Reactions of the *cis*-Dicarbonyl Compound $Ir(\eta^1\text{-}OC(O)CH_3)(CO)_2(PCy_3)$ with $HSnPh_3$, $HSiR_3$ (R = Ph, Et), and $H_{x+1}SiPh_{3-x}$ (x = 1, 2)

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The reactivity of the *cis*-dicarbonyl compound $Ir(\eta^1\text{-}OC(O)CH_3)(CO)_2(PCy_3)$ (**1**) toward $HSnPh_3$, $HSiPh_3$, $HSiEt_3$, H_2SiPh_2, and H_3SiPh is described. **1** reacts with $HSnPh_3$ to afford $Ir(SnPh_3)(CO)_3(PCy_3)$ (**2**). The molecular structure of **2** was determined by X-ray investigations. Crystals of **2** are monoclinic, space group $P2_1/n$, with unit cell dimensions a = 14.643(2) Å, b = 13.048(1) Å, c = 19.510(4) Å, β = 95.26(1)°, and Z = 4. The structure was refined to the following R and R_w values: 0.0192 and 0.0208 (6556 observed data). The coordination polyhedron around the iridium atom can be described as a trigonal bipyramid with the triphenylstannyl group and the tricyclohexylphosphine ligand occupying the axial positions, while the three carbonyl groups define the equatorial plane. **2** reacts with molecular hydrogen and $HSnPh_3$. The first reaction gives $IrH_2(SnPh_3)(CO)_2(PCy_3)$ (**3**) and the second one $IrH(SnPh_3)_2(CO)_2(PCy_3)$ (**4**). The reactions of **1** with $HSiR_3$ (R = Ph, Et) lead to mixtures of products, from which the complexes $Ir(SiR_3)(CO)_3(PCy_3)$ (R = Ph (**5**), Et (**9**)), $IrH_2(SiR_3)(CO)_2(PCy_3)$ (R = Ph (**6**), Et (**7**)), $[IrH(\mu\text{-}O_2CCH_3)(CO)(PCy_3)]_2$ (**8**), and $IrH(\eta^1\text{-}OC(O)CH_3)(SiR_3)(CO)_2(PCy_3)$ (R = Ph (**10**), Et (**11**)) can be isolated or spectroscopically detected. The reaction of **1** with 1 equiv of H_2SiPh_2 gives $IrH_2(Si(OC(O)CH_3)Ph_2)(CO)_2(PCy_3)$ (**12**) along with small amounts of **8** and $Ir(SiHPh_2)(CO)_3(PCy_3)$ (**15**). In the presence of 2 equiv of H_2SiPh_2 and H_3SiPh, **1** affords $IrH(SiHPh_2)_2(CO)_2(PCy_3)$ (**13**) and $IrH(SiH_2Ph)_2(CO)_2(PCy_3)$ (**14**), respectively. **13** in the presence of acetic acid evolves into **12** and $IrH_2(SiHPh_2)(CO)_2(PCy_3)$ (**16**). **13** and **14** react with alcohols such as methanol, ethanol, 2-propanol, and phenol to give $IrH_2(Si(OR)Ph_2)(CO)_2(PCy_3)$ (R = Me (**17**), Et (**18**), ^{i}Pr (**19**), Ph (**20**)) or $IrH_2(Si(OR)_2Ph)(CO)_2(PCy_3)$ (R = Me (**21**), Et (**22**), ^{i}Pr (**23**)). The key intermediates of these alcoholysis processes could be silylene species of iridium(III). The formation of such intermediates may be a consequence of the trend that these types of compounds have to dissociate the tricyclohexylphosphine ligand. In addition, the spectroscopic characterizations of the complexes $IrH_2(Si(OCH_3)Ph_2)(CO)_2(P^iPr_3)$ (**24**), $IrH(SiHPh_2)_2(CO)_2(P^iPr_3)$ (**25**), and $IrH_2(SiHPh_2)(CO)_2(P^iPr_3)$ (**26**) are also reported.

Introduction

Hydridosilyliridium(III) complexes have proved to be useful models for understanding stoichiometric reactions related to the catalytic hydrosilylation of unsaturated organic compounds and the alcoholysis of hydrosilanes.[1] Most of these compounds have been obtained by oxidative addition of $HSiR_3$ to iridium(I) complexes.[2] A few, less common examples involve the reaction of silanes with iridium(III) compounds, which proceed by prior reductive elimination to iridium(I).[3]

The oxidative addition of silanes to iridium(I) complexes is generally viewed as a concerted *cis* addition.[2b,c,4] In agreement with this, Johnson and Eisenberg have shown that the oxidative addition of $HSiR_3$ to the iridium(I) *cis* phosphine complexes IrX(CO)(dppe) (X = Br, CN; dppe = 1,2-bis(diphenylphosphino)ethane) is a diastereoselective process with specific substrate orientation.[5]

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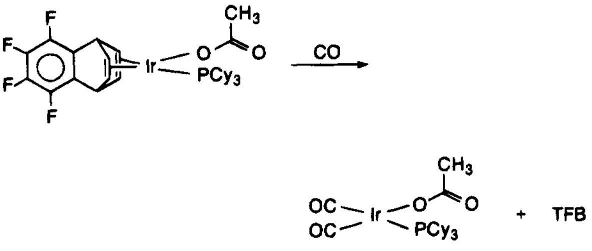
We have previously reported that the alkoxy compounds Ir(OR)(COD)(PR'$_3$) (COD = 1,5-cyclooctadiene; R = Me, PR'$_3$ = PPh$_3$; R = Et, PR'$_3$ = PCy$_3$) react with HSiEt$_3$ and HSiMe$_2$Ph to give ROSiR''$_3$ (SiR''$_3$ = SiEt$_3$, SiMe$_2$Ph) and the silyl dihydrido complexes IrH$_2$(SiR''$_3$)(COD)(PR'$_3$),[6] which have been found to promote silicon−carbon bond formation in hydrosilylation and dehydrogenative silylation of olefins.[7] Subsequently, we observed that the reactions of the acetato complexes Ir(η^1-OC(O)CH$_3$)(TFB)(PR$_3$) (TFB = tetrafluorobenzobarrelene; PR$_3$ = PPh$_3$, P^{i}Pr$_3$, PCy$_3$) with HSiR'$_3$ also lead to silyl dihydrido derivatives of the formula IrH$_2$(SiR'$_3$)(TFB)(PR$_3$) (R' = Et, Ph). The same reactions with H$_2$SiPh$_2$ afford IrH$_2$(Si(OC(O)CH$_3$)Ph$_2$)(TFB)(PR$_3$), which are the first iridium compounds containing an acetoxysilyl ligand.[8]

As a continuation of our work in this field, we have now studied the oxidative addition of HSnPh$_3$, HSiPh$_3$, HSiEt$_3$, H$_2$SiPh$_2$, and H$_3$SiPh to the *cis*-dicarbonyl compound Ir(η^1-OC(O)CH$_3$)(CO)$_2$(PCy$_3$). During these studies, we have isolated dihydrido(silyl)iridium(III) compounds containing two carbonyl ligands. Although dihydrido(silyl)iridium(III) compounds containing a carbonyl ligand are known,[2j,m,3,5] as far as we know, no dicarbonyl complexes of this type have been previously reported. In addition, we have isolated new dihydrido stannyl, bis(silyl), bis(stannyl), alkoxysilyl, and acetoxysilyl complexes of iridium. The X-ray crystal structure of the iridium(I) compound Ir(SnPh$_3$)(CO)$_3$(PCy$_3$) is also reported.

Results and Discussion

The complex Ir(η^1-OC(O)CH$_3$)(CO)$_2$(PCy$_3$) (**1**) was prepared, as a light green solid in 85% yield, by reaction of a hexane suspension of Ir(η^1-OC(O)CH$_3$)(TFB)(PCy$_3$) with carbon monoxide (eq 1).



(1)

1

The Ir and ^{1}H and ^{31}P{^{1}H} NMR spectra of **1** are in good agreement with the structure proposed in eq 1. In the IR spectrum in Nujol there are two strong ν(CO) bands at 2056 and 1980 cm^{-1} consistent with the *cis* geometry. The acetato group is formulated as a monodentate ligand on the basis of the value found for $\Delta\nu$ (ν_{asym}(OCO) − ν_{sym}(OCO) = 286 cm^{-1}), which coincides with those previously found for related rhodium compounds[9] and with those reported by Mitchell et al.,[10] Robinson et al.,[11] and Deacon et al.[12] for the same ligand in other types of compounds. The ^{31}P{^{1}H} NMR spectrum in benzene-d_6 contains a singlet at 31.8 ppm.

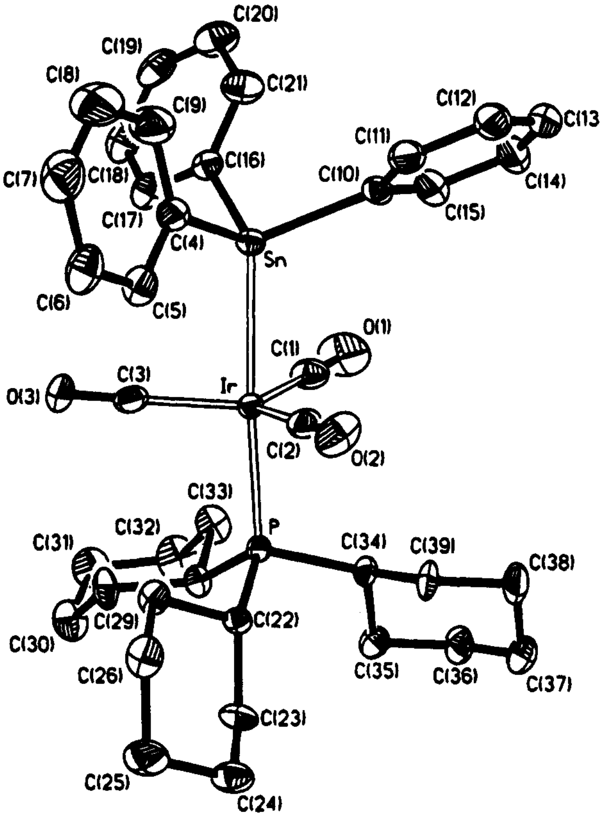
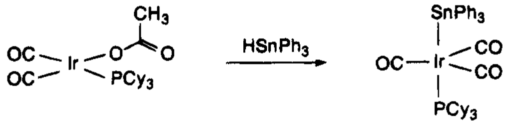


Figure 1. ORTEP diagram of complex **2**. Thermal ellipsoids are shown at the 50% level.

Reaction of Ir(η^1-OC(O)CH$_3$)(CO)$_2$(PCy$_3$) with HSnPh$_3$. The dicarbonyl complex **1** reacts with 1 equiv of HSnPh$_3$ in toluene to give a colorless solution, from which the tricarbonyl complex **2** was isolated as a white powder in 43% yield, by addition of hexane (eq 2).



(2)

1 2

The structure of **2** was determined by an X-ray analysis. Figure 1 shows an ORTEP drawing of the molecule. Selected bond distances and angles are listed in Table 1.

The coordination polyhedron around the iridium atom can be described as a trigonal bipyramid with the triphenylstannyl group and the tricyclohexylphosphine ligands occupying the axial positions; the Sn−Ir−P angle is 176.04(3)°. The equatorial plane is defined by the three carbonyl ligands with C−Ir−C angles in the range 117.4−122.2(1)°.

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Table 1. Selected Bond Lengths (Å) and Angles (deg) for the Complex $Ir(SnPh_3)(CO)_3(PCy_3)$ (2)

Ir—Sn	2.6610(3)	Ir—C(3)	1.910(3)
Ir—P	2.3745(8)	C(1)—O(1)	1.136(4)
Ir—C(1)	1.904(3)	C(2)—O(2)	1.143(4)
Ir—C(2)	1.901(3)	C(3)—O(3)	1.140(4)
Sn—Ir—P	176.04(3)	C(1)—Ir—C(2)	122.2(1)
Sn—Ir—C(1)	86.2(1)	C(1)—Ir—C(3)	118.9(2)
Sn—Ir—C(2)	84.6(1)	C(2)—Ir—C(3)	117.4(1)
Sn—Ir—C(3)	87.2(1)	Ir—C(1)—O(1)	179.2(3)
P—Ir—C(1)	94.0(1)	Ir—C(2)—O(2)	178.9(3)
P—Ir—C(2)	92.0(1)	Ir—C(3)—O(3)	177.9(3)
P—Ir—C(3)	96.2(1)		

The Ir—Sn distance (2.6610(3) Å) is slightly longer than the iridium–tin bond length found for the complex $Ir(SnCl_3)(COD)_2$ (COD = 1,5-cyclooctadiene; 2.642(2) Å)[13] and around 0.07 Å longer than that observed for the pentacoordinated compound $Ir(SnCl_3)(NBD)(PMe_2Ph)_2$ (NBD = 2,5-norbornadiene; 2.5867(6) Å).[14] Each of these distances is significantly shorter than the value of 2.75 Å suggested for an iridium–tin linkage of unit bond order; this has been taken as indicative of multiple-bond character in Ir—Sn linkages.[14]

The Ir—CO distances (1.901(3), 1.904(3), and 1.910(3) Å) compare well with those observed for the equatorial Ir—CO linkage in $Ir(\eta^1:\eta^2\text{-}C_{12}F_4H_7)(CO)_2(PCy_3)$ (1.920(6) and 1.934(6) Å)[8] and $Ir(\eta^1:\eta^2\text{-}C_8H_{13})(CO)_2(PCy_3)$ (1.918(10) and 1.900(10) Å).[6a] In accordance with the local symmetry of the $Ir(CO)_3$ unit, the IR spectrum of **2** in dichloromethane shows a ν(CO) band at 1945 cm^{-1}. The $^{31}P\{^1H\}$ NMR spectrum in benzene-d_6 contains a singlet at 21.9 ppm together with the satellites due to ^{117}Sn and ^{119}Sn. The values of the P—^{117}Sn and P—^{119}Sn coupling constants of 560 and 584 Hz, respectively, are in agreement with the mutually *trans* disposition of these groups.

We note that the synthesis of the complexes $Ir(SnR_3)(CO)_3(PPh_3)$ (R = Et, Ph) has been previously reported. These compounds were prepared by reaction of $Na[Ir(CO)_3(PPh_3)]$ with R_3SnCl. On the basis of their IR and NMR spectra,[15] a structure such as that shown in Figure 1 has been proposed for these complexes.

Complex **2** reacts with molecular hydrogen to give the dihydro derivative **3** (eq 3).

2 **3**

(3)

In agreement with the mutually *cis* disposition of the two carbonyl groups and the two hydrido ligands, the IR spectrum of **3** in Nujol has two ν(CO) absorptions in the terminal carbonyl region and a ν(Ir—H) band at 2100 cm^{-1}. In the ^1H NMR spectrum in benzene-d_6 the hydrido ligands appear as a doublet at −11.1 ppm with a P—H coupling constant of 15.9 Hz. The satellites due to the Sn isotopes are also observed near this resonance. The value of the Sn—H coupling constant, 41 Hz, strongly supports the *cis* disposition of the triphenylstannyl group and the two hydrido ligands.[16] The $^{31}P\{^1H\}$ NMR spectrum shows a singlet at 26.6 ppm, along with the satellites corresponding to the tin active isotopes. The values of the P—Sn coupling constants, 815 and 853 Hz, agree well with the mutually *trans* disposition of the $SnPh_3$ and PCy_3 groups.

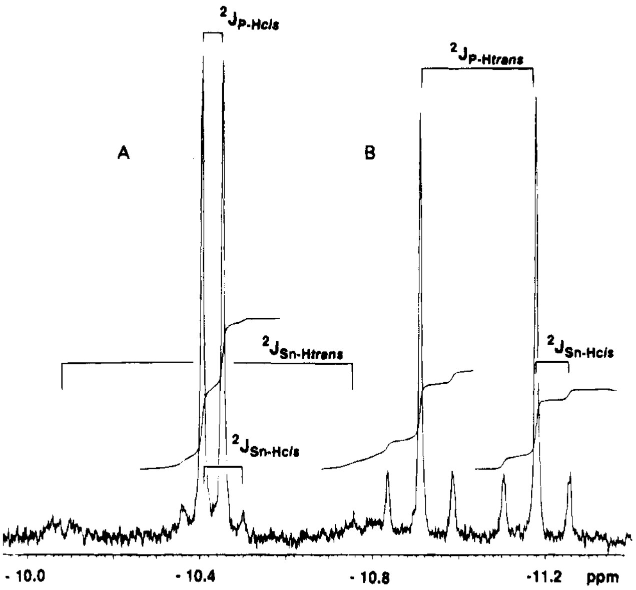
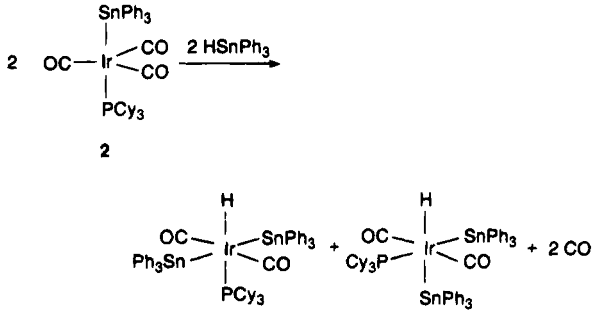


Figure 2. ^1H NMR spectrum (benzene-d_6) of the isomeric mixture of $IrH(SnPh_3)_2(CO)_2(PCy_3)$ (**4a,b**) in the hydride region.

Complex **2** also reacts with $HSnPh_3$ to afford a mixture of isomers **4a,b** in a 1:1 molar ratio (eq 4).



2

4a **4b**

(4)

Although attempts to separate the mixture of isomers by fractional crystallization or column chromatography were unsuccessful, the complexes **4a,b** were characterized by IR and ^1H and $^{31}P\{^1H\}$ NMR spectroscopy. The IR spectrum shows a single ν(CO) band for both isomers at 1990 cm^{-1}, which is in agreement with the mutually *trans* disposition of the carbonyl ligands in both complexes. The ^1H NMR spectrum contains in the hydrido region two doublets, A and B (Figure 2). The doublet A was assigned to **4b**. With regard to the values of the P—H and Sn—H coupling constants, there is no doubt that the hydride is *cis* to the tricyclohexylphosphine ligand and to a triphenylstannyl group and *trans* to the other triphenylstannyl group. The doublet B was assigned to **4a**. With regard to the P—H and Sn—H coupling constants, there is also no doubt that the hydride is *trans* to the tricyclohexylphosphine ligand

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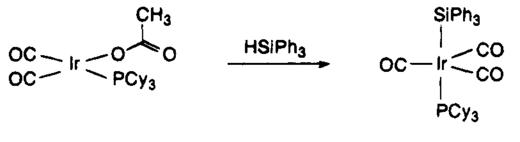
and *cis* to both triphenylstannyl groups. The $^{31}P\{^1H\}$ NMR spectrum shows a singlet for each isomer at 8.2 (**4a**) and 19.4 (**4b**) ppm, along with the corresponding tin satellites. The values of the P—Sn coupling constants, 34 Hz for **4a** and 44 and 613 Hz for **4b**, also agree well with the stereochemistries proposed for these compounds.

Reactions of Ir(η^1-OC(O)CH$_3$)(CO)$_2$(PCy$_3$) with HSiR$_3$ (R = Ph, Et). Treatment of **1** with 1 equiv of $HSiPh_3$ in toluene leads to a colorless solution, from which the tricarbonyl complex **5** was isolated as a white air-stable powder in 59% yield, by addition of hexane (eq 5).

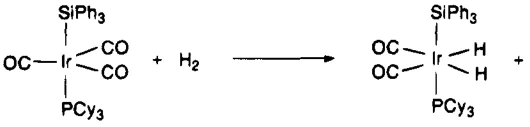


(5)

1 **5**

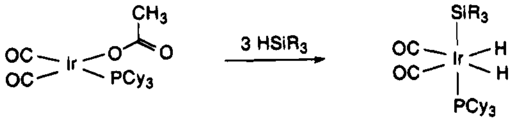
The IR and $^{31}P\{^1H\}$ NMR spectra of **5** strongly support the structure shown in eq 5. The IR spectrum in dichloromethane shows only one ν(CO) band at 1955 cm^{-1}, while the $^{31}P\{^1H\}$ NMR spectrum in benzene-d_6 contains a singlet at 18.4 ppm along with the satellites due to the ^{29}Si isotope. The value of the P—Si coupling constant, 66 Hz, strongly supports the mutually *trans* disposition of the Ph_3Si and PCy_3 ligands.[17] In addition, it should be mentioned that only one (silyl)iridium(I) compound has been previously synthesized. This complex, of formula $\overline{Ir(PPh_2CH_2CH_2SiMe_2})(CO)_2(PPh_3)$, was obtained in low yield (<30%) from $IrH_2(PPh_2CH_2CH_2SiMe_2)(CO)_2(PPh_3)$ by prolonged photolysis.[18]

Complex **5** reacts with molecular hydrogen to give the dihydrido compound **6** (eq 6), which can be directly obtained by reaction of **1** with 3 equiv of $HSiPh_3$. Similarly, the reaction of **1** with 3 equiv of $HSiEt_3$ gives **7** (eq 7).



(6)

5 **6**



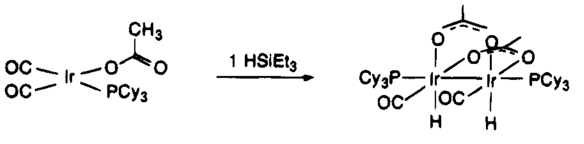
(7)

1

SiR$_3$ = SiPh$_3$ (**6**), SiEt$_3$ (**7**)

The spectroscopic data of **6** and **7** are consistent with the stereochemistry shown in eq 7. The spectra in Nujol contain two ν(CO) absorptions in the terminal carbonyl region and a ν(Ir—H) band at about 2100 cm^{-1}. The hydrido ligands appear in the ^1H NMR spectra as doublets at −10.3 (**6**) and −10.8 (**7**) ppm, with P—H coupling constants of 16.7 and 17.8 Hz, respectively. The $^{31}P\{^1H\}$ NMR spectra show singlets at 23.2 (**6**) and 20.9 (**7**) along with the satellites due to the ^{29}Si isotope. The values of the P—^{29}Si coupling constants are 80 (**6**) and 66 (**7**) Hz, respectively.

The addition of $HSiEt_3$ to a toluene solution of **1** in 1:1 molar ratio leads to a yellow solution, from which the unexpected complex **8** (eq 8) was isolated in 25% yield.



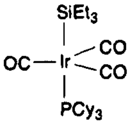
(8)

1 **8**

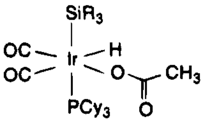
In accordance with the structure shown in eq 8, the IR spectrum of **8** in dichloromethane contains two ν(CO) absorptions at 1980 and 1955 cm^{-1}. The ν(Ir—H) absorptions are only observed in the IR spectrum in Nujol at 2210 and 2190 cm^{-1}. The ^1H NMR spectrum in chloroform-d_1 shows in the hydride region a virtual triplet (AA'XX' splitting pattern) at −20.5 ppm. The $^{31}P\{^1H\}$ NMR spectrum exhibits a singlet at 28.3 ppm.

We note that the synthesis of related compounds of formulas $[IrH(\mu\text{-pz})(CO)(PPh_3)]_2$[19] (pz = pyrazole) and $[IrH(\mu\text{-SBu}^t)(CO)(PR_3)]_2$[20] has been previously reported. These complexes were prepared by reaction of the corresponding dimers of iridium(I) with molecular hydrogen.

Reactions of **1** with $HSiPh_3$ and $HSiEt_3$ were also carried out in an NMR tube. The ^1H and $^{31}P\{^1H\}$ NMR spectra of the solutions formed by addition of ca. 1.5 equiv of $HSiPh_3$ or $HSiEt_3$ to **1** in benzene-d_6 show resonances that were assigned to the complexes **1** and **5**−**8**, by comparison of these spectra with pure samples. In addition, signals indicating the presence of the derivatives **9**−**11** were also observed.



9



R= Ph (**10**), Et (**11**)

The presence of complex **9** was inferred from the $^{31}P\{^1H\}$ NMR spectra of the reaction of **1** with $HSiEt_3$. These spectra show a singlet at 17.3 ppm. Similar chemical shifts are observed for the tricyclohexylphosphine ligands of the related compounds **2** and **5**. The *trans* disposition of the silyl and phosphine groups is supported by the value of the P—Si coupling constant (70 Hz). The most characteristic resonances of **10** are, in the ^1H NMR spectra, a doublet at −6.8 ppm with a P—H coupling constant of 15.4 Hz and, in the $^{31}P\{^1H\}$ NMR spectra, a singlet at 23.5 ppm along with the satellites due to the ^{29}Si isotope (J_{P-Si} = 100 Hz). Characteristic resonances of **11** are a doublet at −7.2 ppm (J_{P-H} = 16.2 Hz) in the ^1H NMR spectra and a singlet at 22.4 ppm along with the satellites due to the ^{29}Si isotope (J_{P-Si} = 82 Hz) in the $^{31}P\{^1H\}$ NMR spectra.

Reactions of Ir(η^1-OC(O)CH$_3$)(CO)$_2$(PCy$_3$) with H$_2$SiPh$_2$ and H$_3$SiPh. Treatment of a toluene solution

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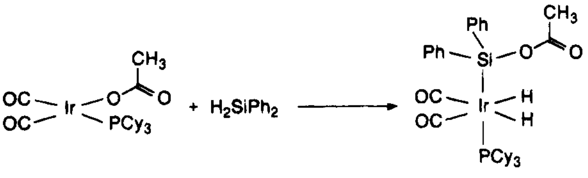
[17] (a) Chang, L. S.; Johnson, M. P.; Fink, M. J. *Organometallics* **1991**, *10*, 1219. (b) Schubert, U.; Müller, C. *J. Organomet. Chem.* **1991**, *418*, C6.

[18] Auburn, M. J.; Grundy, S. L.; Stobart, S. R.; Zaworotko, M. J. *J. Am. Chem. Soc.* **1985**, *107*, 266.

[19] Beveridge, K. A.; Bushnell, G. W.; Dixon, K. R.; Eadie, D. T.; Stobart, S. R. *J. Am. Chem. Soc.* **1982**, *104*, 920.

[20] Thorez, A.; Maisonnat, A.; Poilblanc, R. *J. Chem. Soc., Chem. Commun.* **1977**, 518.

of **1** with H_2SiPh_2 in a 1:1 molar ratio leads, after 30 min, to a light yellow solution from which a white solid was isolated by addition of hexane. In this case, the solid was characterized as the complex $IrH_2(Si(OC(O)CH_3)Ph_2)(CO)_2(PCy_3)$ (**12**, eq 9) by elemental analysis, IR, and ^1H and $^{31}P\{^1H\}$ NMR spectroscopy.

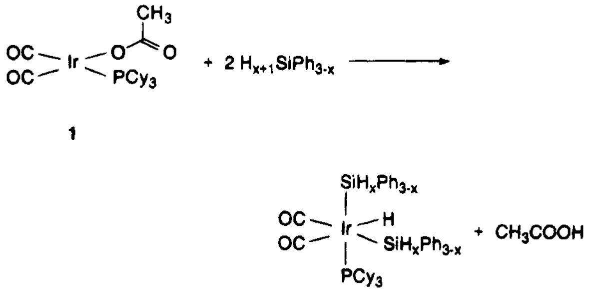


(9)

1 **12**

The presence of the acetoxydiphenylsilyl ligand in **12** is supported by the IR and ^1H NMR spectra. The IR spectrum in Nujol shows absorptions at 1708 and 1015 cm^{-1}, which are assigned to the $\nu(CO)$ and $\nu(SiO)$ vibrations, respectively, while the ^1H NMR spectrum contains a resonance at 2.0 ppm, due to the CH_3 protons. Furthermore, **12** contains two carbonyl and two hydrido ligands. The mutually *cis* disposition of the carbonyl ligands is strongly supported by the IR spectrum in dichloromethane, which shows two $\nu(CO)$ absorptions at 2030 and 1982 cm^{-1}. The presence of two hydrido ligands is inferred from the $^{31}P\{^1H\}$ NMR spectrum, which shows a singlet that under off-resonance conditions due to the P—H coupling is split into a triplet. The hydrido ligands appear in the ^1H NMR spectrum as a doublet at −10.4 ppm with a P—H coupling constant of 16.5 Hz.

In the presence of 2 equiv of H_2SiPh_2, complex **1** reacts with the silane to give the bis(silyl) derivative **13**. Similarly, **1** reacts with H_3SiPh to give **14** (eq 10).



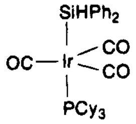
1

(10)

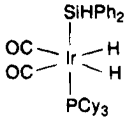
x = 1 (**13**), 2 (**14**)

Assignment of the coordination geometry of **13** and **14** is straightforward on the basis of the NMR and IR spectroscopic data. In agreement with the *cis* disposition of the carbonyl ligands, the IR spectra of **13** and **14** in dichloromethane show two $\nu(CO)$ absorptions in the terminal carbonyl region. The iridium–hydride resonances appear in the ^1H NMR spectra as doublets at −9.8 (**13**) and −10.6 (**14**) ppm, with P—H coupling constants of about 15 Hz. For **13**, the Si—H resonances appear as doublets at 5.8 (Si *trans* to PCy_3) and 5.7 (Si *cis* to PCy_3) ppm, with P—H coupling constants of 16.0 and 8.1 Hz, respectively. For **14**, the Si—H resonances are observed as a very complicated signal between 5.2 and 4.9 ppm. The $^{31}P\{^1H\}$ NMR spectra show singlets at 7.1 (**13**) and 9.4 (**14**) ppm, along with the satellites due to the ^{29}Si isotope of the silyl groups located *trans* to the tricyclohexylphosphine ligands. The P—Si coupling constants are 73 Hz for **13** and 91 Hz for **14**. Couplings between the phosphine ligands and the silyl groups in *cis* positions are not observed.

In order to rationalize the formation of **12**–**14**, the reactions of **1** with 1 equiv and 2 equiv of H_2SiPh_2 were also followed by ^1H and $^{31}P\{^1H\}$ NMR spectroscopy. After 5 min, the ^1H and $^{31}P\{^1H\}$ NMR spectra of the solution formed by addition of ca. 1 equiv of H_2SiPh_2 to **1** in benzene-d_6 contain the resonances of **1** (19%), **8** (7%), and **12** (55%). Furthermore, the $^{31}P\{^1H\}$ NMR spectrum shows a singlet with satellites due to the ^{29}Si isotope (J_{P-Si} = 87 Hz) at 16.9 ppm (19% of intensity ratio). This signal was assigned to the five-coordinate complex **15**, by comparison of the chemical shifts of the singlet with those of the five-coordinate compounds **5** and **9**. After 40 min, the composition of the mixture was 5% of **1**, 9% of **8**, 69% of **12**, and 17% of **15**.



15



16

After 5 min, the ^1H and $^{31}P\{^1H\}$ NMR spectra of the solution formed by addition of ca. 2 equiv of H_2SiPh_2 to **1** in benzene-d_6 contain the resonances of **12** (12%) and **13** (84%). Furthermore, the ^1H NMR spectrum shows the presence of acetic acid (δ 11.1 ppm) and a double doublet at −10.6 ppm (J_{P-H} = 16.7, J_{H-H} = 1.9 Hz). In the $^{31}P\{^1H\}$ NMR spectrum this double doublet fits a singlet with satellites due to the ^{29}Si isotope (J_{P-Si} = 82 Hz) at 23.3 ppm (4% of intensity ratio). With regard to the position, multiplicity, and values of the coupling constants of these signals there is no doubt that they are characteristic of the dihydrido silyl complex **16**. Interestingly, after 45 h, the composition of the mixture is 63% of **12**, 6% of **13**, and 31% of **16**. In addition, the ^1H NMR spectrum shows singlets at 5.1 and 4.5 ppm which were assigned to H_2SiPh_2 and $H_2Si_2Ph_4$, respectively, by comparison of these chemical shifts with those previously reported for pure samples.[21]

The initial formation of **13** (84%) by reaction of **1** with 2 equiv of H_2SiPh_2 indicates that, under the reaction conditions, this complex is kinetically favored. However, the compounds **12** and **16** are thermodynamically more stable. Furthermore, **12** is the kinetic and thermodynamically favored compound, when the reaction between **1** and H_2SiPh_2 is carried out in a 1:1 molar ratio.

The formation of **13** and **16** could be rationalized according to the reaction sequence shown in Scheme 1. In accordance with this, we have observed that the addition of H_2SiPh_2 to a benzene-d_6 solution of **13** in a 1:1 molar ratio leads to a mixture of **13**, **16**, H_2SiPh_2, and $H_2Si_2Ph_4$ in a 2:1:2:1 molar ratio after 26 h.

The formation of **12** merits further consideration. Scheme 2 illustrates two plausible reaction routes that could lead to **12**. According to Scheme 2, for both paths, the first step involves the oxidative addition of H_2SiPh_2 to **1**, giving the hydrido silyl intermediate $IrH(\eta^1\text{-}OC(O)CH_3)(SiHPh_2)(CO)_2(PCy_3)$. Path **a** in Scheme 2 involves reductive elimination and subsequent oxidative

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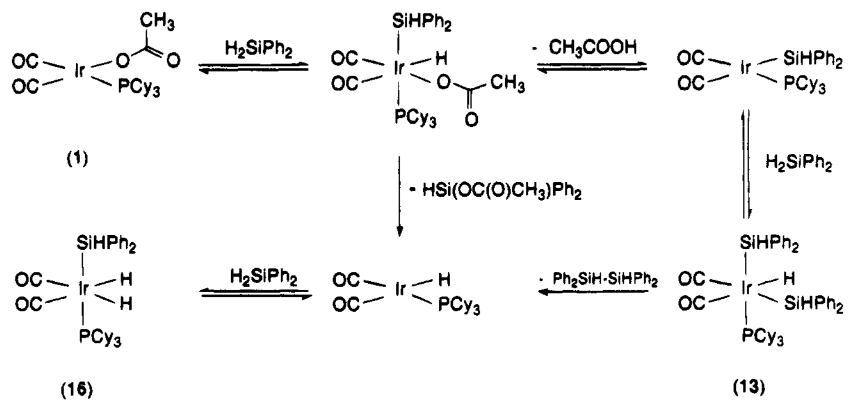
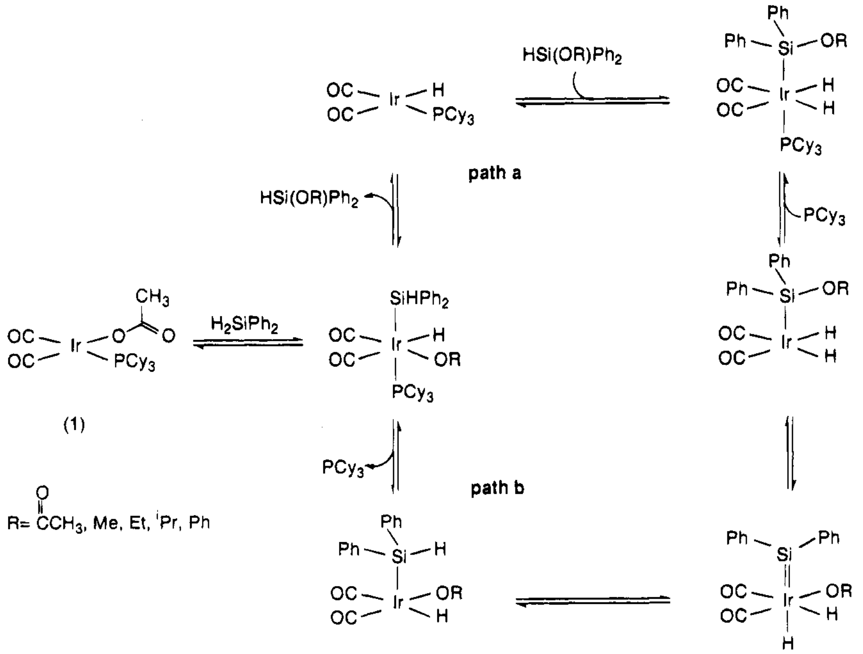
(21) Pham, E. K.; West, R. *J. Am. Chem. Soc.* **1989**, *111*, 7667.

Scheme 1

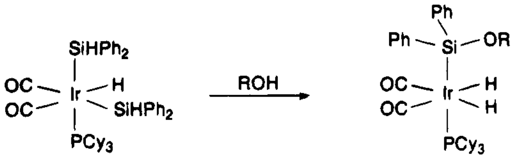


Scheme 2



addition of HSi(OC(O)CH$_3$)Ph$_2$ to IrH(CO)$_2$(PCy$_3$). According to path **b**, the dissociation of the phosphine ligand from IrH(η^1-OC(O)CH$_3$)(SiHPh$_2$)(CO)$_2$(PCy$_3$) could lead to an unsaturated IrH(η^1-OC(O)CH$_3$)(SiHPh$_2$)(CO)$_2$ intermediate, which by an α-elimination reaction should give the silylene derivative IrH$_2$(η^1-OC(O)CH$_3$)(=SiPh$_2$)(CO)$_2$. Then, the silylene group could be attacked by the acetate ligand, to form the unsaturated dihydrido acetoxydiphenylsilyl intermediate IrH$_2$(Si(OC(O)CH$_3$)Ph$_2$)(CO)$_2$, which by coordination of PCy$_3$ should give **12**. The participation of silylene intermediates in the formation of iridium–acetoxysilyl derivatives and related compounds has been previously suggested by Bergman[22] and by us.[8] Evidence for the dissociation of the phosphine ligand was obtained from the study of the reactions of **13** with alcohols.

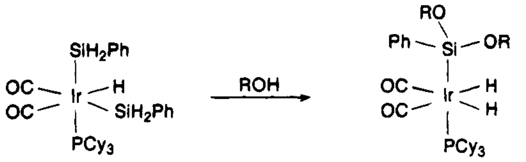
Reactions of IrH(SiH$_x$Ph$_{3-x}$)$_2$(CO)$_2$(PCy$_3$) with Alcohols. The bis(silyl) complexes **13** and **14** have been found to be useful starting materials for the preparation of acetoxysilyl, alkoxysilyl, and dialkoxysilyl compounds. Thus, the reaction of **13** with acetic acid leads to the acetoxysilyl derivative **12**, while **13** in the presence of alcohols such as methanol, ethanol, 2-propanol, and phenol affords the alkoxysilyl complexes **17**–**20** (eq 11).



(11)

13

R= Me (17), Et (18), iPr (19), Ph (20)



(12)

14

R= Me (21), Et (22), iPr (23)

Similarly, the complex **14** reacts with methanol, ethanol, and 2-propanol to give **21**–**23** (eq 12), which contain a dialkoxysilyl group. During the writing of this paper, Caulton and co-workers have reported that the reaction of Cp*Ru(P^{i}Pr$_2$Ph)(OCH$_2$CF$_3$) with H$_2$SiPh$_2$ gives two

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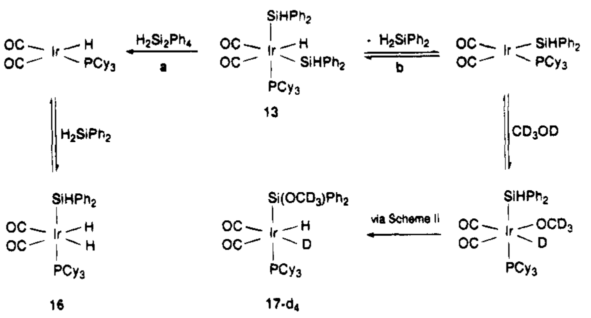
(22) Burger, P.; Bergman, R. G. *J. Am. Chem. Soc.* **1993**, *115*, 10462.

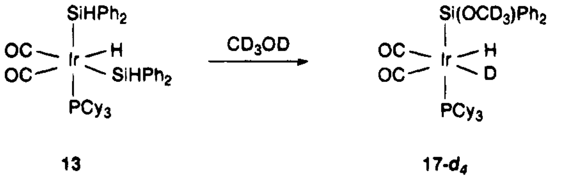
Scheme 3



products, one of which is the alkoxysilyl derivative $Cp^*Ru(P^iPr_2Ph)(H)_2(Si(OCH_2CF_3)Ph_2)$.[23]

The complexes **17**–**23** were isolated as white microcrystalline solids in 50–75% yields and characterized by elemental analysis, IR, and ^1H and $^{31}P\{^1H\}$ NMR spectroscopy. The IR spectra of these compounds show absorptions between 1015 and 1100 cm^{-1} assigned to the ν(Si–O) vibrations. Furthermore, the IR spectra contain two ν(CO) bands in the terminal carbonyl region along with one or two absorptions at about 2100 cm^{-1}, attributable to ν(Ir–H), in agreement with a *cis* arrangement of these ligands. The ^1H NMR spectra show the hydrido resonances as a doublet between −9 and −11 ppm with a P–H coupling constant of about 17 Hz, suggesting that both hydrido ligands are chemically equivalent and are *cis* disposed to the phosphine ligand. This ligand appears in the $^{31}P\{^1H\}$ NMR spectra as a singlet between 20.1 and 21.9 ppm.

In order to obtain information about the mechanism of the reactions shown in eq 11, we have studied the reaction of **13** with methanol-d_4. The stirring of a solution of **13** and methanol-d_4 in toluene leads selectively to **17**-d_4 in quantitative yield after 18 h (eq 13).



(13)

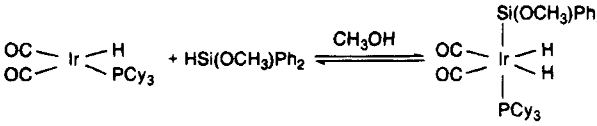
13 **17-d_4**

With regard to the ^1H, ^2H, and $^{31}P\{^1H\}$ NMR of the solid obtained according to eq 13, there is no doubt that it is the complex **17-d_4**. The ^1H NMR spectrum in benzene-d_6 shows a doublet at −10.4 (J_{P-H} = 16.7 Hz) with an intensity corresponding to one proton. The ^2H NMR spectrum, however, contains a singlet at 3.6 ppm and a broad singlet at −10.4 ppm. The $^{31}P\{^1H\}$ NMR spectrum shows a singlet at 20.9 ppm that under off-resonance conditions due to P–H coupling with only one hydride is split into a doublet.

Scheme 3 shows a sequence of reactions that allow the formation of **17-d_4** to be rationalized. According to Scheme 1, **13** could eliminate H_2SiPh_2 to give $Ir(SiHPh_2)(CO)_2(PCy_3)$ and could remove $H_2Si_2Ph_4$ to form $IrH(CO)_2(PCy_3)$. The H_2SiPh_2 formed could react with $IrH(CO)_2(PCy_3)$ to afford **16**. The reaction of $Ir(SiHPh_2)(CO)_2(PCy_3)$ with methanol-d_4 could lead to $IrD(SiHPh_2)(OCD_3)(CO)_2(PCy_3)$, which should evolve to **17-d_4** according to Scheme 2. The oxidative addition of alcohols to iridium(I) fragments has been recently proved by Merola and co-workers.[24]

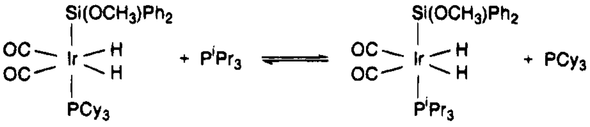
In agreement with Scheme 3, we have observed that the addition of methanol to a benzene-d_6 solution of **13** in a 1:2 molar ratio leads to a mixture of **16** and **17** in 1:2 molar ratio after 24 h.

In excess methanol (or methanol-d_4), **17** (or **17-d_4**) is the only product formed, indicating that under these conditions **13** reacts mainly by path **b** of Scheme 3. Furthermore, the exclusive formation of **17-d_4** from the reaction shown in eq 13 suggests that during the formation of **17** the equilibrium shown in eq 14 does not contribute very significantly to the overall process.[25]



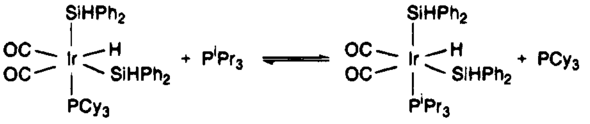
(14)

If the equilibrium shown in eq 14 does not contribute significantly to the overall process, it is clear that path **a** of Scheme 2 is not a useful route to explain the transformation of $IrH(OCH_3)(SiHPh_2)(CO)_2(PCy_3)$ to **17**. Path **b** involves silylene intermediates, which require the dissociation of the phosphine ligand. The dissociation of tricyclohexylphosphine seems to be a general property of these compounds. In fact, the addition of triisopropylphosphine to a benzene-d_6 solution of **17** in a 1:1 molar ratio leads to a mixture of **17**, **24**, PCy_3, and P^iPr_3 in a 4:1:1:4 molar ratio after 24 h (eq 15). Similarly, the addition of triisopropylphosphine to a benzene-d_6 solution of **13** in 1:1 molar ratio gives a mixture of **13**, **25**, PCy_3, and P^iPr_3 in a 1:2:2:1 molar ratio after 24 h (eq 16).



(15)

17 **24**



(16)

13 **25**

The complex **24** was characterized by a singlet at 31.1 ppm in the $^{31}P\{^1H\}$ NMR spectrum of the mixture and by a doublet at −10.6 ppm (J_{P-H} = 17.1 Hz) in the ^1H NMR spectrum, while **25** was characterized by a singlet at 15.6 ppm in the $^{31}P\{^1H\}$ NMR spectrum and a doublet at −10.1 ppm (J_{P-H} = 14.8 Hz) in the ^1H NMR spectrum.

The PCy_3–P^iPr_3 exchange can also be observed when the reaction between **13** and methanol is carried out in the presence of triisopropylphosphine. Figure 3 shows the ^1H and $^{31}P\{^1H\}$ NMR spectra of the reaction mixture after 24 h. These spectra, which are illustrative of the spectra analyzed during this work, show the presence

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[23] Johnson, T. J.; Coan, P. S.; Caulton, K. G. *Inorg. Chem.* **1993**, *32*, 4594.

[24] Ladipo, F. T.; Kooti, M.; Merola, J. S. *Inorg. Chem.* **1993**, *32*, 1681.

[25] If the equilibrium shown in eq 14 takes place, the complexes $IrD_2(Si(OCD_3)Ph_2)(CO)_2(PCy_3)$ and $IrH_2(Si(OCD_3)Ph_2)(CO)_2(PCy_3)$ should also be formed.

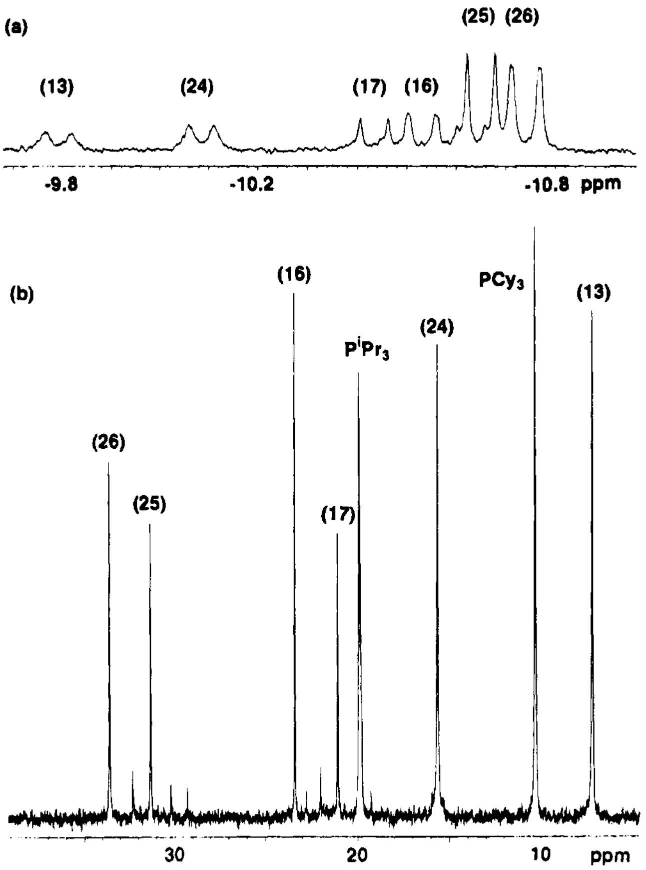
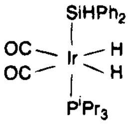


Figure 3. (a) ^{1}H NMR spectrum (benzene-d_6) of the mixture resulting from the reaction of IrH(SiHPh$_2$)$_2$(CO)$_2$(PCy$_3$) (**13**) with methanol in the presence of P^{i}Pr$_3$, in the hydride region. (b) ^{31}P{^{1}H} NMR spectrum of the same reaction mixture.

of **13**, **16**, **17**, and **24**–**26**. The last complex is characterized by a singlet at 33.6 ppm in the ^{31}P{^{1}H} NMR spectrum and by a double doublet at −10.7 ppm (J_{P-H} = 16.7 Hz, J_{H-H} = 1.4 Hz) in the ^{1}H NMR spectrum.



26

Concluding Remarks

This study has shown that the *cis*-dicarbonyl complex Ir(η^1-OC(O)CH$_3$)(CO)$_2$(PCy$_3$) undergoes reactions with HSnPh$_3$ and HSiR$_3$ (HSiR$_3$ = HSiPh$_3$, HSiEt$_3$, H$_2$SiPh$_2$, H$_3$SiPh) to give dihydrido stannyl, bis(stannyl), dihydrido silyl, and bis(silyl) derivatives, depending upon the nature of the reagent used. The complexes IrH(SiHPh$_2$)$_2$(CO)$_2$(PCy$_3$) and IrH(SiH$_2$Ph)$_2$(CO)$_2$(PCy$_3$), which are obtained by reaction of Ir(η^1-OC(O)CH$_3$)(CO)$_2$(PCy$_3$) with H$_2$SiPh$_2$ and H$_3$SiPh, react with alcohols to afford IrH$_2$(Si(OR)Ph$_2$)(CO)$_2$(PCy$_3$) and IrH$_2$(Si(OR)$_2$Ph)(CO)$_2$(PCy$_3$), respectively. The key intermediates of these processes may be silylene species of iridium(III). The formation of these intermediates could be a consequence of the trend that these compounds have to release the tricyclohexylphosphine ligand.

Experimental Section

General Data. All reactions were carried out with the use of standard Schlenk procedures. Solvents were dried and purified by known procedures and distilled prior to use. Elemental analyses were performed with a Perkin-Elmer 240 microanalyzer. ^{1}H NMR spectra were recorded at 299.949 MHz on a Varian UNITY 300 spectrometer at 20 °C. Chemical shifts are measured relative to the residual ^{1}H resonance in the deuterated solvent: C$_6$D$_6$ (δ 7.15 ppm); CDCl$_3$ (δ 7.24 ppm). ^{2}H and ^{13}C{^{1}H} NMR spectra were recorded on a Bruker 300 AXR spectrometer at 46.07 and 75.47 MHz, respectively. ^{31}P{^{1}H} NMR spectra were recorded on Varian UNITY 300 and XL 200 spectrometers at 121.421 and 80.984 MHz, respectively. Chemical shifts are relative to external 85% H$_3$PO$_4$, with downfield values reported as positive. Infrared spectra were run on a Perkin-Elmer 783 spectrophotometer as either solids (Nujol mulls on polyethylene sheets) or solutions (NaCl cell windows). Mass spectral analysis was performed with a VG Auto Spec. Ionization was by electron impact, operating at 70 eV. The reagents triethylsilane, triphenylsilane, diphenylsilane, and phenylsilane (Fluka) and triphenyltin hydride (Aldrich) were used as received. The starting material Ir(η^1-OC(O)CH$_3$)(TFB)(PCy$_3$) was prepared by a published method.[8]

Synthesis of Ir(η^1-OC(O)CH$_3$)(CO)$_2$(PCy$_3$) (1). A suspension of Ir(η^1-OC(O)CH$_3$)(TFB)PCy$_3$ (100 mg, 0.13 mmol) in hexane (10 mL) was stirred under CO for 20 min, and the resulting pale green solid was decanted, washed with hexane, and dried in vacuo; yield 66 mg (85%). Anal. Calcd for C$_{22}$H$_{36}$IrO$_4$P: C, 44.96; H, 6.17. Found: C, 44.93; H, 6.61. IR (Nujol, cm^{-1}): ν(C≡O) 2056 (s), 1980 (vs); ν_{asym}(OCO) 1642 (s); ν_{sym}(OCO) 1356 (s). IR (CH$_2$Cl$_2$, cm^{-1}): ν(C≡O) 2065 (s), 1980 (s). ^{1}H NMR (C$_6$D$_6$): δ 2.2−1.0 (m, 33H, Cy), 2.1 (s, 3H, OCOCH$_3$). ^{13}C{^{1}H} NMR (C$_6$D$_6$): δ 181.29 (d, J_{P-C} = 113.7 Hz, *C*O *trans* to PCy$_3$), 174.20 (d, J_{P-C} = 3.4 Hz, −O*C*OCH$_3$), 173.04 (d, J_{P-C} = 11.9 Hz, *C*O *cis* to PCy$_3$), 33.43 (d, J_{P-C} = 26.7 Hz, P*Cy*$_3$), 30.02 (s, P*Cy*$_3$), 27.72 (d, J_{P-C} = 11.0 Hz, P*Cy*$_3$), 26.43 (s, P*Cy*$_3$), 21.74 (s, −OCO*C*H$_3$). ^{31}P{^{1}H} NMR (C$_6$D$_6$, 121.421 MHz): δ 31.8 (s).

Synthesis of Ir(SnPh$_3$)(CO)$_3$(PCy$_3$) (2). A solution of **1** (100 mg, 0.17 mmol) in toluene (6 mL) was treated with HSnPh$_3$ (59.7 mg, 0.17 mmol). The solution was stirred for 90 min at room temperature and the resulting yellow solution concentrated under reduced pressure to ca. 0.5 mL. Addition of hexane caused the precipitation of a white solid, which was decanted, washed with hexane, and dried in vacuo; yield 66.3 mg (43%). Anal. Calcd for C$_{39}$H$_{48}$IrO$_3$PSn: C, 51.66; H, 5.34. Found: C, 51.69; H, 5.24. IR (Nujol, cm^{-1}): ν(C≡O) 1950 (vs); ν(Sn−Ph) 260 (s). IR (CH$_2$Cl$_2$, cm^{-1}): ν(C≡O) 1945 (s). ^{1}H NMR (C$_6$D$_6$): δ 8.1−7.1 (m, 15H, Ph), 1.9−0.9 (m, 33H, Cy). ^{31}P{^{1}H} NMR (C$_6$D$_6$, 121.421 MHz): δ 21.9 (s with ^{117}Sn and ^{119}Sn satellites, J_{P-Sn} = 560 and 584 Hz, respectively).

Synthesis of IrH$_2$(SnPh$_3$)(CO)$_2$(PCy$_3$) (3). A solution of **2** (100 mg, 0.11 mmol) in toluene (10 mL) was stirred under H$_2$ for 72 h. The resulting solution was filtered through Kieselguhr. The yellow filtrate was concentrated to ca. 0.5 mL, and hexane was added to give a white solid, which was decanted, washed with hexane, and dried in vacuo; yield 65 mg (67%). Anal. Calcd for C$_{38}$H$_{50}$IrO$_2$PSn: C, 51.82; H, 5.72. Found: C, 51.70; H, 6.00. IR (Nujol, cm^{-1}): ν(Ir−H) 2100 (s); ν(C≡O) 2020 (s), 1970 (vs); ν(Sn−Ph) 265 (s). IR (CH$_2$Cl$_2$, cm^{-1}): ν(Ir−H) 2090 (m); ν(C≡O) 2015 (s), 1975 (s). ^{1}H NMR (C$_6$D$_6$): δ 8.2−7.2 (m, 15H, Ph), 1.9−1.1 (m, 33H, Cy), −11.1 (d with Sn satellites, $^2J_{Sn-H}$ = 41 Hz, $^2J_{P-H}$ = 15.9 Hz, 2H, Ir−H). ^{31}P{^{1}H} NMR (C$_6$D$_6$, 121.421 MHz): δ 26.6 (s with ^{117}Sn and ^{119}Sn satellites, $^2J_{P-Sn}$ = 815 and 853 Hz, respectively).

Synthesis of the Isomeric Mixture of IrH(SnPh$_3$)$_2$(CO)$_2$(PCy$_3$) (4a,b). A solution of **2** (100 mg, 0.11 mmol) in toluene (10 mL) was treated with HSnPh$_3$ (38.7 mg, 0.11 mmol) and then stirred for 20 h at room temperature. The yellow solution was concentrated to ca. 0.5 mL, and methanol was added to give a white solid, which was decanted, washed with methanol, and dried in vacuo; yield 93.5 mg (65%). Anal. Calcd for $C_{56}H_{64}IrO_2PSn_2$: C, 54.69; H, 5.24. Found: C, 55.22; H, 5.62. IR (Nujol, cm^{-1}): ν(C≡O) 1995 (s); ν(Sn−Ph) 270 (s). IR (CH_2Cl_2, cm^{-1}): ν(C≡O) 1990 (s). Attempts to separate the two isomers, formed in the ratio **4a**:**4b** = 1:1, by fractional crystallization or chromatographic techniques were unsuccessful. Data for **4a** are as follows. ^{1}H NMR (C_6D_6): δ 8.0−7.0 (m, 15H, Ph), 1.8−0.9 (m, 33H, Cy), −11.0 (d with Sn satellites, $^2J_{Sn-H}$ = 23 Hz, $^2J_{P-H}$ = 81.0 Hz, 1H, Ir−H). ^{31}P{^{1}H} NMR (C_6D_6, 121.421 MHz): δ 8.2 (s with Sn satellites, $^2J_{P-Sn}$ = 34 Hz). Data for **4b** are as follows. ^{1}H NMR (C_6D_6): δ 8.0−7.0 (m, 15H, Ph), 1.8−0.9 (m, 33H, Cy), −10.4 (d with Sn satellites, $^2J_{Sn-H}$ = 27.6 Hz, $^2J_{Sn-H}$ = 208 Hz, $^2J_{P-H}$ = 14.0 Hz, 1H, Ir−H). ^{31}P{^{1}H} NMR (C_6D_6, 121.421 MHz): δ 19.4 (s with Sn satellites, $^2J_{P-Sn}$ = 44 Hz, $^2J_{P-Sn}$ = 613 Hz).

Synthesis of Ir(SiPh$_3$)(CO)$_3$(PCy$_3$) (5). This compound was prepared analogously as described for **2**, with **1** (100 mg, 0.17 mmol) and $HSiPh_3$ (44.3 mg, 0.17 mmol) as starting materials. It is a white solid; yield 82 mg (59%). Anal. Calcd for $C_{39}H_{48}IrO_3PSi$: C, 57.40; H, 5.93. Found: C, 57.65; H, 5.87. IR (Nujol, cm^{-1}): ν(C≡O) 1949 (vs). IR (CH_2Cl_2, cm^{-1}): ν(C≡O) 1955 (s). ^{1}H NMR (C_6D_6): δ 8.1−7.2 (m, 15H, Ph), 2.0−1.1 (m, 33H, Cy). ^{31}P{^{1}H} NMR (C_6D_6, 121.421 MHz): δ 18.4 (s with ^{29}Si satellites, J_{P-Si} = 66 Hz).

Synthesis of IrH$_2$(SiPh$_3$)(CO)$_2$(PCy$_3$) (6). This complex can be prepared by using two different procedures.

(a) A solution of **5** (100 mg, 0.12 mmol) in toluene (5 mL) was stirred under H_2 for 72 h at room temperature and filtrated through Kieselguhr. The yellow filtrate was concentrated under reduced pressure to ca. 0.5 mL. Addition of hexane caused the precipitation of a white solid, which was decanted, washed with hexane, and dried in vacuo; yield 76.5 mg (79%).

(b) A solution of **1** (100 mg, 0.17 mmol) in toluene (5 mL) was treated with $HSiPh_3$ (133 mg, 0.51 mmol). After 2 h the light yellow solution was concentrated under reduced pressure to ca. 0.5 mL, and methanol was added to give a white solid, which was decanted, washed with methanol, and dried in vacuo; yield 84 mg (65%). Anal. Calcd for $C_{38}H_{50}IrO_2PSi$: C, 57.77; H, 6.38. Found: C, 57.85; H, 6.83. IR (Nujol, cm^{-1}): ν(Ir−H) 2120 (s); ν(C≡O) 2025 (s), 1980 (vs). IR (CH_2Cl_2, cm^{-1}): ν(Ir−H) 2115 (m); ν(C≡O) 2030 (s), 1985 (s). ^{1}H NMR (C_6D_6): δ 7.9−7.1 (m, 15H, Ph), 1.8−0.9 (m, 33H, Cy), −10.3 (d, $^2J_{P-H}$ = 16.7 Hz, 2H, Ir−H). ^{31}P{^{1}H} NMR (C_6D_6, 121.421 MHz): δ 23.2 (s with ^{29}Si satellites, J_{P-Si} = 80 Hz).

Synthesis of IrH$_2$(SiEt$_3$)(CO)$_2$(PCy$_3$) (7). This compound was prepared analogously as described for **6** (method b), with **1** (100 mg, 0.17 mmol) and $HSiEt_3$ (81 μL, 0.51 mmol) as starting materials. It is a white solid, yield 74 mg (68%). Anal. Calcd for $C_{26}H_{50}IrO_2PSi$: C, 48.34; H, 7.80. Found: C, 48.36; H, 8.14. IR (Nujol, cm^{-1}): ν(Ir−H) 2100 (s); ν(C≡O) 2010 (s), 1965 (vs). IR (CH_2Cl_2, cm^{-1}): ν(Ir−H) 2080 (m); ν(C≡O) 2015 (m), 1960 (s). ^{1}H NMR (C_6D_6): δ 1.8−1.2 (m, 48H, Cy, Et), −10.8 (d, J_{P-H} = 17.8 Hz, 2H, Ir−H). ^{31}P{^{1}H} NMR (C_6D_6, 121.421 MHz): δ 20.9 (s with ^{29}Si satellites, $^2J_{P-Si}$ = 66 Hz).

Synthesis of [IrH(μ-O$_2$CCH$_3$)(CO)(PCy$_3$)]$_2$ (8). This compound was prepared analogously as described for **2**, starting from **1** (100 mg, 0.17 mmol) and $HSiEt_3$ (27.1 μL, 0.17 mmol). It is a white solid; yield 47.7 mg (25%). Anal. Calcd for $C_{42}H_{74}Ir_2O_6P_2$: C, 44.98; H, 6.65. Found: C, 45.58; H, 7.44. IR (Nujol, cm^{-1}): ν(Ir−H) 2210 (m), 2190 (m); ν(C≡O) 1970−1940 (vs); ν_{asym}(OCO) 1580 (s), ν_{sym}(OCO) 1430 (s). IR (CH_2Cl_2, cm^{-1}): ν(C≡O) 1980 (s), 1955 (s). ^{1}H NMR ($CDCl_3$): δ 2.2−1.2 (m, 72H, Cy, −CH_3), −20.5 (vt, N = 7.1 Hz, 2H, Ir−H). ^{31}P{^{1}H} NMR ($CDCl_3$, 80.984 MHz): δ 28.3 (s).

Reaction of 1 with HSiPh$_3$. In a 5-mm NMR tube a solution of **1** (20 mg, 0.034 mmol) in benzene-d_6 (0.6 mL) was treated with $HSiPh_3$ (13.3 mg, 0.05 mmol). The reaction was monitored by ^{1}H and ^{31}P{^{1}H} NMR spectroscopy. After 20 min the ^{1}H and ^{31}P{^{1}H} NMR spectra show signals corresponding to **1** (8%), **5** (30%), **6** (7%), **8** (4%), and **10** (51%). ^{1}H and ^{31}P{^{1}H} NMR spectra after 2 h show **5** (67%), **6** (21%), and **8** (12%). In addition, in the ^{1}H NMR spectra were observed signals assigned to CH_3CHO (δ 9.2 (q, J_{H-H} = 3 Hz, −C*H*O)) and $Ph_3SiOSiPh_3$ (δ 7.8−7.2 (m, Ph)). Spectroscopic data for IrH(η^1-OC(O)CH$_3$)(SiPh$_3$)(CO)$_2$(PCy$_3$) (**10**) are as follows: ^{1}H NMR (C_6D_6): δ 8.1−7.1 (m, 15H, Ph), 1.9−0.85 (m, 33H, Cy), 1.66 (s, 3H, $OCOCH_3$), −6.8 (d, 1H, $^2J_{P-H}$ = 15.4 Hz, Ir−H). ^{31}P{^{1}H} NMR (C_6D_6, 121.421 MHz): δ 23.5 (s with ^{29}Si satellites, $^2J_{P-Si}$ = 100 Hz).

Reaction of 1 with HSiEt$_3$. In a 5-mm NMR tube a solution of **1** (20 mg, 0.034 mmol) in benzene-d_6 (0.6 mL) was treated with $HSiEt_3$ (8 μL, 0.05 mmol). The reaction was monitored by ^{1}H and ^{31}P{^{1}H} NMR spectroscopy. After 5 min the ^{1}H and ^{31}P{^{1}H} NMR spectra show signals corresponding to **1** (6%), **7** (5%), **8** (12%), **9** (26%), and **11** (51%). ^{1}H and ^{31}P{^{1}H} NMR spectra after 40 min show **1** (2%), **7** (11%), **8** (22%), **9** (43%), and **11** (22%). ^{1}H and ^{31}P{^{1}H} NMR spectra after 44 h show **7** (34%), **8** (23%), and **9** (43%). Spectroscopic data for Ir(SiEt$_3$)(CO)$_3$(PCy$_3$) (**9**) are as follows. ^{1}H NMR (C_6D_6): δ 1.9−0.8 (m, 48H, Cy, Et). ^{31}P{^{1}H} NMR (C_6D_6, 121.421 MHz): δ 17.3 (s with ^{29}Si satellites, $^2J_{P-Si}$ = 70 Hz). Spectroscopic data for IrH(η^1-OC(O)CH$_3$)(SiEt$_3$)(CO)(PCy$_3$) (**11**) are as follows. ^{1}H NMR (C_6D_6): δ 1.9−0.8 (m, 51H, Cy, Et, −CH_3), −7.2 (d, 1H, $^2J_{P-H}$ = 16.2 Hz, Ir−H). ^{31}P{^{1}H} NMR (C_6D_6, 121.421 MHz): δ 22.4 (s with ^{29}Si satellites: $^2J_{P-Si}$ = 82 Hz).

Reaction of 5 with HSiPh$_3$. In a 5-mm NMR tube a solution of **5** (20 mg, 0.024 mmol) in benzene-d_6 (0.6 mL) was treated with $HSiPh_3$ (6.4 mg, 0.024 mmol). The reaction was monitored by ^{1}H and ^{31}P{^{1}H} NMR spectroscopy. After 55 h the ^{1}H and ^{31}P{^{1}H} NMR spectra show signals corresponding to **5**, **6**, and $Ph_3Si−SiPh_3$ in a 1:1:1 molar ratio. The mass spectrum of the solution shows a peak at *m/e* 517, which can be assigned to $Ph_3Si−SiPh_3$.

Synthesis of IrH$_2$(Si(OC(O)CH$_3$)Ph$_2$)(CO)$_2$(PCy$_3$) (12). This complex can be prepared by using two different procedures.

(a) A solution of **1** (100 mg, 0.17 mmol) in toluene (6 mL) was treated with H_2SiPh_2 (33 μL, 0.17 mmol). After 30 min the light yellow solution was concentrated under reduced pressure to ca. 0.5 mL, and 3 mL of hexane was added. A white precipitate was formed, which was decanted, washed with hexane, and dried in vacuo; yield 34 mg (26%).

(b) A solution of **13** (100 mg, 0.11 mmol) in toluene (6 mL) was treated with acetic acid (19 μL, 0.33 mmol). After 20 h the light yellow solution was concentrated under reduced pressure to ca. 0.5 mL, and 3 mL of hexane was added. A white precipitate was formed, which was decanted, washed with hexane, and dried in vacuo; yield 39 mg (45%). This reaction was quantitative by ^{31}P{^{1}H} NMR spectroscopy (C_6D_6). Anal. Calcd for $C_{34}H_{48}IrO_4PSi$: C, 52.89; H, 6.27. Found: C, 53.34; H, 6.62. IR (Nujol, cm^{-1}): ν(Ir−H) 2130 (s); ν(C≡O) 2040 (s), 1985 (vs); ν(C=O) 1708 (s); ν(Si−O) 1015. IR (CH_2Cl_2, cm^{-1}): ν(Ir−H) 2100 (m), ν(C≡O) 2030 (m), 1982 (s). ^{1}H NMR (C_6D_6): δ 8.1−7.1 (m, 10H, Ph), 2.0 (s, 3H, $OCOCH_3$), 1.9−1.0 (m, 33H, Cy), −10.4 (d, 2H, $^2J_{P-H}$ = 16.5 Hz, Ir−H). ^{31}P{^{1}H} NMR (C_6D_6, 121.421 MHz): δ 22.7 (s with ^{29}Si satellites, $^2J_{P-Si}$ = 102 Hz; t in off-resonance).

Synthesis of IrH(SiHPh$_2$)$_2$(CO)$_2$(PCy$_3$) (13). A solution of **1** (100 mg, 0.17 mmol) in toluene (6 mL) was treated with H_2SiPh_2 (66 μL, 0.34 mmol), resulting in a rapid color change from green to light yellow. After 1 h the solution was concentrated to ca. 0.5 mL in vacuo, and 4 mL of hexane was added. A white precipitate was formed, which was decanted, washed with hexane, and dried in vacuo; yield 106 mg (70%). Anal. Calcd for $C_{44}H_{56}IrO_2PSi_2$: C, 58.97; H, 6.30. Found: C, 59.08; H, 6.85. IR (Nujol, cm^{-1}): ν(Si−H) 2144; ν(Ir−H) 2115 (m); ν(C≡O) 2037 (s), 1995 (s). IR (CH_2Cl_2, cm^{-1}): ν(Ir−H) 2121 (w), ν(C≡O) 2047 (m), 1999 (m). ^{1}H NMR (C_6D_6): δ 8.0−7.0 (m, 20H, Ph), 5.8 (d, 1H, $^3J_{P-H}$ = 16 Hz, Si−H), 5.7 (d, 1H, $^3J_{P-H}$ = 8.1 Hz, Si−H), 2.0−0.8 (m, 33H, Cy), −9.8 (d, 1H, $^2J_{P-H}$

= 15.3 Hz, Ir—H). $^{31}P\{^1H\}$ NMR (C_6D_6, 121.421 MHz): δ 7.1 (s with ^{29}Si satellites, $^2J_{P-Si}$ = 73 Hz).

Synthesis of $IrH(SiH_2Ph)_2(CO)_2(PCy_3)$ (14). A solution of **1** (100 mg, 0.17 mmol) in 6 mL of toluene was treated with H_3SiPh (42 μL, 0.34 mmol), resulting in a rapid color change from green to light yellow. After 1 h the solution was concentrated under reduced pressure, and a light yellow oil was formed. Unfortunately, all attempts to crystallize **14** were unsuccessful. The compound was thus characterized in solution. IR (CH_2Cl_2, cm^{-1}): ν(Ir—H) 2105 (m); ν(C≡O) 2045 (s), 1990 (s). ^1H NMR (C_6D_6): δ 7.9–7.0 (m, 10H, Ph), 5.2–4.9 (m, 4H, Si—H), 1.9–0.9 (m, 33H, Cy), −10.6 (d, 1H, $^2J_{P-H}$ = 15.3 Hz, Ir—H). $^{31}P\{^1H\}$ NMR (C_6D_6, 121.421 MHz): δ 9.4 (s with ^{29}Si satellites, $^2J_{P-Si}$ = 91 Hz).

Reaction of 1 with 1 Equiv of H_2SiPh_2. In a 5-mm NMR tube a solution of **1** (20 mg, 0.034 mmol) in benzene-d_6 (0.6 mL) was treated with H_2SiPh_2 (6.6 μL, 0.034 mmol). The reaction was monitored by ^1H and $^{31}P\{^1H\}$ NMR spectroscopy. After 5 min the ^1H and $^{31}P\{^1H\}$ NMR spectra show signals corresponding to **1** (19%), **8** (7%), **12** (55%), and **15** (19%). ^1H and $^{31}P\{^1H\}$ NMR spectra after 40 min **1** (5%), **8** (9%), **12** (69%), and **15** (17%). Spectroscopic data for $Ir(SiHPh_2)(CO)_3(PCy_3)$ (**15**) are as follows. ^1H NMR (C_6D_6): δ 8.1–7.1 (m, 15H, Ph), 6.3 (d, 1H, $^3J_{P-H}$ = 6.3 Hz, Si—H), 1.9–0.8 (m, 33H, Cy). $^{31}P\{^1H\}$ NMR (C_6D_6, 121.421 MHz): δ 16.9 (s with ^{29}Si satellites, $^2J_{P-Si}$ = 87 Hz).

Reaction of 1 with 2 Equiv of H_2SiPh_2. In a 5-mm NMR tube a solution of **1** (20 mg, 0.034 mmol) in benzene-d_6 (0.6 mL) was treated with H_2SiPh_2 (13.3 μL, 0.068 mmol). The reaction was monitored by ^1H and $^{31}P\{^1H\}$ NMR spectroscopy. After 5 min the ^1H and $^{31}P\{^1H\}$ NMR spectra show signals corresponding to **12** (12%), **13** (84%), and **16** (4%). In addition, in the ^1H NMR spectrum were observed signals assigned to CH_3COOH (δ 11.1 (br, —O*H*)), H_2SiPh_2 (δ 5.1 (s, Si—H)), and $H_2Si_2Ph_4$ (δ 4.5 (s, Si—H)). ^1H and $^{31}P\{^1H\}$ NMR spectra after 45 h show **12** (63%), **13** (6%), and **16** (31%). Spectroscopic data for $IrH_2(SiHPh_2)(CO)_2(PCy_3)$ (**16**) are as follows. ^1H NMR (C_6D_6): δ 8.1–7.1 (m, 10H, Ph), 6.3 (dt, 1H, $^3J_{P-H}$ = 6.9 Hz, $^3J_{H-H}$ = 1.9 Hz, Si—H), 1.8–0.9 (m, 33H, Cy), −10.6 (dd, 2H, $^2J_{P-H}$ = 16.7 Hz, $^3J_{H-H}$ = 1.9 Hz, Ir—H). $^{31}P\{^1H\}$ NMR (C_6D_6, 121.421 MHz): δ 23.3 (s with ^{29}Si satellites, $^2J_{P-Si}$ = 82 Hz).

Reaction of 13 with 1 Equiv of H_2SiPh_2. In a 5-mm NMR tube a solution of **13** (20 mg, 0.022 mmol) in benzene-d_6 (0.6 mL) was treated with H_2SiPh_2 (4.3 μL, 0.022 mmol). The reaction was monitored by ^1H and $^{31}P\{^1H\}$ NMR spectroscopy. After 26 h the ^1H and $^{31}P\{^1H\}$ NMR spectra show signals corresponding to **13**, **16**, H_2SiPh_2, and $H_2Si_2Ph_4$ in a 2:1:2:1 molar ratio.

Synthesis of $IrH_2(Si(OMe)Ph_2)(CO)_2(PCy_3)$ (17). A solution of **13** (100 mg, 0.11 mmol) in toluene (5 mL) was treated with methanol (13.5 μL, 0.33 mmol). After 18 h the light yellow solution was concentrated to ca. 0.5 mL in vacuo and 3 mL of methanol was added. A white precipitate was formed, which was decanted, washed with methanol, and dried in vacuo; yield 62 mg (75%). Anal. Calcd for $C_{33}H_{48}IrO_3PSi$: C 53.27; H, 6.50. Found: C, 53.65; H, 7.01. IR (Nujol, cm^{-1}): ν(Ir—H) 2114 (s), 2096 (s); ν(C≡O) 2025 (s), 1981 (vs); ν(Si—O) 1092 (m). IR (CH_2Cl_2, cm^{-1}): ν(Ir—H) 2106 (m); ν(C≡O) 2031 (m), 1983 (s). ^1H NMR (C_6D_6): δ 8.1–7.2 (m, 10H, Ph), 3.7 (s, 3H, OMe), 1.8–0.9 (m, 33H, Cy), −10.4 (d, 2H, $^2J_{P-H}$ = 17.0 Hz, Ir—H). $^{31}P\{^1H\}$ NMR (C_6D_6, 80.984 MHz): δ 21.1 (s).

Synthesis of $IrHD(Si(OCD_3)Ph_2)(CO)_2(PCy_3)$ (17-d_4). This compound was prepared analogously as described for **17**, with **13** (100 mg, 0.11 mmol) and methanol-d_4 (15.2 μL, 0.33 mmol) as starting materials. It is a white solid; yield 58.4 mg (70%). Anal. Calcd for $C_{33}D_4H_{44}IrO_3PSi$: C, 52.99; H, 5.93. Found: C, 53.37; H, 6.42. IR (Nujol, cm^{-1}): ν(Ir—H) 2114 (s); ν(C≡O) 2025 (s), 1981 (vs); ν(Si—O) 1090 (m). IR (CH_2Cl_2, cm^{-1}): ν(Ir—H) 2106 (m); ν(C≡O) 2031 (m), 1983 (s). ^1H NMR (C_6D_6): δ 8.1–7.2 (m, 10H, Ph), 1.8–0.9 (m, 33H, Cy), −10.4 (d, 1H, $^2J_{P-H}$ = 17.0 Hz, Ir—H). ^2H NMR (C_6H_6): δ 3.6 (s, —OCD_3), −10.4 (br, Ir—D). $^{31}P\{^1H\}$ NMR (C_6D_6, 121.421 MHz): δ 21.1 (s, d in off-resonance).

Synthesis of $IrH_2(Si(OEt)Ph_2)(CO)_2(PCy_3)$ (18). This compound was prepared analogously as described for **17**, with **13** (100 mg, 0.11 mmol) and ethanol (19.5 μL, 0.33 mmol) as starting materials; this mixture was stirred for 40 h at room temperature. **18** is a white solid; yield 45 mg (53%). Anal. Calcd for $C_{34}H_{50}IrO_3PSi$: C, 53.87; H, 6.65. Found: C, 53.81; H, 6.73. IR (Nujol, cm^{-1}): ν(Ir—H) 2096 (s); ν(C≡O) 2024 (s), 1982 (vs); ν(Si—O) 1075 (m). IR (CH_2Cl_2, cm^{-1}): ν(Ir—H) 2100 (m); ν(C≡O) 2025 (m), 1980 (s). ^1H NMR (C_6D_6): δ 8.1–7.1 (m, 10H, Ph), 4.0 (q, 2H, J_{H-H} = 6.5 Hz, —OC*H*$_2CH_3$), 1.8–1.0 (m, 33H, Cy), 1.4 (t, 6H, J_{H-H} = 6.5 Hz, —OCH_2C*H*$_3$; this resonance is partially masked by the resonances of Cy), −10.4 (d, 2H, $^2J_{P-H}$ = 16.9 Hz, Ir—H). $^{31}P\{^1H\}$ NMR (C_6D_6, 80.984 MHz): δ 21.1 (s).

Synthesis of $IrH_2(Si(O^iPr)Ph_2)(CO)_2(PCy_3)$ (19). This compound was prepared analogously as described for **17**, with **13** (100 mg, 0.11 mmol) and 2-propanol (26 μL, 0.33 mmol) as starting materials; this mixture was stirred for 48 h at room temperature. **19** is a white solid; yield 43 mg (50%). Anal. Calcd for $C_{35}H_{52}IrO_3PSi$: C, 54.45; H, 6.79. Found: C, 54.64; H, 7.06. IR (Nujol, cm^{-1}): ν(Ir—H) 2105 (s); ν(C≡O) 2020 (s), 1980 (vs); ν(Si—O) 1015 (m). IR (CH_2Cl_2, cm^{-1}): ν(Ir—H) 2100 (m); ν(C≡O) 2040 (m), 1985 (s). ^1H NMR (C_6D_6): δ 8.1–7.2 (m, 10H, Ph), 4.4 (stp, 1H, J_{H-H} = 5.9 Hz, —OC*H*(CH_3)$_2$), 1.8–1.0 (m, 33H, Cy), 1.3 (d, 6H, J_{H-H} = 5.9 Hz, —OCH(C*H*$_3$)$_2$; this resonance is partially masked by the resonances of Cy), −10.4 (d, 2H, $^2J_{P-H}$ = 16.9 Hz, Ir—H). $^{31}P\{^1H\}$ NMR (C_6D_6, 80.984 MHz): δ 21.3 (s).

Synthesis of $IrH_2(Si(OPh)Ph_2)(CO)_2(PCy_3)$ (20). This compound was prepared analogously as described for **17**, with **13** (100 mg, 0.11 mmol) and phenol (31.5 mg, 0.33 mmol) as starting materials; the mixture was stirred for 72 h at room temperature. **20** is a white solid; yield 43 mg (48%). This reaction was quantitative by $^{31}P\{^1H\}$ NMR spectroscopy (C_6D_6). Anal. Calcd for $C_{38}H_{50}IrO_3PSi$: C, 56.62; H, 6.25. Found: C, 56.93; H, 6.90. IR (Nujol, cm^{-1}): ν(Ir—H) 2145 (s), 2130 (s); ν(C≡O) 2035 (s), 1985 (vs); ν(C=C) phenyl vibration 1605 (m); ν(Si—O) 1100 (m). IR (CH_2Cl_2, cm^{-1}): ν(Ir—H) 2105 (m); ν(C≡O) 2038 (m), 1985 (s). ^1H NMR (C_6D_6: δ 8.2–6.8 (m, 15H, Ph), 1.8–1.0 (m, 33H, Cy), −10.4 (d, 2H, $^2J_{P-H}$ = 16.8 Hz, Ir—H). $^{31}P\{^1H\}$ NMR (C_6D_6, 80.984 MHz): δ 21.9 (s).

Synthesis of $IrH_2(Si(OMe)_2Ph)(CO)_2(PCy_3)$ (21). A solution of **1** (100 mg, 0.17 mmol) in toluene (6 mL) was treated with H_3SiPh (42 μL, 0.34 mmol). The mixture was stirred at room temperature for 1 h and then was filtered. The light yellow filtrate was treated with an excess of methanol (1 mL), and the resulting solution was stirred for 2 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 89 mg (75%). Anal. Calcd for $C_{28}H_{46}IrO_4PSi$: C, 48.19; H, 6.64. Found: C, 48.13; H, 7.22. IR (Nujol, cm^{-1}): ν(Ir—H) 2120 (s); ν(C≡O) 2030 (s), 1985 (vs); ν(Si—O) 1060 (m). IR (CH_2Cl_2, cm^{-1}): ν(Ir—H) 2100 (m); ν(C≡O) 2030 (m), 1980 (s). ^1H NMR (C_6D_6): δ 8.2–7.2 (m, 5H, Ph), 3.6 (s, 6H, OMe), 1.8–1.0 (m, 33H, Cy), −10.7 (d, 2H, $^2J_{P-H}$ = 16.8 Hz, Ir—H). $^{31}P\{^1H\}$ NMR (C_6D_6, 80.984 MHz): δ 20.6 (s).

Synthesis of $IrH_2(Si(OEt)_2Ph)(CO)_2(PCy_3)$ (22). The same procedure used for **21** was employed, with **1** (100 mg, 0.17 mmol), H_3SiPh (42 μL, 0.34 mmol), and an excess of ethanol (1 mL) as starting materials. The resulting yellow solution was stirred for 6 h. **22** is a white solid; yield 84 mg (68%). Anal. Calcd for $C_{30}H_{50}IrO_4PSi$: C, 49.63; H, 6.94. Found: C, 49.37; H, 7.47. IR (Nujol, cm^{-1}): ν(Ir—H) 2110 (s); ν(C≡O) 2025 (s), 1985 (vs); ν(Si—O) 1060 (m). IR (CH_2Cl_2, cm^{-1}): ν(Ir—H) 2100 (m); ν(C≡O) 2020 (m), 1980 (s). ^1H NMR (C_6D_6): δ 8.2–7.2 (m, 5H, Ph), 4.1 (q, 4H, J_{H-H} = 6.9 Hz, OC*H*$_2$$CH_3$), 1.8–1.0 (m, 33H, Cy), 1.4 (t, 6H, J_{H-H} = 6.9 Hz, OCH_2C*H*$_3$; this resonance is partially masked by Cy), −10.6

Table 2. Atomic Coordinates (×10⁴; ×10⁵ for Ir, Sn, and P Atoms) and Equivalent Isotropic Displacement Coefficients (Å² × 10³; Å² × 10⁴ for Ir, Sn, and P Atoms) for the Compound $Ir(SnPh_3)(CO)_3(PCy_3)$ (2)

atom	*x/a*	*y/b*	*z/c*	U_{eq}[a]
Ir	49211(1)	9908(1)	20005(1)	182(1)
Sn	43132(1)	29120(1)	20128(1)	208(1)
P	55683(5)	−6774(6)	19946(4)	172(2)
O(1)	4718(2)	1183(2)	441(1)	62(1)
O(2)	6575(2)	1834(2)	2882(1)	43(1)
O(3)	3254(2)	428(2)	2751(2)	49(1)
C(1)	4791(2)	1104(3)	1024(2)	33(1)
C(2)	5959(2)	1518(2)	2545(2)	28(1)
C(3)	3877(2)	620(2)	2465(2)	27(1)
C(4)	4158(2)	3396(2)	3054(2)	26(1)
C(5)	4476(2)	2792(3)	3606(2)	30(1)
C(6)	4390(2)	3101(3)	4279(2)	39(1)
C(7)	3978(3)	4017(3)	4402(2)	49(1)
C(8)	3644(3)	4614(3)	3866(2)	59(2)
C(9)	3730(3)	4309(3)	3189(2)	48(1)
C(10)	5223(2)	4003(2)	1606(2)	24(1)
C(11)	5687(2)	4749(2)	2009(2)	32(1)
C(12)	6271(2)	5449(2)	1730(2)	36(1)
C(13)	6389(2)	5416(3)	1037(2)	37(1)
C(14)	5939(3)	4693(3)	622(2)	38(1)
C(15)	5359(3)	3988(2)	903(2)	34(1)
C(16)	3040(2)	3182(2)	1394(2)	23(1)
C(17)	2344(2)	2456(3)	1314(2)	32(1)
C(18)	1531(2)	2654(3)	910(2)	38(1)
C(19)	1401(2)	3583(3)	588(2)	39(1)
C(20)	2083(3)	4314(3)	659(2)	44(1)
C(21)	2902(3)	4117(3)	1061(2)	36(1)
C(22)	6175(2)	−991(2)	2839(1)	19(1)
C(23)	6592(2)	−2069(2)	2899(2)	27(1)
C(24)	7189(2)	−2183(3)	3578(2)	35(1)
C(25)	6640(3)	−1963(3)	4188(2)	40(1)
C(26)	6210(2)	−897(3)	4123(2)	31(1)
C(27)	5618(2)	−764(3)	3453(1)	25(1)
C(28)	4785(2)	−1740(2)	1722(2)	23(1)
C(29)	4117(2)	−2091(3)	2237(2)	30(1)
C(30)	3581(2)	−3023(3)	1939(2)	39(1)
C(31)	3077(2)	−2817(3)	1243(2)	42(1)
C(32)	3744(3)	−2442(3)	741(2)	45(1)
C(33)	4260(2)	−1493(3)	1031(2)	32(1)
C(34)	6442(2)	−720(2)	1355(2)	22(1)
C(35)	6662(2)	−1774(2)	1046(2)	29(1)
C(36)	7328(2)	−1642(3)	493(2)	37(1)
C(37)	8197(3)	−1096(3)	758(2)	41(1)
C(38)	7983(2)	−55(3)	1064(2)	39(1)
C(39)	7332(2)	−183(3)	1632(2)	29(1)

[a] Equivalent isotropic *U*, defined as one-third of the trace of the orthogonalized U_{ij} tensor.

(d, 2H, $^2J_{P-H}$ = 17.1 Hz, Ir—H). $^{31}P\{^1H\}$ NMR (C_6D_6, 80.984 MHz): δ 20.6 (s).

Synthesis of $IrH_2(Si(O^iPr)_2Ph)(CO)_2(PCy_3)$ (23). The same procedure used for **21** was employed, with **1** (100 mg, 0.17 mmol), H_3SiPh (42 μL, 0.34 mmol), and an excess of 2-propanol (1 mL) as starting materials. The resulting yellow solution was stirred for 8 h. **23** is a white solid; yield 60 mg (47%). Anal. Calcd for $C_{32}H_{54}IrO_4PSi$: C, 50.97; H, 7.22. Found: C, 51.15; H, 7.91. IR (Nujol, cm⁻¹): ν(Ir—H) 2100 (s); ν(C≡O) 2030 (s), 1982 (vs); ν(Si—O) 1015 (m). IR (CH_2Cl_2, cm⁻¹): ν(Ir—H) 2100 (m); ν(C≡O) 2030 (m), 1980 (s). ^1H NMR (C_6D_6): δ 8.2−7.2 (m, 5H, Ph), 4.6 (spt, 2H, J_{H-H} = 5.9 Hz, $OCH(CH_3)_2$), 1.8−1.0 (m, 33H, Cy), 1.5 (d, 6H, J_{H-H} = 5.9 Hz, $OCH(CH_3)_2$), 1.4 (d, 6H, J_{H-H} = 5.9 Hz, $OCH(CH_3)_2$; these resonances are partially masked by Cy), −10.7 (d, 2H, $^2J_{P-H}$ = 17.1 Hz, Ir—H). $^{31}P\{^1H\}$ NMR (C_6D_6, 80.984 MHz): δ 20.1 (s).

Reaction of 13 with Methanol. In a 5-mm NMR tube was dissolved **13** (20 mg, 0.022 mmol) in benzene-d_6 (0.6 mL), and MeOH (1.8 μL, 0.044 mmol) was added. The reaction was monitored by ^1H and $^{31}P\{^1H\}$ NMR spectroscopy. After 24 h the ^1H and $^{31}P\{^1H\}$ NMR spectra show signals corresponding to **16**, **17**, H_2SiPh_2, and $H_2Si_2Ph_4$ in a 1:2:1:2 molar ratio.

Table 3. Crystal Data and Data Collection and Refinement Details for $Ir(SnPh_3)(CO)_3(PCy_3)$ (2)

Crystal Data	
formula	$C_{39}H_{48}IrO_3PSn$
mol wt	906.69
color and habit	colorless, transparent prism
cryst size, mm	0.228 × 0.304 × 0.476
cryst syst	monoclinic
space group	$P2_1/n$ (No. 14)
a, Å	14.643(2)
b, Å	13.048(1)
c, Å	19.510(4)
β, deg	95.26(1)
V, Å³	3712(1)
Z	4
D(calcd), g cm⁻³	1.622
Data Collection and Refinement	
diffractometer	4-circle Siemens-STOE AED
λ(Mo Kα), Å; technique	0.710 73; bisecting geometry
monochromator	graphite oriented
μ, mm⁻¹	4.32
scan type	ω/2θ
2θ range, deg	3 ≤ 2θ ≤ 50
temp, K	173
no. of data collected	7160
no. of unique data	6556 (R_{int} = 0.014)
no. of unique obsd data	5999 ($F_o \geq 4.0\sigma(F_o)$)
no. of params refined	408
R, R_w[a]	0.0192, 0.0208
max/min transmissn factor	0.416, 0.280

[a] $R = (\Sigma[|F_o| - |F_c|])/\Sigma F_o$. $R_w = (\Sigma([|F_o| - |F_c|])w^{1/2})/\Sigma(|F_o|w^{1/2})$; $w^{-1} = \sigma^2(F_o) + 0.0001(F_o)^2$.

Reaction of 17 with P^iPr_3. In a 5-mm NMR tube was dissolved **17** (20 mg, 0.027 mmol) in benzene-d_6 (0.6 mL), and P^iPr_3 (4.3 μL, 0.027 mmol) was added. The reaction was monitored by ^1H and $^{31}P\{^1H\}$ NMR spectroscopy. After 24 h the ^1H and $^{31}P\{^1H\}$ NMR spectra show signals corresponding to **17**, **24**, PCy_3, and P^iPr_3 in a 4:1:1:4 molar ratio. Spectroscopic data for $IrH_2(Si(OMe)Ph_2)(CO)_2(P^iPr_3)$ (**24**) are as follows. ^1H NMR (C_6D_6): δ 8.1−7.2 (m, 10H, Ph), 3.6 (s, 3H, OMe), 0.8 (dd, 18H, J_{H-H} = 7.2 Hz, J_{P-H} = 14.7 Hz, $P(CH(CH_3)_2)_3$), −10.6 (d, 2H, $^2J_{P-H}$ = 17.1 Hz, Ir—H), the multiplet of P—C*H* is masked by Cy. $^{31}P\{^1H\}$ NMR (C_6D_6, 121.421 MHz): δ 31.1 (s).

Reaction of 13 with P^iPr_3. In a 5-mm NMR tube was dissolved **13** (20 mg, 0.022 mmol) in benzene-d_6 (0.6 mL), and P^iPr_3 (3.6 μL, 0.022 mmol) was added. The reaction was monitored by ^1H and $^{31}P\{^1H\}$ NMR spectroscopy. After 24 h the ^1H and $^{31}P\{^1H\}$ NMR spectra show signals corresponding to **13**, **25**, PCy_3, and P^iPr_3 in a 1:2:2:1 molar ratio. Spectroscopic data for $IrH(SiHPh_2)_2(CO)_2(P^iPr_3)$ (**25**) are as follows: ^1H NMR (C_6D_6): δ 8.0−7.1 (m, 20H, Ph), 5.7 (d, 1H, $^3J_{P-H}$ = 16.3 Hz, Si—H), 5.6 (d, 1H, $^3J_{P-H}$ = 8 Hz, Si—H), 0.7 (dd, 18H, J_{H-H} = 7.7 Hz, J_{P-H} = 14.5 Hz, $P(CH(CH_3)_2)_3$), −10.1 (d, 1H, $^2J_{P-H}$ = 14.8 Hz, Ir—H); the multiplet of P—C*H* is masked by Cy. $^{31}P\{^1H\}$ NMR (C_6D_6, 121.421 MHz): δ 15.6 (s with ^{29}Si satellites, $^2J_{P-Si}$ = 77 Hz).

Reaction of 13 with Methanol in the Presence of P^iPr_3. In a 5-mm NMR tube was dissolved **13** (20 mg, 0.022 mmol) in benzene-d_6 (0.6 mL), and P^iPr_3 (3.6 μL, 0.022 mmol) and methanol (0.9 μL, 0.022 mmol) were added. The reaction was monitored by ^1H and $^{31}P\{^1H\}$ NMR spectroscopy. After 24 h the ^1H and $^{31}P\{^1H\}$ NMR spectra show signals corresponding to **13**, **16**, **17**, and **24**−**26**. Spectroscopic data for $IrH_2(SiHPh_2)(CO)_2(P^iPr_3)$ (**26**) are as follows. ^1H NMR (C_6D_6): δ 8.1−7.1 (m, 20H, Ph), 6.3 (dt, 1H, $^3J_{P-H}$ = 7.5 Hz, J_{H-H} = 1.4 Hz, Si—H), 0.7 (dd, 18H, J_{H-H} = 7.4 Hz, J_{P-H} = 14.2 Hz, $P(CH(CH_3)_2)_3$), −10.7 (dd, 2H, $^2J_{P-H}$ = 16.7 Hz, J_{H-H} = 1.4 Hz, Ir—H); the multiplet of P—C*H* is masked by Cy. $^{31}P\{^1H\}$ NMR (C_6D_6, 121.421 MHz): δ 33.6 (s).

X-ray Structure Analysis of $Ir(SnPh_3)(CO)_3(PCy_3)$ (2). Crystals suitable for an X-ray diffraction experiment were obtained by slow diffusion of hexane into a concentrated solution of **2** in toluene. Atomic coordinates and U_{eq} values are listed in Table 2. A summary of crystal data, intensity collection procedure, and refinement data is reported in Table 3. The prismatic crystal studied was glued on a glass fiber and mounted on a Siemens-STOE AED-2 diffractometer. Cell constants were obtained from the least-squares fit of the setting angles of 56 reflections in the range $20 \leq 2\theta \leq 50°$. The 7160 recorded reflections were corrected for Lorentz and polarization effects. Three orientation and intensity standards were monitored every 55 min of measuring time; no variation was observed. Reflections were also corrected for absorption by a numerical method based on indexed morphological faces.[26]

The structure was solved by Patterson (Ir atom) and conventional Fourier techniques. Refinement was carried out by full-matrix least squares with initial isotropic thermal parameters. Anisotropic thermal parameters were used in the last cycles of refinement for all non-hydrogen atoms. Hydrogen atoms were located from difference Fourier maps and included in the refinement riding on carbon atoms with a common isotropic thermal parameter. Atomic scattering factors, corrected for anomalous dispersion for Ir, P, and Sn, were taken from ref 27. The function minimized was $\sum w(|F_o| - |F_c|)^2$, with the weight defined as $w = 1/(\sigma^2(F_o) + 0.0001(F_o)^2)$. Final R and R_w values were 0.0192 and 0.0208. All calculations were performed by use of the SHELXTL-PLUS system of computer programs.[28]

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Supplementary Material Available: Tables of anisotropic thermal parameters, atomic coordinates for hydrogen atoms, experimental details of the X-ray study, bond distances and angles, and interatomic distances for **2** (11 pages). Ordering information is given on any current masthead page.

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