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Synthesis and Reactions of New Hydridosilyliridium(III) Complexes Containing the Diolefin Tetrafluorobenzobarrelene

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Treatment of the complex $[Ir(\mu\text{-}OMe)(TFB)]_2$ (1) with acetic acid leads to the dimeric carboxylate compound $[Ir(\mu,\eta^2\text{-}O_2CCH_3)(TFB)]_2$ (2). The acetate bridges of 2 are split by monodentate ligands to give the square-planar derivatives $Ir(OCOCH_3)(TFB)L$ (L = py (3), PPh_3 (4), PCy_3 (5), P^iPr_3 (6)). The complexes 4–6 react with $HSiEt_3$, $HSiPh_3$, and H_2SiPh_2 to give the dihydride silyl complexes $IrH_2(SiR'_3)(TFB)(PR_3)$ (R′ = Et (7, 9, 11), Ph (8, 10, 12); R = Ph (7, 8), Cy (9, 10), ^{i}Pr (11, 12)) and $IrH_2(Ph_2SiOCOCH_3)(TFB)(PR_3)$ (R = Ph (13), Cy (14), ^{i}Pr (15)). In the presence of 7, 9, and 11, phenylacetylene undergoes reaction with triethylsilane. In all experiments carried out $PhCH{=}CH_2$, $PhC{\equiv}CSiEt_3$, *cis*-$PhCH{=}CH(SiEt_3)$, *trans*-$PhCH{=}CH(SiEt_3)$, and $Ph(SiEt_3)C{=}CH_2$ were obtained. Reactions of 7–12 with CO cause reductive elimination of $HSiR'_3$ and the formation of $Ir(\eta^1{:}\eta^2\text{-}C_{12}F_4H_7)(CO)_2(PR_3)$ (R = Ph (16), Cy (17), ^{i}Pr (18)). The molecular structure of 17 has been determined by X-ray investigation. 17 crystallizes with a toluene molecule in the monoclinic space group $P2_1/n$ with $a = 10.158(3)$ Å, $b = 15.075(2)$ Å, $c = 21.539(7)$ Å, and $\beta = 92.50(2)°$. The coordination geometry around the iridium center can be described as a distorted trigonal bipyramid with the phosphorus atom of the phosphine ligand and the C–Ir carbon atom occupying the axial positions. The equatorial plane is defined by the two carbon monoxide ligands and by the midpoint of the double carbon–carbon bond of the carbocyclic ligand.

Introduction

Six years ago, we reported that the dinuclear complex $[Ir(\mu\text{-}OMe)(COD)]_2$ reacts with $HSiMe_2Ph$ to give $[(Me_2SiC_6H_5)_4Ir_2H_2]$, in which each iridium atom is η^6-bonded to a phenyldimethylsilyl group. This ligand, furthermore, is in turn σ-bonded to the other metallic center through the silicon. In addition, each iridium atom has another σ-bonded $PhMe_2Si$ and a hydride ligand.[1] When the reaction was carried out in the presence of $AsPh_3$, PPh_3, and PCy_3 the silyl dihydride complexes $IrH_2(SiMe_2Ph)(COD)L$ were isolated. The same reactions with $HSiMe_2Ph$ replaced by $HSiEt_3$ lead to the related compounds $IrH_2(SiEt_3)(COD)L$,[2] which have been found to promote silicon–carbon bond formation in hydrosilylation and dehydrogenative silylation of olefins as in eq 1.[3]

$$C_6H_{12} + HSiEt_3 \xrightarrow{IrH_2(SiEt_3)(COD)L} C_6H_{14} + C_6H_{11}SiEt_3 + C_6H_{13}SiEt_3 \quad (1)$$

We have previously reported that treatment of $IrCl_3 \cdot xH_2O$ with tetrafluorobenzobarrelene (TFB) in refluxing methanol/water leads to the complex $IrCl(TFB)_2$ in nearly quantitative yield.[4] The accessibility of this compound has promoted the development of an extensive chemistry of neutral and cationic complexes containing the iridium–tetrafluorobenzobarrelene moiety, which shows significant differences with respect to the chemistry of the typical iridium–1,5-cyclooctadiene moiety.[4,5]

As a continuation of our work on the chemical properties of iridium–diolefin systems in the presence of silanes, we have now studied the reactivity of mononuclear complexes of the type $Ir(OCOCH_3)(TFB)(PR_3)$ toward $HSiEt_3$, $HSiPh_3$, and H_2SiPh_2. During these studies, we have isolated the first iridium compounds containing an acetoxysilyl ligand, and in addition, it has been also observed that some of the new complexes prepared catalyze the hydrosilylation and dehydrogenative silylation of alkynes.

The hydrosilylation of alkynes catalyzed by platinum metal complexes gives predominantly the corresponding

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[1] Fernández, M. J.; Esteruelas, M. A.; Oro, L. A.; Ruiz, J.; Smith, A. J.; Maitlis, P. M. *J. Organomet. Chem.* **1987**, *330*, 179.

[2] (a) Fernández, M. J.; Esteruelas, M. A.; Oro, L. A.; Apreda, M. C.; Foces-Foces, C.; Cano, F. H. *Organometallics* **1987**, *6*, 1751. (b) Fernández, M. J.; Esteruelas, M. A.; Covarrubias, M.; Oro, L. A.; Apreda, M. C.; Foces-Foces, C.; Cano, F. H. *Organometallics* **1989**, *8*, 1158.

[3] (a) Oro, L. A.; Fernández, M. J.; Esteruelas, M. A.; Jiménez, M. S. *J. Mol. Catal.* **1986**, *37*, 151. (b) Fernández, M. J.; Esteruelas, M. A.; Jiménez, M. S.; Oro, L. A. *Organometallics* **1986**, *5*, 1519.

[4] Usón, R.; Oro, L. A.; Carmona, D.; Esteruelas, M. A.; Foces-Foces, C.; Cano, F. H.; García-Blanco, S. *J. Organomet. Chem.* **1983**, *254*, 249.

[5] (a) Usón, R.; Oro, L. A.; Carmona, D.; Esteruelas, M. A. *J. Organomet. Chem.* **1984**, *263*, 109. (b) Usón, R.; Oro, L. A.; Carmona, D.; Esteruelas, M. A.; Foces-Foces, C.; Cano, F. H.; García-Blanco, S.; Vázquez de Miguel, A. *J. Organomet. Chem.* **1984**, *273*, 111. (c) Oro, L. A.; Carmona, D.; Esteruelas, M. A.; Foces-Foces, C.; Cano, F. H. *J. Organomet. Chem.* **1986**, *307*, 83. (d) Fernández, M. J.; Esteruelas, M. A.; Covarrubias, M.; Oro, L. A. *J. Organomet. Chem.* **1986**, *316*, 343. (e) Esteruelas, M. A.; Oro, L. A.; Apreda, M. C.; Foces-Foces, C.; Cano, F. H.; Claramunt, R. M.; López, C.; Elguero, J.; Begtrup, M. *J. Organomet. Chem.* **1988**, *344*, 93. (f) García, M. P.; López, A. M.; Esteruelas, M. A.; Lahoz, F. J.; Oro, L. A. *J. Chem. Soc., Dalton Trans.* **1990**, 3465. (g) García, M. P.; López, A. M.; Esteruelas, M. A.; Lahoz, F. J.; Oro, L. A. *J. Organomet. Chem.* **1990**, *388*, 365. (h) Esteruelas, M. A.; García, M. P.; López, A. M.; Oro, L. A. *Organometallics* **1991**, *10*, 127.

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trans-alkenylsilanes.[6] However, it has been reported that significant amounts of *cis*-alkenylsilanes are formed when certain rhodium complexes are used as catalysts.[7] Hydridosilyliridium complexes have proved to be useful models for understanding stoichiometric reactions related to the catalytic hydrosilylation of unsaturated organic compounds.[8] However, iridium complexes have scarcely been studied as catalysts in these reactions. Crabtree has recently reported that the complexes $Ir(triso)H(SiPh_3)(C_2H_4)$ and $Ir(triso)H_2(SiPh_2Me)_2$ (triso = $C(Ph_2PO)_3$) catalyze the net *anti* addition of silanes to phenylacetylene.[9] 1-Hexyne also undergoes reaction with triethylsilane in the presence of iridium catalysts formed by adding triarylarsines and triarylphosphines to $[Ir(\mu\text{-}OMe)(COD)]_2$.[10]

In this paper we report the synthesis, characterization, catalytic activity, and some reactivity of new dihydridosilyliridium compounds containing the diolefin tetrafluorobenzobarrelene.

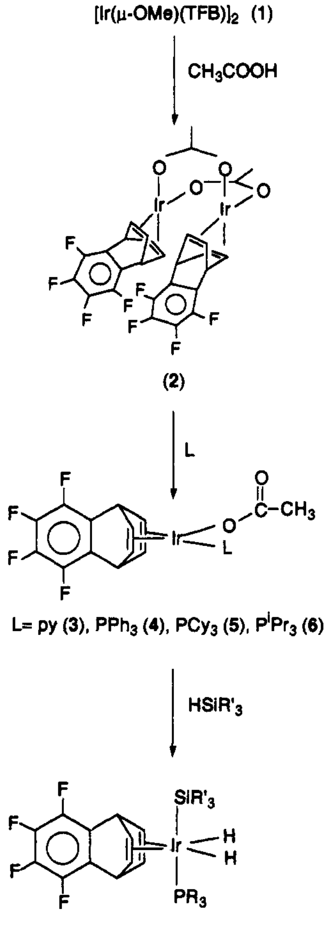
Results and Discussion

Synthesis, Characterization, and Catalytic Activity of $IrH_2(SiR'_3)(TFB)(PR_3)$. Treatment of $[Ir(\mu\text{-}OMe)(TFB)]_2$ (1) with acetic acid in acetone/2-propanol (1:5) leads to the dimeric carboxylate compound $[Ir(\mu,\eta^2\text{-}O_2CCH_3)(TFB)]_2$ (2) in 80% yield. The acetate bridges of this complex are readily split by monodentate ligands such as pyridine (py) and phosphines (PPh_3, PCy_3, and P^iPr_3) to give the square-planar derivatives $Ir(OCOCH_3)(TFB)py$ (3) and $Ir(OCOCH_3)(TFB)(PR_3)$ (4–6) (Scheme I).

The acetate ligand in these compounds is formulated as monodentate in 3–6 and as bidentate in 2 on the basis of the values calculated for $\Delta\nu$ (Table I), which coincide with those previously reported for related rhodium compounds.[11]

The ^1H NMR spectra of 2, 5, and 6 agree well with a square-planar structure. The spectrum of 2 contains two peaks at 6.00 and 3.32 ppm, assigned to the aliphatic and olefinic protons of two chemically equivalent diolefins. The spectra of 5 and 6 show two signals at about 4.70 and 2.11 ppm due to two groups of two chemically inequivalent vinyl protons, indicating furthermore that 5 and 6 have a rigid structure in solution. In contrast, to the spectra of 5 and 6, the spectrum of 4 is temperature-dependent. At room temperature, it does not show olefinic resonances. However, at −55 °C two signals at 4.70 and 1.73 ppm are observed. This behavior suggests the existence of a slow (on the NMR time scale) intramolecular exchange process, which involves the triphenylphosphine and acetate ligands. This process, most probably, proceeds via a five-coordinated intermediate where the acetate group acts as a bidentate ligand. In the ^1H NMR spectra of 3, only a single vinylic resonance is observed at room temperature and at −55 °C, suggesting the existence of a rapid exchange process (on the NMR time scale) between the pyridine and acetate ligands. Interestingly, in this case, the process is rapid even at −55 °C.

Scheme I



R' \ R	Ph	Cy	^{i}Pr
Et	7	9	11
Ph	8	10	12

The complexes 4–6 react with $HSiEt_3$ and $HSiPh_3$ to give the dihydride silyl derivatives $IrH_2(SiR'_3)(TFB)(PR_3)$ (7–12) (Scheme I). These complexes were isolated as white, air-stable powders in good yields (64–69%). The presence of the hydride ligands in the complexes is inferred from the IR and ^1H NMR spectra. The IR spectra in Nujol show one or two strong absorptions at about 2100 cm^{-1}, attributable to $\nu(IrH)$, in agreement with a *cis* arrangement of these ligands. The ^1H NMR spectra show the hydride resonances as one doublet between −14 and −16 ppm with P–H coupling constants of about 20 Hz, suggesting that both hydride ligands are chemically equivalent and are disposed *cis* to the phosphine ligands. This disposition

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(6) (a) Speier, J. L. *Adv. Organomet. Chem.* **1979**, *17*, 407. (b) Green, M.; Spencer, J. L.; Stone, F. G. A.; Tsipis, C. A. *J. Chem. Soc., Dalton Trans.* **1977**, 1525.

(7) (a) Ojima, I.; Kumagai, M.; Nagai, Y. *J. Organomet. Chem.* **1974**, *66*, C14. (b) Hill, J. E.; Nile, T. A. *J. Organomet. Chem.* **1977**, *139*, 293. (c) Watanabe, H.; Kitahara, T.; Motegi, T.; Nagai, Y. *J. Organomet. Chem.* **1977**, *137*, 215. (d) Dickers, H. M.; Haszeldine, R. N.; Mather, A. P.; Parish, R. V. *J. Organomet. Chem.* **1978**, *161*, 91. (e) Dickers, H. M.; Haszeldine, R. N.; Malkin, L. S.; Mather, A. P.; Parish, R. V. *J. Chem. Soc., Dalton Trans.* **1980**, 308. (f) Lappert, M. F.; Maskell, R. K. *J. Organomet. Chem.* **1984**, *264*, 217.

(8) (a) Johnson, C. E.; Eisenberg, R. *J. Am. Chem. Soc.* **1985**, *107*, 6531. (b) Rappoli, B. J.; Janik, T. S.; Churchill, M. R.; Thompson, J. S.; Atwood, J. D. *Organometallics* **1988**, *7*, 1939. (c) Luo, X.-L.; Crabtree, R. H. *J. Am. Chem. Soc.* **1989**, *111*, 2527. (d) Rappoli, B. J.; McFarland, J. M.; Thompson, J. S.; Atwood, J. D. *J. Coord. Chem.* **1990**, *21*, 147. (e) Hays, M. K.; Eisenberg, R. *Inorg. Chem.* **1991**, *30*, 2623. (f) Schubert, U. *Transition Met. Chem.* **1991**, *16*, 136. (g) Tanke, R. S.; Crabtree, R. H. *Organometallics* **1991**, *10*, 415. (h) Hostetler, M. J.; Bergman, R. G. *J. Am. Chem. Soc.* **1992**, *114*, 7629. (i) Cleary, B. P.; Eisenberg, R. *Organometallics* **1992**, *11*, 2335.

(9) Tanke, R. S.; Crabtree, R. H. *J. Chem. Soc., Chem. Commun.* **1990**, 1056.

(10) Fernández, M. J.; Oro, L. A.; Manzano, B. R. *J. Mol. Catal.* **1988**, *45*, 7.

(11) (a) Lahoz, F. J.; Martín, A.; Esteruelas, M. A.; Sola, E.; Serrano, J. L.; Oro, L. A. *Organometallics* **1991**, *10*, 1794. (b) Esteruelas, M. A.; Lahuerta, O.; Modrego, J.; Nürnberg, O.; Oro, L. A.; Rodríguez, L.; Sola, E.; Werner, H. *Organometallics* **1993**, *12*, 266.

Table I. IR[a] and $^{31}P\{^1H\}$[b] NMR Data for the Complexes 2–18

			$\nu(OCOCH_3)$				
complex	ν(Ir–H)	ν(CO)	$\nu_{asym}(OCO)$	$\nu_{sym}(OCO)$	$\Delta\nu$	ν(Si–O)	$^{31}P\{^1H\}$ (δ)
2			1560	1445	115		
3			1625	1365	260		
4			1615	1355	260		18.78
5			1645	1365	280		18.71
6			1645	1375	270		29.54
7	2145, 2085						3.81
8	2150						3.67
9	2145, 2120						8.90
10	2140, 2120						8.38
11	2140, 2115						22.97
12	2175						22.39
13	2140		1710			1040	3.96
14	2130		1715			1050	8.64
15	2120		1712			1040	23.89
16		2035–1940 (2020, 1975)[c]					4.10
17		2010–1955 (2005, 1955)[c]					6.92
18		2020–1925 (2012, 1950)[c]					16.81

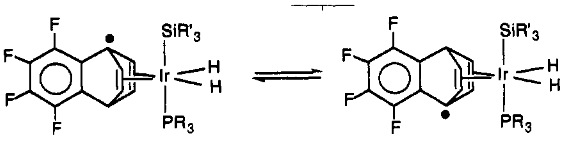
[a] IR: mull in Nujol; ν in cm^{-1}. The resonances of the TFB diolefin appear in all IR spectra at about 1490, 1090, 890, and 850 cm^{-1}. [b] NMR: δ in ppm; $^{31}P\{^1H\}$ NMR spectra in $CDCl_3$ (**4–12**) and in C_6D_6 (**13–18**). [c] In CH_2Cl_2 solution.

Table II. ^1H NMR[a] Spectral Data for the Complexes 2–15

	T^a		TFB				
	(°C)	L	CH	=CH	–SiR′$_3$	–OCOCH$_3$	Ir–H
2	20		6.00 (4H)	3.32 (8H)		1.95 (s, 6H)	
3	–55	8.44 (2H), 7.84 (1H), 7.4 (2H)	5.61 (2H)	3.17 (4H)		1.97 (s, 3H)	
4	20	7.62–7.42 (15H)	5.51 (2H)			1.69 (s, 3H)	
	–55	*b*	*b*	4.70 (2H), 1.73 (2H)		*b*	
5	20	1.88–1.10 (33H)	5.54 (2H)	4.72 (2H), 2.11 (2H)		1.90 (s, 3H)	
6	20	2.17 (m, 3H), 1.32 (dvt, 18H, $N = 13$, $J_{H-H} = 7.2$)	5.57 (2H)	4.76 (2H), 2.17 (2H)		1.90 (s, 3H)	
7	20	7.65–7.39 (15H)			1.25–0.89 (15H)		–14.84 (d, 2H, $J_{P-H} = 20.5$)
	–55	*b*	5.11 (1H), 3.51 (1H)	3.26 (2H), 2.38 (2H)	*b*		*b*
8	20	7.74–7.25 (15H)			7.74–7.25 (15H)		–14.15 (d, 2H, $J_{P-H} = 19.0$)
	–55	*b*	4.74 (1H), 3.51 (1H)	3.10 (2H), 2.62 (2H)	*b*		*b*
9	20	1.87–1.28 (33H)	5.50 (2H)	2.83 (4H)	0.89 (15H)		–15.57 (d, 2H, $J_{P-H} = 21.2$)
	–55	*b*	5.03 (1H), 4.61 (1H)	2.84 (2H), 2.60 (2H)	*b*		*b*
10	20	1.81–1.21 (33H)	4.67 (2H)	2.88 (4H)	7.69–7.22 (15H)		–14.80 (d, 2H, $J_{P-H} = 19.9$)
	–55	*b*	4.75 (1H), 4.63 (1H)	2.84 (2H), 2.73 (2H)	*b*		*b*
11	20	2.39 (m, 3H), 1.24 (dvt, 18H, $N = 13$, $J_{H-H} = 6.6$)	4.89 (2H)	2.87 (4H)	0.97–0.82 (15H)		–15.66 (d, 2H, $J_{P-H} = 21.1$)
	–55	*b*	5.04 (1H), 4.65 (1H)	2.80 (2H), 2.68 (2H)	*b*		*b*
12	20	2.40 (m, 3H), 1.17 (dvt, 18H, $N = 11$, $J_{H-H} = 5.2$)	4.66 (2H)	2.94 (4H)	7.68–7.28 (15H)		–14.93 (d, 2H, $J_{P-H} = 20.1$)
	–55	*b*	4.68 (2H)	2.92 (2H), 2.80 (2H)	*b*		*b*
13	20	7.61–7.14 (15H)			7.61–7.14 (10H)	2.23 (s, 3H)	–14.30 (d, 2H, $J_{P-H} = 18.8$)
	–55	*b*	4.90 (1H), 3.37 (1H)	3.12 (2H), 2.56 (2H)	*b*	*b*	*b*
14	20	2.10–1.00 (33H)	4.76 (2H)	3.00 (4H)	7.60–7.00 (10H)	2.20 (s, 3H)	–14.89 (d, 2H, $J_{P-H} = 19.2$)
	–55	*b*	5.20 (1H), 4.60 (1H)	3.10 (2H), 2.80 (2H)	*b*	*b*	*b*
15	20	2.20 (m, 3H), 0.90 (dvt, 18H, $N = 14$, $J_{H-H} = 7.1$)	4.95 (2H)	3.45 (4H)	8.10–7.20 (10H)	2.02 (s, 3H)	–14.70 (d, 2H, $J_{P-H} = 19.9$)
	–55	*b*	5.50 (1H), 4.50 (1H)	3.05 (2H), 2.60 (2H)	*b*	*b*	*b*

[a] ^1H NMR in ppm, in $CDCl_3$ (**2**, **4–1 1**) and in C_6D_6 at 20 °C and in C_7D_8 at –55 °C (**3**, **13–15**), *J* and *N* in Hz. Abbreviations used: br = broad, s = singlet, m = multiplet, d = doublet, vt = virtual triplet. All TFB resonances are broad. L = py (**2**), PPh_3 (**4**, **7**, **8**, **13**), PCy_3 (**5**, **9**, **10**, **14**), P^iPr_3 (**6**, **11**, **12**, **15**). –SiR′$_3$ = –$SiEt_3$ (**7**, **9**, **11**), –$SiPh_3$ (**8**, **10**, **12**), –$Ph_2Si(OCOCH_3)$ (**13–15**). [b] Resonance(s) is the same as that at 20 °C.

leads to a situation where the aliphatic CH protons of the tetrafluorobenzobarrelene diolefin are chemically inequivalent; furthermore, the protons of each double carbon–carbon bond are also mutually inequivalent, although both olefinic bonds are chemically equivalent. As would be expected for this arrangement, the ^1H NMR spectra display two aliphatic and two olefinic signals at –55 °C (Table II). At room temperature, the ^1H NMR spectra of **7** and **8** do not contain resonances due to the diolefin, while the ^1H NMR spectra of **9–12** show two resonances, one due to the aliphatic protons and the other one to the olefinic protons. This behavior suggests that the complexes **7–12** have a rigid structure (Scheme I) only at low temperature. At room temperature an intramolecular exchange process takes place, which involves the relative positions of the atoms of the diolefin (eq 2).



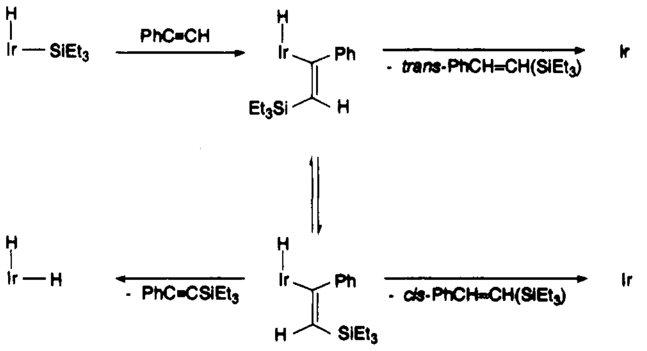
(2)

Table III. Hydrosilylation of Phenylacetylene Catalyzed by $IrH(SiEt_3)(TFB)(PR_3)$[a]

				yield, %			
R	*T*, °C	*t*, h	[Prod], M	$PhC{\equiv}CSiEt_3$	$Ph(SiEt_3)C{=}CH_2$	*cis*-$PhCH{=}CH(SiEt_3)$	*trans*-$PhCH{=}CH(SiEt_3)$
Ph	60	2.33	0.20	13.9	3.4	33.9	48.8
	20	6.67	0.19	12.6	2.6	61.8	23
Cy	60	0.33	0.19	20.8	11.9	59.8	7.5
	20	4.2	0.21	8.4	5.5	66.5	19.6
^iPr	60	1.1	0.19	16.3	11.5	49.9	22.3
	20	8	0.17	13.2	10.2	54.6	22

[a] $[IrH_2(SiEt_3)(TFB)(PR_3)] = 2.4 \times 10^{-3}$ M; $[PhC_2H] = [HSiEt_3] = 0.24$ M. C_6H_{12} (0.125 M) is used as the internal standard.

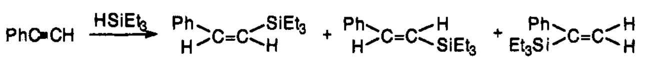
Scheme II



The fluxional process could proceed via a five-coordinated intermediate of the type $IrH_2(SiR'_3)(TFB)$, which could be formed by dissociation of the phosphine ligand from **7**–**12**. In accordance with this, we have observed that the addition of P^iPr_3 to a benzene solution of **9** in a 1:1 molar ratio leads to a mixture of **11**, **9**, PCy_3, and P^iPr_3 in 1:1:1:1 molar ratio after 22 h.

In the presence of the complexes **7**, **9**, and **11**, phenylacetylene undergoes reaction with triethylsilane. The reactions were performed in 1,2-dichloroethane solution at 60 and 20 °C, and the results are listed in Table III. In all experiments carried out, $PhCH{=}CH_2$, $PhC{\equiv}CSiEt_3$, *cis*-$PhCH{=}CH(SiEt_3)$, *trans*-$PhCH{=}CH(SiEt_3)$, and $Ph(SiEt_3)C{=}CH_2$ were obtained. The amount of $PhCH{=}CH_2$ formed was very similar to that of $PhC{\equiv}CSiEt_3$. This may be rationalized in terms of a dehydrogenative silylation (eq 3), along with a normal hydrosilylation (eq 4).

$$2PhC{\equiv}CH + HSiEt_3 \longrightarrow PhC{\equiv}CSiEt_3 + PhHC{=}CH_2 \qquad (3)$$



$$PhC{\equiv}CH \xrightarrow{HSiEt_3} (Ph)(H)C{=}C(SiEt_3)(H) + (Ph)(H)C{=}C(H)(SiEt_3) + (Ph)(Et_3Si)C{=}C(H)(H) \qquad (4)$$

The major product in almost all cases is *cis*-$PhCH{=}CH(SiEt_3)$, resulting from *anti* addition of the silane to the alkyne. In this context, it should be mentioned that Crabtree et al.[8g,9,12] and Ojima et al.[13] have proposed that, in general, the *anti*-addition product is formed by initial insertion of the unsaturated substrate into a M–Si bond; in this way, the isomerization of the resulting (*Z*)-silylvinyl intermediate to the less sterically congested *E* isomer is favored (Scheme II).

In our previous work on the addition of triethylsilane to phenylacetylene catalyzed by the complexes $MHCl(CO)(P^iPr_3)_2$ (M = Ru, Os), we also found predominant *anti* addition of the silane to the alkyne.[14] In this case, on the basis of spectroscopic studies, we have proposed that the formation of *cis*-$PhCH{=}CH(SiEt_3)$ involves the insertion of phenylacetylene into the M–Si bond of the intermediates $M(SiEt_3)Cl(CO)(P^iPr_3)_2$ (M = Ru, Os), followed by the isomerization of the resulting (*Z*)-silylvinyl derivatives to the *E* isomers.

The reactions catalyzed by **7**–**12**, in contrast to those catalyzed by $MHCl(CO)(P^iPr_3)_2$ (M = Ru, Os), furthermore lead to $PhC{\equiv}CSiEt_3$. The formation of *cis*-$PhCH{=}CH(SiEt_3)$ together with $PhC{\equiv}CSiEt_3$ could be rationalized in terms of the proposal of Crabtree and Ojima. Thus, once the (*E*)-silylvinyl intermediate has been formed, β-elimination of the *endo*-hydrogen atom of the silylvinyl group could lead to the dehydrogenative silylation product (Scheme II). However, the participation of alkynyl intermediates cannot be excluded. Studies recently carried out in our laboratory, on the addition of triethylsilane to phenylacetylene catalyzed by the cationic complex $[Ir(COD)(\eta^2\text{-}^iPr_2PCH_2CH_2OMe)]BF_4$, strongly suggest that these types of intermediates could also play a main role in these reactions.[15]

Raising the temperature favors *syn* addition, resulting in the *trans* isomer, as seen in Table III. The same behavior has been observed for the addition of silanes to alkynes catalyzed by $[IrH(H_2O)(bq)(PPh_3)_2]SbF_6$ (bq = 7,8-benzoquinolinato).[16] In this case, it has been argued that high temperature favors reductive elimination of the products before $Z \rightarrow E$ equilibrium is reached. In our case, the formation of *trans*-$PhCH{=}CH(SiEt_3)$ can also be due to a *cis*–*trans* isomerization process. Thus, it was observed that, at 60 °C in the presence of **7** and triethylsilane, a mixture of 41% of *cis*-$PhCH{=}CH(SiEt_3)$ and 59% of *trans*-$PhCH{=}CH(SiEt_3)$ is converted into 13% of *cis*-$PhCH{=}CH(SiEt_3)$ and 87% of *trans*-$PhCH{=}CH(SiEt_3)$ after 2 h.

Previously, we have reported that the complexes $IrH_2(SiEt_3)(COD)(AsPh_3)$ and $IrH_2(SiEt_3)(COD)(PPh_3)$ catalyze the hydrosilylation and dehydrogenative silylation of 1-hexene and ethylene.[3b] In addition, we have now observed that related complexes containing the tetrafluorobenzobarrelene diolefin are active catalysts for the hydrosilylation and the dehydrogenative silylation of phenylacetylene. So, there is now accumulating evidence proving that the systems $IrH_2(SiEt_3)(diolefin)L$ are active catalysts for the hydrosilylation and the dehydrogenative silylation of unsaturated organic substrates.

Synthesis and Characterization of $IrH_2(Ph_2SiOCOCH_3)(TFB)(PR_3)$. The complexes **4**–**6** also react

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(12) Tanke, R. S.; Crabtree, R. H. *J. Am. Chem. Soc.* **1990**, *112*, 7984.

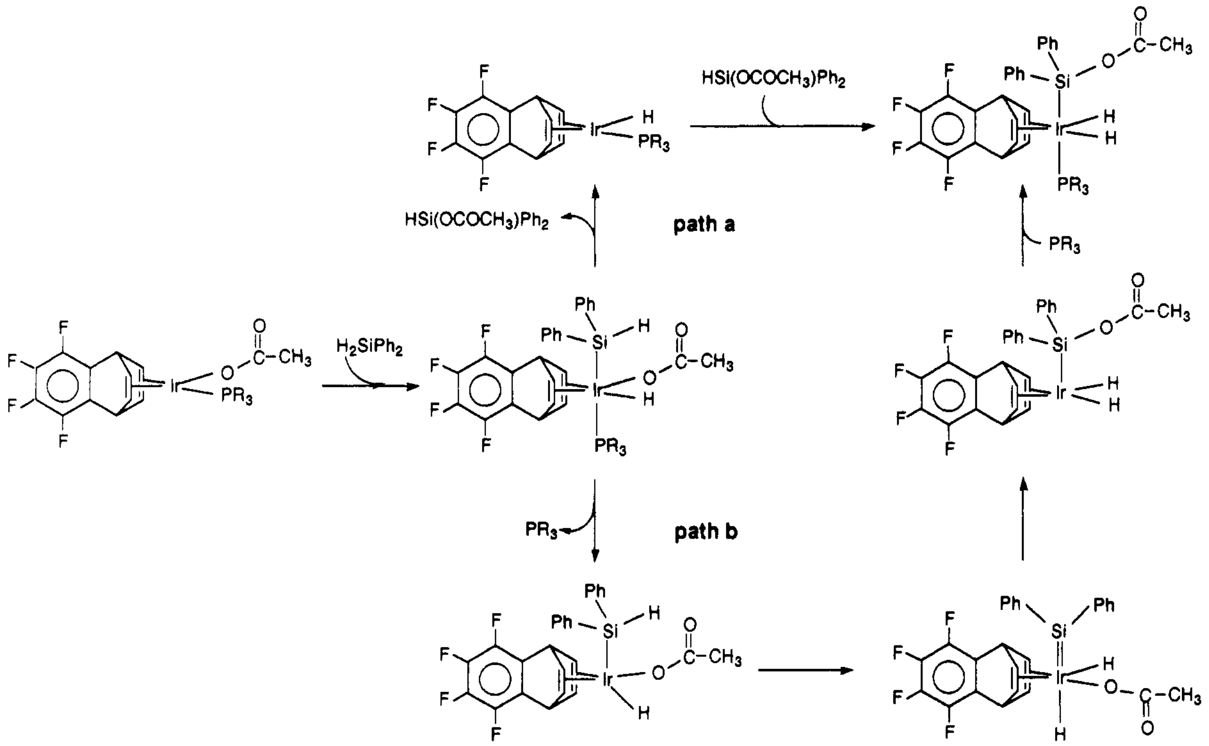
(13) Ojima, I.; Clos, N.; Donovan, R. J.; Ingallina, P. *Organometallics* **1990**, *9*, 3127.

(14) (a) Esteruelas, M. A.; Oro, L. A.; Valero, C. *Organometallics* **1991**, *10*, 462. (b) Esteruelas, M. A.; Herrero, J.; Oro, L. A. *Organometallics* **1993**, *12*, 2377.

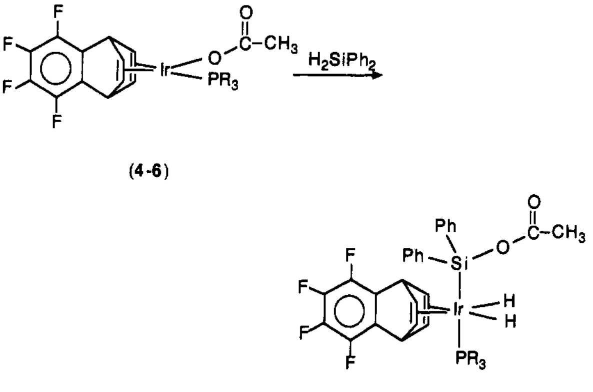
(15) (a) Esteruelas, M. A.; López, A. M.; Oro, L. A.; Pérez, A.; Schulz, M.; Werner, H. *Organometallics* **1993**, *12*, 1823. (b) Esteruelas, M. A.; Oliván, M.; Oro, L. A.; Tolosa, J. I., manuscript in preparation.

(16) Jun, C.-H.; Crabtree, R. H. *J. Organomet. Chem.* **1993**, *447*, 177.

Scheme III



with H_2SiPh_2. These reactions lead to $IrH_2(Ph_2SiOCOCH_3)(TFB)(PR_3)$ (R = Ph (**13**), Cy (**14**), iPr (**15**)), which contain an acetoxydiphenylsilyl ligand (eq 5).



(4-6)

(5)

(13-15)

The presence of this ligand in **13**–**15** is supported by the IR and ^1H NMR spectra. The IR spectra show absorptions at about 1715 and 1040 cm^{-1}, which are assigned to the ν(CO) and ν(Si-O) vibrations, respectively, while the ^1H NMR spectra contain a resonance at about 2.10 ppm, due to the CH_3 protons of the acetate group of the acetoxydiphenylsilyl ligand. Furthermore, **13**–**15** contain two hydrides. Their presence is strongly supported by the ^{31}P NMR spectra, which show singlets that under off-resonance conditions due to P–H coupling are split into triplets. The presence of two hydrides is also inferred from IR and ^1H NMR spectra. The IR spectra have a ν(IrH) absorption at about 2100 cm^{-1} and the ^1H NMR spectra a doublet between −14.3 and −14.90 ppm, with P–H coupling constants of about 20 Hz. Similarly to **7**–**12**, the signals of the tetrafluorobenzobarrelene diolefin in the ^1H NMR spectra are temperature-dependent. At room temperature the spectrum of **13** does not contain diolefinic resonances, while the spectra of **14** and **15** show two CH resonances, one aliphatic and the other one olefinic. At −55 °C, the three spectra contain two aliphatic and two olefinic resonances. All these spectroscopic data suggest that the complexes **13**–**15** possess an octahedral structure in solution (eq 5), but only at low temperature.

Scheme III illustrates two plausible reaction routes that allow the formation of **13**–**15** to be rationalized. For both paths, the first step could involve the oxidative addition of H_2SiPh_2 to **4**–**6**, giving hydride silyl intermediates of the type $IrH(SiHPh_2)(\eta^1\text{-}OCOCH_3)(TFB)(PR_3)$. Most of the silyl complexes of iridium(III) previously reported have been obtained by oxidative addition of $HSiR_3$ to iridium(I) compounds.[8] Path a involves reductive elimination of $HSi(OCOCH_3)Ph_2$ and subsequent oxidative addition of $HSi(OCOCH_3)Ph_2$ to $IrH(TFB)(PR_3)$. According to path b, the dissociation of the phosphine ligand from $IrH(SiHPh_2)(\eta^1\text{-}OCOCH_3)(TFB)(PR_3)$ could lead to the unsaturated species $IrH(SiHPh_2)(\eta^1\text{-}OCOCH_3)(TFB)$, which by an α-elimination reaction should give the silylene derivative $IrH_2(=SiPh_2)(\eta^1\text{-}OCOCH_3)(TFB)$.[17] Then, the silylene group could be attacked by the acetate ligand, to form the unsaturated dihydride acetoxydiphenylsilyl intermediate $IrH_2(Ph_2SiOCOCH_3)(TFB)$, which by coordination of the phosphine ligands should give **13**–**15**.

When the reactions of formation of **13**–**15** were carried out with an excess of H_2SiPh_2 (2 equiv) in toluene or acetone as solvents, the only products detected during the reactions were **13**–**15**. This, in our opinion, suggests that path a does not contribute very significantly to the overall reactions, because complexes of formulation $IrH_2(SiHPh_2)(TFB)(PR_3)$ are not visibly formed. Furthermore, it is interesting to note that the presence of $IrH_2(Ph_2SiOCOCH_3)(TFB)$ is essential in order to rationalize the fluxional process observed in solution for **13**–

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(17) Evidence for the existence of base-free silylene compounds of the type $L_nM{=}Si(Ph)_2$ has been previously reported. See: Straus, D. A.; Zhong, C.; Chimbita, G. E.; Grumbine, S. D.; Heyn, R. H.; Tilley, T. D.; Rheingold, A. L.; Geib, S. J. *J. Am. Chem. Soc.* **1990**, *112*, 2673.

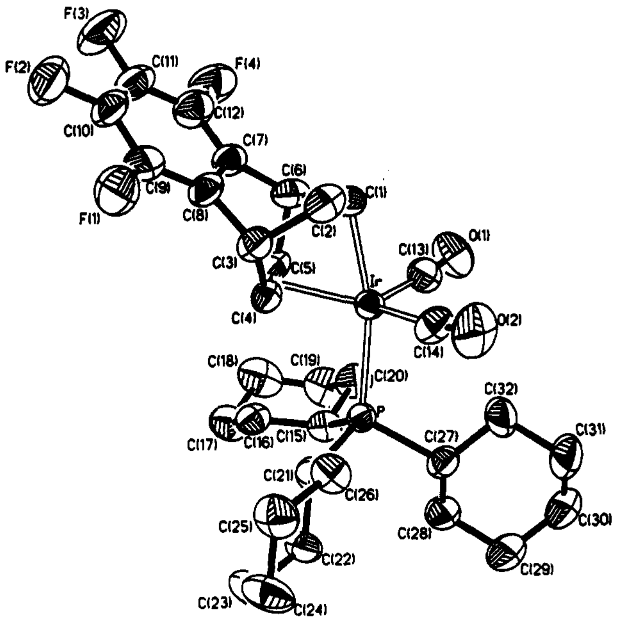
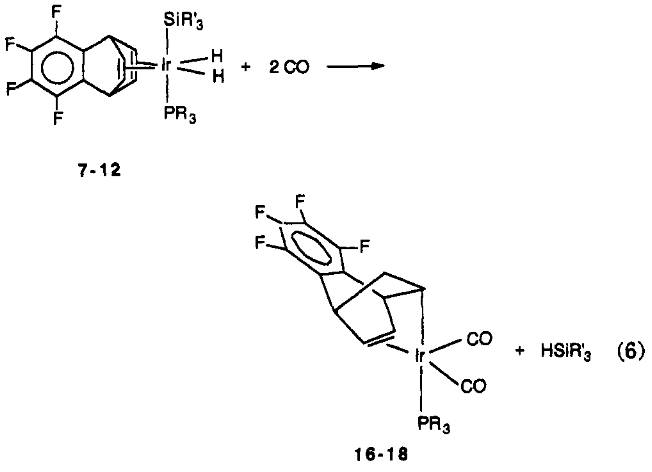


Figure 1. ORTEP diagram of $Ir(\eta^1:\eta^2\text{-}C_{12}F_4H_7)(CO)_2(PCy_3)$.

15, which most probably proceeds via the same mechanism as that described for 7–12.

Reactions of 7–12 with CO. Reactions of 7–12 with carbon monoxide (room temperature, 1 atm) cause reductive elimination of $HSiR'_3$ (R′ = Et, Ph) and the formation of $Ir(\eta^1:\eta^2\text{-}C_{12}F_4H_7)(CO)_2(PR_3)$ (R = Ph (16), Cy (17), ^{i}Pr (18)) (eq 6).



The complexes 16–18 were fully characterized by elemental analysis, IR, and ^1H, $^{31}P\{^1H\}$, and $^{13}C\{^1H\}$ NMR spectroscopy (Tables I and V). 17 was furthermore characterized by X-ray crystallography. An ORTEP drawing of the molecular structure of 17 is presented in Figure 1. Selected bond distances and angles are listed in Table IV. The coordination polyhedron around the iridium atom can be described as a distorted trigonal bipyramid with the C(1) and P atoms occupying the axial positions; the P–Ir–C(1) angle is 166.1(1)°. The equatorial plane is defined by the two carbonyl ligands and by the midpoint of the side-on-coordinated carbon–carbon double bond of the carbocyclic ligand.

The Ir–C(1) distance (2.162(5) Å) is in the expected range for an iridium to carbon single bond (sum of covalent radii 2.07 Å) and is quite similar to that found for the Ir–C σ-bond in the compounds $Ir(\eta^1:\eta^2\text{-}C_8H_{13})(PNP)$ (PNP = $Pr^nN(CH_2CH_2PPh_2)_2$; 2.109(5) Å),[18] $Ir(\eta^1:\eta^2\text{-}C_8H_{13})(CO)_2(PCy_3)$ (2.150(11) Å),[2a] $(\eta^4\text{-}C_8H_{12})Ir(\mu\text{-pz})(\mu\text{-PPh}_2)Ir(\eta^1:\eta^2\text{-}C_8H_{13})$ (2.159(13) Å),[19] $Ir(\eta 1:\eta^2\text{-}C_8H_{12}OCH_3)(NC{-}CH{=}CH{-}CN)(phen)$ (phen = 1,10-phenanthroline; 2.13(3) Å),[20] $Ir(\eta^1:\eta^2\text{-}C_8H_{12}\text{-}Ind)(PMe_3)_3$ (Ind = indenyl; 2.18 Å),[21] and $Ir(\eta^1:\eta^3\text{-}C_8H_{12})H(dppm)$ (dppm = bis(diphenylphosphino)methane; 2.115(6) Å).[22] The distance between the iridium atom and the midpoint of the C(4)–C(5) double bond is 2.028(5) Å, which compares well with the values found previously for equatorial iridium–olefin bonds.[23] Similarly, the olefinic C(4)–C(5) bond distance, 1.439(7) Å, is in the range found in transition-metal–olefin complexes, in agreement with the usual Chatt–Dewar metal–olefin bonding scheme. Furthermore, it should be mentioned that the carbon–carbon double bond lies practically in the equatorial plane as is usual in trigonal bipyramids, in contrast to the situation in square-based-pyramidal arrangements, where the double bonds are orthogonal to the coordination plane.[24] The Ir–P and Ir–CO distances are also clearly in the range expected and deserve no further comment.

Table IV. Selected Bond Distances (Å) and Bond Angles (deg) with Estimated Standard Deviations

	Bond Distances		
Ir–P	2.406(1)	C1–C2	1.493(7)
Ir–C1	2.162(5)	C1–C6	1.573(7)
Ir–C4	2.177(4)	C2–C3	1.543(7)
Ir–C5	2.128(4)	C3–C4	1.540(7)
Ir–C13	1.920(6)	C3–C8	1.500(7)
Ir–C14	1.934(6)	C4–C5	1.439(7)
O1–C13	1.117(6)	C5–C6	1.527(7)
O2–C14	1.122(6)	C6–C7	1.503(7)
	Bond Angles		
P–Ir–C1	166.1(1)	Ir–C1–C2	105.3(3)
P–Ir–C13	97.2(2)	Ir–C1–C6	94.7(3)
P–Ir–C14	93.8(2)	C1–C2–C6	111.8(4)
C1–Ir–C13	91.3(2)	C1–C2–C3	104.4(4)
C1–Ir–C14	94.8(2)	C2–C3–C4	106.0(4)
C4–Ir–C13	142.7(2)	C2–C3–C8	102.2(4)
C4–Ir–C14	109.7(2)	C4–C3–C8	107.5(4)
P–Ir–C4	96.9(1)	C3–C4–C5	115.8(4)
P–Ir–C5	102.4(1)	C4–C5–C6	108.8(4)
C5–Ir–C13	104.0(2)	C1–C6–C5	95.6(4)
C5–Ir–C14	145.7(2)	C1–C6–C7	111.4(4)
C13–Ir–C14	103.7(2)	C5–C6–C7	106.5(4)

Concluding Remarks

This study has shown that the complexes $Ir(OCOCH_3)(TFB)(PR_3)$ (R = Ph, Cy, ^{i}Pr) react with $HSiR'_3$ (R′ = Et, Ph) to give dihydride silyl compounds of the type $IrH_2(SiR'_3)(TFB)(PR_3)$, which catalyze the hydrosilylation and dehydrogenative silylation of phenylacetylene. The reactions of the complexes $Ir(OCOCH_3)(TFB)(PR_3)$ with H_2SiPh_2 lead to $IrH_2(Ph_2SiOCOCH_3)(TFB)(PR_3)$, which are iridium compounds containing an acetoxydiphenylsilyl ligand.

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(18) Bianchini, C.; Farnetti, E.; Graziani, M.; Nardin, G.; Vacca, A.; Zanobini, F. *J. Am. Chem. Soc.* **1990**, *112*, 9190.

(19) Bushnell, G. W.; Stobart, R. S.; Vefghi, R.; Zaworotko, M. J. *J. Chem. Soc., Chem. Commun.* **1984**, 282.

(20) Bresciani-Pahor, N.; Calligaris, M.; Nardin, G.; Delise, P. *J. Chem. Soc., Dalton Trans.* **1976**, 762.

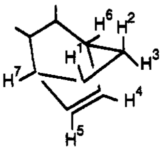
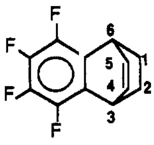
(21) Merola, J. S.; Kacmarcik, R. T. *Organometallics* **1989**, *8*, 778.

(22) Esteruelas, M. A.; Oliván, M.; Oro, L. A.; Schulz, M.; Sola, E.; Werner, H. *Organometallics* **1992**, *11*, 3659.

(23) Churchill, M. R.; Bezman, S. A. *Inorg. Chem.* **1972**, *11*, 2243; **1973**, *12*, 260, 531.

(24) Oro, L. A.; Carmona, D.; Esteruelas, M. A.; Foces-Foces, C.; Cano, F. H. *J. Organomet. Chem.* **1983**, *258*, 357.

Table V. ^{1}H and ^{13}C{^{1}H} NMR Spectral Data for 16–18[a]

	^{1}H NMR (δ)		^{13}C NMR (δ)		
	PR$_3$		CO	PR$_3$	
16	4.40–7.00 (15H)	4.40 (br, 1H, H^6) 4.06 (br, 1H, H^7) 2.74 (br, 1H, H^5) 2.28 (ddd, 1H, J_{H-H} = 12, J_{H-H} = 5.4, J_{H-H} = 5.4, H^3) 2.22 (br, 1H, H^4) 2.04 (br, 1H, H^2) 1.44 (ddd, 1H, J_{P-H} = 12, J_{H-H} = 12, J_{H-H} = 5.2, H^1)	176.24 (d, J_{P-C} = 6) 175.12 (d, J_{P-C} = 5)	132.00 (d, J_{P-C} = 12) 129.90 (d, J_{P-C} = 2.5) 127.00 (d, J_{P-C} = 10)	53.71 (s, C^4) 53.39 (d, J_{P-C} = 3, C^5) 43.73 (s, C^3) 30.27 (d, J_{P-C} = 2.5, C^6) 27.49 (s, C^2) –1.04 (d, J_{P-C} = 59, C^1)
17	1.84–1.21 (33H)	4.35 (br, 1H, H^6) 4.05 (br, 1H, H^7) 3.15 (br, 1H, H^5) 2.83 (br, 2H, H^4 and H^2) 2.15 (m, 1H, H^3)	177.30 (d, J_{P-C} = 5.5) 176.29 (d, J_{P-C} = 3.5)	33.92 (d, J_{P-C} = 20.6) 28.55 (d, J_{P-C} = 45) 25.76 (d, J_{P-C} = 21.1) 25.24 (d, J_{P-C} = 78.5)	52.29 (d, J_{P-C} = 2.5, C^5) 51.11 (s, C^4) 44.94 (s, C^3) 30.88 (s, C^6) 27.98 (s, C^2) –0.38 (d, J_{P-C} = 57, C^1)
18	1.46–1.28 (m, 3H) 0.75 (dd, 9H, J_{H-H} = 7.2, J_{P-H} = 14.1) 0.69 (dd, 9H, J_{H-H} = 6.9, J_{P-H} = 13.8)	4.40 (br, 1H, H^6) 4.10 (br, 1H, H^7) 2.90 (dd, 1H, J_{H-H} = 10, J_{H-H} = 5.5, H^5) 2.72 (dd, 1H, J_{H-H} = 10, J_{H-H} = 5.5, H^4) 2.22 (ddd, 1H, J_{H-H} = 12, J_{H-H} = 5, J_{H-H} = 5, H^3) 1.99 (dd, 1H, J_{H-H} = 5, J_{H-H} = 5, H^2) 1.40 (ddd, 1H, J_{P-H} = 12, J_{H-H} = 12, J_{H-H} = 5, H^1)	178.80 (d, J_{P-C} = 6.5) 177.80 (d, J_{P-C} = 6)	25.31 (d, *N* = 21.6, δ(P*C*H)) 19.91 (s, δ(PH*C*H$_3$)) 19.30 (s, δ(PH*C*H$_3$))	53.76 (d, J_{P-C} = 2.5, C^5) 52.77 (s, C^4) 46.56 (s, C^3) 32.48 (s, C^6) 25.89 (s, c^2 1.57 (d, J_{P-C} = 57, C^1)

[a] In C_6D_6, δ in ppm. *J* and *N* in Hz. The signal of H^1 is masked by PCy$_3$ resonance in **17** and partially masked by P^{i}Pr$_3$ resonance in **18**. Abbreviations used: m = multiplet, br = broad, d = doublet, dd = double doublet, ddd = double doublet of doublets.

In addition, we have also observed that the complexes $IrH_2(SiR'_3)(TFB)(PR_3)$ react with carbon monoxide to give $Ir(\eta^1{:}\eta^2\text{-}C_{12}F_4H_7)(CO)_2(PR_3)$ and $HSiR'_3$. The X-ray diffraction analysis of the structure of $Ir(\eta^1{:}\eta^2\text{-}C_{12}F_4H_7)(CO)_2(PCy_3)$ shows that the coordination polyhedron around the iridium atom can be described as a distorted trigonal bipyramid with the C–Ir carbon atom of the carbocyclic ligand and the P atom of the PCy$_3$ ligand occupying the axial positions.

Experimental Section

General Considerations. All reactions were carried out with the use of standard Schlenk procedures. Solvents were dried and purified by known procedures and distilled under argon prior to use. Triethylsilane (Fluka), triphenylsilane (Fluka), and diphenylsilane (Fluka) were used without further purification. Phenylacetylene (Merck) was purified by distillation. The starting material $[Ir(\mu\text{-OMe})(TFB)]_2$ (1) was prepared by a published method.[5b]

Physical Measurements. Elemental analyses were performed with a Perkin-Elmer 240 microanalyzer. NMR spectra were recorded on Varian 200 XL and Varian Unity 300 instruments. Chemical shifts are expressed in parts per million upfield from $Si(CH_3)_4$ (^{1}H and ^{13}C{^{1}H} NMR spectra) or 85% H_3PO_4 (^{31}P{^{1}H} and ^{31}P NMR spectra). Infrared spectra were run on a Perkin-Elmer 783 spectrophotometer, either as solids (Nujol mulls on polyethylene sheets) or solutions (NaCl cell windows). The catalytic reactions were followed by measuring the silane consumption as a function of time using C_6H_{12} as the internal standard with a 15% β,β'-oxobis(propionitrile) on Chromosorb W-HP 80/100-mesh column at 40 °C on a Perkin-Elmer 8500 gas chromatograph with a flame ionization detector. Silicon-containing products were analyzed by using a FFAP on Chromosorb GHP 80/100-mesh column at 175 °C. Mass spectral analyses were performed with a VG Auto Spec instrument equipped with an HP-1 capillary column. Ionization was by electron impact, operating at 70 eV.

Preparation of $[Ir(\mu\text{-OCOCH}_3)(TFB)]_2$ (2). A suspension of 1 (250 mg, 0.28 mmol) in 1/5 acetone/2-propanol (10 mL) was treated with an excess of acetic acid (1 mL) and stirred for 30 min. Distilled water was then added to complete the precipitation of a violet solid, which was filtered off, washed with water, and dried in vacuo; yield 214 mg (81%). Anal. Calcd for $C_{28}F_8H_{18}Ir_2O_4$: C, 35.22; H, 1.90. Found: C, 35.38; H, 1.98.

Preparation of $Ir(OCOCH_3)(TFB)(py)$ (3). Pyridine (33 μL, 0.42 mmol) was added to a suspension of 2 (100 mg, 0.105 mmol) in 10 mL of hexane, and the mixture was stirred at room temperature for 30 min. The resulting pale brown solid was decanted, washed with hexane, and dried in vacuo; yield 56 mg (48%). Anal. Calcd for $C_{19}F_4H_{14}IrNO_2$: C, 41.00; H, 2.53; N, 2.52. Found: C, 41.54; H, 2.52, N, 2.40.

Preparation of $Ir(OCOCH_3)(TFB)(PPh_3)$ (4). PPh_3 (54.9 mg, 0.21 mmol) was added to a suspension of 2 (100 mg, 0.105 mmol) in 10 mL of hexane and the mixture stirred at room temperature for 2 h. The resulting orange powder was decanted, washed with hexane, and dried in vacuo; yield 138.7 mg (89%). Anal. Calcd for $C_{32}F_4H_{24}IrO_2P$: C, 51.96; H, 3.27. Found: C, 52.44; H, 3.25.

Preparation of $Ir(OCOCH_3)(TFB)(PCy_3)$ (5). This compound was prepared analogously as described for 4, starting from 2 (100 mg, 0.105 mmol) and PCy_3 (58.7 mg, 0.21 mmol). It is a microcrystalline orange solid, yield 129 mg (73%). The crystals contained 1 mol of hexane/mol of 5. Anal. Calcd for $C_{38}F_4H_{56}IrO_2P$: C, 54.07; H, 6.69. Found: C, 54.13; H, 6.65.

Preparation of $Ir(OCOCH_3)(TFB)(P^iPr_3)$ (6). This compound was prepared analogously as described for 4, starting from 2 (100 mg, 0.105 mmol) and P^iPr_3 (34 μL, 0.21 mmol). The

Table VI. Crystallographic Data for 17

formula	$C_{32}F_4H_{37}IrO_2P$
fw	752.61
cryst size, mm	0.3 × 0.3 × 0.4
cryst syst	monoclinic
space group	$P2_1/n$ (No. 14)
cell dimens determn	23 rflns, 13° < θ < 14°
a, Å	10.158(3)
b, Å	15.075(2)
c, Å	21.539(7)
β, deg	92.50(2)
V, Å^3	3295(2)
Z	4
d_{calcd}, g cm^{-3}	1.518
diffractometer	Enraf-Nonius CAD4
radiation (graphite monochromated)	Mo Kα (0.709 30 Å)
temp, °C	20 ± 1
μ, cm^{-1}	41.3
scan method	$\omega/2\theta$
2θ(max), deg	46
total no. of rflns scanned	5086
no. of unique rflns	4480
no. of obsd rflns ($F_o > 3\sigma(F_o)$)	3065
no. of params refined	381
R	0.030
R_w	0.034
refln/param ratio	8.04
residual electron density, e Å^{-3}	+1.24/−0.41

resulting orange solution was cooled during 24 h at −20 °C, and then an orange solid was formed; yield 27 mg (20%). Anal. Calcd for $C_{23}F_4H_{39}IrO_2P$: C, 42.71; H, 6.08. Found: C, 43.09; H, 4.91.

Preparation of $IrH_2(SiEt_3)(TFB)(PPh_3)$ (7). An orange solution of 4 (100 mg, 0.135 mmol) in 10 mL of acetone was treated with $HSiEt_3$ (65 μL, 0.41 mmol), and the solution changed to dark yellow. After 1 h the solution was concentrated to ca. 0.5 mL in vacuo, and 5 mL of methanol was added. A white precipitate was formed, which was decanted, washed with methanol, and dried in vacuo; yield 62 mg (67%). Anal. Calcd for $C_{36}F_4H_{38}IrPSi$: C, 54.19; H, 4.80. Found: C, 53.68; H, 4.95.

Preparation of $IrH_2(SiPh_3)(TFB)(PPh_3)$ (8). This compound was prepared analogously as described for 7, starting from 4 (100 mg, 0.135 mmol) and $HSiPh_3$ (105.6 mg, 0.41 mmol). It is a white solid, yield 88 mg (69%). Anal. Calcd for $C_{48}F_4H_{38}IrPSi$: C, 61.20; H, 4.07. Found: C, 60.60; H, 4.33.

Preparation of $IrH_2(SiEt_3)(TFB)(PCy_3)$ (9). This compound was prepared analogously as described for 7, starting from 5 (100 mg, 0.12 mmol) and $HSiEt_3$ (47 μL, 0.29 mmol). It is a white solid, yield 61 mg (63%). Anal. Calcd for $C_{36}F_4H_{56}IrPSi$: C, 52.98; H, 6.92. Found: C, 53.14; H, 7.30.

Preparation of $IrH_2(SiPh_3)(TFB)(PCy_3)$ (10). This compound was prepared analogously as described for 7, starting from 5 (100 mg, 0.12 mmol) and $HSiPh_3$ (77.1 mg, 0.29 mmol). It is a white solid, yield 77 mg (68%). Anal. Calcd for $C_{48}F_4H_{56}IrPSi$: C, 60.04; H, 5.88. Found: C, 60.21; H, 6.49.

Preparation of $IrH_2(SiEt_3)(TFB)(P^iPr_3)$ (11). A violet suspension of 2 (100 mg, 0.105 mmol) in 10 mL of acetone was treated with P^iPr_3 (34 μL, 0.21 mmol) and the mixture stirred at room temperature for 30 min. Then, $HSiEt_3$ (100 μL, 0.63 mmol) was added to the orange solution, and the solution changed slowly to pale orange. After 1 h the solution was concentrated to ca. 0.5 mL in vacuo and 5 mL of methanol was added. A white precipitate was formed, which was decanted, washed with methanol, and dried in vacuo; yield 99 mg (68%). Anal. Calcd for $C_{27}F_4H_{44}IrPSi$: C, 46.60; H, 6.37. Found: C, 46.16; H, 6.86.

Preparation of $IrH_2(SiPh_3)(TFB)(P^iPr_3)$ (12). This compound was prepared analogously as described for 11, starting from 2 (100 mg, 0.105 mmol), P^iPr_3 (34 μL, 0.21 mmol), and $HSiPh_3$ (163.3 mg, 0.63 mmol). It is a white solid, yield 113 mg (64%). Anal. Calcd for $C_{39}F_4H_{44}IrPSi$: C, 55.76; H, 5.28. Found: C, 55.95; H, 5.56.

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

atom	x	y	z	B_{eq}, Å^2
Ir	−0.03902(3)	0.33859(2)	0.38124(1)	2.840(6)
P	−0.0997(2)	0.4358(1)	0.2961(1)	2.82(4)
F1	0.5263(5)	0.3667(4)	0.4844(3)	6.4(2)
F2	0.6796(5)	0.2229(5)	0.4849(3)	6.9(2)
F3	0.5828(6)	0.0654(5)	0.4416(3)	8.3(2)
F4	0.3308(6)	0.0525(4)	0.3999(3)	6.9(2)
O1	−0.2383(7)	0.1920(4)	0.3545(3)	5.9(2)
O2	−0.1650(7)	0.4486(5)	0.4817(3)	6.6(2)
C1	0.0625(8)	0.2542(6)	0.4489(4)	3.7(2)
C2	0.1415(9)	0.3157(6)	0.4901(4)	4.3(2)
C3	0.2424(8)	0.3570(6)	0.4472(4)	3.9(2)
C4	0.1719(7)	0.3645(6)	0.3826(4)	3.3(2)
C5	0.1399(8)	0.2818(6)	0.3522(4)	3.5(2)
C6	0.1500(9)	0.2073(6)	0.4001(4)	4.0(2)
C7	0.2920(8)	0.2032(6)	0.4227(4)	3.7(2)
C8	0.3436(8)	0.2849(6)	0.4437(4)	3.8(2)
C9	0.4736(9)	0.2897(7)	0.4629(4)	4.8(2)
C10	0.5527(9)	0.2168(7)	0.4636(4)	5.1(2)
C11	0.5044(9)	0.1374(7)	0.4419(5)	5.5(2)
C12	0.374(1)	0.1314(7)	0.4223(5)	4.9(2)
C13	−0.1686(9)	0.2484(6)	0.3631(4)	4.2(2)
C14	−0.1202(9)	0.4123(6)	0.4424(4)	4.1(2)
C15	−0.0804(8)	0.3888(6)	0.2174(4)	3.5(2)
C16	0.0640(8)	0.3861(6)	0.1990(4)	3.9(2)
C17	0.077(1)	0.3436(7)	0.1349(4)	5.2(2)
C18	0.014(1)	0.2513(7)	0.1325(4)	6.3(3)
C19	−0.129(1)	0.2565(7)	0.1471(5)	5.9(3)
C20	−0.1451(9)	0.2976(6)	0.2114(4)	4.2(2)
C21	0.0006(8)	0.5380(5)	0.2965(4)	3.3(2)
C22	−0.0325(9)	0.6045(6)	0.2438(4)	4.0(2)
C23	0.069(1)	0.6794(6)	0.2438(5)	5.2(2)
C24	0.075(1)	0.7276(6)	0.3056(5)	6.1(3)
C25	0.1053(9)	0.6624(7)	0.3595(5)	5.2(2)
C26	0.0052(9)	0.5862(6)	0.3590(4)	4.2(2)
C27	−0.2753(8)	0.4772(6)	0.2954(4)	3.6(2)
C28	−0.3344(9)	0.4996(7)	0.2312(4)	4.5(2)
C29	−0.4701(9)	0.5452(7)	0.2360(5)	5.8(3)
C30	−0.564(1)	0.4878(8)	0.2709(6)	6.6(3)
C31	−0.5045(9)	0.4629(9)	0.3340(5)	7.0(3)
C32	−0.3693(9)	0.4179(8)	0.3287(5)	5.7(3)

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

Preparation of $IrH_2(Ph_2SiOCOCH_3)(TFB)(PPh_3)$ (13). An orange solution of 4 (100 mg, 0.135 mmol) in 5 mL of toluene was treated with H_2SiPh_2 (26 μL, 0.135 mmol), and the solution changed to pale orange. After 1 h the solution was concentrated to ca. 0.5 mL in vacuo and 5 mL of methanol was added. A white precipitate was formed, which was decanted, washed with methanol, and dried in vacuo; yield 50 mg (40%). Anal. Calcd for $C_{44}F_4H_{36}IrO_2PSi$: C, 57.19; H, 3.93. Found: C, 57.47; H, 4.09.

Preparation of $IrH_2(Ph_2SiOCOCH_3)(TFB)(PCy_3)$ (14). This compound was prepared analogously as described for 13, starting from 5 (100 mg, 0.12 mmol) and H_2SiPh_2 (23 μL, 0.12 mmol). It is a white solid, yield 48 mg (43%). Anal. Calcd for $C_{44}F_4H_{54}IrO_2PSi$: C, 56.09; H, 5.78. Found: C, 55.86; H, 6.02.

Preparation of $IrH_2(Ph_2SiOCOCH_3)(TFB)(P^iPr_3)$ (15). A violet suspension of 2 (100 mg, 0.105 mmol) in 5 mL of toluene was treated with P^iPr_3 (34 μL, 0.21 mmol). The mixture was stirred at room temperature for 30 min and then was filtered. The orange filtrate was treated with H_2SiPh_2 (41 μL, 0.21 mmol), and the resulting solution was stirred for 1 h. The solution was concentrated under reduced pressure, and a yellow oil was formed. The complex was characterized by IR and ^1H and $^{31}P\{^1H\}$ NMR spectra.

Preparation of $Ir(\eta^1{:}\eta^2\text{-}C_{12}F_4H_7)(CO)_2(PPh_3)$ (16). A solution of 7 (100 mg, 0.125 mmol) in dichloromethane (50 mL) was stirred under CO for 24 h and the resulting solution concentrated under reduced pressure to 0.5 mL. Methanol was added, and the solution was cooled to −20 °C over 24 h, causing the precipitation of a white solid, which was decanted, washed with methanol, and dried in vacuo; yield 66 mg (72%). Anal. Calcd for $C_{32}F_4H_{22}IrO_2P$: C, 52.10; H, 3.01. Found: C, 51.68; H, 3.17.

Preparation of Ir(η^1:η^2-$C_{12}F_4H_7$)(CO)$_2$(PCy$_3$) (17). This compound was prepared analogously as described for **16**, starting from **9** (100 mg, 0.122 mmol). It is a white solid, yield 63 mg (68%). Anal. Calcd for $C_{32}F_4H_{40}IrO_2P$: C, 50.85; H, 5.33. Found: C, 50.57; H, 5.66.

Preparation of Ir(η^1:η^2-$C_{12}F_4H_7$)(CO)$_2$(P^{i}Pr$_3$) (18). This compound was prepared analogously as described for **16**, starting from **11** (100 mg, 0.14 mmol). It is a white solid, yield 48 mg (49%). Anal. Calcd for $C_{23}F_4H_{28}IrO_2P$: C, 43.46; H, 4.44. Found: C, 43.89; H, 4.62.

Catalytic Studies. The hydrosilylation reactions were performed under argon at 60 or 20 °C. The reactions were carried out in a two-necked flask fitted with a condenser and a magnetic stirring bar. The second neck was capped with a septum to be removed without opening the system.

For **7** and **9**, the procedure was as follows: The complexes were dissolved in a 1,2-dichloroethane solution (8 mL) containing HSiEt$_3$, PhC$_2$H, and C_6H_{12}. The flask was then immersed in a bath at 60 or 20 °C, and the reaction mixture was magnetically stirred. For **11** the procedure was as follows: To a solution of **2** (9.2 mg, 0.0096 mmol) in 2 mL of 1,2-dichloroethane was added P^{i}Pr$_3$ (3 μL, 0.0192 mmol) and the mixture stirred at room temperature for 10 min; then HSiEt$_3$ (6 μL, 0.0384 mmol) was added, and the solution was stirred at room temperature for 30 min. To this solution was added a 1,2-dichloroethane solution (6 mL) containing HSiEt$_3$, PhC$_2$H, and C_6H_{12}. The flask was then immersed in a bath at 60 or 20 °C and the reaction mixture was magnetically stirred. Silicon-containing products were isolated by column chromatography (silica gel, 70–230 mesh; hexane) and characterized by ^{1}H NMR and GC-MS ^{1}H NMR spectra of the Si-containing products in CDCl$_3$: *cis*-PhCH=CH(SiEt$_3$), 7.49 (d, PhC*H*=, J_{H-H} = 15.4 Hz), 7.38–7.29 (Ph), 5.8 (d, =C*H*(SiEt$_3$), J_{H-H} = 15.4 Hz), 0.86 (t, SiCH$_2$C*H*$_3$, J_{H-H} = 7.6 Hz), 0.58 (q, SiC*H*$_2$CH$_3$, J_{H-H} = 7.6 Hz); *trans*-PhCH=CH(SiEt$_3$), 7.38–7.29 (Ph), 6.93 (d, PhC*H*=, J_{H-H} = 19 Hz), 6.46 (d, =C*H*(SiEt$_3$), J_{H-H} = 19 Hz), 0.91 (t, SiCH$_2$C*H*$_3$, J_{H-H} = 7.8 Hz), 0.58 (q, SiC*H*$_2$CH$_3$, J_{H-H} = 7.8 Hz); Ph(SiEt$_3$)C=CH$_2$, 7.38–7.29 (Ph), 5.90 (d, one H of =CH$_2$, J_{H-H} = 3.2 Hz), 5.60 (d, one H of =CH$_2$, J_{H-H} = 3.2 Hz), 0.98 (t, SiCH$_2$C*H*$_3$, J_{H-H} = 7.6 Hz), 0.75 (q, SiC*H*$_2$CH$_3$, J_{H-H} = 7.6 Hz); PhC≡C(SiEt$_3$), 7.38–7.29 (Ph), 1.1 (t, SiCH$_2$C*H*$_3$, J_{H-H} = 7.7 Hz), 0.73 (q, SiC*H*$_2$CH$_3$, J_{H-H} = 7.7 Hz). Mass fragmentation patterns (*m*/*e*): PhC≡C(SiEt$_3$), 216 (M$^+$), 187 (–29, –Et), 159 (–28, –CH$_2$CH$_2$), 131 (–28, –CH$_2$CH$_2$), 105; *cis*-PhCH=CH(SiEt$_3$), 218 (M$^+$), 189 (–29, –Et), 161 (–28, –CH$_2$CH$_2$), 131 (–30, –CH$_3$ – CH$_3$), 105; *trans*-PhCH=CH(SiEt$_3$), 218 (M$^+$), 189 (–29, –Et), 161 (–28, –CH$_2$CH$_2$), 131 (–30, –CH$_3$ – CH$_3$), 105; Ph(SiEt$_3$)C=CH$_2$, 218 (M$^+$), 189 (–29, –Et), 161 (–28, –CH$_2$CH$_2$), 133 (–28, –CH$_2$CH$_2$), 107.

X-ray Data Collection. Crystals of **17** suitable for X-ray diffraction studies were obtained by the slow diffusion of methanol into a toluene solution of the compound. Crystal data collection parameters are summarized in Table VI. An empirical absorption correction was applied (ψ-scan method, minimum transmission 88.95%). The structure was solved by direct methods (SHELXS-86).[25] One molecule of toluene is present in the crystal. The toluene molecule lies on the center of symmetry, and it is therefore disordered. Atomic coordinates (see Table VII) and anisotropic thermal parameters of all non-hydrogen atoms were refined by full-matrix least-squares. The positions of the hydrogen atoms were calculated according to ideal geometry (C–H distance 0.95 Å) and refined using the riding method. All calculations were performed on a Micro-VAX computer using the program package SDP from Enraf-Nonius.[26]

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Supplementary Material Available: Tables of positional parameters for hydrogen atoms, general displacement parameter expressions, and additional bond lengths and bond angles and a view of the disordered toluene molecule for **17** (9 pages). Ordering information is given on any current masthead page.

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[25] G. M. Sheldrick, University of Göttingen, 1986.

[26] Frenz, B. A. The Enraf-Nonius CAD4 SDP-a Real Time System for Concurrent X-ray Data Collection and Structure Determination. In *Computing in Crystallography*; Delft University Press: Delft, Holland, 1978; pp 64–71.