4. Residual peaks in the final difference map of both structures were about 1.0 e $Å^{-3}$ and were localized in the proximity of metal atoms. Atomic scattering factors, corrected for anomalous dispersion, were used as implemented in the refinement programs.[16]

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Supporting Information Available: Listings of atomic coordinates, hydrogen positional parameters, isotropic and anisotropic displacement parameters, and complete bond distances and angles for compounds **1** and **2** (CIF format). This material is available free of charge via the Internet at http://pubs.acs.org.

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