New Dihydride− and Alkene−η^6-Arene Complexes of Iridium

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The synthesis of iridium derivatives of general formula [(η^6-arene)$IrH_2(PR_3)$]BF_4 {arene = benzene: R = ^{i}Pr (**1**), Cy (**2**); R = ^{i}Pr: arene = toluene (**4**), 1,3,5-trimethylbenzene (**5**), 1,2,4-trimethylbenzene (**6**), hexamethylbenzene (**7**), 1-methylstyrene (**8**), phenol (**9**), aniline (**10**)} and [(η^6-arene)Ir(η^2-C_2H_4)(P^iPr_3)]BF_4 {arene = benzene (**23**), toluene (**24**), 1,3,5-trimethylbenzene (**25**), hexamethylbenzene (**26**)} is described. **1** and **2** have been obtained by treatment of [Ir(μ-OMe)(cod)]$_2$ with [HPR_3]BF_4, followed by reaction with H_2, in acetone/benzene mixtures. A similar synthetic methodology has been used to prepare the naphthalene complex [(η^6-$C_{10}H_8$)$IrH_2(P^iPr_3)$]BF_4 (**16**) and the thiophene derivative [(η^5-SC_4H_4)$IrH_2(P^iPr_3)$]BF_4 (**17**). Compounds **4**−**10** have been prepared from **1** by arene substitution in acetone solutions. The substitution reactions involved a tris-acetone intermediate, which has been characterized in acetone-d_6, [$IrH_2(OC(CD_3)_2)_3(P^iPr_3)]^+$ (**3**). The η^6-aniline ligand of **10** can be displaced by three N-bonded anilines, to give the complex [$IrH_2(\kappa$-*N*, $NH_2Ph)_3(P^iPr_3)$]BF_4 (**11**). Other N-containing arenes such as quinoline and isoquinoline gave only products with N-coordinating ligands, **12**−**15**. The treatment of **1** with $NaBPh_4$ led to the zwitterionic compound [$Ph_3B(\eta^6$-Ph)$IrH_2(P^iPr_3)$] (**18**). This complex has been used as an arene ligand to obtain the compounds [$Ph_2B\{(\eta^6$-Ph)$IrH_2(P^iPr_3)\}_2$]BF_4 (**19**), [$PhB\{(\eta^6$-Ph)$IrH_2(P^iPr_3)\}_3$]$(BF_4)_2$ (**20**), and [$B\{(\eta^6$-Ph)$IrH_2(P^iPr_3)\}_4$]$(BF_4)_3$ (**21**), in which the BPh_4^- anion is coordinated to two, three, or four iridium centers, respectively. Treatment of **1** with styrene afforded the Ir(I) compound [(η^6-C_6H_5Et)Ir(η^2-CH_2=CHPh)(P^iPr_3)]BF_4 (**22**). Under similar conditions, the reaction of **1**, **4**, and **5** with ethylene produced ethane and the ethylene complexes **23**−**25**. Compound **26** and the zwitterionic complex [$Ph_3B(\eta^6$-Ph)Ir(η^2-C_2H_4)(P^iPr_3)] (**27**) have been prepared by arene displacement from **23**. **1** has been found to catalyze, under mild conditions, the hydrogenation of several unsaturated substrates, including imines. The molecular structure of **23** has been determined by X-ray crystallography.

Introduction

η^6-Arene complexes of iridium and rhodium have been known for approximately 30 years, and some of them, especially those of rhodium, have been found to be good catalyst precursors in a variety of catalytic transformations.[1] Despite these facts, the relative significance of such compounds within the organometallic chemistry of rhodium and iridium is still minor, in contrast to the relevance of complexes containing η^6-arene ligands in the chemistry of other late transition metals such as ruthenium and osmium.[2] This situation is, most likely, a consequence of the scarcity of synthetic procedures leading to rhodium and iridium η^6-arene complexes, since, in fact, the vast majority of complexes of this type reported so far correspond to only two formulations: $[CpM(arene)]^{2+}$ [3] and $[M(arene)(diene)]^+$.[4] In addition to the latter, few particular examples of complexes containing phosphines,[5] phosphites,[6] carbonyl ligands,[7] and diphosphines[8] have been described, although, to the best

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(5) (a) Crabtree, R. H.; Mellea, M. F.; Mihelcic, J. M.; Quirk, J. M. *J. Am. Chem. Soc.* **1982**, *104*, 107. (b) Bleeke, J. R.; Donaldson, A. J. *Organometallics* **1988**, *7*, 1588.

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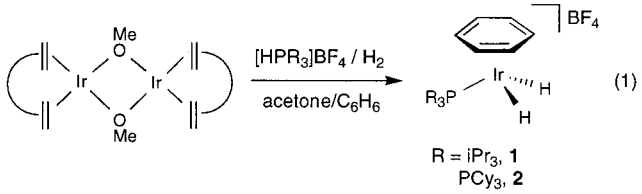
of our knowledge, systematic synthetic methods leading to such derivatives are still unknown. Only very recently have Werner et al. described an original synthetic procedure, based on the use of the solvento complex $[Rh(C_8H_{14})_2(acetone)_2]PF_6$, that may largely contribute to extend the amount and variety of η^6-arene complexes of rhodium.[9] In this work, we describe a versatile synthetic route to dihydride−η^6-arene complexes of Ir(III) containing bulky alkylphosphines. These new complexes, which have been found to be active catalysts for the hydrogenation of a variety of unsaturated substrates, are also convenient precursors for the synthesis of new η^6-arene complexes of Ir(I) with alkene ligands. Part of this work has been previously communicated.[10]

Results and Discussion

1. Cationic Iridium(III) Complexes. In a recent paper, we reported on the synthesis and reactivity of the tris-acetonitrile dihydride complex $[IrH_2(NCCH_3)_3(P^iPr_3)]BF_4$, which was obtained after treatment of the iridium dimer $[Ir(\mu\text{-OMe})(cod)]_2$ with the phosphonium salt $[HP^iPr_3]BF_4$ in acetone/acetonitrile, followed by reaction with hydrogen.[11] A similar one-pot synthesis, in the absence of acetonitrile and in the presence of benzene, affords the η^6-arene complex $[(\eta^6\text{-}C_6H_6)IrH_2(P^iPr_3)]BF_4$ (**1**), as a white solid in diethyl ether/THF mixtures (eq 1). This procedure is also applicable to

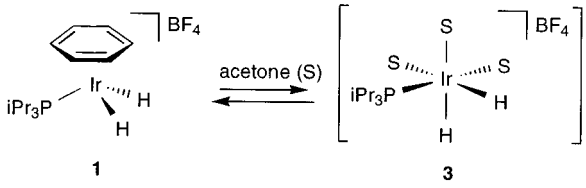


(1)

R = iPr_3, **1**
PCy_3, **2**

phosphonium salts of other bulky phosphines such as PCy_3, which afforded the complex $[(\eta^6\text{-}C_6H_6)IrH_2(PCy_3)]BF_4$ (**2**), but fails for the salts obtained by protonation of smaller ligands such as PMe_3 or pyridine. In the case of pyridine, the treatment of the starting iridium dimer with $[Hpy]BF_4$, in acetone/benzene, led to an equimolar mixture of the known complexes $[Ir(cod)(py)_2]BF_4$[12] and $[(\eta^6\text{-}C_6H_6)Ir(cod)]BF_4$.[4] This result suggests that, in the case of small ligands, the reaction intermediates could undergo facile disproportionation processes, in agreement with the behavior previously observed for related $[Ir(cod)LL']^+$ compounds.[12]

In $CDCl_3$ solutions, the spectroscopic data of **1** and **2** support the proposed structures. The ^1H NMR spectra of these compounds show high-field doublets ($J_{HP} = 27$ Hz) corresponding to the hydride ligands and singlets at about δ 6.7 for the η^6-benzene ligands. These ligands appear in the $^{13}C\{^1H\}$ NMR spectra as doublets, with J_{CP} coupling constants of about 2 Hz. Moreover, the ^{31}P *off-resonance* spectra of both compounds show triplets, indicative of two equivalent hydride ligands. The spectra of compound **1** in acetone-d_6 solutions show, together with the signals corresponding to **1**, those due to the cation $[IrH_2(OC(CD_3)_2)_3(P^iPr_3)]^+$ (**3**), indicating that the labile benzene ligand can be substituted by three acetone ligands (eq 2). This cationic species, which is

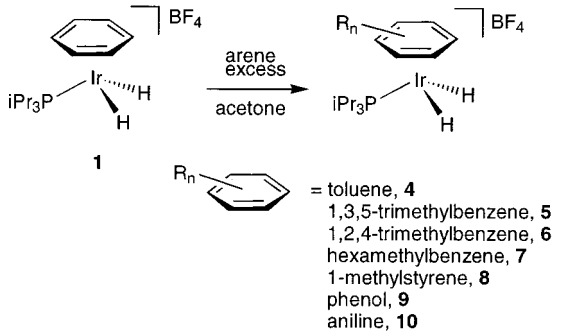


(2)

1 **3**

similar to the aforementioned tris-acetonitrile complex $[IrH_2(NCCH_3)_3(P^iPr_3)]^+$, is characterized by a doublet at δ −31.08 ($J_{HP} = 23.7$ Hz) in the ^1H NMR spectrum and a singlet at δ 31.32 in the $^{31}P\{^1H\}$ NMR spectrum. Even though this labile tris-acetone compound seems to be rather stable in acetone solutions, our attempts to isolate it by following the procedure described for **1**, in the absence of benzene, led only to intractable black solids (nonisolated complexes such as **3** are drawn between brackets).

The equilibrium depicted in eq 2 allows the facile preparation of other arene derivatives by substitution of the benzene ligand, provided that the desired arene coordinates to the iridium better than benzene. This is the case for methyl-substituted arenes, 1-methylstyrene, phenol, or aniline (eq 3). The spectroscopic data of the



(3)

1

complexes shown in eq 3 are consistent with the fast rotation of the arene ligands around the Ir−arene axis. This rotation results in the chemical equivalence of the hydride ligands in the 293 K ^1H NMR spectra, except for complex **6**, in which the asymmetry of the arene ligand allows the observation of nonequivalent hydrides showing a mutual coupling constant of 5.1 Hz. The X-ray structure of the mesitylene derivative **5**, which has been described in a previous communication,[10] supports the structural proposals for these dihydride derivatives.

The reactions of eq 3 were typically carried out by treatment of acetone solutions of **1** with an excess of the desired arene, except in the case of complex **10**,

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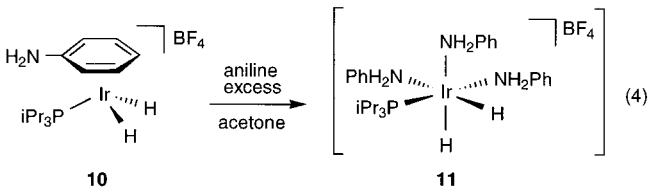
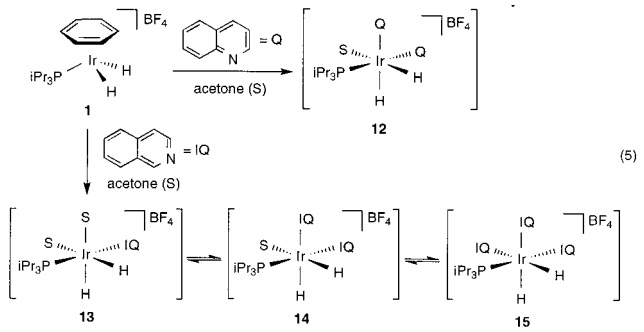
which required the use of a stoichiometric amount of aniline. This is due to the fact that, in the presence of an excess of this ligand, the η^6-aniline is replaced by three N-bonded aniline ligands, affording the complex $[IrH_2(\kappa\text{-}N,NH_2Ph)_3(P^iPr_3)]BF_4$ (**11**) analogous to **3** (eq 4).



(4)

Complex **11** can be formed in quantitative yield in solution by using a moderate excess of ligand. However, the elemental analyses and the NMR spectra of the solids isolated from these solutions revealed that significant amounts of complex **10** (ca. 20%) precipitate together with **11**. This has been found to occur even at high aniline concentrations.

Other aromatic molecules such as quinoline and isoquinoline, which may also coordinate to the metal either as an arene or through the nitrogen atom, have been found to prefer N-coordination at any concentration (eq 5). Thus, treatment of acetone-d_6 solutions of **1**



(5)

with quinoline produced the compound $[IrH_2(\kappa\text{-}N,\text{quinoline})_2(OC(CD_3)_2)(P^iPr_3)]BF_4$ (**12**), as the unique observable species by NMR. This complex displays two different hydride resonances in the ^{1}H NMR spectrum, indicating that the quinoline ligands coordinate one trans to the phosphine and the other trans to one hydride ligand. The use of the less sterically demanding isoquinoline allowed the observation of three different species, complexes **13**, **14**, and **15**, corresponding respectively to the coordination of one (trans to phosphine), two, and three N-donor ligands (eq 5). None of these quinoline or isoquinoline products could be isolated as an analytically pure solid. In fact, although the products crystallized from acetone/ether solutions at low temperature, the crystals so obtained slowly melted into oils after isolation.

The synthetic procedure of eq 3 requires the displacement of benzene by a better donating arene ligand. The relative coordinating capabilities of the different arenes can be estimated in the equilibrium mixtures generated by the arene complexes in acetone-d_6 (eq 2), by evaluating to what extent each coordinated arene is displaced by the solvent to give complex **3**. Table 1 shows the values of the equilibrium constant K, defined as $K = [\mathbf{3}][\text{arene}]/[\eta^6\text{-arene complex}]$, obtained by ^{1}H NMR for various complexes at 297 K and a 3.6×10^{-2} M initial

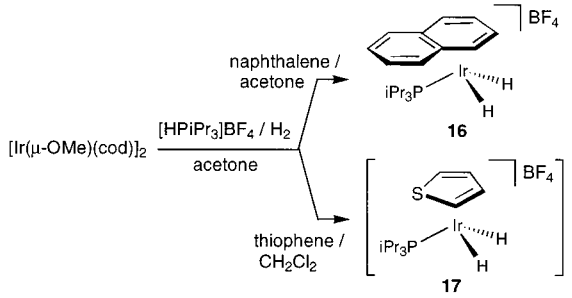
Table 1. Equilibrium Constants for Arene Replacement by Acetone-d_6

complex	arene ligand	K (M)
1	benzene	3.5×10^{-1}
2	benzene	3.6×10^{-1}
4	toluene	7.5×10^{-2}
5	1,3,5-trimethylbenzene	7.2×10^{-3}
7	hexamethylbenzene	*a*
10	aniline	3.2×10^{-5}

[a] Complex **3** was not detected by ^{1}H NMR.

concentration of arene complex. In agreement with previous observations in related complexes,[4k] the more electron-rich arene ligands lead to the more stable complexes.

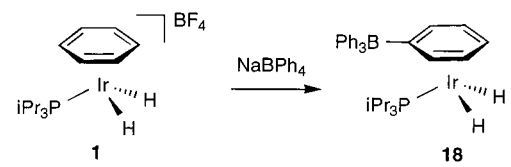
Even though poorly donating arene ligands cannot displace benzene from complex **1**, their complexes can be obtained by using these ligands instead of benzene in the synthetic procedure of eq 1. This alternative has been used for the preparation of the naphthalene complex $[(\eta^6\text{-}C_{10}H_8)IrH_2(P^iPr_3)]BF_4$ (**16**) (eq 6). More-



(6)

over, a similar reaction scheme in CH_2Cl_2 as solvent, and under excess of thiophene, allows the preparation of the compound $[(\eta^5\text{-}SC_4H_4)IrH_2(P^iPr_3)]BF_4$ (**17**). The lifetime of this complex in $CDCl_3$ is short, and decomposition to unidentified species is completed in a few hours at room temperature. This low stability precluded the isolation of an analytically pure solid, but still allowed the spectroscopic characterization of the complex in solution. The proposed η^5-coordination of the thiophene in **17** (eq 6) is inferred from the $^{13}C\{^1H\}$ NMR signals of this ligand, which consist of two doublets at δ 93.52 and 95.57 with J_{CP} coupling constants of 3.7 and 2.4 Hz, respectively. Interestingly, this unusual coordination mode is the only one observed even in the presence of an excess of thiophene.[13]

2. Zwitterionic Complexes. The η^6-benzene ligand of **1** can be readily displaced by the BPh_4^- anion to give the zwitterionic complex $[Ph_3B(\eta^6\text{-}Ph)IrH_2(P^iPr_3)]$ (**18**) (eq 7). This compound seems to be much more stable

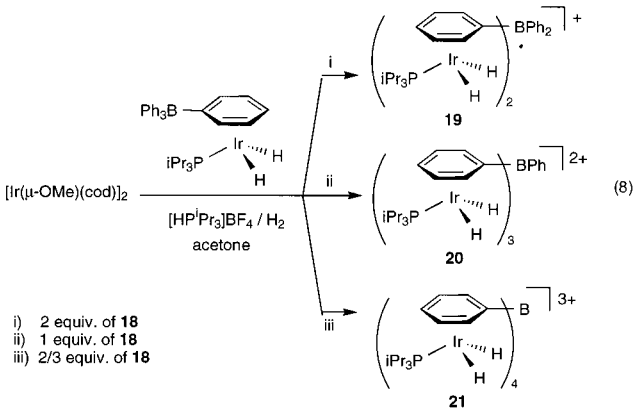


(7)

than the cationic species described above and can be also

(13) Precedents for such a coordination mode of thiophene to Rh and Cr are known; see: (a) Sánchez-Delgado, R. A.; Marquez-Silva, R. L.; Puga, J.; Tiripicchio, A.; Tiripicchio Camellini, M. *J. Organomet. Chem.* **1986**, *316*, C35. (b) Spies, G. H.; Angelici, R. J. *J. Am. Chem. Soc.* **1985**, *107*, 5569.

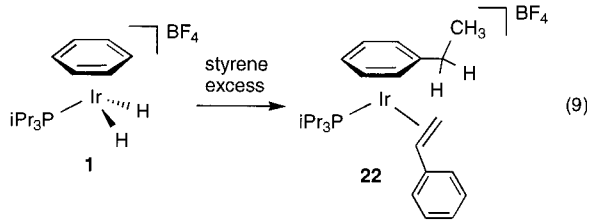
conveniently prepared by displacement of the three acetonitrile ligands of the complex $[IrH_2(NCCH_3)_3(P^iPr_3)]BF_4$[11] in CH_2Cl_2 as solvent. Compound **18**, which still has three arene rings available for coordination, can be introduced as an arene ligand in the general synthetic procedure of eq 1. Through this method, and depending on the ratio [Ir(μ-OMe)(cod)]$_2$/**18** employed in the synthesis, the complexes $[Ph_2B\{(\eta^6\text{-Ph})IrH_2(P^iPr_3)\}_2]BF_4$ (**19**), $[PhB\{(\eta^6\text{-Ph})IrH_2(P^iPr_3)\}_3](BF_4)_2$ (**20**), and $[B\{(\eta^6\text{-Ph})IrH_2(P^iPr_3)\}_4](BF_4)_3$ (**21**) can be obtained (eq 8).



(8)

The identity of these cationic complexes has been established by NMR spectroscopy, elemental analyses, and conductivity measurements in acetone. Precedents for BPh_4^- coordination to a cationic metal fragment are relatively abundant,[1,4a,14] but, to the best of our knowledge, the simultaneous coordination of this anion to various metal centers has been reported only for $[Rh(C_2H_4)_2]^+$ moieties.[15] In this case, the BPh_4^- anion, which is generally considered a noncoordinating anion, can coordinate up to three rhodium centers. In this respect, complex **21**, which represents the first example of the η^2[4] coordination of BPh_4^-, can properly illustrate the wide range of synthetic possibilities opened up by the method herein described.

3. Hydrogenation Reactions and Ir(I) Complexes. In contrast to that shown in eq 3 for 1-methylstyrene, the reaction of **1** with styrene did not give the arene substitution product. In turn, styrene was hydrogenated to ethylbenzene, which remained coordinated to the final reaction product $[(\eta^6\text{-}C_6H_5Et)Ir(\eta^2\text{-}CH_2{=}CHPh)(P^iPr_3)]BF_4$ (**22**) (eq 9).[16] This reaction



(9)

suggests that Ir(I) arene derivatives are accessible by

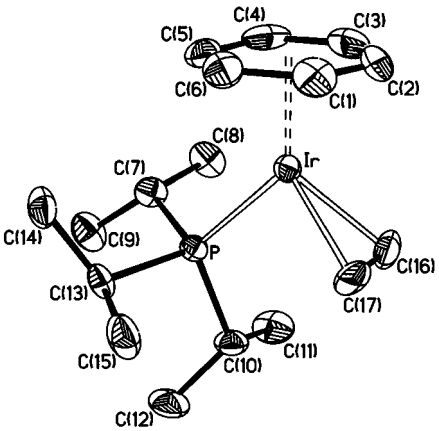


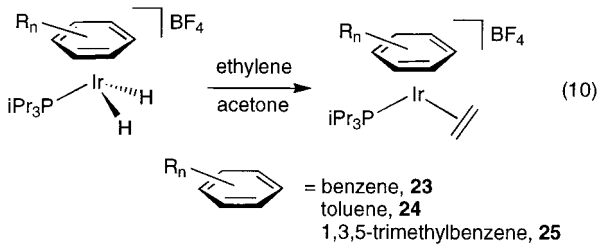
Figure 1. Molecular structure of the cation of complex **23**. The thermal ellipsoids correspond to 50% probability.

Table 2. Selected Bond Lengths (Å) and Angles (deg) for $[(\eta^6\text{-}C_6H_6)Ir(\eta^2\text{-}C_2H_4)(P^iPr_3)]BF_4$ (23)

Ir−P	2.2933(12)	P−Ir−G[a]	133.6(2)
Ir−C(1)	2.266(5)	P−Ir−C(16)	93.3(2)
Ir−C(2)	2.244(5)	P−Ir−C(17)	91.5(2)
Ir−C(3)	2.288(5)	G−Ir−C(16)	130.5(2)
Ir−C(4)	2.310(5)	G−Ir−C(17)	130.9(2)
Ir−C(5)	2.252(5)	C(16)−Ir−C(17)	39.7(2)
Ir−C(6)	2.301(5)		
Ir−C(16)	2.108(5)		
Ir−C(17)	2.105(5)		
C(16)−C(17)	1.430(7)		

[a] G represents the centroid of the C(1)−C(6) ring.

treatment of the Ir(III) dihydride complexes with hydrogen acceptors such as alkenes. Indeed, the treatment of the cationic dihydride complexes **1**, **3**, and **4** with ethylene produced ethane and, respectively, the Ir(I) complexes $[(\eta^6\text{-}C_6H_6)Ir(\eta^2\text{-}C_2H_4)(P^iPr_3)]BF_4$ (**23**), $[(\eta^6\text{-}C_6H_5Me)Ir(\eta^2\text{-}C_2H_4)(P^iPr_3)]BF_4$ (**24**), and $[(\eta^6\text{-}1,3,5\text{-}C_6H_3(Me)_3)Ir(\eta^2\text{-}C_2H_4)(P^iPr_3)]BF_4$ (**25**) (eq 10). The reaction



(10)

conditions required for these syntheses were different, depending on the coordinating abilities of the corresponding arene ligands. Thus, the formation of the benzene derivative **23** was fast and took place at room temperature, whereas the synthesis of the mesitylene complex **25** required treatment with ethylene during 12 h at 313 K. The structure of complex **23** determined by X-ray diffraction is shown in Figure 1. Important distances and angles are collected in Table 2.

In the solid state, the ethylene and benzene ligands of **23** are disposed parallel to each other. Such arrangement seems to be maintained in solution for the three ethylene derivatives **23**−**25**, since they show ^{1}H NMR patterns indicating nonrotating alkene ligands.[17] In

(14) (a) Bochmann, M. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 1181, and references therein. (b) Oro, L. A.; Pinilla, E.; Tenajas, M. L. *J. Organomet. Chem.* **1978**, *148*, 81.

(15) (a) Aresta, M.; Quaranta, E.; Tommasi *New J. Chem.* **1997**, *21*, 595. (b) Aresta, M.; Quaranta, E.; Albinati, A. *Organometallics* **1993**, *12*, 2032.

(16) An analogous reaction leading to the cation $[Ir(\eta^6\text{-}C_6H_5Et)(PPh_3)_2]^+$ was reported in ref 5a.

(17) A hindered rotation of the ethylene has been also observed for the rhodium analogue of **23**. See ref 9.

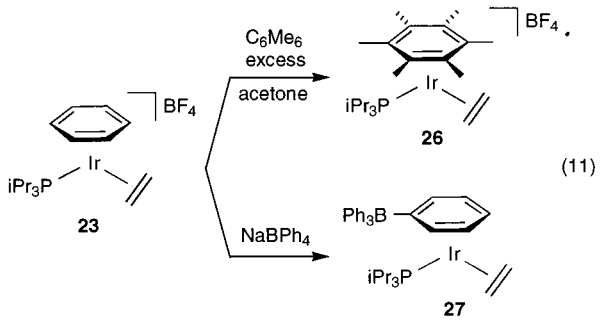
Table 3. Hydrogenation Reactions Catalyzed by Complex 1

substrate	substrate/catalyst	T (K)	time (h)	yield
styrene	200	298	6	90
phenylacetylene	200	298	10	87[a]
2-cyclohexenone	500	298	18	100[b]
cinnamaldehyde	500	323	24	100[c]
N-benzylydenaniline	100	313	24	97

[a] Conditions: solvent, 1,2-dichloroethane; $P(H_2) = 1$ atm. Products: (a) ethylbenzene; (b) cyclohexanone (100%); (c) 3-phenyl-2-propen-1-ol (55%), 3-phenylpropionaldehyde (45%).

turn, the NMR spectra of compounds **24** and **25** indicate that rotation of the arenes around the Ir−arene axis is fast on the NMR time scale.

The features of complex **22** suggest that the cationic Ir(I) species are less labile than the corresponding Ir(III) dihydrides, since the substitution of the η^6-ethylbenzene ligand did not take place in the presence of an excess of styrene. In agreement with this, the solutions of the Ir(I) complexes **22**−**25** in acetone-d_6 did not show any detectable product of arene substitution by solvent molecules. Despite this fact, the benzene ligand of **23** could be replaced by hexamethylbenzene or BPh_4^- in refluxing acetone, affording the complexes $[(\eta^6\text{-}C_6Me_6)Ir(\eta^2\text{-}C_2H_4)(P^iPr_3)]BF_4$ (**26**) and $[Ph_3B(\eta^6\text{-}Ph)Ir(\eta^2\text{-}C_2H_4)(P^iPr_3)]$ (**27**), respectively (eq 11). For these strong coordinating



(11)

arene ligands, this synthetic approach (substitution) led to higher yields and shorter reaction times than the treatment of the dihydrides **7** and **18** with ethylene (hydrogenation).

The above-described synthetic strategies leading to Ir(I) compounds strongly suggested that the η^6-arene complexes herein described could be efficient hydrogenation catalysts. Table 3 summarizes the results of some representative catalytic reactions performed by **1**. The hydrogenation of carbon−carbon double and triple bonds catalyzed by **1** took place under very mild conditions, even for an arene-substituted alkene such as styrene. α,β-Unsaturated ketones such as 2-hexenone were selectively reduced at the alkene position, whereas the hydrogenation of cinnamaldehyde occurred unselectively at both alkene and carbonyl groups. Noteworthily, imine substrates, which are commonly found to be rather reluctant to hydrogenation,[18] were also efficiently hydrogenated under mild conditions. Current work in our laboratory is aimed at the development of chiral versions of these η^6-arene derivatives that may catalyze the enantioselective reduction of imines.

Experimental Section

All experiments were carried out under an atmosphere of argon by Schlenk techniques. Oxygen-free solvents were employed throughout. Diethyl ether, THF, and acetone were distilled immediately prior to use from sodium/benzophenone, and anhydrous $CaCl_2$, respectively. $CDCl_3$ and CD_2Cl_2 were dried from activated molecular sieves. Acetone-d_6 (<0.02% D_2O) was purchased from Euriso-top and used as received. The complex $[Ir(\mu\text{-}OMe)(cod)]_2$ was prepared by published methods.[19] All other reagents were obtained from common commercial sources unless otherwise stated and were used as received. IR spectra were recorded as Nujol mulls on polyethylene sheets using a Nicolet 550 spectrometer. Elemental analyses were carried out with a Perkin-Elmer 2400 CHNS/O analyzer. Conductivities were measured in ca. 5×10^{-4} M solutions using a Philips PW 9501/01 conductometer. NMR spectra were recorded on a Varian UNITY, a Varian Gemini 2000, and a Bruker ARX 300 MHz instrument. ^{1}H (300 MHz) and ^{13}C (75.19 MHz) NMR chemical shifts were referenced to TMS by using known shifts of residual proton or carbon signals in the solvents. ^{31}P (121 MHz) NMR were measured relative to external 85% phosphoric acid. NMR coupling constants are given in Hz. MS data were recorded on a VG Autospec double-focusing mass spectrometer operating in the positive mode; ions were produced with the Cs^+ gun at ca. 30 kV, and 3-nitrobenzyl alcohol (NBA) was used as the matrix.

The salts $[HP^iPr_3]BF_4$ and $[HPCy_3]BF_4$ were prepared in quantitative yields by slow addition of HBF_4 solutions (54% in diethyl ether) to diethyl ether solutions of P^iPr_3 and PCy_3, respectively. The white solids obtained were filtered, washed with ether, and dried in vacuo. Data for $[HP^iPr_3]BF_4$: ^{1}H NMR ($CDCl_3$, 293 K) δ 1.41 (dd, $J_{HP} = 17.6$, $J_{HH} = 7.2$, 18H, PCHCH_3), 2.75 (m, 3H, PCHCH$_3$), 5.71 (dq, $J_{HP} = 468.4$, $J_{HH} = 4.2$, 1H, PH); ^{31}P{^{1}H} NMR ($CDCl_3$, 293 K) δ 42.37 (s). Data for $[HPCy_3]BF_4$: ^{1}H NMR ($CDCl_3$, 293 K) δ 1.1−2.6 (m, 33 H) 5.75 (dq, $J_{HP} = 474.3$, $J_{HH} = 3.9$, 1H, PH); ^{31}P{^{1}H} NMR ($CDCl_3$, 293 K) δ 29.20 (s).

Preparation of $[(\eta^6\text{-}C_6H_6)IrH_2(P^iPr_3)]BF_4$ (1). A suspension of $[Ir(\mu\text{-}OMe)(cod)]_2$ (300 mg, 0.45 mmol) in acetone/benzene (20:1, 10 mL) was treated with $[HP^iPr_3]BF_4$ (223 mg, 0.90 mmol), and the resulting orange solution was stirred for 1 h under hydrogen atmosphere ($P = 1$ atm). The dark solution obtained was filtered through Celite and dried in vacuo. After treatment of the resulting residue with a mixture of diethyl ether/THF (4:1) a white solid precipitated. The solution was decanted and the solid washed with ether and dried in vacuo: yield 327 mg (70%); IR 2237, 2208 ν(Ir−H); ^{1}H NMR ($CDCl_3$, 293 K) δ −16.66 (d, $J_{HP} = 27.2$, 2H, Ir−H), 1.08 (dd, $J_{HP} = 15.6$, $J_{HH} = 7.2$, 18H, PCHCH_3), 2.14 (m, 3H, PCHCH$_3$), 6.71 (s, 6H, C_6H_6); ^{31}P{^{1}H} NMR ($CDCl_3$, 293 K) δ 51.23 (s); ^{13}C{^{1}H} NMR ($CDCl_3$, 293 K) δ 19.78 (d, $J_{CP} = 1.3$, PCHCH$_3$), 28.16 (d, $J_{CP} = 34.4$, PCHCH$_3$), 97.99 (d, $J_{CP} = 2.3$, C_6H_6); MS (FAB+, m/z (%)) 433 (100) [M$^+$]; Λ_M (acetone) = 135 Ω^{-1} cm^2 mol^{-1} (1:1). Anal. Calcd for $C_{15}H_{29}BF_4IrP$: C, 34.69; H, 5.63. Found: C, 34.28; H, 5.87.

Preparation of $[(\eta^6\text{-}C_6H_6)IrH_2(PCy_3)]BF_4$ (2). The compound was prepared following the procedure described for **1**, by using $[HPCy_3]BF_4$ (330 mg, 0.90 mmol): yield 437 mg (76%); IR 2237, 2208 ν(Ir−H); ^{1}H NMR ($CDCl_3$, 293 K) δ −16.67 (d, $J_{HP} = 27.0$, 2H, Ir−H), 1.12−1.32 (m, 16H), 1.68−1.98 (m, 17H), 6.68 (s, 6H, C_6H_6); ^{31}P{^{1}H} NMR ($CDCl_3$, 293 K) δ 38.71 (s); ^{13}C{^{1}H} NMR (CD_2Cl_2, 293 K) δ 26.52 (s, CH_2), 27.32 (d, $J_{CP} = 11.0$, CH_2), 30.54 (d, $J_{CP} = 2.5$, CH_2), 38.55 (d, $J_{CP} = 33.3$, PCH), 98.15 (d, $J_{CP} = 2.0$, C_6H_6). Anal. Calcd for $C_{24}H_{41}BF_4IrP$: C, 45.07; H, 6.46. Found: C, 45.55; H, 6.42.

$[IrH_2(OC(CD_3)_2)_3(P^iPr_3)]BF_4$ (3). The NMR spectra of acetone-d_6 (0.5 mL) solutions of complex **1** (26 mg, 0.05 mmol) at 293 K showed the presence of complex $[IrH_2(OC(CD_3)_2)_3$-

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(19) Usón, R.; Oro, L. A.; Cabeza, J. A. *Inorg. Synth.* **1985**, *23*, 126.

(P^iPr_3)]BF_4 as the major species in solution, in equilibrium with **1**. Data for **3**: ^{1}H NMR (acetone-d_6, 253 K) δ −31.08 (d, J_{HP} = 23.7, 2H, Ir−H), 1.15 (dd, J_{HP} = 13.5, J_{HH} = 6.8, 18H, PCHCH_3), 2.12 (m, 3H, PCHCH$_3$); ^{31}P{^{1}H} NMR (acetone-d_6, 253 K) δ 31.32 (s); ^{13}C{^{1}H} NMR (acetone-d_6, 253 K) δ 16.49 (s, PCHCH$_3$), 22.53 (d, J_{CP} = 35.2, PCHCH$_3$).

Preparation of Complexes 4−9. Solutions of **1** (100 mg, 0.19 mmol) in acetone (5 mL) were treated with a ca. 10-fold excess of the desired arene and stirred for 1 h. The resulting solutions were concentrated to ca. 0.5 mL and treated with a mixture of diethyl ether/THF (4:1) to give white solids, which were filtered, washed with ether, and dried in vacuo.

[(η^6-C_6H_5Me)$IrH_2(P^iPr_3)$]BF_4 (4). Yield: 91 mg (90%); IR 2245, 2201 ν(Ir−H); ^{1}H NMR ($CDCl_3$, 293 K) δ −16.81 (d, J_{HP} = 27.3, 2H, Ir−H), 1.07 (dd, J_{HP} = 15.3, J_{HH} = 7.2, 18H, PCHCH_3), 2.13 (m, 3H, PCHCH$_3$), 2.64 (s, 3H, CH$_3$), 6.54 (d, J_{HH} = 6.0, 2H, CH), 6.59 (t, J_{HH} = 6.0, 1H, CH), 6.77 (t, J_{HH} = 6.0, 2H, CH); ^{31}P{^{1}H} NMR ($CDCl_3$, 293 K) δ 50.93 (s); ^{13}C{^{1}H} NMR ($CDCl_3$, 293 K) δ 19.61 (d, J_{CP} = 1.0, PCHCH$_3$), 20.85 (s, CH$_3$), 27.90 (d, J_{CP} = 35.1, PCHCH$_3$), 95.53 (d, J_{CP} = 3.2, CH), 95.62, 100.11 (both s, CH), 116.54 (d, J_{CP} = 3.0, C); MS (FAB+, m/z (%)) 447 (100) [M$^+$]. Anal. Calcd for $C_{16}H_{31}BF_4IrP$: C, 36.03; H, 5.86. Found: C, 36.37; H, 5.76.

[(η^6-1,3,5-$C_6H_3(Me)_3$)$IrH_2(P^iPr_3)$]BF_4 (5). Yield: 98 mg (92%); IR 2220 (br) ν(Ir−H); ^{1}H NMR ($CDCl_3$, 293 K) δ −17.72 (d, J_{HP} = 28.5, 2H, Ir−H), 1.07 (dd, J_{HP} = 15.3, J_{HH} = 6.9, 18H, PCHCH_3), 2.03 (m, 3H, PCHCH$_3$), 2.64 (s, 9H, CH$_3$), 6.39 (s, CH); ^{31}P{^{1}H} NMR ($CDCl_3$, 293 K) δ 48.16 (s); ^{13}C{^{1}H} NMR ($CDCl_3$, 293 K) δ 19.57 (d, J_{CP} = 1.3, PCHCH$_3$), 20.48 (s, CH$_3$), 26.74 (d, J_{CP} = 35.0, PCHCH$_3$), 94.30 (d, J_{CP} = 1.9, CH), 118.41 (d, J_{CP} = 1.8, C); MS (FAB+, m/z (%)) 475 (100) [M$^+$]; Anal. Calcd for $C_{18}H_{35}BF_4IrP$: C, 38.50; H, 6.28. Found: C, 38.62; H, 6.24.

[(η^6-1,2,4-$C_6H_3(Me)_3$)$IrH_2(P^iPr_3)$]BF_4 (6). Yield: 98 mg (92%); IR 2241, 2210 ν(Ir−H); ^{1}H NMR (CD_2Cl_2, 293 K) δ −17.38 (A part of a ABX spin system (X = ^{31}P) J_{HP} = 27.9, J_{HH} = 5.1, 1H, Ir−H), −17.36 (B part of a ABX spin system (X = ^{31}P) J_{HP} = 27.9, J_{HH} = 5.1, 1H, Ir−H), 1.11, 1.12 (both dd, J_{HP} = 15.3, J_{HH} = 6.9, 9H, PCHCH_3), 2.11 (m, 3H, PCHCH$_3$), 2.48 (s, 3H, CH$_3$), 2.58 (s, 3H, CH$_3$), 2.60 (s, 3H, CH$_3$), 6.40 (d, J_{HH} = 6.0, 1H, CH), 6.44 (s, 1H, CH), 6.60 (d, J_{HH} = 6.0, 1H, CH); ^{31}P{^{1}H} NMR ($CDCl_3$, 293 K) δ 49.86 (s); ^{13}C{^{1}H} NMR ($CDCl_3$, 293 K) δ 18.42, 19.47 (both s, CH$_3$), 19.61, 19.69 (both d, J_{CP} = 1.5, PCHCH$_3$), 20.09 (s, CH$_3$), 28.11 (d, J_{CP} = 34.8, PCHCH$_3$), 95.13 (d, J_{CP} = 5.8, CH), 97.11, 101.33 (both s, CH), 100.57 (s, C), 113.69 (d, J_{CP} = 4.5, C), 114.88 (s, C); MS (FAB+, m/z (%)) 475 (100) [M$^+$]. Anal. Calcd for $C_{18}H_{35}BF_4IrP$: C, 38.50; H, 6.28. Found: C, 38.66; H, 6.23.

[(η^6-C_6Me_6)$IrH_2(P^iPr_3)$]BF_4 (7). Yield: 101 mg (88%); IR 2220 (br) ν(Ir−H); ^{1}H NMR ($CDCl_3$, 293 K) δ −18.91 (d, J_{HP} = 29.7, 2H, Ir−H), 1.02 (dd, J_{HP} = 15.0, J_{HH} = 7.2, 18H, PCHCH_3), 1.98 (m, 3H, PCHCH$_3$), 2.50 (s, 18H, CH$_3$); ^{31}P{^{1}H} NMR ($CDCl_3$, 293 K) δ 45.41 (s); ^{13}C{^{1}H} NMR ($CDCl_3$, 293 K) δ 17.65 (s, CH$_3$), 19.50 (d, J_{CP} = 1.3, PCHCH$_3$), 27.33 (d, J_{CP} = 34.3, PCHCH$_3$), 110.29 (d, J_{CP} = 2.2, C); MS (FAB+, m/z (%)) 517 (100) [M$^+$]. Anal. Calcd for $C_{21}H_{41}BF_4IrP$: C, 41.79; H, 6.85. Found: C, 41.39; H, 6.73.

[(η^6-$C_6H_5(C(Me)=CH_2)$)$IrH_2(P^iPr_3)$]BF_4 (8). Yield: 95 mg (90%); IR 2222 (br) ν(Ir−H); ^{1}H NMR ($CDCl_3$, 293 K) δ −16.80 (d, J_{HP} = 27.0, 2H, Ir−H), 1.09 (dd, J_{HP} = 15.3, J_{HH} = 6.9, 18H, PCHCH_3), 2.09 (d, J_{HH} = 1.5, 3H, CH$_3$), 2.15 (m, 3H, PCHCH$_3$), 5.41 (q, J_{HH} = 1.5, 1H, =CH$_2$), 5.66 (s, 1H, =CH$_2$), 6.75 (m, 3H, CH), 6.84 (m, 2H, CH); ^{31}P{^{1}H} NMR ($CDCl_3$, 293 K) δ 51.07 (s); ^{13}C{^{1}H} NMR ($CDCl_3$, 293 K) δ 19.80 (d, J_{CP} = 4.3, PCHCH$_3$), 21.73 (s, CH$_3$), 28.44 (d, J_{CP} = 34.8, PCHCH$_3$), 92.81 (d, J_{CP} = 3.2, CH), 98.17 (d, J_{CP} = 1.9, CH), 99.31 (d, J_{CP} = 1.2, CH), 118.29 (d, J_{CP} = 3.3, C), 120.68 (s, CH$_2$), 137.20 (s, C); MS (FAB+, m/z (%)) 473 (30) [M$^+$]. Anal. Calcd for $C_{18}H_{33}BF_4IrP$: C, 38.64; H, 5.94. Found: C, 38.33; H, 6.00.

[(η^6-C_6H_5OH)$IrH_2(P^iPr_3)$]BF_4 (9). Yield: 91 mg (90%); IR 3286 (br) ν(O−H), 2218 (br) ν(Ir−H); ^{1}H NMR ($CDCl_3$, 293 K) δ −17.64 (d, J_{HP} = 27.3, 2H, Ir−H), 1.09 (dd, J_{HP} = 15.5, J_{HH} = 7.2, 18H, PCHCH_3), 2.11 (m, 3H, PCHCH$_3$), 5.97 (t, J_{HH} = 6.6, 1H, CH), 6.42 (d, J_{HH} = 6.6, 2H, CH), 6.57 (t, J_{HH} = 6.6, 2H, CH), 9.10 (br, 1H, OH); ^{31}P{^{1}H} NMR ($CDCl_3$, 293 K) δ 48.38 (s); ^{13}C{^{1}H} NMR ($CDCl_3$, 293 K) δ 19.68 (s, PCHCH$_3$), 27.35 (d, J_{CP} = 34.7, PCHCH$_3$), 82.53 (s, CH), 83.22 (d, J_{CP} = 3.6, CH), 100.54 (s, CH), 149.39 (s, C); Anal. Calcd for $C_{15}H_{29}BF_4IrOP$: C, 33.65; H, 5.46. Found: C, 34.00; H, 5.17.

Preparation of [(η^6-$C_6H_5(NH_2)$)$IrH_2(P^iPr_3)$]BF_4 (10). The compound was prepared following the procedure described for **4**, by using a stoichiometric amount of aniline (18 μL): yield 83 mg (82%); IR 3364, 3259 ν(N−H), 2177, 2226 ν(Ir−H); ^{1}H NMR ($CDCl_3$, 293 K) δ −18.25 (d, J_{HP} = 27.6, 2H, Ir−H), 1.09 (dd, J_{HP} = 15.0, J_{HH} = 6.9, 18H, PCHCH_3), 2.10 (m, 3H, PCHCH$_3$), 5.67 (dd, J_{HH} = 6.9, 5.7, 2H, CH), 5.72 (br, 2H, NH$_2$), 6.09 (d, J_{HH} = 6.9, 2H, CH), 6.28 (t, J_{HH} = 5.7, 1H, CH); ^{31}P{^{1}H} NMR ($CDCl_3$, 293 K) δ 45.62 (s); ^{13}C{^{1}H} NMR ($CDCl_3$, 293 K) δ 19.47 (d, J_{CP} = 1.2, PCHCH$_3$), 26.73 (d, J_{CP} = 34.5, PCHCH$_3$), 76.14 (s, CH), 99.92 (d, J_{CP} = 1.7, CH), 129.5 (br, CH), 146.28 (d, J_{CP} = 2.4, C); MS (FAB+, m/z (%)) 448 (100) [M$^+$]. Anal. Calcd for $C_{15}H_{30}NBF_4IrP$: C, 33.71; H, 5.66; N, 2.62 Found: C, 33.88; H, 6.00; N, 2.70.

[IrH_2(κN-NH_2Ph)$_3$(P^iPr_3)]BF_4 (11). A solution of complex **10** (80 mg, 0.15 mmol) in acetone (5 mL) was treated with an excess of aniline (100 μL, 1.1 mmol) and stirred for 30 min at room temperature. The resulting solution was concentrated to ca. 0.5 mL, and diethyl ether was slowly added to give a white solid. The solid was filtered, washed with ether, and dried in vacuo. The NMR spectrum of this material in $CDCl_3$ shows a mixture of complexes **11** and **10** and aniline in a ca. 5:2:1 molar ratio. The elemental analysis of this material was also consistent with the presence of 20% of the starting complex **10**. Several attempts to obtain analytically pure **11** by using a larger excess of aniline yielded, in all cases, materials containing 20% of **10**. Data for **11**: IR 3442, 3344, 3292, 3242 ν(N−H), 2206 (br) ν(Ir−H); ^{1}H NMR ($CDCl_3$, 253 K) δ −26.37 (d, J_{HP} = 22.5, 2H, Ir−H), 1.13 (dd, J_{HP} = 13.5, J_{HH} = 6.9 Hz, 18H, PCHCH_3), 2.07 (m, 3H, PCHCH$_3$), 3.71 (d, J_{HP} = 3.0, 2H, NH_2Ph), 5.18 (d, J_{HH} = 10.2, 2H, NH_2Ph), 5.75 (d, J_{HH} = 10.2, 2H, NH_2Ph), 5.99 (d, J_{HH} = 7.8, 2H, CH), 6.84 (t, J_{HH} = 7.8, 1H, CH), 6.97 (t, J_{HH} = 7.8, 2H, CH), 7.07 (t, J_{HH} = 7.5, 2H, CH), 7.17 (d, J_{HH} = 7.5, 4H, CH), 7.36 (t, J_{HH} = 7.5, 4H, CH); ^{31}P{^{1}H} NMR ($CDCl_3$, 253 K) δ 26.65 (s); ^{13}C{^{1}H} NMR ($CDCl_3$, 253 K) δ 19.33 (s, PCHCH$_3$), 24.92 (d, J_{CP} = 32.5, PCHCH$_3$), 119.98, 120.54, 124.20, 124.80, 128.51, 130.12 (all s, CH), 142.47, 145.66 (both s, C).

[IrH_2(κ-*N*,quinoline)$_2$($OC(CD_3)_2$)(P^iPr_3)]BF_4 (12). The treatment of a solution of complex **1** (26 mg, 0.05 mmol) in acetone-d_6 (0.5 mL) with quinoline (13 mg, 0.1 mmol) produced C_6H_6 and complex **12**, in quantitative yield. Our attempts to isolate **12** from its acetone solutions, by addition of diethyl ether, afforded yellow oils which gave incorrect elemental analyses. Data for **12**: ^{1}H NMR (acetone-d_6, 233 K) δ −28.94 (dd, J_{HP} = 24.0, J_{HH} = 6.3, 1H, Ir−H), −23.22 (dd, J_{HP} = 23.4, J_{HH} = 6.3, 1H, Ir−H), 0.85 (dd, J_{HP} = 13.8, J_{HH} = 7.2, 9H, PCHCH_3), 1.18 (dd, J_{HP} = 12.6, J_{HH} = 6.9, 9H, PCHCH_3), 2.15 (m, 3H, PCHCH$_3$), 7.12 (dd, J_{HH} = 8.1, 5.7, 1H, CH), 7.28 (t, J_{HH} = 7.5, 1H, CH), 7.43 (t, J_{HH} = 7.2, 1H, CH), 7.59 (t, J_{HH} = 7.8, 1H, CH), 7.80 (t, J_{HH} = 7.2, 1H, CH), 7.91 (dd, J_{HH} = 7.8, 5.7, 1H, CH), 7.97 (d, J_{HH} = 5.7, 1H, CH), 8.12 (m, 2H, CH), 8.42 (d, J_{HH} = 9.0, 1H, CH), 8.52 (d, J_{HH} = 8.1, 1H, CH), 8.72 (d, J_{HH} = 8.1, 1H, CH), 9.61 (d, J_{HH} = 9.0, 1H, CH), 10.18 (d, J_{HH} = 4.5, 1H, CH); ^{31}P{^{1}H} NMR (acetone-d_6, 233 K) δ 23.95 (s); ^{13}C{^{1}H} NMR (acetone-d_6, 233 K) δ 18.77 (d, J_{CP} = 1.4, PCHCH$_3$), 19.74 (s, PCHCH$_3$), 26.11 (d, J_{CP} = 33.0, PCHCH$_3$), 123.26, 123.69, 127.80, 128.80, 129.27, 129.36, 129.60 (all s, CH), 130.33 (s, C), 130.84, 131.61 (both s, CH), 132.14 (s, C), 133.48, 139.58, 139.77 (all s, CH), 147.70, 148.56 (both s, C), 154.51, 155.86 (both s, CH).

Isoquinoline Complexes 13−15. A solution of complex **1** (26 mg, 0.05 mmol) in acetone-d_6 (0.5 mL) was treated with isoquinoline (6 mg, 0.05 mmol). The ^{1}H and ^{31}P{^{1}H} NMR spectra of this solution at room temperature showed several broad resonances. After cooling this solution at 233 K, the NMR spectra revealed the presence of a mixture of complexes, consisting of compounds **1** and **3** (ca. 30% of the reaction mixture), and two new species. On the basis of their spectroscopic data (see below), these new species were identified as the compounds [IrH_2(κ-*N*,isoquinoline)($OC(CD_3)_2$)$_2$(P^iPr_3)]BF_4 (**13**) and [IrH_2(κ-*N*,isoquinoline)$_2$($OC(CD_3)_2$)(P^iPr_3)]BF_4 (**14**). The addition to the previous solution of six more equivalents of isoquinoline (39 mg, 0.6 mmol) produced a new mixture of complexes, consisting of complex **14** together with the new complex [IrH_2(κ-*N*,isoquinoline)$_3$(P^iPr_3)]BF_4 (**15**) in about equimolar amounts. Partial data for **13**: ^{1}H NMR (acetone-d_6, 233 K) δ −29.58 (d, J_{HP} = 21.3, 2H, Ir−H), 1.07 (dd, J_{HP} = 13.8, J_{HH} = 6.9, 18H, PCHCH_3), 2.10 (m, 3H, PCHCH_3), 8.27 (d, J_{HH} = 7.8, 1H, CH), 8.47 (dd, J_{HH} = 6.4, 2.2, 1H, CH), 9.44 (d, J_{HH} = 3.0, 1H, CH); ^{31}P{^{1}H} NMR (acetone-d_6, 233 K) δ 28.32 (s). Partial data for **14**: ^{1}H NMR (acetone-d_6, 233 K) δ −29.31 (dd, J_{HP} = 22.2, J_{HH} = 7.8, 1H, Ir−H), −22.35 (dd, J_{HP} = 22.2, J_{HH} = 7.8, 1H, Ir−H), 1.05 (dd, J_{HP} = 14.7, J_{HH} = 6.9, 9H, PCHCH_3), 1.19 (dd, J_{HP} = 13.6, J_{HH} = 7.2, 9H, PCHCH_3), 2.14 (m, 3H, PCHCH_3), 7.72 (t, J_{HH} = 7.2 Hz, 1H, CH), 8.37 (dd, J_{HH} = 6.3, 2.2 Hz, 1H, CH), 8.96 (br, 1H, CH), 9.51 (d, J_{HH} = 3.0 Hz, 1H, CH), 9.93 (br, 1H, CH); ^{31}P{^{1}H} NMR (acetone-d_6, 233 K) δ 24.46 (s). Partial data for **15**: ^{1}H NMR (acetone-d_6, 233 K) δ −22.36 (d, J_{HP} = 23.4, 2H, Ir−H), 1.00 (dd, J_{HP} = 13.8, J_{HH} = 6.9, 18H, PCHCH_3), 2.27 (m, 3H, PCHCH_3), 8.64 (t, J_{HH} = 7.8, 1H, CH), 8.15 (dd, J_{HH} = 6.3, 7.4, 2H, CH), 8.30 (d, J_{HH} = 7.4, 2H, CH), 8.93 (dd, J_{HH} = 6.3, 2.2 Hz, 1H, CH), 8.97 (d, J_{HH} = 6.3, 2H, CH), 9.85 (d, J_{HH} = 3.0, 1H, CH), 10.02 (br, 2H, CH); ^{31}P{^{1}H} NMR (acetone-d_6, 233 K) δ 24.94 (s).

Preparation of [(η^6-$C_{10}H_8$)IrH_2(P^iPr_3)]BF_4 (16). The compound was prepared following the procedure described for **1**, by using [Ir(μ-OMe)(cod)]$_2$ (100 mg, 0.15 mmol), [HP^iPr_3]BF_4 (74 mg, 0.30 mmol), naphthalene (300 mg, 2.3 mmol), and acetone (5 mL): yield 113 mg (66%); IR 2220 (br) ν(Ir−H); ^{1}H NMR ($CDCl_3$, 293 K) δ −19.65 (d, J_{HP} = 25.5, 2H, Ir−H), 0.81 (dd, J_{HP} = 15.3, J_{HH} = 7.2, 18H, PCHCH_3), 1.86 (m, 3H, PCHCH_3), 6.66 (A part of an AA′BB′X spin system (X = ^{31}P), J_{AB} = 5.70, $J_{AB'}$ = 1.2, $J_{AA'}$ = 3.5, J_{AX} = 0.6, 2H, CH), 7.44 (B part of an AA′BB′X spin system, $J_{BB'}$ = J_{BX} = 0, 2H, CH), 7.75 (m, 2H, CH), 7.86 (m, 2H, CH); ^{31}P{^{1}H} NMR ($CDCl_3$, 293 K) δ 49.52 (s); ^{13}C{^{1}H} NMR ($CDCl_3$, 293 K) δ 19.24 (d, J_{CP} = 1.3, PCHCH$_3$), 27.57 (d, J_{CP} = 34.5, PCHCH$_3$), 93.87 (d, J_{CP} = 2.8, CH), 94.43 (d, J_{CP} = 2.2, CH), 111.90 (s, C), 127.95, 132.61 (both s, CH). Anal. Calcd for $C_{19}H_{33}BF_4IrP$: C, 39.93; H, 5.82. Found: C, 40.12; H, 5.88.

[(η^5-SC_4H_4)IrH_2(P^iPr_3)]BF_4 (17). A solution of [Ir(μ-OMe)(cod)]$_2$ (100 mg, 0.15 mmol) in CH_2Cl_2/thiophene (20:1, 5 mL) was treated with [HP^iPr_3]BF_4 (74 mg, 0.30 mmol), and the resulting orange solution was stirred for 30 min under hydrogen atmosphere (P = 1 atm). The dark solution obtained was filtered through Celite and dried in vacuo. The resulting residue was then washed with diethyl ether to give a beige oil. The spectroscopic analysis of this oil in $CDCl_3$ (see below) shows the presence of complex **17** and traces of thiophene. All our attempts to crystallize **17** from its freshly prepared solutions were unsuccessful. Data for **17**: ^{1}H NMR ($CDCl_3$, 293 K) δ −17.88 (d, J_{HP} = 25.2, 2H, Ir−H), 1.07 (dd, J_{HP} = 15.3, J_{HH} = 7.2, 18H, PCHCH_3), 2.15 (m, 3H, PCHCH_3), 6.57 (m, 2H, CH), 6.94 (m, 2H, CH); ^{31}P{^{1}H} NMR ($CDCl_3$, 293 K) δ 52.53 (s); ^{13}C{^{1}H} NMR ($CDCl_3$, 293 K) δ 19.67 (d, J_{CP} = 1.0, PCHCH$_3$), 27.53 (d, J_{CP} = 34.3, PCHCH$_3$), 93.52 (d, J_{CP} = 3.7, CH), 95.57 (d, J_{CP} = 2.4, CH).

Preparation of [Ph_3B(η^6-Ph)IrH_2(P^iPr_3)] (18). A solution of **1** (100 mg, 0.19 mmol) in acetone (5 mL) was treated with $NaBPh_4$ (130 mg, 0.40 mmol) and stirred for 30 min at room temperature. The resulting solution was dried and methanol added to give a white solid, which was filtered, washed with methanol, and dried in vacuo: yield 116 mg (91%); IR 2225, 2205 ν(Ir−H); ^{1}H NMR ($CDCl_3$, 293 K) δ −16.78 (d, J_{HP} = 28.1, 2H, Ir−H), 0.97 (dd, J_{HP} = 14.9, J_{HH} = 7.1, 18H, PCHCH_3), 1.89 (m, 3H, PCHCH_3), 6.03 (t, J_{HH} = 6.0, 1H, CH), 6.20 (t, J_{HH} = 6.0, 2H, CH), 6.45 (d, J_{HH} = 6.0, 2H, CH), 7.00 (t, J_{HH} = 6.9, 3H, CH), 7.11 (t, J_{HH} = 6.9, 6H, CH), 7.44 (d, J_{HH} = 6.9, 6H, CH); ^{31}P{^{1}H} NMR ($CDCl_3$, 293 K) δ 46.79 (s); ^{13}C{^{1}H} NMR ($CDCl_3$, 293 K) δ 19.67 (s, PCHCH$_3$), 28.21 (d, J_{CP} = 34.3, PCHCH$_3$), 90.99 (s, CH), 98.30 (d, J_{CP} = 3.5, CH), 99.03, 123.06, 126.18, 135.72 (all s, CH). Anal. Calcd for $C_{33}H_{43}BIrP$: C, 58.83; H, 6.43. Found: C, 58.82; H, 6.89.

Preparation of [Ph_2B{(η^6-Ph)IrH_2(P^iPr_3)}$_2$]BF_4 (19). A suspension of [Ir(μ-OMe)(cod)]$_2$ (100 mg, 0.15 mmol) in acetone (5 mL) was treated with [HP^iPr_3]BF_4 (74.3 mg, 0.30 mmol) and with complex **18** (202 mg, 0.3 mmol). The resulting orange solution was stirred under hydrogen atmosphere (P = 1 atm) for 1 h, and the resulting brown solution was filtered through Celite and dried in vacuo. Treatment of the residue with a mixture of diethyl ether/THF (4:1) produced a white solid, which was filtered, washed with ether, and dried in vacuo: yield 271 mg (82%); IR 2210 (br) ν(Ir−H); ^{1}H NMR ($CDCl_3$, 293 K) δ −16.79 (d, J_{HP} = 27.9, 4H, Ir−H), 0.97 (dd, J_{HP} = 15.0, J_{HH} = 7.2, 36H, PCHCH_3), 1.98 (m, 6H, PCHCH_3), 6.36 (t, J_{HH} = 6.0, 2H, CH), 6.44 (t, J_{HH} = 6.0, 4H, CH), 6.52 (d, J_{HH} = 6.0, 4H, CH), 7.03 (t, J_{HH} = 6.9, 2H, CH), 7.12 (t, J_{HH} = 6.9, 4H, CH), 7.43 (d, J_{HH} = 6.9, 4H, CH); ^{31}P{^{1}H} NMR ($CDCl_3$, 293 K) δ 48.59 (s); ^{13}C{^{1}H} NMR ($CDCl_3$, 293 K) δ 19.69 (s, PCHCH$_3$), 28.21 (d, J_{CP} = 34.8, PCHCH$_3$), 93.98 (s, CH), 98.04 (d, J_{CP} = 3.1, CH), 99.80, 124.59, 126.77, 135.35 (all s, CH); MS (FAB+, *m*/*z* (%)) 1027 (100) [M$^+$]; Λ_M (acetone) = 124 Ω^{-1} cm^2 mol^{-1} (1:1). Anal. Calcd for $C_{42}H_{66}B_2F_4Ir_2P_2$: C, 45.24; H, 5.97. Found: C, 45.73; H, 6.06.

Preparation of [PhB{(η^6-Ph)IrH_2(P^iPr_3)}$_3$]$(BF_4)_2$ (20). The compound was prepared following the procedure described for **19**, by using 50 mg (0.07 mmol) of [Ir(μ-OMe)(cod)]$_2$, 37.1 mg (0.15 mmol) of [HP^iPr_3]BF_4, and 202 mg (0.3 mmol) of complex **18**: yield 182 mg (78%); IR 2210 (br) ν(Ir−H); ^{1}H NMR ($CDCl_3$, 293 K) δ −16.71 (d, J_{HP} = 27.3, 6H, Ir−H), 1.00 (dd, J_{HP} = 15.0, J_{HH} = 7.2, 54H, PCHCH_3), 2.10 (m, 9H, PCHCH_3), 6.48 (m, 3H, CH), 6.60 (m, 12H, CH), 7.12 (m, 3H, CH), 7.51 (m, 2H, CH); ^{31}P{^{1}H} NMR ($CDCl_3$, 293 K) δ 49.49 (s); ^{13}C{^{1}H} NMR ($CDCl_3$, 293 K) δ 19.66 (d, J_{CP} = 1.4, PCHCH$_3$), 28.14 (d, J_{CP} = 35.0, PCHCH$_3$), 95.93 (s, CH), 98.51 (d, J_{CP} = 3.0, CH), 100.00, 125.89, 127.44, 134.96 (all s, CH); MS (FAB+, *m*/*z* (%)) 1469 (25) [M(BF_4)$^+$], 691 (50) [M$_2$+]; Λ_M (acetone) = 241 Ω^{-1} cm^2 mol^{-1} (2:1). Anal. Calcd for $C_{51}H_{89}B_3F_8Ir_3P_3$: C, 39.36; H, 5.76. Found: C, 38.95; H, 5.99.

Preparation of [B{(η^6-Ph)IrH_2(P^iPr_3)}$_4$]$(BF_4)_3$ (21). The compound was prepared following the procedure described for **19**, by using 50 mg (0.07 mmol) of [Ir(μ-OMe)(cod)]$_2$, 37.1 mg (0.15 mmol) of [HP^iPr_3]BF_4, and 303 mg (0.45 mmol) of complex **18**: yield 258 mg (72%); IR 2210 (br) ν(Ir−H); ^{1}H NMR ($CDCl_3$, 293 K) δ −16.51 (d, J_{HP} = 27.0, 8H, Ir−H), 1.04 (dd, J_{HP} = 15.3, J_{HH} = 7.2, 72H, PCHCH_3), 2.12 (m, 12H, PCHCH_3), 6.45 (t, J_{HH} = 6.0, 4H, CH), 6.71 (t, J_{HH} = 7.2, 18H, CH), 6.78 (br, 18H, CH); ^{31}P{^{1}H} NMR ($CDCl_3$, 293 K) δ 49.95 (s); ^{13}C{^{1}H} NMR ($CDCl_3$, 293 K) δ 19.70 (d, J_{CP} = 1.4, PCHCH$_3$), 28.28 (d, J_{CP} = 35.0, PCHCH$_3$), 96.85 (s, CH), 98.95 (br, CH), 99.98 (s, CH); Λ_M (CH_3NO_2) = 268 Ω^{-1} cm^2 mol^{-1} (3:1). Anal. Calcd for $C_{60}H_{112}B_4F_{12}Ir_4P_4$: C, 36.10; H, 5.65. Found: C, 36.40; H, 5.49.

Preparation of [(η^6-C_6H_5Et)Ir(η^2-CH_2=CHPh)(P^iPr_3)]BF_4 (22). A solution of **1** (100 mg, 0.19 mmol) in acetone (5 mL) was treated with styrene (ca. 500 μL) and stirred for 30 min at room temperature. The resulting solution was concentrated, and diethyl ether was added to give a pale yellow solid, which was filtered, washed with ether, and dried in vacuo: yield 100 mg (81%); ^{1}H NMR ($CDCl_3$, 293 K) δ 1.09 (t, J_{HH} = 7.5, 3H, CH_3), 1.15, 1.18 (both dd, J_{HP} = 14.4, J_{HH} = 7.8, 9H, PCHCH_3),

1.88 (ddd, J_{HH} = 8.4, 3.6, J_{HP} = 5.1, 1H, =CH_2), 2.00 (m, 3H, PC*H*CH_3), 2.16, 2.17 (both q, J_{HH} = 7.5, 1H, CH_2), 3.14 (dd, J_{HH} = 10.8, 3.6, 1H, =CH_2), 3.75 (ddd, J_{HH} = 10.8, 8.4, J_{HP} = 6.0, 1H, =CH), 5.26 (d, J_{HH} = 6.3, 1H, CH), 5.49 (td, J_{HH} = 6.3, 1.2, 1H, CH), 5.71 (d, J_{HH} = 6.3, 1H, CH), 6.41 (td, J_{HH} = 6.3, 1.2, 1H, CH), 6.78 (t, J_{HH} = 6.3, 1H, CH), 7.02 (tt, J_{HH} = 7.2, 1.2, 1H, CH), 7.07, 7.22 (both m, 2H, CH); $^{31}P\{^1H\}$ NMR ($CDCl_3$, 293 K) δ 20.41 (s); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 293 K) δ 14.12 (s, CH_3), 17.38 (s, CH_2), 19.32, 19.44 (both s, PCH*C*H_3), 24.27 (d, J_{CP} = 30.7, P*C*HCH$_3$), 25.66 (s, =CH_2), 41.35 (s, =CH), 93.58 (d, J_{CP} = 4.2, CH), 93.79 (s, CH), 94.83 (d, J_{CP} = 3.0, CH), 95.39 (d, J_{CP} = 1.0, CH), 100.61 (d, J_{CP} = 1.0, CH), 123.31 (d, J_{CP} = 2.7, C), 126.14, 126.82, 128.77 (all s, CH), 144.48 (s, C); MS (FAB+, *m*/*z* (%)) 563 (20) [M^+]. Anal. Calcd for $C_{25}H_{39}BF_4IrP$: C, 46.22; H, 6.05. Found: C, 46.06; H, 5.77.

Preparation of [(η^6-C_6H_6)Ir(η^2-C_2H_4)(P^iPr_3)]BF_4 (23). Ethylene was bubbled through a solution of **1** (100 mg, 0.19 mmol) in acetone (5 mL) for 30 min at room temperature. The resulting solution was concentrated, and diethyl ether was added to give a pale yellow solid, which was filtered, washed with ether, and dried in vacuo: yield 88 mg (85%); ^1H NMR ($CDCl_3$, 293 K) δ 1.60 (dd, J_{HP} = 14.1, J_{HH} = 7.2, 18H, PCHC*H*$_3$), 2.07 (A-part of a AA′MM′X spin system (X = ^{31}P), $J_{AA'}$ = 8.5, J_{AM} = 11.3, $J_{AM'}$ = 2.3, J_{AX} = 4.9, 2H, CH_2), 2.39 (m, 3H, PC*H*CH_3), 3.32 (M-part of a AA′MM′X spin system (X = ^{31}P), $J_{MM'}$ = 8.5, J_{MX} = 0.8, 2H, CH_2), 7.01 (s, 6H, C_6H_6); $^{31}P\{^1H\}$ NMR ($CDCl_3$, 293 K) δ 22.43 (s); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 293 K) δ 19.31 (d, J_{CP} = 1.4, PCH*C*H_3), 19.53 (d, J_{CP} = 2.2, C_2H_4), 24.43 (d, J_{CP} = 32.2, P*C*HCH$_3$), 95.89 (d, J_{CP} = 2.2, C_6H_6); MS (FAB+, *m*/*z* (%)) 459 (100) [M^+]; Λ_M (acetone) = 129 Ω^{-1} cm^2 mol^{-1} (1:1). Anal. Calcd for $C_{17}H_{31}BF_4IrP$: C, 37.37; H, 5.90. Found: C, 37.02; H, 5.55.

Preparation of [(η^6-C_6H_5Me)Ir(η^2-C_2H_4)(P^iPr_3)]BF_4 (24). The compound was prepared following the procedure described for **23**, but starting from complex **4** (100 mg, 0.19 mmol). The reaction time under ethylene atmosphere was 3 h: yield 76 mg (73%); ^1H NMR ($CDCl_3$, 293 K) δ 1.16 (dd, J_{HP} = 14.4, J_{HH} = 7.2, 18H, PCHC*H*$_3$), 1.74 (A-part of a AA′BB′X spin system (X = ^{31}P), $J_{AA'}$ = 8.5, J_{AB} = 11.2, $J_{AB'}$ = 2.1, J_{AX} = 4.2, 2H, CH_2), 1.98 (m, 3H, PC*H*CH_3), 2.34 (s, 3H, CH_3), 3.32 (B-part of a AA′BB′X spin system (X = ^{31}P), $J_{BB'}$ = 8.5, J_{BX} = 1.8, 2H, CH_2), 6.17 (d, J_{HH} = 6.3, 2H, CH), 6.64 (dd, J_{HH} = 6.3, 6.0, 2H, CH), 6.72 (t, J_{HH} = 6.0, 1H, CH); $^{31}P\{^1H\}$ NMR ($CDCl_3$, 293 K) δ 22.43 (s); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 293 K) δ 19.26 (d, J_{CP} = 1.3, PCH*C*H_3), 21.96 (d, J_{CP} = 2.0, C_2H_4), 24.35 (d, J_{CP} = 30.7, P*C*HCH$_3$), 94.30 (d, J_{CP} = 3.2, CH), 94.88, 96.50 (both s, CH), 113.12 (d, J_{CP} = 3.0, C); MS (FAB+, *m*/*z* (%)) 473 (100) [M^+]; Anal. Calcd for $C_{18}H_{33}BF_4IrP$: C, 38.64; H, 5.94. Found: C, 38.34; H, 5.76.

Preparation of [(η^6-1,3,5-$C_6H_3(Me)_3$)Ir(η^2-C_2H_4)(P^iPr_3)]-BF_4 (25). The compound was prepared following the procedure described for **23**, but starting from complex **5** (150 mg, 0.27 mmol). In this case, the reaction with ethylene required 12 h at 313 K: yield 125 mg (80%); ^1H NMR ($CDCl_3$, 293 K) δ 1.15 (dd, J_{HP} = 14.1, J_{HH} = 7.2, 18H, PCHC*H*$_3$), 1.82−1.90 (m, 5H, CH_2 and PC*H*CH_3), 2.22 (B-part of a AA′BB′X spin system (X = ^{31}P), J_{AB} = 11.1, $J_{AB'}$ = 2.2, $J_{BB'}$ = 8.1, J_{BX} = 0.9, 2H, CH_2), 2.47 (s, 9H, CH_3), 6.10 (s, 3H, CH); $^{31}P\{^1H\}$ NMR ($CDCl_3$, 293 K) δ 19.69 (s); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 293 K) δ 19.28 (d, J_{CP} = 1.4, PCH*C*H_3), 19.47 (s, CH_3), 22.68 (d, J_{CP} = 30.9, P*C*HCH$_3$), 23.58 (d, J_{CP} = 2.3, C_2H_4), 94.41 (d, J_{CP} = 2.3, CH), 114.35 (d, J_{CP} = 2.3, C); MS (FAB+, *m*/*z* (%)) 501 (100) [M^+]. Anal. Calcd for $C_{20}H_{37}BF_4IrP$: C, 40.84; H, 6.53. Found: C, 40.77; H, 6.38.

Preparation of [(η^6-C_6Me_6)Ir(η^2-C_2H_4)(P^iPr_3)]BF_4 (26). A solution of **23** (200 mg, 0.37 mmol) in acetone (5 mL) was treated with hexamethylbenzene (450 mg, 2.8 mmol) and stirred for 48 h at room temperature. The resulting solution was concentrated to ca. 0.5 mL, and then diethyl ether was added, causing the precipitation of a white solid. The solid was separated by decantation, washed with ether, and dried in vacuo: yield 145 mg (63%); ^1H NMR ($CDCl_3$, 293 K) δ 1.09 (dd, J_{HP} = 13.8, J_{HH} = 7.2, 18H, PCHC*H*$_3$), 1.43 (A-part of a AA′BB′X spin system (X = ^{31}P), $J_{AA'}$ = 7.5, J_{AB} = 9.9, $J_{AB'}$ = 2.1, J_{AX} = 0, 2H, CH_2), 1.70 (B-part of a AA′BB′X spin system (X = ^{31}P), $J_{BB'}$ = 7.5, J_{BX} = 2.7, 2H, CH_2), 1.82 (m, 3H, PC*H*CH_3), 2.19 (s, 18H, CH_3); $^{31}P\{^1H\}$ NMR ($CDCl_3$, 293 K) δ 17.83 (s); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 293 K) δ 16.33 (s, CH_3), 19.38 (d, J_{CP} = 0.9, PCH*C*H_3), 23.53 (d, J_{CP} = 30.2, P*C*HCH$_3$), 23.85 (d, J_{CP} = 1.2, C_2H_4), 107.95 (d, J_{CP} = 1.6, C); MS (FAB+, *m*/*z* (%)) 543 (75) [M^+]; Λ_M (acetone) = 100 Ω^{-1} cm^2 mol^{-1} (1:1). Anal. Calcd for $C_{23}H_{43}BF_4IrP$: C, 43.88; H, 6.88. Found: C, 43.40; H, 7.01.

Preparation of [Ph_3B(η^6-Ph)Ir(η^2-C_2H_4)(P^iPr_3)] (27). A solution of **23** (100 mg, 0.18 mmol) in acetone (5 mL) was treated with $NaBPh_4$ (65 mg, 0.20 mmol) and stirred for 8 h at 323 K. The resulting suspension was taken to dryness and the residue treated with methanol, to give a white solid. The solid was filtered off, washed with methanol, and dried in vacuo: yield 103 mg (82%); ^1H NMR ($CDCl_3$, 293 K) δ 1.11 (dd, J_{HP} = 13.5, J_{HH} = 6.9, 18H, PCHC*H*$_3$), 1.41 (A-part of a AA′BB′X spin system (X = ^{31}P), $J_{AA'}$ = 8.5, J_{AB} = 10.9, $J_{AB'}$ = 2.2, J_{AX} = 4.8, 2H, CH_2), 1.84 (m, 3H, PC*H*CH_3), 2.31 (B-part of a AA′BB′X spin system (X = ^{31}P), $J_{BB'}$ = 8.5, J_{BX} = 0.9, 2H, CH_2), 5.96 (t, J_{HH} = 6.3, 2H, CH), 6.08 (d, J_{HH} = 6.3, 2H, CH), 6.47 (t, J_{HH} = 6.3, 1H, CH), 7.02 (tt, J_{HH} = 7.2, 2.1, 3H, CH), 7.12 (t, J_{HH} = 7.2, 6H, CH), 7.33 (brd, J_{HH} = 7.2, 6H, CH); $^{31}P\{^1H\}$ NMR ($CDCl_3$, 293 K) δ 18.01 (s); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 293 K) δ 18.80 (s, C_2H_4), 19.23 (s, PCH*C*H_3), 24.21 (d, J_{CP} = 30.7, P*C*HCH$_3$), 91.57, 94.22 (both s, CH), 95.86 (d, J_{CP} = 4.1, CH), 123.35, 126.14, 136.16 (all s, CH). Anal. Calcd for $C_{35}H_{45}$-BIrP: C, 60.08; H, 6.48. Found: C, 59.98; H, 6.75.

Catalytic Reactions. The reactions were carried out in a conventional glass hydrogenation apparatus equipped with a shaker. The reaction solvent was 1,2-dichloroethane (8 mL), the hydrogen pressure was set to 1 atm, and 1 mmol of substrate was used in each reaction. The course of the catalytic reactions was followed by GC in a HP 5890 series II gas chromatograph with a HP-Innowax cross-linked poly(ethylene glycol) column (30 m × 0.53 mm × 1.0 μm).

X-ray Structural Determination of Compound 23. A summary of crystal data and refinement parameters for **23** is given in Table 4. Suitable crystals for X-ray diffraction were obtained by slow diffusion of *n*-hexane into a concentrated solution of **23** in acetone. The selected crystal was a pale yellow irregular block of approximate dimensions 0.24 × 0.09 × 0.08

Table 4. Crystallographic Data for 23

formula	$C_{17}H_{31}BF_4IrP$
fw	545.40
temp, K	173(2)
cryst syst	monoclinic
space group	$P2_1/c$ (no. 14)
Z	4
a, Å	8.3723(7)
b, Å	17.1013(15)
c, Å	13.8467(12)
β, deg	91.913(2)
V, Å^3	1981.4(3)
F(000)	1064
ρ(calcd), g cm^{-3}	1.828
μ(Mo Kα), mm^{-1}	6.851
θ range data collec, deg	1.89−27.0
no. of collected reflns	12 459
no. of unique reflns	4323 (R_{int} = 0.0379)
no. of obsd reflns [$I \geq 2\sigma(I)$]	3516
min., max. transmn factors	0.6102, 0.2901
no. of data/restraints/params	4323/21/227
GOF[a]	0.934
$R_1(F)$, $wR_2(F^2)$ [obsd][b]	0.0338, 0.0616
$R_1(F)$, $wR_2(F^2)$ [all data]	0.0437, 0.0639

[a] GOF = $(\sum[w(F_o^2 - F_c^2)^2]/(n - p))^{1/2}$, where *n* and *p* are the number of data and parameters. [b] $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$, $wR_2 = (\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2])^{1/2}$ where $w = 1/[\sigma^2(F_o^2) + (0.0196P)^2]$ and $P = [\mathrm{Max}(0,F_o^2) + 2F_c^2]/3$.

mm. Diffraction data were recorded at 173 K on a Bruker SMART APEX diffractometer with a CCD area detector, using graphite-monochromated Mo Kα radiation ($\lambda = 0.71073$ Å). Cell constants were obtained from the least-squares refinement of three-dimensional centroids of 3837 reflections in the range $4.76° \leq 2\theta \leq 52.28°$. A total of 1771 frames of data were collected with scan widths of 0.3° in ω and exposure times of 10 s/frame. Data were corrected for absorption with the SADABS routine, based on the method of Blessing,[20] integrated in the Bruker SAINT program.[21]

The structure was solved by the Patterson method (SHELXS97)[22] and difference Fourier techniques and refined by full-matrix least-squares on F^2 (SHELXL97),[22] first with isotropic and then with anisotropic displacement parameters for the non-hydrogen atoms. The hydrogen atoms were introduced in calculated positions or localized in a difference Fourier map (for the olefinic ligand) and refined riding on the corresponding carbon atoms. Scattering factors, corrected for anomalous dispersion, were as implemented in the refinement program.[22]

(20) Blessing, R. H. *Acta Crystallogr., Sect. A* **1995**, *51*, 33.
(21) *SAINT+*, version 6.01; Bruker AXS, Inc., Madison, WI, 2000.
(22) Sheldrick, G. M. *SHELX97*; University of Göttingen, Germany, 1997.

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Supporting Information Available: Full listings of crystallographic data, complete atomic coordinates, isotropic and anisotropic thermal parameters, and bond distances and angles for complex **23**. This material is available free of charge via the Internet at http://pubs.acs.org.

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