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Silicon–Oxygen Bond-Forming Reactions upon Addition of Silanes and Silyl Halides to the 16-Electron Alkoxyiridium Complexes *trans*-ROIr(CO)[P(*p*-tol)$_3$]$_2$ (R = Me or Ph; *p*-tol = *p*-Tolyl). Crystal and Molecular Structure of H_2Ir(CO)(SiMe$_2$Ph)[P(*p*-tol)$_3$]$_2$

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The reactions of silanes and silyl halides with the 16-electron alkoxyiridium complexes *trans*-ROIr(CO)[P(*p*-tol)$_3$]$_2$ (R = Me or Ph; *p*-tol = *p*-tolyl) are reported. The silanes add oxidatively to the alkoxyiridium complex; the resulting complex undergoes reductive elimination of an alkoxysilane with ultimate formation of H_2Ir(CO)(SiR$_3$)[P(*p*-tol)$_3$]$_2$. Reactions of silyl halides with the alkoxy complex results in formation of silicon–oxygen bonds. The dihydride H_2Ir(CO)(SiMe$_2$Ph)[P(*p*-tol)$_3$]$_2$, which is an active hydrogenation catalyst, was subjected to structural analysis. It crystallizes in the centrosymmetric triclinic space group $P\bar{1}$ with a = 10.692 (1) Å, b = 11.199 (2) Å, c = 20.557 (4) Å, α = 75.991 (14)°, β = 84.505 (14)°, γ = 77.503 (11)°, V = 2329 (1) Å^3, and Z = 2. Diffraction data (Mo Kα, 2θ = 4.5–45.0°) were collected with a Syntex P2$_1$ automated diffractometer; the structure was solved and refined to R_F = 4.9% for all 6119 reflections (R_F = 3.6% for those 5094 data with $|F_o| > 6\sigma(|F_o|)$). The non-hydride ligands occupy expanded sites in an octahedral iridium(III) complex with Ir–P(1) = Ir–P(2) = 2.366 (2) Å, Ir–Si = 2.414 (2) Å, and Ir–CO = 1.900 (8) Å. The SiMe$_2$Ph ligand is trans to a P(*p*-tol)$_3$ ligand (P(1)–Ir–Si = 146.39 (7)°). The hydride ligands were located and refined; their positions are of limited accuracy, but they lie in mutually cis sites, trans to a P(*p*-tol)$_3$ ligand (P(2)–Ir–H(1) = 169.2 (21)°) and to the CO ligand (C(1)–Ir–H(2) = 169.4 (22)°).

A number of transition-metal complexes have been used as catalysts in the commercially important process of O-silylation, which involves silicon–oxygen bond formation.[3] In this paper we report a stoichiometric Si–O bond formation by reductive elimination from the intermediate formed by addition of a silane or a silyl halide to *trans*-ROIr(CO)[P(*p*-tol)$_3$]$_2$.

Addition of group 14 hydrides to square-planar iridium complexes has been extensively studied.[4]

$$trans\text{-Ir(CO)(PPh}_3)_2\text{Cl} + \text{HMR}_3 \rightleftharpoons \text{Ir(H)(MR}_3\text{)(CO)(PPh}_3)_2\text{Cl}$$

$$\text{M} = \text{Si, Ge, Sn; R} = \text{alkyl, aryl}$$

Under forcing conditions the silyl chloride (M = Si in above equation) could be eliminated and a second molecule of silane added.[4] These reactions depended strongly on the steric and electronic nature of the substituents on the silane.[4]

We have been examining various reactions of alkoxy[5] and alkyliridium[6] complexes and now report the addition of silanes and silyl halides which result in Si–O bond formation for the alkoxyiridium complexes.

Experimental Section

All solvents were purified according to standard techniques and were then distilled from appropriate drying agents under a dry nitrogen atmosphere. All syntheses were accomplished under an argon atmosphere. Dimethylphenylsilane (Petrach), trimethoxysilane (Petrach), and trimethylchlorosilane (Aldrich) were vacuum distilled from anhydrous sodium carbonate. Iridium trichloride, IrCl$_3$·3H_2O, was loaned by Johnson Matthey Inc. Sodium methoxide and sodium phenoxide were prepared from the reaction of dry alcohol with sodium. Triphenylphosphine and tri-*p*-tolylphosphine (Strem Chemical) were used as received. The complex *trans*-IrCl(CO)[P(*p*-tol)$_3$]$_2$ (*p*-tol = *p*-tolyl) was prepared as previously described.[4e] Infrared spectra were recorded on a Beckman 4240 spectrophotometer. ^{1}H NMR spectra were recorded on a Varian EM390 or a Joelco FX90Q spectrometer. ^{13}C and ^{31}P NMR spectra were recorded on a Joelco FX90Q spectrometer.

Preparation of *trans*-CH$_3$OIr(CO)[P(*p*-tol)$_3$]$_2$. In the drybox, a solution of 0.514 g (0.595 mmol) of IrCl(CO)[P(*p*-tol)$_3$]$_2$ in 15 mL of THF was prepared and 0.158 g (2.92 mmol) of NaOCH$_3$ was added. The suspension was stirred at ambient temperature for 17 h, and then the solvent was removed under vacuum. To ensure complete removal of the THF, the yellow solid was dissolved in a minimal volume of toluene and the toluene was removed under vacuum. The yellow solid was extracted with benzene, and the extract was filtered through a fine frit. Removal of the benzene yielded a yellow solid that was dissolved in 20 mL of 10:1 Et$_2$O/THF. The solution was diluted by the addition of

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75 mL of hexanes. The volume was reduced to 20 mL, and the resulting yellow precipitate was collected by vacuum filtration and washed with hexanes; yield 0.430 g (84%). IR (cyclohexane) ν_{CO} 1944 cm^{-1}; ^{1}H NMR (THF)-d_8) 2.17 (s), 2.93 (s), 6.5–7.6 (m) ppm. Anal. Calcd: C, 61.4; H, 5.28; P, 7.20. Found: C, 61.9; H, 5.35; P, 6.43.

Preparation of *trans*-$C_6H_5OIr(CO)[P(p\text{-tol})_3]_2$. In the drybox, a flask was charged with 0.462 g (0.534 mmol) of *trans*-$IrCl(CO)[P(p\text{-tolyl})_3]_2$, 10 mL of THF, and 0.32 g of $NaOC_6H_5$. The suspension was stirred at ambient temperature for 20 h, and then the solvent was removed under vacuum. To ensure complete removal of the THF, the yellow solid was dissolved in a minimal volume of toluene and then the toluene was removed under vacuum. The yellow solid was extracted with cyclohexane, and the extract was filtered through a fine frit. Removal of the solvent provided a pale yellow solid; yield 0.460 g (93%); IR (cyclohexane) ν_{CO} 1952 cm^{-1}. Anal. Calcd: C, 63.8; H, 5.15; P, 6.72. Found: C, 65.5; H, 5.70; P, 5.96.

Reaction of Alkoxyiridium Complexes with Silanes. In a typical reaction, the alkoxy complex was dissolved in benzene or THF and an excess (4 equiv) of dimethylphenylsilane was added. The reaction mixture was stirred at ambient temperature for several hours, and the reaction products were then identified by ^{1}H NMR spectroscopy. $H_2Ir(CO)(SiMe_2Ph)[P(p\text{-tol})_3]_2$, a product for each alkoxide, was typically purified by column chromatography on alumina or Florisil, eluting with benzene or toluene, followed by recrystallization from hexanes; yield 75–85%. Crystallographic grade crystals were grown from a saturated cyclohexane solution at 10 °C over a period of 14 days: ^{1}H NMR −9.98 (ddd, $J_{P(trans)-H}$ = 112.5 Hz, $J_{P(cis)-H}$ = 21.0 Hz, J_{H-H} = 4.5 Hz) −9.25 (td, $J_{P(cis)-H}$ = 19.5 Hz, J_{H-H} = 4.5 Hz), 0.92 (dd, $J_{P(trans)-H}$ = 12.0 Hz, $J_{P(cis)-H}$ = 2.3 Hz), 2.00 (s), 6.8–7.8 (m) ppm; ^{13}C NMR 9.44 (d, J_{P-C} = 43.6 Hz), 21.02 (s), 130–140 (m) ppm; ^{31}P NMR 21.81 (d, J_{P-P} = 14.7 Hz), 29.45 (d, J_{P-P} = 14.7 Hz) ppm; IR (KBr) ν_{Ir-H} 2103 (m), 2052 (s), ν_{CO} 1960 (vs) cm^{-1}. Anal. Calcd for $C_{51}H_{55}IrOP_2Si$: C, 63.40; H, 5.74; Ir, 19.89; P, 6.41; Si, 2.91. Found: C, 63.01; H, 6.08; Ir, 19.78; P, 6.31; Si, 3.23.

Reaction of *trans*-$CH_3OIr(CO)[P(p\text{-tol})_3]_2$ with $HSiMe_2Ph$. In the drybox, a suspension was prepared by charging a flask with 0.135 g (0.157 mmol) of *trans*-$CH_3OIr(CO)[P(p\text{-tol})_3]_2$ and 0.5 mL of benzene. On a high-vacuum line the suspension was degassed and 0.05 mL (0.3 mmol) of $HSiMe_2Ph$ was condensed into the flask. Upon thawing, the suspension became a yellow solution which gradually faded in color. After 16 h, the volatile products were collected and analyzed by ^{1}H NMR spectroscopy. The product CH_3OSiMe_2Ph was identified: 0.30 (s) and 3.25 (s) ppm. Integration is consistent with this formulation.

Reaction of *trans*-$CH_3OIr(CO)[P(p\text{-tol})_3]_2$ with $HSiPh_3$. In the drybox, an NMR tube equipped with a 14/20 joint was charged with 0.040 g (0.047 mmol) of *trans*-$CH_3OIr(CO)[P(p\text{-tol})_3]_2$ and 0.038 g (0.16 mmol) of triphenylsilane. On a high-vacuum line, approximately 0.5 mL of THF-d_8 was condensed into the NMR tube that was then flame-sealed. The tube was removed from liquid nitrogen and placed in the NMR probe. ^{1}H spectra were recorded at −49.0, −40.7, −32.1, −19.2, −8.6, 3.3, and 11.8 °C. A hydride resonance grew as the temperature was increased to 3.3 °C, and then the resonance diminished as the temperature further increased. At 3.3 °C a triplet centered at −15.61 ppm (J_{P-H} = 27.2 Hz) was observed. After warming to 23 °C, $H_2Ir(CO)(SiPh_3)[P(p\text{-tol})_3]_2$ and CH_3OSiPh_3 were formed. CH_3OSiPh_3 was characterized by ^{1}H NMR spectroscopy: 3.47 (s) ppm.

Reaction of *trans*-$C_6H_5OIr(CO)[P(p\text{-tol})_3]_2$ with $HSiMe_2Ph$. In the drybox, an NMR tube was charged with 0.100 g (0.108 mmol) of *trans*-$C_6H_5OIr(CO)[P(p\text{-tol})_3]_2$, 0.040 mL (0.24 mmol) of $HSiMe_2Ph$, and approximately 0.5 mL of benzene-d_6. The reaction was monitored by ^{1}H NMR for a period of 1 h. During this period, the doublet at 0.22 ppm, due to $HSiMe_2Ph$, decreased in amplitude while the doublet of doublets and singlet at 0.92 and 0.39 ppm, due to $H_2Ir(CO)(SiMe_2Ph)[P(p\text{-tol})_3]_2$ and $C_6H_5OSiMe_2Ph$, respectively, increased in amplitude.

Hydrogenation of Alkenes by $H_2Ir(CO)(SiMe_2Ph)[P(p\text{-tol})_3]_2$. In a typical reaction, a tube was charged with 20–30 mg of $H_2Ir(CO)(SiMe_2Ph)[P(p\text{-tol})_3]_2$ and 1–2 mL of toluene. On a high-vacuum line, the solution was degassed and an excess of alkene was condensed into the tube. The tube was then filled with hydrogen to a pressure of 1 atmosphere. After being thawed, the tube was placed in a 100 °C oil bath. After the desired period of time, volatile products were collected by vacuum distillation. Products were identified by GC analysis.

Hydrogenation of 1-Octene. In the drybox, a tube was charged with 0.018 g (0.019 mmol) of catalyst, 0.250 mL (1.59 mmol) of 1-octene, and approximately 2 mL of toluene. After 88 h, the volatile components were identified by GC: octane, 68%; 2- and 3-octenes, 17%; 1-octene, 15% with hydrogenation at 0.66 turnover/h.

Hydrogenation of 1-Octene in the Presence of PPh_3. In the drybox, a tube was charged with 0.0388 g (0.0410 mmol) of catalyst, 0.0120 g (0.0458 mmol) of PPh_3, 0.070 mL (0.45 mmol) of 1-octene, and 2 mL of toluene. After 50 h, the volatile components were identified by GC: octane, 52%; 1-octene, 37%; octenes, 11% with hydrogenation at 0.12 turnover/h.

Hydrogenation of Cyclohexene. In the drybox, a tube was charged with 0.036 g (0.037 mmol) of catalyst, 0.040 mL (0.390 mmol) of cyclohexene, and 1 mL of toluene. After 17 h, the volatile products were identified by GC: cyclohexene, 99.7%; cyclohexane, 0.3% with less than 0.01 turnover/h.

Reaction of *trans*-$C_6H_5OIr(CO)[P(p\text{-tol})_3]_2$ with Me_3SiCl. In the drybox, an NMR tube equipped with a 14/20 joint was charged with 0.108 g (0.117 mmol) of *trans*-$PhOIr(CO)[P(p\text{-tol})_3]_2$. On a high-vacuum line, 0.5 mL of benzene-d_6 was condensed into the tube. With use of a calibrated manometer, 0.126 mmol of Me_3SiCl was also condensed into the tube. After the reaction mixture was thawed, a yellow precipitate formed within 10 min. ^{1}H NMR spectroscopy indicated the formation of Me_3SiOPh: 0.16 (s) ppm. The yellow precipitate was found to be *trans*-$IrCl(CO)[P(p\text{-tol})_3]_2$.

Reaction of *trans*-$CH_3OIr(CO)[P(p\text{-tol})_3]_2$ with Me_3SiCl. In the drybox, an NMR tube equipped with a 14/20 joint was charged with 0.102 g (0.119 mmol) of *trans*-$MeOIr(CO)[P(p\text{-tol})_3]_2$. On a high-vacuum line, 0.5 mL of benzene-d_6 and 0.126 mmol of trimethylchlorosilane, measured by using a calibrated manometer, were condensed into the tube. When the reaction mixture was warmed $IrCl(CO)[P(p\text{-tol})_3]_2$ was rapidly formed as shown by IR. ^{1}H NMR spectroscopy indicated the formation of Me_3SiOMe: 0.07 (s) and 3.26 (s) ppm.

Kinetic Studies. In the drybox, a saturated solution of *trans*-$CH_3OIr(CO)[P(p\text{-tol})_3]_2$ was prepared by adding 0.02 g of the complex to 100 mL of cyclohexane. A stock solution of $HSiMe_2Ph$ or $HSi(OMe)_3$, in cyclohexane, was used to prepare silane solutions used in the kinetic experiments. The solutions were stored under an inert atmosphere prior to being introduced to the stopped-flow apparatus. The concentration of *trans*-$CH_3OIr(CO)[P(p\text{-tol})_3]_2$ was measured by the change in absorbance at 365.7 nm.

Collection of X-ray Diffraction Data on $H_2Ir(CO)(SiMe_2Ph)[P(p\text{-tol})_3]_2$. A colorless crystal of approximate orthogonal dimension 0.2 × 0.2 × 0.3 mm^3 was mounted along its extended axis in a thin-walled glass capillary. Unit-cell dimensions and diffraction data were obtained as described previously;[7] details appear in Table I. There were no systematic absences in the diffraction data; the only diffraction symmetry present was the Friedel condition (C_i; $\bar{1}$). Possible triclinic space groups are the centrosymmetric $P\bar{1}$ (C_i^1; No. 2) and the noncentrosymmetric $P1$ (C_1^1; No. 1). The centrosymmetric possibility ($P\bar{1}$) was strongly indicated by the number of molecules per unit cell ($Z = 2$) and was confirmed by successful solution of the structure in this higher symmetry space group.

All data were corrected for absorption and for Lorentz and polarization factors. Symmetry equivalent reflections were averaged and data were converted to unscaled $|F_o|$ values; any reflection with $I < 0$ was given a value of $|F_o| = 0$. A Wilson plot was used to place data on an approximate absolute scale.

Solution and Refinement of the Structure of $H_2Ir(CO)(SiMe_2Ph)[P(p\text{-tol})_3]_2$. All calculations were performed on the SUNY—Buffalo modified version of the Syntex XTL system.[8] The position of the iridium atom was determined from a Patterson map; all remaining non-hydrogen atoms and the two

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Table I. Experimental Data for the X-ray Diffraction Study of $H_2Ir(CO)(SiMe_2Ph)[P(p\text{-}tol)_3]_2$

(A) Unit-Cell Data

$a = 10.692$ (1) Å	cryst system: triclinic
$b = 11.199$ (2) Å	space group: $P\bar{1}$ (C_i^1; No. 2)
$c = 20.557$ (4) Å	$Z = 2$
$\alpha = 75.991$ (14)°	formula: $C_{51}H_{55}IrOP_2Si$
$\beta = 84.505$ (14)°	mol wt = 966 amu
$\gamma = 77.503$ (11)°	D(calcd) = 1.38 g/cm^3
$V = 2329$ (1) Å^3	T = 24 °C (297 K)

(B) Collection of X-ray Diffraction Data

diffractometer: Syntex $P2_1$
radiatn: Mo Kα ($\bar{\lambda}$ = 0.710730 Å)
monochromator: highly oriented (pyrolytic) graphite; equatorial mode with 2θ(max) = 12.160°; assumed to be 50% perfect/50% ideally mosaic for polarization correction
reflctns measd: $+h,\pm k,\pm l$ for $2\theta = 4.5° \rightarrow 45°$, yielding 6119 unique data
scan type: coupled θ(crystal)–2θ(counter)
scan width: $[2\theta(K\alpha_1) - 1.0]° \rightarrow [2\theta(K\alpha_2) + 1.0]°$
scan speed: 4.0 deg/min (2θ)
bkgnds: stationary-crystal, stationary-counter at the two extremes of the 2θ scan; each for one-fourth of the total scan time
std reflctns: three approximately mutually orthogonal reflections collected before each set of 97 data points; no decay observed
abs correctn: μ(Mo Kα) = 31.7 cm^{-1}; corrected empirically by interpolation (in 2θ and ϕ) for six close-to-axial (Ψ-scan) reflctns

hydride ligands were located by use of difference-Fourier maps. Hydrogen atoms of the aromatic organic fragments were included in idealized locations by assuming a carbon–hydrogen distance of 0.95 Å.[9] These positions were updated as refinement proceeded but were not refined. Methyl hydrogens were not included in the calculations. The structure was refined by using a full-matrix least-squares program minimizing the function $\sum w(|F_o| - |F_c|)^2$, where $w = \{[\sigma(|F_o|)]^2 + [0.015|F_o|]^2\}^{-1}$. The F_c values were based upon the analytical expressions for the neutral atoms scattering factors; both the real ($\Delta f'$) and imaginary ($i\Delta f''$) components of anomalous dispersion were included for all non-hydrogen and hydride atoms.[10] Anisotropic thermal parameters were used for all non-hydrogen atoms, except for the carbon atoms of the phosphine ligands.

Final convergence was reached with $R_F = 4.9\%$, $R_{wF} = 4.5\%$, and GOF = 1.61 for all 6119 reflections ($R_F = 3.6\%$, $R_{wF} = 4.2\%$, GOF = 1.68 for those 5094 reflections with $|F_o| > 6\sigma(|F_o|)$). A final difference map showed no significant features; the largest peaks (~0.8 e/Å^3) were in the vicinity of the isotropically refined carbon atoms of the phosphine ligands. (Unfortunately, limitations in computer core prevent the anisotropic refinement of all atoms.) Final positional and thermal parameters are shown in Table II.

Results and Discussion

Reaction of Alkoxyiridium Complexes with Silanes. Alkoxyiridium complexes react with silanes to produce alkoxysilanes and dihydridoiridium complexes:

$$trans\text{-}ROIr(CO)L_2 + 2HSiR'_3 \rightarrow ROSiR'_3 + H_2Ir(CO)(SiR'_3)L_2$$

$$L = P(p\text{-}tol)_3;\ R = CH_3, C_6H_5;\ R'_3 = (CH_3)_2Ph, Ph_3, (OCH_3)_3$$

Unlike the reactions of silanes with Vaska's compound (*trans*-$IrCl(CO)(PPh_3)_2$), the reactions of silanes with alkoxyiridium complexes occur readily at ambient temperature. The formation of dihydridoiridium complexes from the reaction of silanes with Vaska's compound is slow even at high temperatures, while here it occurs readily.

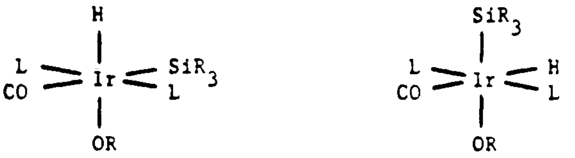

Figure 1. Possible geometries of $HIr(CO)(SiPh_3)(OCH_3)[P(p\text{-}tol)_3]_2$ with trans phosphines from cis addition of the silane to *trans*-$CH_3OIr(CO)[P(p\text{-}tol)_3]_2$ (L = $P(p\text{-}tol)_3$).

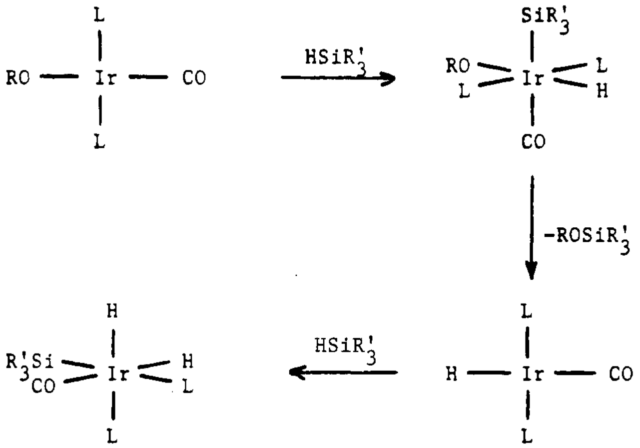

Figure 2. Suggested mechanism for the reaction of silanes with *trans*-$MeOIr(CO)[P(p\text{-}tol)_3]_2$ (L = $P(p\text{-}tol)_3$).

The reaction of triphenylsilane and *trans*-$CH_3OIr(CO)[P(p\text{-}tol)_3]_2$ was studied by using NMR spectroscopy at low temperatures. The ^1H NMR spectra were recorded between the temperatures of −44.0° and 11.8 °C. A hydride resonance was first observed at −8.6 °C. At 3.3 °C, the resonance (−15.61 (t) ppm (J_{P-H} = 27.2 Hz)) due to the intermediate hydride complex had increased in amplitude, but the intermediate was only a minor component of the reaction mixture. When the reaction was warmed to 11.8 °C, the triplet was no longer observed in the spectrum. Since silanes undergo a concerted cis oxidative addition,[12] the intermediate hydride complex has two possible geometries that are consistent with the ^1H NMR spectra. These are shown in Figure 1. The most probable geometry of the hydride complex is one in which the hydride ligand is trans to the methoxy ligand. This geometry is favored for two reasons: (1) the chemical shift of the hydride is consistent with the hydride being trans to an electronegative ligand and (2) reductive elimination of methyl alcohol is not observed as might be expected for a mutually cis arrangement of the hydride and methoxy ligands.

The reactions of *trans*-$CH_3OIr(CO)[P(p\text{-}tol)_3]_2$ with dimethylphenylsilane and trimethoxysilane have been monitored by UV–visible spectroscopy under pseudo-first-order conditions using stopped-flow techniques. Observed rate constants and initial concentrations of silane are given in the supplementary material. The rate law observed was of the form:

$$\text{rate} = k[HSiR_3][CH_3OIr(CO)L_2]$$

$$L = P(p\text{-}tol)_3;\ R_3 = Me_2Ph, (OMe)_3$$

The rate constants, at 23.5 °C, for the reactions with dimethylphenylsilane and trimethoxysilane are (9 ± 2) × 10^{-1} and (9 ± 3) × 10^{1} $M^{-1}\,s^{-1}$, respectively. As expected, the silane with the more electronegative substituents has the larger rate constant, consistent with the known reactivity of silanes with Vaska's compound.[4a,b,d,13]

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[9] Churchill, M. R. *Inorg. Chem.* **1973**, *12*, 1213.

[10] *International Tables for X-ray Crystallography*; Kynoch: Birmingham, England, 1974; Vol. 4, pp 99–101, 149–150.

[11] R_F (%) = $100\sum||F_o| - |F_c||/\sum|F_o|$, R_{wF} (%) = $100[\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$, and GOF = $[\sum w(|F_o| - |F_c|)^2/(NO - NV)]^{1/2}$, where NO = number of observations and NV = number of variables.

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Table II. Final Fractional Atomic Coordinates and Isotropic Thermal Parameters (Å^2) for $H_2Ir(CO)(SiMe_2Ph)[P(p\text{-tol})_3]_2$

atom	*x*	*y*	*z*	*B*(iso), Å^2
Ir	0.03050 (3)	0.16097 (3)	0.24305 (1)	
H(1)	−0.0849 (45)	0.1900 (43)	0.2705 (23)	1.1 (10)
H(2)	0.0532 (51)	0.0998 (51)	0.3124 (27)	2.7 (13)
P(1)	0.04005 (16)	0.35190 (15)	0.27066 (9)	
P(2)	0.24320 (17)	0.07548 (16)	0.21102 (9)	
Si	−0.05758 (19)	−0.02727 (18)	0.27279 (10)	
O(1)	−0.05588 (65)	0.25715 (64)	0.09933 (32)	
C(1)	−0.02160 (71)	0.22178 (70)	0.15317 (42)	
C(2)	−0.18250 (77)	−0.02669 (79)	0.21112 (42)	
C(3)	0.05772 (84)	−0.18638 (69)	0.28127 (47)	
C(4)	−0.14552 (67)	−0.03965 (64)	0.35793 (38)	
C(5)	−0.27228 (78)	0.01623 (80)	0.36750 (41)	
C(6)	−0.33572 (84)	0.00709 (89)	0.43068 (51)	
C(7)	−0.2723 (10)	−0.05980 (91)	0.48584 (44)	
C(8)	−0.1480 (10)	−0.1162 (11)	0.47900 (47)	
C(9)	−0.08558 (81)	−0.1072 (10)	0.41789 (46)	
C(11)	−0.04612 (61)	0.37295 (61)	0.34999 (32)	2.87 (13)
C(12)	−0.04104 (68)	0.48052 (68)	0.37376 (36)	3.78 (15)
C(13)	−0.10061 (71)	0.49751 (71)	0.43433 (38)	4.09 (15)
C(14)	−0.16520 (69)	0.41064 (69)	0.47444 (36)	3.77 (15)
C(15)	−0.16825 (71)	0.30570 (71)	0.45171 (37)	4.06 (15)
C(16)	−0.11133 (66)	0.28554 (66)	0.39093 (35)	3.58 (14)
C(17)	−0.22748 (81)	0.43046 (81)	0.54324 (43)	5.29 (19)
C(21)	−0.03543 (62)	0.48930 (62)	0.20845 (33)	2.99 (13)
C(22)	0.02174 (76)	0.51684 (77)	0.14425 (41)	4.75 (17)
C(23)	−0.03695 (79)	0.61583 (78)	0.09481 (41)	4.96 (18)
C(24)	−0.15510 (76)	0.68755 (75)	0.10739 (40)	4.54 (17)
C(25)	−0.21154 (75)	0.65983 (74)	0.17016 (40)	4.53 (17)
C(26)	−0.15475 (68)	0.56260 (67)	0.22053 (36)	3.68 (15)
C(27)	−0.2199 (10)	0.7973 (10)	0.05125 (53)	7.36 (25)
C(31)	0.19372 (62)	0.38607 (61)	0.28591 (32)	2.92 (13)
C(32)	0.23989 (72)	0.49499 (72)	0.25589 (38)	4.24 (16)
C(33)	0.35497 (80)	0.51202 (79)	0.27458 (42)	5.02 (18)
C(34)	0.42732 (79)	0.42296 (78)	0.32291 (41)	4.87 (18)
C(35)	0.38152 (76)	0.31540 (75)	0.35414 (39)	4.58 (17)
C(36)	0.26478 (72)	0.29684 (71)	0.33527 (38)	4.18 (16)
C(37)	0.5582 (10)	0.4386 (10)	0.34274 (54)	7.54 (26)
C(41)	0.25972 (62)	−0.00142 (61)	0.13986 (32)	2.98 (13)
C(42)	0.15751 (72)	−0.04287 (71)	0.12213 (38)	4.16 (16)
C(43)	0.17179 (79)	−0.10798 (78)	0.07123 (42)	4.91 (18)
C(44)	0.28732 (76)	−0.13319 (76)	0.03627 (40)	4.61 (17)
C(45)	0.38776 (72)	−0.08959 (72)	0.05233 (38)	4.22 (16)
C(46)	0.37512 (67)	−0.02204 (67)	0.10221 (36)	3.66 (14)
C(47)	0.3035 (10)	−0.2081 (10)	−0.01978 (52)	7.16 (24)
C(51)	0.34936 (61)	0.18869 (61)	0.18011 (32)	2.88 (13)
C(52)	0.45731 (72)	0.19024 (71)	0.21194 (38)	4.15 (16)
C(53)	0.52932 (77)	0.28577 (77)	0.18682 (41)	4.79 (17)
C(54)	0.49356 (78)	0.37802 (77)	0.13217 (41)	4.79 (17)
C(55)	0.38657 (77)	0.37718 (75)	0.09922 (40)	4.70 (17)
C(56)	0.31473 (69)	0.28287 (68)	0.12279 (36)	3.77 (15)
C(57)	0.5723 (10)	0.4835 (10)	0.10671 (54)	7.66 (26)
C(61)	0.33838 (60)	−0.04293 (60)	0.27522 (32)	2.81 (13)
C(62)	0.45138 (78)	−0.11912 (77)	0.26019 (41)	4.90 (18)
C(63)	0.52838 (83)	−0.20116 (83)	0.30979 (45)	5.54 (19)
C(64)	0.49436 (72)	−0.20996 (71)	0.37670 (39)	4.13 (16)
C(65)	0.38203 (76)	−0.13538 (76)	0.39223 (40)	4.67 (17)
C(66)	0.30559 (70)	−0.05311 (70)	0.34271 (37)	4.04 (15)
C(67)	0.57992 (89)	−0.30065 (88)	0.43204 (46)	6.01 (21)

A possible mechanism for the reaction of silanes with alkoxyiridium complexes is shown in Figure 2. The initial step involves oxidative addition of the silicon–hydrogen bond to the iridium complex to form a transient hydride complex, $HIr(CO)(SiR'_3)(OR)[p(p\text{-tol})_3]_2$. Oxidative addition may be preceded by the formation of a molecular complex. The formation of such molecular complexes have been implicated in the reaction of silanes with Wilkinson's catalyst.[4e,14] Elimination of alkoxysilane from $HIr(CO)(SiR'_3)(OR)[P(p\text{-tol})_3]_2$ produces an unsaturated hydridoiridium complex, $HIr(CO)[P(p\text{-tol})_3]_2$, which undergoes rapid oxidative addition of silane to yield a dihydridoiridium complex, $H_2Ir(CO)(SiR'_3)[P(p\text{-tol})_3]_2$. Although the unsaturated hydridoiridium complex was not observed, it has frequently been postulated as an intermediate in iridium(I) chemistry.[15]

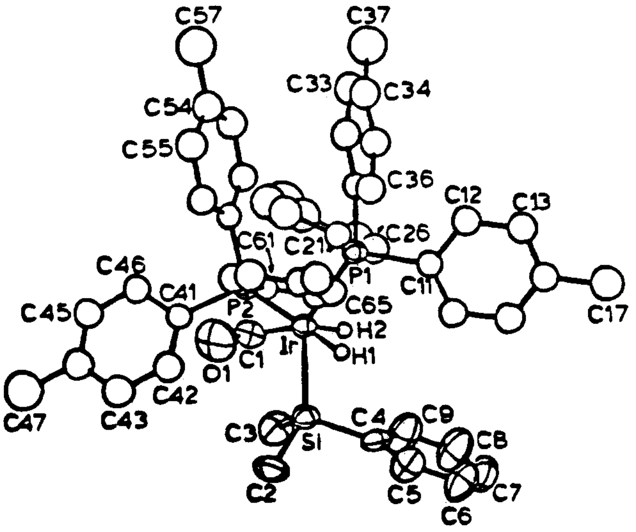

Figure 3. Labeling of atoms in the $H_2Ir(CO)(SiMe_2Ph)[P(p\text{-tol})_3]_2$ molecule (ORTEP diagram).

Table III. Selected Interatomic Distances (Å) in $H_2Ir(CO)(SiMe_2Ph)[P(p\text{-tol})_3]_2$

Distances around the Iridium Atom			
Ir–P(1)	2.366 (2)	Ir–H(1)	1.32 (5)
Ir–P(2)	2.366 (2)	Ir–H(2)	1.44 (5)
Ir–Si	2.414 (2)	C(1)–O(1)	1.148 (11)
Ir–C(1)	1.900 (8)		
Phosphorus–Carbon Distances			
P(1)–C(11)	1.835 (7)	P(2)–C(41)	1.846 (7)
P(1)–C(21)	1.833 (7)	P(2)–C(51)	1.842 (7)
P(1)–C(31)	1.837 (7)	P(2)–C(61)	1.833 (7)
Distances in the SiMe$_2$Ph ligand			
Si–C(2)	1.925 (9)	Si–C(3)	1.914 (8)
Si–C(4)	1.895 (8)	C(4)–C(5)	1.382 (11)
C(5)–C(6)	1.398 (13)	C(6)–C(7)	1.350 (14)
C(7)–C(8)	1.352 (16)	C(8)–C(9)	1.357 (13)
C(9)–C(4)	1.411 (12)		

Description of the Crystal Structure of $H_2Ir(CO)(SiMe_2Ph)[P(p\text{-tol})_3]_2$. The crystal contains an ordered arrangement of $H_2Ir(CO)(SiMe_2Ph)[P(p\text{-tol})_3]_2$ molecules that are separated by normal van der Waals' distances. The overall geometry and atomic labelling scheme are shown in Figure 3. Figure 4 provides a stereoscopic view. Interatomic distances and angles are listed in Tables III and IV, respectively.

The central iridium(III) atom has a rather distorted octahedral stereochemistry. Angles between the four accurately located non-hydride ligands are substantially different from the idealized trans and cis values of 180° and 90°, respectively; the deviations, in general, are a function of ligand size ("cone angle"). Thus, cis angles (in decreasing order) are P(1)–Ir–P(2) = 105.68 (6)°, P(1)–Ir–C(1) = 100.29 (25)°, P(2)–Ir–Si = 99.89 (7)°, Si–Ir–C(1) = 99.38 (25)°, and P(2)–Ir–C(1) = 93.81 (25)°; the sole trans angle is P(1)–Ir–Si = 146.39 (7)°. Thus, the non-

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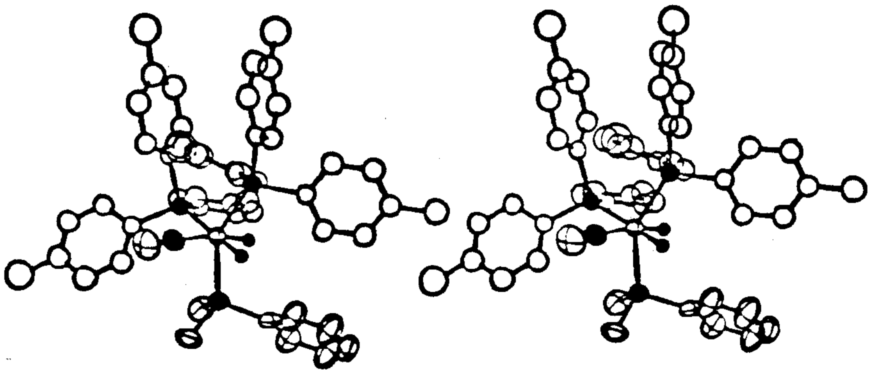

Figure 4. Stereoscopic view of the $H_2Ir(SiMe_2Ph)[P(p\text{-tol})_3]_2$ molecule.

Table IV. Selected Interatomic Angles (deg) for $H_2Ir(CO)(SiMe_2Ph)[P(p\text{-tol})_3]_2$

Angles around the Iridium Atom			
P(1)–Ir–P(2)	105.68 (6)	H(1)–Ir–H(2)	79.5 (30)
P(1)–Ir–Si	146.39 (7)	H(1)–Ir–P(1)	78.9 (21)
P(1)–Ir–C(1)	100.29 (25)	H(1)–Ir–P(2)	169.2 (21)
P(2)–Ir–Si	99.89 (7)	H(1)–Ir–Si	72.5 (21)
P(2)–Ir–C(1)	93.81 (25)	H(1)–Ir–C(1)	95.0 (21)
Si–Ir–C(1)	99.38 (25)	H(2)–Ir–P(1)	87.7 (22)
		H(2)–Ir–P(2)	90.7 (22)
		H(2)–Ir–Si	70.3 (22)
		H(2)–Ir–C(1)	169.4 (22)
Ir–P–C and C–P–C Angles			
Ir–P(1)–C(11)	113.86 (22)	Ir–P(2)–C(41)	115.43 (22)
Ir–P(1)–C(21)	112.15 (23)	Ir–P(2)–C(51)	115.99 (22)
Ir–P(1)–C(31)	121.03 (23)	Ir–P(2)–C(61)	117.16 (22)
C(11)–P(1)–C(21)	103.85 (31)	C(41)–P(2)–C(51)	100.35 (30)
C(11)–P(1)–C(31)	98.65 (31)	C(41)–P(2)–C(61)	103.23 (30)
C(21)–P(1)–C(31)	105.24 (31)	C(51)–P(2)–C(61)	102.32 (30)
Ir–C–O and Ir–Si–C Angles			
Ir–C(1)–O(1)	178.20 (73)	Ir–Si–C(2)	112.26 (27)
Ir–Si–C(3)	118.52 (28)	Ir–Si–C(4)	110.18 (24)
Angles in the $SiMe_2Ph$ Ligand			
C(2)–Si–C(3)	105.54 (38)	C(2)–Si–C(4)	105.74 (35)
C(3)–Si–C(4)	103.57 (56)	C(5)–C(4)–C(9)	113.84 (73)
C(6)–C(5)–C(4)	123.27 (80)	C(7)–C(6)–C(5)	119.57 (90)
C(8)–C(7)–C(6)	119.32 (96)	C(9)–C(8)–C(7)	121.4 (10)
C(4)–C(9)–C(8)	122.56 (90)		

hydride ligands have opened up the interligand angles toward a tetrahedral arrangement and are now clearly "encroaching" on the stereochemical sites of the hydride ligands. Such effects have been noted before[16] and reach their zenith in $HRh(PPh_3)_4$[17] and $HRh(PPh_3)_3(AsPh_3)$,[18] in which the triphenylpnictide ligands are distributed with regular tetrahedral interligand angles.

Iridium–ligand bond lengths are normal with Ir–P(1) = 2.366 (2) Å, Ir–P(2) = 2.366 (2) Å, Ir–Si = 2.414 (2) Å, and Ir–C(1) = 1.900 (8) Å.

The positions of the hydride ligands were determined from a difference-Fourier map after all non-hydrogen atoms had been located and refined. At that stage the two hydride ligands showed up as the two largest features (~1.0 e/Å^3) on the map; there were no other features above 0.5 e/Å^3 within 2 Å of the iridium atom. The hydride ligands were subsequently refined, giving rise to iridium–hydrogen bond distances of Ir–H(1) = 1.32 (5) Å (trans to P(2), with H(1)–Ir–P(2) = 169.2 (21)°) and Ir–H(2) = 1.44 (5) Å (trans to the carbonyl ligand, with H(2)–Ir–C(1) = 169.4 (22)°). The refined Ir–H distances are substantially shorter than those determined previously (1.57 (7)–1.82 (17) Å; average = 1.67 (7) Å).[19] Our refined values are clearly of limited accuracy, and we attach little significance to the refined Ir–H bond lengths. The basic stereochemical sites do, however, make chemical sense.

All other distances and angles have the expected values.

Alkene Hydrogenation by Silyliridium Complexes. The compound $H_2Ir(CO)(SiMe_2Ph)[P(p\text{-tol})_3]_2$ has been found to catalyze the isomerization and hydrogenation of alkenes. The rate of hydrogenation is markedly dependent upon the nature of the alkene. At 100 °C and 1 atm of H_2, the turnover rates for the hydrogenation of 1-octene and cyclohexene are 0.66/h and 0.048/day, respectively. An analogous germyliridium complex, $H_2Ir(CO)(GeMe_3)(PPh_3)_2$, has been reported to be a stoichiometric reagent for the hydrogenation of ethylene and hex-2-yne.[4c,d,20]

A reaction pathway can be proposed for the hydrogenation of alkenes by $H_2Ir(CO)(SiMe_2Ph)[P(p\text{-tol})_3]_2$. As a coordinatively saturated complex, the initial step must involve either formation of a seven-coordinate complex or ligand dissociation. The addition of 1 equiv of triphenylphosphine greatly reduces the rate of 1-octene hydrogenation. Such a large decrease, 82%, strongly suggests that triphenylphosphine dissociation takes place in the hydrogenation process. Phosphine dissociation has been reported to take place in the hydrogenation of alkenes and alkynes by cobalt, rhodium, and iridium catalysts.[21] Phosphine dissociation is followed by alkene coordination. Insertion of the coordinated alkene into the iridium–hydrogen bond produces an alkyliridium hydride. The observation of alkene isomerization (see Experimental Section for details) indicates that the insertion reaction is reversible. Subsequent alkane elimination produces an unsaturated complex that undergoes oxidative addition of hydrogen and coordination of either an alkene or a phosphine. An alternate mechanism involving silane elimination to open a coordination site cannot be excluded, though observation of the $H_2Ir(CO)(SiMe_2Ph)[P(p\text{-tol})_3]_2$ after the reaction would be less likely in this case.

Competitive Reductive Elimination from Hydridoiridium Complexes. The addition of silanes to square-

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planar iridium(I) complexes leads to four distinct reductive elimination reactions: (1) re-formation of the silicon–hydrogen bond occurs for $Ir(CO)(PPh_3)_2Cl(SiR_3)(H)$, (2) formation of a silicon–chlorine bond for $Ir(CO)(PPh_3)_2Cl(SiR_3)(H)$, (3) formation of a silicon–oxygen bond for alkoxyiridium complexes, and (4) formation of carbon–hydrogen bonds for alkyliridium complexes.[23] The suggested geometry for addition of silane to *trans*-$IrCl(CO)(PPh_3)_2$ has a trans distribution of the Cl and SiR_3 groups such that isomerization is required before elimination of SiR_3Cl.[15d] Similar isomerization would be required for formation of Si–O bonds if addition to the alkoxide occurs with the same geometry. That isomerization is possible is shown by the addition of stannanes to *trans*-$IrCl(CO)(PPh_3)_2$ which gives two isomers directly.[22] If we assume that isomerization is not the rate-determining step for the reductive elimination reactions, the following order of ease of bond forming to silicon is observed.

$$\text{Si–O} > \text{Si–H} > \text{Si–Cl}$$

Silicon–carbon bond formation cannot be included because of the rapid elimination of CH_4 through C–H bond formation.[23]

Further (if isomerization is not rate-limiting) our data suggest that formation of Si–O bonds occurs more readily than formation of O–H bonds.

Reaction of Alkoxyiridium Complexes with Chlorosilanes. The reaction of chlorotrimethylsilane with alkoxyiridium complexes results in formation of an alkoxysilane and an analogue of Vaska's compound:

$$\textit{trans}\text{-}ROIr(CO)L_2 + ClSiMe_3 \rightarrow ROSiMe_3 + IrCl(CO)L_2$$

$$L = P(p\text{-tol})_3;\ R = CH_3,\ C_6H_5$$

The ready reaction of chlorotrimethylsilane with the alkoxyiridium complexes is in contrast to the lack of reaction of chlorotrimethylsilane with the methyliridium complex.[23] Alkyliridium complexes generally show a greater tendency to undergo oxidative addition of substrates than their alkoxyiridium analogues.[5,6] This tendency is demonstrated by the rapid reaction of the methyliridium complex with hydrogen at low temperatures while the alkoxyiridium complexes fail to react with hydrogen at ambient temperatures.[24] The lesser tendency of alkoxyiridium complexes to undergo oxidative addition and the inactivity of the methyliridium complex toward oxidative addition of chlorotrimethylsilane suggest that oxidative addition is not involved in the reaction of the chlorosilane with alkoxyiridium complexes. This reaction may result from the alkoxy ligand acting as a Lewis base and undergoing an S_N2 attack on the silicon atom. The ability of the alkoxy ligand to act as a nucleophile has been demonstrated by the formation of carboalkoxyiridium (IrC(=O)OR) complexes via nucleophilic attack on carbon monoxide.[5b,c] Similarly, a common feature of the mechanisms of a variety of O-silylation catalysts is the formation of alkoxysilanes via nucleophilic attack of an alcohol on a silyl ligand.[3]

Addendum: Similarly tetrahedrally distorted arrays of non-hydrogenic ligands are found in the *cis*-dihydroiridium(III) species $H_2Ir(SiEt_3)(COD)(AsPh_3)$[25] and $H_2Ir(GeMe_3)(CO)(PPh_3)_2$.[26]

Acknowledgment. We acknowledge the National Science Foundation (CHE8709563) and the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research. A loan of $IrCl_3{\cdot}xH_2O$ was provided by Johnson Matthey Corp. We are grateful to Professor C. D. Ritchie for use of his stopped-flow kinetic system.

Registry No. *trans*-$CH_3OIr(CO)[P(p\text{-tol})_3]_2$, 115338-91-5; *trans*-$IrCl(CO)[P(p\text{-tol})_3]_2$, 28195-56-4; *trans*-$C_6H_5OIr(CO)[p(p\text{-tol})_3]_2$, 115338-92-6; $HSiMe_2Ph$, 766-77-8; CH_3OSiMe_2Ph, 17881-88-8; $HSiPh_3$, 789-25-3; $H_2Ir(CO)(SiPh_3)[P(p\text{-tol})_3]_2$, 115338-93-7; CH_3OSiPh_3, 1829-41-0; $H_2Ir(CO)(SiMe_2Ph)_P(p\text{-tol})_3]_2$, 115338-94-8; $C_6H_5OSiMe_2Ph$, 17915-17-2; $CH_2{=}CH(CH_2)_5CH_3$, 111-66-0; $CH_3(CH_2)_6CH_3$, 111-65-9; $CH_3CH{=}CH(CH_2)_4CH_3$, 111-67-1; $CH_3CH_2CH{=}CH(CH_2)_3CH_3$, 592-98-3; Me_3SiCl, 75-77-4; Me_3SiOPh, 1529-17-5; Me_3SiOMe, 1825-61-2; $HSi(OMe)_3$, 2487-90-3; $HIr(CO)(SiPh_3)(OCH_3)[P(p\text{-tol})_3]_2$, 115338-95-9; $H_2Ir(CO)(SiCOMe)_3)[P(p\text{-tol})_3]_2$, 115338-96-0; $Si(OCH_3)_4$, 681-84-5; octene, 25377-83-7; cyclohexene, 110-83-8.

Supplementary Material Available: A table and a plot of kinetic data for reaction of silanes with *trans*-$MeOIr(CO)[P(p\text{-tol})_3]_2$ and tables of bond distances and angles, anisotropic thermal parameters, and fractional atomic coordinates for H's (7 pages); a table of observed and calculated structure factor amplitudes (29 pages). Ordering information is given on any current masthead page.

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