Another comparison of interest concerns the SO_2-addition reactions to a number of metal hydroxo complexes (Table IV). It is noted that in all cases, with the exception of $Cr(OH_2)_5OH^{2+}$, studied in this work the direct SO_2 addition to the mono and dihydroxo forms of the various species are very rapid, ranging from a low of 6.8×10^6 s^{-1} for the monohydroxoplatinum(IV) to a high of 2.2×10^{10} s^{-1} for the *cis*-dihydrobis(ethylenediamine)cobalt(III) complex, a value within only 1 or less order of magnitude of the diffusion-controlled limit. The value of 4.4×10^2 s^{-1} M^{-1} for $Cr(OH_2)_5OH^{2+}$ obtained in this work is clearly an exception especially when compared to the pentaammine analogue, 2.9×10^8 s^{-1} M^{-1}. The value, however, of 4.38 s^{-1} M^{-1} obtained by using a mechanism in which the reacting species are $Cr(OH_2)_6^{3+}$ and HSO_3^- is of comparable magnitude to that observed for the reactions of $Co(NH_3)_5OH^{2+}$ and $HSeO_3$ (8 s^{-1} M^{-1}) and *cis*-$Co(en)_2(OH_2)OH^{2+}$ and $HSeO_3^-$ (4 s^{-1} M^{-1}) (see Table IV), suggesting very strongly that this is the preferred route in the present system.

It has previously been shown[27,30] that log *k* for the CO_2 uptake by various metal hydroxo complexes depends linearly with the p*K* value of the corresponding aquo form. Analysis of the data given in Table IV suggests the possibility of such a trend over the limited range of available data. The observed variations, however, suggest that the nature of the central metal atom and/or other ligands must play an important role in determining the value of the rate-limiting step for the SO_2-addition reactions.

Acknowledgment. Financial support of this research from the Charles D. and Francis H. Larkin Foundation of the State University of New York at Buffalo and from Western Illinois University is gratefully acknowledged.

Registry No. $[Cr(OH_2)_5(OSO_2)]^+$, 94233-45-1; $Cr(H_2O)_4(OH)(SO_3)$, 94136-83-1; $Cr(H_2O)_6^{3+}$, 14873-01-9.

Contribution from the Department of Chemistry,
University of Victoria, British Columbia, Canada V8W 2Y2

(Phosphinoalkyl)silyl Complexes. 5.[1] Synthesis and Reactivity of Congeneric Chelate-Stabilized Disilyl Complexes of Rhodium(III) and Iridium(III): Chlorobis[[(diphenylphosphino)ethyl]dimethylsilyl]rhodium and -iridium

MARY J. AUBURN and STEPHEN R. STOBART*

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Reaction of $[M(COD)Cl]_2$ (M = Rh, Ir; COD = cycloocta-1,5-diene) with excess $PPh_2CH_2CH_2SiMe_2H$ in THF solution affords the 5-coordinate M(III) complexes $\overline{M(PPh_2CH_2CH_2Si}Me_2)_2Cl$ (**1**, M = Rh; **2**, M = Ir), which are enantiomeric with the two P atoms trans; the common geometry for **1** and **2** deduced from spectroscopic data has been substantiated with X-ray diffraction that shows crystals of the two compounds to be isomorphous. Halide ion exchange reactions yield the analogues **3–6** $\overline{M(PPh_2CH_2CH_2Si}Me_2)_2X$ in which X = Br or I. Treatment of $[Ir(COD)Cl]_2$ with 2 mol equiv of $PPh_2CH_2CH_2SiMe_2H$ allows the 6-coordinate intermediate $\overline{Ir(PPh_2CH_2CH_2Si}Me_2)(COD)(H)(Cl)$ (**7**) to be recovered, in which the chelating ligands occupy a plane with H and Cl mutually trans and from which chel (diphos, dpm, $PPh_2CH_2CH_2SiMe_2H$) displaces COD, yielding respectively $\overline{Ir(PPh_2CH_2CH_2Si}Me_2)(chel)(H)(Cl)$ (**8**, diphos; **9**, dpm) or compound **2**, although under similar reaction conditions a Rh analogue of **7** could not be obtained. The coordinatively unsaturated Ir complex **2** reacts rapidly with a variety of neutral molecules (CO, PF_3, $P[OR]_3$, RNC), generating 6-coordinate adducts as single isomers possessing a common structure with L entering cis to Cl, trans to Si; with L = *t*-BuNC, $Me_3CCH_2CMe_2NC$, or Me_2CHNC, Rh analogues **10–12** are also formed from **1**. Compounds **1** and **10–12** offer the first fully characterized examples respectively of bis(silyl)rhodium, octahedral silylrhodium species, the stability of which contrasts remarkably with the sensitivity toward dissociative cleavage of unsupported Si–Rh bonds.

Conversion of **1** or **2** to the corresponding hydrido complexes $\overline{M(PPh_2CH_2CH_2Si}Me_2)_2H$ (**23**, M = Rh; **24**, M = Ir) has been demonstrated in solution with NMR spectroscopy, and although the structures of these species remain uncertain since attempted isolation leads to decomposition, compound **24** has been intercepted to form 6-coordinate CO or *t*-BuNC adducts.

Introduction

Silyl complexes of rhodium and iridium have been studied in considerable detail,[2] principally because of putative intermediacy in metal-catalyzed hydrosilylation of olefins.[3] To date, all examples of such species, regardless of whether M = Rh or Ir, are M(III) derivatives,[2,4] accessed virtually without exception via oxidative addition of silanes to d^8 precursors including $[M(PPh_3)_3Cl]$ or *trans*-$[M(PPh_3)_2(CO)X]$ (M = Rh, Ir; X = Cl, Br), $[IrH(PPh_3)_3CO]$, or $[Ir(diphos)_2]^+$ (diphos = $PPh_2CH_2CH_2PPh_2$). In other respects, however, it has become clear that silyl compounds formed by the two elements are conspicuously dissimilar, rather than resembling one another; in particular, most representative rhodium species are 5-coordinate at the metal center and are very sensitive to reductive cleavage of the Rh–Si bond,[2,5] while iridium analogues, which are ac-

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cordingly more numerous, are typically octahedral and are chemically more inert.[2–4,6]

In extending our investigation of the coordination properties[1,7,8] of the functionalized silanes[9] $R_2P(CH_2)_nSiR^1R^2H$, we have examined the action of [(diphenylphosphino)ethyl]dimethylsilane, $PPh_2(CH_2)_2SiMe_2H$, on the labile diolefin dimers $[M(COD)Cl]_2$ (M = Rh, Ir; COD = cycloocta-1,5-diene). Although reactions of the latter with simple silanes have been almost completely ignored,[10,11] bridge cleavage and displacement of COD proved to be remarkably facile, accompanying *chelate-assisted*[7a,12] silane addition to afford congeneric M(III) complexes. These products are unusual in that they share a common geometry, existing in the solid state as markedly distorted, chiral 5-coordinate structures that are isomorphous;[13] they are atypical also in a number of other ways, including (a) greatly enhanced stability toward M–Si bond cleavage (especially[2,5] for Rh), (b) increased resistance toward reductive elimination (emphasized[2–5] by addition of neutral ligands to give isolable adducts for M = Rh as well as Ir), and (c) characterization of a stable octahedral intermediate establishing that formation of the iridium complex occurs via two discrete, consecutive hydrosilylation steps.

Experimental Section

General methods including details of spectroscopic measurements have been described previously.[8] In the present work, more extensive use was made of in situ ^{31}P NMR spectroscopy (Nicolet TT-14 FT-NMR spectrometer, 24.3 MHz) to elucidate the course of preliminary reactions and ^1H NMR spectra were routinely recorded at 250 MHz with a Bruker WM250 FT-NMR instrument. [(Diphenylphosphino)ethyl]dimethylsilane was synthesized as reported earlier,[9] $[M(COD)Cl]_2$ (M = Rh, Ir) were prepared by well-established[14] routes, and the alkyl isocyanides were provided by Dr. D. E. Berry of this department. Analytical data were supplied by Canadian Microanalytical Services Ltd.

Syntheses. (Phosphinoethyl)silyl Complexes. A. Five-Coordinate Compounds. $[Rh(PPh_2CH_2CH_2SiMe_2)_2Cl]$ (1). To a stirred solution in THF (10 mL) of $[Rh(COD)Cl]_2$ (0.20 g, 0.41 mmol) was added a solution of $PPh_2(CH_2)_2SiMe_2H$ (0.45 g, 1.70 mmol) also in THF (5 mL). After gas evolution had ceased, the reaction mixture was stirred (30 min) and then volatiles were removed by evacuation at 10^{-2} mmHg to leave a bright yellow oil. On addition of Et_2O (2 mL), the product (0.45 g, 0.66 mmol, 81%) deposited as translucent yellow crystals. Anal. Calcd for $C_{32}H_{40}ClP_2RhSi_2$: C, 56.42; H, 5.91; Cl, 5.20. Found: C, 56.05; H, 5.86; Cl, 5.96.

$Ir(PPh_2CH_2CH_2SiMe_2)_2Cl$ (2). Addition of $Ph_2P(CH_2)_2SiMe_2H$ (0.32 g, 1.20 mmol) in THF (5 mL) to a stirred solution of $[Ir(COD)Cl]_2$ (0.20 g, 0.30 mmol) also in THF (10 mL) resulted in gas evolution accompanied by a color change from red to yellow. After stirring (30 min), the yellow mixture was filtered (alumina column, 5 × 3 cm^2) and then solvent was pumped away, affording an orange oil. Addition of Et_2O (1 mL) gave chrome yellow crystals of the product (0.33 g, 0.21 mmol, 35%). Anal. Calcd for $C_{32}H_{40}ClIrP_2Si_2$: C, 49.88; H, 5.23. Found: C, 50.20; H, 5.55.

$[Rh(PPh_2CH_2CH_2SiMe_2)_2Br]$ (3). After complex 1 (50 mg, 0.07 mmol) was stirred (24 h) with excess NaBr in acetone (20 mL), removal of solvent was followed by extraction with benzene (20 mL). Filtration of the resulting solution and then evaporation of benzene afforded an oily residue that was dissolved in Et_2O (1 mL); addition of hexane precipitated the product (ca. 80%) as a pale yellow powder. Anal. Calcd for $C_{32}H_{40}BrP_2RhSi_2$: C, 52.97; H, 5.56. Found: C, 51.61, H, 5.50.

$[Rh(PPh_2CH_2CH_2SiMe_2)_2I]$ (4). A procedure similar to that described above using NaI in acetone led to isolation of the yellow product (ca. 90%). Anal. Calcd for $C_{32}H_{40}IP_2RhSi_2$: C, 49.75; H, 5.22. Found: C, 49.84; H, 5.39.

$[Ir(PPh_2CH_2CH_2SiMe_2)_2Br]$ (5). Compound 2 (50 mg, 0.06 mmol) was stirred in acetone (20 mL) with excess NaBr for 24 h, and then solvent was removed to leave a whitish residue. Extraction by stirring (30 min) with benzene (30 mL) followed by filtration and concentration precipitated the yellow product in essentially quantitative yield. Anal. Calcd for $C_{32}H_{40}BrIrP_2Si_2$: C, 47.16; H, 4.95. Found: C, 46.97; H, 4.95.

$[Ir(PPh_2CH_2CH_2SiMe_2)I]$ (6). In a similar manner to that described above, treatment of compound 2 with NaI in acetone yielded the product as a yellow powder. Anal. Calcd for $C_{32}H_{40}IIrP_2Si_2$: C, 44.59; H, 4.68. Found: C, 44.73; H, 4.83.

B. Six-Coordinate Compounds. $[Ir(PPh_2CH_2CH_2SiMe_2)(COD)(H)(Cl)]$ (7). Drop-by-drop addition of a solution of $Ph_2P(CH_2)_2SiMe_2H$ (0.08 g, 0.30 mmol) in THF (5 mL) to a stirred solution in THF (10 mL) of $[Ir(COD)Cl]_2$ (0.10 g, 0.15 mmol) rapidly discharged the red color of the latter, and after 5 min, removal of solvent left a pale yellow oil. Addition of Et_2O (1 mL) gave the product (0.12 g, 0.20 mmol, 67%) as ivory crystals. Anal. Calcd for $C_{24}H_{33}ClIrPSi$: C, 47.39; H, 5.47; Cl, 5.83. Found: C, 47.53; H, 5.33; Cl, 6.27.

$[Ir(PPh_2CH_2CH_2SiMe_2)(Ph_2PCH_2CH_2PPh_2)(H)(Cl)]$ (8). diphos (bis(diphenylphosphino)ethane; 32 mg, 0.08 mmol) dissolved in THF (10 mL) was added dropwise to a stirred solution of complex 7 (50 mg, 0.08 mmol) in THF (10 mL). After 5 min the mixture was filtered through an alumina plug (5 × 3 cm^2); removal of solvent gave a yellow oil that was redissolved in a minimum amount of Et_2O, and then hexane was added, precipitating the pale yellow powdery product (35 mg, 0.04 mmol, 50%). Anal. Calcd for $C_{42}H_{45}ClIrP_3Si$: C, 56.14; H, 5.05. Found: C, 55.98; H, 5.40.

$[Ir(PPh_2CH_2CH_2SiMe_2)(PPh_2CH_2PPh_2)(H)(Cl)]$ (9). Addition of dpm (bis(diphenylphosphino)methane; 30 mg, 0.08 mmol) in THF (5 mL) to a solution in THF (10 mL) of complex 7 (50 mg, 0.08 mmol) followed by stirring (5 min) and then removal of solvent afforded a yellow oil. Redissolution in Et_2O (2 mL) and then addition of hexane (15 mL) precipitated the pale yellow product (59 mg, 0.07 mmol, 83%). Anal. Calcd for $C_{41}H_{43}ClIrP_3Si$: C, 55.68; H, 4.90. Found: C, 56.29; H, 5.34.

C. Six-Coordinate Adducts of Complexes 1 and 2. $[Rh(PPh_2CH_2CH_2SiMe_2)_2(Cl)(CN\text{-}t\text{-}Bu)]$ (10). On addition of *t*-BuNC (ca. 6 mg, 0.07 mmol) in THF (1 mL) to a solution of compound 1 (50 mg, 0.07 mmol) in THF (2 mL), an immediate lightening in color was observed and removal of volatiles followed by addition of Et_2O (1 mL) yielded the cream microcrystalline product (51 mg, 0.066 mmol, 91%). Anal. Calcd for $C_{37}H_{49}ClNP_2RhSi_2$: C, 58.15; H, 6.46; N, 1.83. Found: C, 57.28; H, 6.72; N, 1.79.

$[Rh(PPh_2CH_2CH_2SiMe_2)_2(Cl)(CNCMe_2CH_2CMe_3)]$ (11) and $[Rh(PPh_2CH_2CH_2SiMe_2)_2(Cl)(CNCHMe_2)]$ (12). In parallel reactions to that used to obtain compound 10, complex 1 was treated with $Me_3CCH_2CMe_2NC$ or Me_2CHNC to give cream-colored, crystalline products in 89 and 86% yields, respectively. Anal. Calcd for $C_{41}H_{57}ClNP_2RhSi_2$: C, 60.03; H, 7.00; Ni, 1.71. Found: C, 59.94; H, 7.33; N, 1.71. Anal. Calcd for $C_{36}H_{47}ClNP_2RhSi_2$: C, 57.63; H, 6.32; N, 1.87. Found: C, 57.58; H, 6.52; N, 1.84.

$[Ir(PPh_2CH_2CH_2SiMe_2)_2(Cl)(CO)]$ (13). Carbon monoxide gas was bubbled through a solution of compound 2 (50 mg, 0.06 mmol) in THF (5 mL) for 5 min during which time the initially bright yellow color was discharged. Addition of hexane (10 mL) to the resulting clear solution and then concentration afforded the product (46 mg, 0.057 mmol, 88%) as a white powder. Anal. Calcd for $C_{33}H_{40}ClIrOP_2Si_2$: C, 49.63; H, 5.05. Found: C, 49.77; H, 5.46.

$[Ir(PPh_2CH_2CH_2SiMe_2)_2(Cl)(PF_3)]$ (14). Bubbling PF_3 into a solution of complex 2 (50 mg, 0.06 mmol) in THF (5 mL) led to rapid decolorization, and after 5 min the reaction mixture was treated in a manner similar to that described above to give the product (45 mg, 0.053 mmol, 81%) as a white solid. Anal. Calcd for $C_{32}H_{40}ClF_3IrP_3Si_2$: C, 44.77; H, 4.70. Found: C, 44.75; H, 5.08.

$[Ir(PPh_2CH_2CH_2SiMe_2)_2(Cl)(P(OMe)_3)]$ (15). Dropwise addition of

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(13) Auburn, M. J.; Stobart, S. R.; Brennan, E. T.; Cameron, T. S., unpublished results. Crystals of either complex are monoclinic, space group $P2_1/c$ with a = 12.348 (2) Å, b = 15.338 (8) Å, c = 17.277 (6) Å, and β = 96.33 (4)° for M = Rh and a = 12.321 (2) Å, b = 15.358 (2) Å, c = 17.212 (2) Å, and β v 96.30 (2)° for M = Ir. Complete details of the X-ray structure determinations will be published separately.

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Table I. NMR Data for Compounds 1-6

compd[a]	$\delta(\mathrm{SiCH_3})$[b]	$\delta(^{31}\mathrm{P})$[c]
Rh(chel)$_2$Cl (1)	0.43, 0.11	-88.0 ($^1J = 119$ Hz)[d]
Ir(chel)$_2$Cl (2)	0.48, 0.08	-87.5
Rh(chel)$_2$Br (3)	0.43, 0.05	-86.4 ($^1J = 119$ Hz)
Rh(chel)$_2$I (4)	0.44, -0.08	-84.4 ($^1J = 119$ Hz)
Ir(chel)$_2$Br (5)	0.48, 0.01	-86.3
Ir(chel)$_2$I (6)	0.48, -0.14	-85.1

[a] chel = $\mathrm{PPh_2(CH_2)_2SiMe_2}$-. [b] Measured at 250 MHz, $\mathrm{C_6D_6}$ solution, δ 0.00 for $\mathrm{Me_4Si}$. [c] Measured at 24.3 MHz, THF solution, relative to external TMP. [d] ^1J(Rh-P).

a solution of $\mathrm{P(OMe)_3}$ (8 mg, 0.06 mmol) in THF (1 mL) to a stirred solution of complex **2** (50 mg, 0.06 mmol) also in THF (5 mL) resulted in immediate decolorization. Removal of solvent in vacuo and then addition to the residual oil of $\mathrm{Et_2O}$ (1 mL) afforded colorless crystals of the product (45 mg, 0.05 mmol, 78%). Anal. Calcd for $\mathrm{C_{35}H_{49}ClIrO_3P_3Si_2}$: C, 46.99; H, 5.52. Found: C, 47.45; H, 5.46.

$[\overline{\mathrm{Ir(PPh_2CH_2CH_2Si}}\mathrm{Me_2)_2(Cl)(P(OEt)_3)}]$ (16). This adduct was isolated as a colorless, crystalline product (81% yield) by a method identical with that described for the trimethyl phosphite analogue **15**. Anal. Calcd for $\mathrm{C_{38}H_{55}ClIrO_3P_3Si_2}$: C, 48.73; H, 5.92. Found: C, 48.45; H, 5.93.

$[\overline{\mathrm{Ir(PPh_2CH_2CH_2Si}}\mathrm{Me_2)_2(Cl)(CN\text{-}\mathit{t}\text{-}Bu)}]$ (17). Complex **2** (50 mg, 0.06 mmol) was dissolved in THF (6 mL), and *t*-BuNC (6 mg, 0.06 mmol) was added drop-by-drop with stirring. After 5 min, solvent was removed from the colorless mixture, leaving an oil to which was added $\mathrm{Et_2O}$ (1 mL). The product (53 mg, 0.062 mmol, 95%) was obtained as colorless crystals. Anal. Calcd for $\mathrm{C_{37}H_{49}ClIrNP_2Si_2}$: C, 52.06; H, 5.79; N, 1.64. Found: C, 51.23; H, 5.61; N, 1.60.

$[\overline{\mathrm{Ir(PPh_2CH_2CH_2Si}}\mathrm{Me_2)_2(Cl)(CNCMe_2CH_2CMe_3)}]$ (18) and $[\overline{\mathrm{Ir(PPh_2CH_2CH_2Si}}\mathrm{Me_2)_2(Cl)(CNCHMe_2)}]$ (19). These compounds were prepared by a procedure similar to that described above for complex **17**, by using $\mathrm{Me_3CCH_2CMe_2NC}$ or $\mathrm{Me_2CHNC}$, respectively. Yields of the colorless crystalline products were essentially quantitative. Anal. Calcd for $\mathrm{C_{41}H_{57}ClIrNP_2Si_2}$: C, 54.13; H, 6.32; N, 1.53. Found: C, 54.09; H, 6.39; N, 1.53. Anal. Calcd for $\mathrm{C_{36}H_{47}ClIrNP_2Si_2}$: C, 51.50; H, 5.64; N, 1.67. Found: C, 50.37; H, 5.42; N, 1.60.

D. Related Six-Coordinate Ir(III) Complexes. $[\overline{\mathrm{Ir(PPh_2CH_2CH_2Si}}\mathrm{Me_2)_2(CO)_2}]\mathrm{BF_4}$ (20). Under an atmosphere of CO gas a solution of $\mathrm{AgBF_4}$ (13 mg, 0.07 mmol) in acetone (5 mL) was added to a stirred solution of complex **2** (50 mg, 0.06 mmol), also in acetone (10 mL). After 30 min, the cloudy brown reaction mixture was filtered through a 5 × 3 cm^2 column packed with Celite, and then solvent was removed, leaving an oily residue that was dissolved in a minimum amount of $\mathrm{CH_2Cl_2}$. On addition of hexane the product (42 mg, 0.047 mmol, 73%) was precipitated as a white powder. Anal. Calcd for $\mathrm{C_{34}H_{40}BF_4IrO_2P_2Si_2}$: C, 46.52; H, 4.59. Found: C, 45.42; H, 4.14.

$[\overline{\mathrm{Ir(PPh_2CH_2CH_2Si}}\mathrm{Me_2)_2(H)(CO)}]$ (21). Method A. A suspension of complex **13** (52 mg, 0.065 mmol) in 100% EtOH (15 mL) was stirred for 24 h after addition of excess $\mathrm{NaBH_4}$ in 10 mL of EtOH. Replacement of EtOH by benzene (25 mL) was followed by stirring (30 min). Subsequent filtration and slow removal of solvent precipitated the product (37 mg, 0.048 mmol, 74%) as a cream-colored powder. Anal. Calcd for $\mathrm{C_{33}H_{41}IrOP_2Si_2}$: C, 51.88; H, 5.41. Found: C, 51.92; H, 5.54.

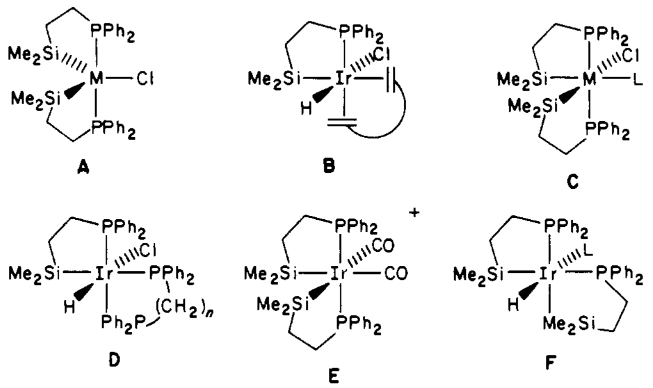
Method B. To a stirred suspension of compound **2** (50 mg, 0.06 mmol) in 100% EtOH (10 mL) was added excess $\mathrm{NaBH_4}$ in 5 mL of EtOH. After 60 min, the EtOH was removed, THF (10 mL) was added, and the resulting mixture was filtered to give a pale brown solution into which was bubbled CO gas (5 min). Recovery from $\mathrm{Et_2O}$/hexane afforded a product identical (IR, NMR) with that obtained from method A.

$[\overline{\mathrm{Ir(PPh_2CH_2CH_2Si}}\mathrm{Me_2)_2(H)(CN\text{-}\mathit{t}\text{-}Bu)}]$ (22). Compound **2** was dissolved in THF (5 mL), and excess $\mathrm{LiAlH_4}$ in THF (1 mL) was added with stirring. After 5 min, introduction of excess *t*-BuNC was followed by stirring for a further 20 h. Filtration through a plug of alumina and then removal of solvent in vacuo gave a grayish residue that was extracted into $\mathrm{Et_2O}$ (1 mL). Slow addition of hexane precipitated the white, powdery product (36 mg, 0.044 mmol, 67%). Anal. Calcd for $\mathrm{C_{37}H_{50}IrNP_2Si_2}$: C, 54.25; H, 6.15; N, 1.71. Found: C, 53.75; H, 6.07; N, 1.91.

Results

Addition of the modified silane[9] $\mathrm{Ph_2P(CH_2)_2SiMe_2H}$ to THF solutions of the chloro-bridged dimers $\mathrm{[M(COD)Cl]_2}$ (M = Rh, Ir; COD = cycloocta-1,5-diene) resulted in either case in gas evolution accompanied by formation in good yield of a bright yellow, air-stable crystalline product. IR and ^{1}H NMR spectra for the two compounds were virtually identical and showed no evidence for the presence of M–H bonds. On the basis of microanalytical figures together with the resolution of two $\mathrm{SiCH_3}$ environments (Table I) but only a single ^{31}P resonance (coupled to ^{103}Rh, 100%, for the rhodium-containing species), a mononuclear 5-coordinate structure (**A**; Chart I) seemed likely. Additional support for this conclusion was provided by the characteristic reactivity of the iridium complex (see below), and the formulation $[\overline{\mathrm{M(PPh_2CH_2CH_2Si}}\mathrm{Me_2)_2Cl}]$ (**1**, M = Rh; **2**, M = Ir) was subsequently confirmed unequivocally by a single-crystal X-ray structure determination for each compound.[13] The reaction may thus be represented as in eq 1. It was also found that slow addition

Chart I



$$\mathrm{[M(COD)Cl]_2 + 4PPh_2(CH_2)_2SiMe_2H =} \\ 2[\overline{\mathrm{M(PPh_2CH_2CH_2Si}}\mathrm{Me_2)_2Cl] + 2COD + 2H_2} \qquad (1)$$

of only 2 mol equiv of the silane to $\mathrm{[M(COD)Cl]_2}$ under identical conditions afforded for M = Rh a mixture of compound **1** and unreacted dimer. By contrast for M = Ir, no initial gas evolution was observed and a further new product proved to be isolable, the ivory-yellow crystalline $[\overline{\mathrm{Ir(PPh_2CH_2CH_2Si}}\mathrm{Me_2)(COD)(H)(Cl)}]$ (**7**): IR (cm^{-1}) ν(Ir–H) 2239; ^{1}H NMR δ(IrH) -16.91. These values are respectively at high energy and to high field in relation to established ranges[8,15] in other hydridoiridium(III) species, consistent with H trans to a weakly trans-influencing ligand[15] like Cl; with this assumption the constraints associated with the two chelating ligands therefore imply a stereochemistry (**B**) for compound **7**. This structural assignment has also been confirmed crystallographically.[16]

When either complex **1** or **2** was stirred with excess sodium halide in acetone, halide ion exchange occurred (eq 2) to give the

$$[\overline{\mathrm{M(PPh_2CH_2CH_2Si}}\mathrm{Me_2)_2Cl]} \xrightarrow{\mathrm{X^-}} \\ [\overline{\mathrm{M(PPh_2CH_2CH_2Si}}\mathrm{Me_2)_2X]} \qquad (2)$$

$$\mathrm{M = Rh, Ir;\ X = Br, I}$$

corresponding bromo and iodo complexes **3** and **5**, and **4** and **6**, respectively. IR spectra contained absorptions attributable to characteristic vibrations of the chelating (phosphinoethyl)silyl ligands but were otherwise uninformative; NMR parameters for all six compounds were virtually identical (Table I), with the ^{31}P resonance shifting slightly to lower field along the series I < Br < Cl.

A more dramatic effect was distinguishable on treatment of solutions of the iridium complex **2** with neutral ligands including CO, $\mathrm{PF_3}$, trialkyl phosphites, or alkyl isocyanides, i.e. those capable

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Table II. Spectral Data for 6-Coordinate Adducts **10–20**

compd[a]	$\delta(SiCH_3)$[b]	$\delta(^{31}P)$[c]	${}^2J(P_A-P_B)$/ Hz	IR/cm^{-1}
$[Rh(chel)_2(Cl)(CN\text{-}t\text{-}Bu)]$ (**10**)	0.33, −0.10, −0.26, −0.50	−95.5, −85.1	343[d]	2155[e]
$[Rh(chel)_2(Cl)(CNCMe_2CH_2CMe_3)]$ (**11**)	0.79, −0.05, −0.26, −0.47	−96.1, −86.5	343[d]	2130[e]
$[Rh(chel)_2(Cl)(CNCHMe_2)]$ (**12**)	0.33, −0.01, −0.26, −0.59	−95.0, −85.4	343[d]	2156[e]
$[Ir(chel)_2(Cl)(CO)]$ (**13**)	0.06, −0.07, −0.47, −0.71	−127.2, −110.9	298	2002[f]
$[Ir(chel)_2(Cl)(PF_3)]$ (**14**)	0.12, 0.09,[g] −0.47, −0.56[h]	−138.1, −121.5[i]	283	850 br[j]
$[Ir(chel)_2(Cl)(P(OMe)_3)]$ (**15**)	0.35, −0.08,[k] −0.58,[l] −0.65	−133.4[m,n]		
$[Ir(chel)_2(Cl)(P(OEt)_3)]$ (**16**)	0.38, −0.08,[o] −0.64,[p] −0.67	−133.4[m,q]		
$[Ir(chel)_2(Cl)(CN\text{-}t\text{-}Bu)]$ (**17**)	−0.06, −0.26, −0.50, −0.70	−130.2, −112.5	325	2150[e]
$[Ir(chel)_2(Cl)(CNCMe_2CH_2CMe_3)]$ (**18**)	−0.06, −0.23, −0.55, −0.67	−130.8, −114.1	326	2138[e]
$[Ir(chel)_2(Cl)(CNCMe_2)]$ (**19**)	−0.03, −0.31, −0.50, −0.67	−129.2, −112.8	326	2151[e]
$[Ir(chel)_2(CO)_2]BF_4$ (**20**)	0.24, −0.32	−117.6		2078, 2040,[f] 1050 br[r]

[a] chel = $PPh_2(CH_2)_2SiMe_2$–. [b] Measured at 250 MHz; $CDCl_3$ (**10–13**, **18**, **19**), CD_2Cl_2 (**14**, **16**, **17**, **20**), or THF-d_8 (**15**); δ 0.00 for Me_4Si. [c] $\delta(P_A)$, $\delta(P_B)$ of $[(P_APh_2CH_2CH_2SiMe_2)M(P_BPh_2CH_2CH_2SiMe_2)(Cl)(Y)]$ measured at 24.3 MHz, THF solution, relative to external TMP. [d] ${}^1J(Rh-P) = 111$ Hz. [e] $\nu(C{\equiv}N)$. [f] $\nu(C{\equiv}O)$. [g] ${}^4J(H-C-Si-Ir-P) = 3.5$ Hz. [h] ${}^4J(H-P) = 2.7$ Hz. [i] $\delta(P_CF_3)$ −50.4, ${}^2J(P_C-P_{A,B}) = 35$ Hz, ${}^1J(P_C-F) = 1391$ Hz. [j] $\nu(P-F)$. [k] ${}^4J(H-P) = 3.5$ Hz. [l] ${}^4J(H-P) = 2.0$ Hz. [m] $\delta(P_A)$, $\delta(P_B)$ coincident. [n] $\delta(P_D(OMe)_3)$ −45.9, ${}^2J(P_D-P_{A,B}) = 33$ Hz. [o] ${}^4J(H-P) = 3.5$ Hz. [p] ${}^4J(H-P) = 2.1$ Hz. [q] $\delta(P_E(OEt)_3)$ −47.9, ${}^2J(P_E-P_{A,B}) = 34$ Hz. [r] $\nu(B-F)$.

Table III. Spectral Data for Hydrido-Rhodium(III) and -Iridium(III) Complexes

compd[a]	IR[b]/cm^{-1}	$\delta(^{31}P)$[c]	$\delta(SiCH_3)$[d]	$\delta(MH)$[d]
$[Ir(chel)(COD)(H)(Cl)]$ (**7**)	2239	−103.4	0.70, 0.41	−16.91[e]
$[Ir(chel)(diphos)(H)(Cl)]$ (**8**)	2210	−109.2,[f] −122.9[g]	0.53,[h] 0.11[i]	−21.01[j]
$[Ir(chel)(dpm)(H)(Cl)]_x$ (**9**)	2194	−104.1,[k] −175.6,[l] −191.5[m]	0.69,[n] 0.40[o]	−19.40[p]
$[Ir(chel)_2(H)(CO)]$ (**21**)	2056, 1949[q]	−117.1	0.98,[r] 0.89[s]	−10.47[t]
$[Ir(chel)_2(H)(CN\text{-}t\text{-}Bu)]$ (**22**)	2130,[u] 2079	−116.3	0.47,[v] 0.35[w]	−12.76[x]
$[Rh(chel)_2H]$ (**23**)	nm[y]	−72.5[z]	0.20	−9.78[aa]
$[Ir(chel)_2H]$ (**24**)	nm	−99.5	0.29	−13.13[bb]

[a] chel = $PPh_2(CH_2)_2SiMe_2$–; COD = cycloocta-1,5-diene; diphos = $PPh_2(CH_2)_2PPh_2$; dpm = $PPh_2CH_2PPh_2$; $x = 1, 2$ (see text). [b] KBr pellet, $\nu(Ir-H)$ unless indicated otherwise. [c] Measured at 24.3 MHz, THF, relative to external trimethyl phosphate. [d] Measured at 250 MHz; C_6D_6 (**7–9**, **21**, **23**, **24**), CD_2Cl_2 (**22**); δ 0.00 for Me_4Si. [e] ${}^2J(H-P) = 10.6$ Hz. [f] P_A(chel). [g] P_B(diphos); ${}^2J(P_A-P_B) = 13$ Hz. [h] ${}^4J(H-C-Si-Ir-P) = 2.6$ Hz. [i] ${}^4J(H-P) = 1.7$ Hz. [j] ${}^2J(H-P) = 12.9, 8.0$ Hz. [k] P_A(chel). [l] P_B(dpm); ${}^2J(P_A-P_B) = 341$ Hz. [m] P_C(dpm); ${}^2J(P_A-P_C) = 22$ Hz, ${}^2J(P_B-P_C) = 17.5$ Hz. [n] ${}^4J(H-P) = 2.1$ Hz. [o] ${}^4J(H-P) = 2.9$ Hz. [p] ${}^2J(H-P) = 13.5, 5.0$ Hz. [q] $\nu(CO)$. [r] ${}^4J(H-P) = 1.1$ Hz. [s] ${}^4J(H-P) = 1.9$ Hz. [t] ${}^2J(H-P) = 17.9$ Hz. [u] $\nu(CN)$. [v] ${}^4J(H-P) = 1.2$ Hz. [w] ${}^4J(H-P) = 1.9$ Hz. [x] ${}^2J(H-P) = 16.0$ Hz. [y] nm = not measured. [z] ${}^1J(P-Rh) = 96$ Hz. [aa] ${}^1J(H-Rh) = 22$ Hz, ${}^2J(H-P) = 16$ Hz. [bb] ${}^2J(H-P) = 13$ Hz.

of functioning as strong π acceptors: instantaneous decolorization was apparent due to formation of white or colorless octahedral adducts **13–19** (eq 3) with L = CO, PF_3, $P(OMe)_3$, $P(OEt)_3$,

$$[Ir(PPh_2CH_2CH_2SiMe_2)_2Cl] + L = [Ir(PPh_2CH_2CH_2SiMe_2)_2(Cl)(L)] \quad (3)$$

t-BuNC, $Me_3CCH_2CMe_2NC$, or Me_2CHNC, respectively. A corresponding reaction with PEt_3 was slow, giving an indeterminate mixture of products, while PPh_3 did not appear to react at all. The rhodium analogue **1** was less reactive than **2** under similar conditions, but cream-colored 6-coordinate adducts were obtained in excellent yield from experiments using equal mole ratios of the isocyanides, compounds **10–12**. Spectroscopic data for all these complexes are collected in Table II and are consistent with a common stereochemistry (**C**) throughout. In particular, in most examples trans inequivalent phosphorus atoms gave rise to characteristic[8,17] AB patterns in ^{31}P NMR spectra with appropriately large values of ${}^2J(P-P)$ (>280 Hz); while as demanded by the asymmetry of the (enantiomeric) arrangement (**C**), the ^1H NMR spectrum for each compound included four well-resolved diastereotopic silyl methyl resonances near δ 0. Two out of the latter were split by long-range coupling to P in the phosphine adducts **14–16**, where cis coupling ($J = 35$ Hz; Table II) with the chelate PPh_2 groups was also clearly evident although in the phosphite complexes (**15**, **16**) resonant frequencies of the P_A,P_B nuclei appear to be accidentally degenerate.

The reactivity of compound **7** and in particular its intermediacy in eq 1 was further corroborated by COD displacement using diphos or dpm (eq 4). The structural identity of the pale yellow

$$[Ir(PPh_2CH_2CH_2SiMe_2)(COD)(H)(Cl)] \xrightarrow{\text{chel}} [Ir(PPh_2CH_2CH_2SiMe_2)(chel)(H)(Cl)] + COD \quad (4)$$

chel = diphos, dpm

products **8** and **9** was established with IR and NMR spectroscopy (Table III); like the precursor **7**, both complexes showed $\nu(Ir-H)$ at high energy with large negative shifts for δ(IrH), ca. −20 ppm, suggesting[8,15] a trans relationship between H and Cl. Multiplicity of the IrH resonance (250 MHz) for the diphos compound **8**, apparent doublet of triplets with two cis spin-coupling constants to P (12.9, 8.0 Hz), was irreconcilable with the ^{31}P NMR spectrum at 24.3 MHz (Table III), which consisted of a deceptively simple, weakly coupled doublet (−109 ppm) and triplet (−123 ppm) pattern in a 2:1 ratio; however, at 101.3 MHz (Bruker WM250 spectrometer) the signals were further split, that at higher frequency being recognizable as a limiting AB pattern, doublet of doublets symmetrically flanked by weak but distinct outer lines, while the triplet was perturbed by superimposition of an additional small *J*. Analysis of this ABX spectrum yielded the following parameters: $\delta(P_A)$ −103.8, $\delta(P_B)$ −105.0, $\delta(P_C)$ −117.9 ppm; ${}^2J_{AB} = 336$ Hz, ${}^2J_{AC} = 15$ Hz, ${}^2J_{BC} = 10$ Hz. A stereochemistry (**D**), i.e. the analogue of configuration **B** for complex **7**, may therefore be unequivocally assigned to **8**, accidental coincidence existing at low applied magnetic field between frequencies for one P atom in the diphos chelate and that of the (phosphinoethyl)silyl group. Compound **9** also exhibited an ABX pattern in the ^{31}P NMR spectrum (Table III), but in this case the AB part was unmistakable, approaching a limit in the opposite sense, i.e. large $|\delta_A - \delta_B|$ (70 ppm at 24.3 MHz vs. $J_{AB} = 341$ Hz). Although a

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disposition in which P nuclei are trans with a third P mutually cis is conclusively established, neither this result nor other spectroscopic data offer any immediate distinction between a chelate structure for complex **9** resembling **B** or **D** or a binuclear arrangement possessing bridging dpm ligands. However, the second of these alternatives was ruled out by osmometric molecular weight determination, giving M_r(obsd) = 917 compared with M_r = 884.4 required for $x = 1$ in Table III.

Attempts to displace Cl in compound **2** using AgBF_4 in acetone solution resulted only in gradual decomposition when conducted in a N_2 atmosphere, but on replacement of the latter with CO gas a further octahedral species was obtained, the cationic iridium complex $[\overline{\text{Ir}(\text{PPh}_2\text{CH}_2\text{CH}_2\text{Si}}\text{Me}_2)_2(\text{CO})_2]\text{BF}_4$ (**20**). A single ^{31}P resonance together with only two distinguishable silyl methyl environments and two IR-active ν(CO) absorptions support a *cis*-dicarbonyl formulation (**E**). Treatment of complexes **1** or **2** with NaBH_4 or LiAlH_4 in EtOH or THF as solvent generated the corresponding hydrides $[\overline{\text{M}(\text{PPh}_2\text{CH}_2\text{CH}_2\text{Si}}\text{Me}_2)_2\text{H}]$ (**23**, M = Rh; **24**, M = Ir), characterized in situ by NMR spectroscopy (Table III) although efforts at isolation from solution were unsuccessful. The iridium hydride **24** however could be trapped as its CO or *t*-BuNC adducts **21** and **22**, respectively, the first of these also being accessible via NaBH_4 reduction of compound **13**. NMR spectra of complexes **21** and **22** (Table III) are consistent with coplanarity of the chelating (phosphinoethyl)silyl ligands with cis equivalent phosphorus atoms, i.e. configuration **F**.

Discussion

It is evident from our earlier reports that introduction[9] of a phosphino function into an organosilane structure lends new versatility to the hydrosilylation reaction as a route to transition-metal silyl complexes.[7,8] Considerations that may account for this effect include (a) ligand displacement by the phosphorus atom, leading to attachment at a coordinatively unsaturated metal center that renders subsequent Si–H addition intramolecular and (b) kinetic stability of the chelate arrangement[7a] adopted by the (phosphinoethyl)silyl ligand. The importance of the second of these factors is emphasized in the reaction represented by eq 1, from which rhodium- or iridium-containing products proved to be accessible with equal facility. Such a situation is unprecedented in the sense that simple silylrhodium complexes have hitherto been isolated only under special conditions[2,5,18] and apparently without exception dissociate in solution through reductive Si–Rh bond cleavage at or near ambient temperature.[18] So far as we are aware therefore compound **1** provides the first properly characterized example of a bis(silyl)rhodium configuration; that this complex is stable in solution for prolonged periods is demonstrated by the conditions under which the halide ion exchange reactions of eq 2 were conducted.

Formation of the rhodium complex **1** from $[\text{Rh(COD)Cl}]_2$ occurred with no evidence (^{31}P NMR spectroscopy) for any intermediate species, but in the corresponding iridium chemistry careful control of the reaction stoichiometry enabled the precursor **7** to the analogue **2** of **1** to be recovered in excellent yield. The reactivity of compound **7** sheds further light on the degree of stabilization offered by the chelating function of the "anchored" silyl ligand: displacement of COD from **7** by $\text{Ph}_2\text{PCH}_2\text{CH}_2\text{SiMe}_2\text{H}$ to afford compound **2** was found to be qualitatively identical, in terms of rate and progress to completion, with similar reactions with the α,ω-diphosphines diphos or dpm, use of which generated two further new products **8** and **9**, respectively (cf. eq 4).

Spectroscopic data (Table III) established that each of the mixed bis(chelate) complexes **8** and **9** is octahedral as expected for Ir(III), the dpm product **9** therefore joining a small but growing group of compounds in which this bis(phosphine) coordinates as a chelating[19] (rather than bridging) ligand. By contrast the bis[(phosphinoethyl)silyl] complexes **1** and **2** exhibit NMR properties (Table I) consistent with a 5-coordinate geometry (equivalent P atoms with diastereotopic silyl methyl groups), the detail of which, resolved with X-ray crystallography,[13] is most unusual. Thus, for M = Ir (compound **2**), the disposition of the chelating ligands about the metal center places the two P atoms trans with the Si atoms adjacent to one another, but while the P(1)–Ir–P(2) axis is almost exactly linear [177.9 (4)°], each of the chelate "bite" angles and Si(1)–Ir–Si(2) are[20] slightly less than 90°. The Cl atom lies in the IrSi_2 plane, but with Ir–Cl rather long;[20] the Si–Ir–Cl angles are extraordinary, at 139.7 (4)° for Si(1) and 133.5 (4)° for Si(2). This arrangement, which is propelloid along the Ir–Cl axis and therefore dissymmetric (point group C_2), may best be described as follows: the two chelate units span two edges of an octahedron occupying four noncoplanar vertices while the fifth ligand (Cl) sits approximately midway between the two remaining, adjacent, vacant vertices. There is no close relationship with either of the classic 5-coordinate stereochemistries,[21] nor with the configuration intermediate between these two typified[22] by the solid-state structure of the fluxional complex $(\text{PMe}_2\text{Ph})_2\text{Ir(NBD)(SnCl}_3)$; unlike the latter, compound **2** maintains a rigid geometry in solution (^{31}P NMR spectrum invariant in the range −70 to +80 °C). The rhodium congener **1**, which is isomorphous with **2**, possesses an almost identical structure.

For M = Ir the coordinatively unsaturated configuration (A) is subject to facile reaction with a range of neutral molecules, completing octahedral coordination around the metal center through formation of a single isomer with sterochemistry C. Adduction of CO to the 5-coordinate compounds $\text{IrHCl(SiX}_3)(\text{PPh}_3)_2$ (X = Cl, OEt) has been noted[23] previously but generates mixtures of isomers. Under similar conditions however even the most stable Rh analogues lose silane, so that uptake of isocyanide (RNC: R = *t*-Bu, $\text{Me}_3\text{CCH}_2\text{CMe}_2$, CHMe_2) by compound **1** presents a unique parallel with the behavior of the congeneric silyliridium species. The octahedral geometry of adducts **10**–**12** therefore illustrates further the stabilizing effect of chelate attachment of the silyl fragment.

Compounds **10**–**19** (configuration C) are chiral like **1**–**6** (configuration A), but unlike these latter are asymmetric rather than dissymmetric and accordingly exhibit nonequivalent ^{31}P resonances and four (rather than two) diastereotropic silyl methyl signals in ^{1}H NMR spectra (Table II). The influence of chirality at M is also transmitted to the more distant *i*-Pr methyl groups in the isopropyl isocyanide adducts **12** and **19**, for both of which ^{1}H NMR spectra contain two doublets near δ 1.1 separated by a diastereotopic shift of ca. 0.1 ppm. This observation is important for M = Rh since it confirms the stability of the octahedral structure for **12**, ruling out rapid dissociative exchange of L in configuration C. The 6-coordinate silylrhodium complexes **10**–**12** show a considerable chemical shift (ca. 30 ppm; Table II) in δ (^{31}P) to low frequency of iridium analogues **17**–**19**, unlike the 5-coordinate species $\overline{\text{M}(\text{PPh}_2\text{CH}_2\text{CH}_2\text{Si}}\text{Me}_2)_2\text{X}$ (i.e., compounds **1**–**6**) for which ^{31}P resonant frequencies vary very little (Table I) with M or indeed with X.

Attempts to generate a cationic species by chloride ion displacement from the iridium complex **2** led only to decomposition in acetone or THF solution in the absence of added ligand, but under a CO atmosphere treatment of **2** with AgBF_4 led to formation of a tetrafluoroborate salt **20**, assigned the *cis*-dicarbonyl structure **E** (i.e., the analogue of C) on the basis of two strong ν(CO) absorptions (IR) and the presence of equivalent phosphorus nuclei (^{31}P NMR; Table II). Displacement of chloride by hydride ion (NaBH_4/EtOH or LiAlH_4/THF) afforded the hydridometal(III) complexes $\overline{\text{M}(\text{PPh}_2\text{CH}_2\text{CH}_2\text{Si}}\text{Me}_2)_2\text{H}$ (**23**, M = Rh; **24**, M = Ir) characterized in solution by NMR measurements

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(Table III). These compounds decomposed on attempted recovery from solution, and their structures remain uncertain; however, the Ir species afforded the stable octahedral adducts **21** and **22** from reactions with excess CO or *t*-BuNC, respectively. That these products were formed with a new but again specific octahedral stereochemistry (**F**) was apparent from consideration of pertinent NMR data (Table III): H is coupled to equivalent P atoms with a small J (16 Hz) indicative of a mutually cis relationship while long-range coupling (^4J) between P and each of two distinguishable types of silyl methyl proton was resolvable. Comparisons among spectroscopic data for the series of hydridoiridium(III) complexes listed in Table III are of some further interest in that they reinforce a set of useful arguments assembled[24] recently by Olgemöler and Beck. Thus, while the well-established[8,15] and concerted effect on ν(Ir–H) and δ(IrH) of strongly trans-influencing ligands is exemplified by values for compounds **21** and **22**, the absence of a similar systematic dependence on donor properties of ligands cis to H is confirmed since for compounds **7–9** ν(Ir–H) varies as COD > diphos > dpm while δ(IrH) is shifted as diphos > dpm > COD.

An unusual degree of selectivity is apparent in the formation of the octahedral (phosphinoethyl)silyl complexes **10–22** as single isomers, most of which possess structures **C** or **F**, a situation that parallels the adherence to a common geometry of enantiomeric or diastereoisomeric products[8] of the addition to *trans*-[Ir(CO)(Cl)(PPh$_3$)$_2$] of Ph$_2$PCH$_2$CH$_2$SiR^{1}R^{2}H (R^1, R^2 = Me, Ph; R^1 = Me, R^2 = Ph). Considered together with the regiospecificity[1] of the addition of Ph$_2$PCH$_2$CH$_2$SiMe$_2$H to IrH(CO)(PPh$_3$)$_3$ and the unexpected irregularity of the 5-coordinate arrangement around the central metal atom in compounds **1** and **2**, these observations suggest that the incipiency of bidentate complexation by the PSi ligand exerts a powerful orientating effect at the metal center that is translated into control over ligand addition/substitution behavior at the resulting chelated M(III) site. It seems plausible that these sterochemical predilections may be a consequence of the unusual electronic character of silyl ligands, which on the basis of structural and spectroscopic evidence have come to be regarded[25] as very strongly electron releasing.

Complexes of configurations **A**, **C**, or **E** exhibit trans P and cis Si atoms while those with structure **F** are all-cis within the planar framework. In no instance, however (here or elsewhere[1,2,7,8]), have two silyl groups been found trans to each other at a single metal center, a situation that would be predicted if relevant arguments[25] regarding trans-influence are correct. Likewise in the bis(chelate) systems (**C** and **F**), a change in geometry accompanies introduction of two (rather than one) strongly trans-influencing unidentate ligands; thus, the same isomer (structure **F**) of the hydridocarbonyliridium(III) complex **21** is isolated regardless of the order in which the required synthetic steps (NaBH$_4$ reduction, CO addition) are applied. A further indication of the extent to which bond weakening occurs trans to silicon is provided by recent NMR evidence[26] for intramolecular ligand exchange trans to SiR$_3$ in *cis*-[PtH(SiR$_3$)(PPh$_3$)$_2$] (R = Ph, *p*-ClC$_6$H$_4$, *p*-MeC$_6$H$_4$). While such a trans-labilizing effect has yet to be exploited in relation to catalytic substrate activation, stabilization by chelate incorporation of bonds from silicon to reactive transition-metal centers may allow this idea to be examined.

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Registry No. **1**, 93842-29-6; **2**, 93842-30-9; **3**, 93842-31-0; **4**, 93842-32-1; **5**, 93842-33-2; **6**, 93842-34-3; **7**, 93842-35-4; **8**, 93842-36-5; **9**, 93842-37-6; **10**, 93842-38-7; **11**, 93842-39-8; **12**, 93842-40-1; **13**, 93842-41-2; **14**, 93842-42-3; **15**, 93842-43-4; **16**, 93842-44-5; **17**, 93842-45-6; **18**, 93842-46-7; **19**, 93842-47-8; **20**, 93842-49-0; **21**, 88453-33-2; **22**, 93842-50-3; **23**, 93842-51-4; **24**, 93842-52-5; [Rh(COD)Cl]$_2$, 12092-47-6; [Ir(COD)Cl]$_2$, 12112-67-3.

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Contribution from the Department of Chemistry,
The University of Newcastle, N.S.W. 2308, Australia

Solvolysis Kinetics of Pentaammine(trifluoromethanesulfonato-*O*) Complexes of Cobalt(III), Rhodium(III), and Iridium(III)

GEOFFREY A. LAWRANCE

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Rate constants for solvolysis of [M(NH$_3$)$_5$(OSO$_2$CF$_3$)](CF$_3$SO$_3$)$_2$ (M = Co, Rh, Ir) have been determined in a range of pure solvents where reaction proceeds smoothly to yield solvent pentaammine complexes (water, methanol, dimethyl sulfoxide, dimethylformamide, acetonitrile, and pyridine for all three metals and the additional solvents ethanol, formamide, methylformamide, and trimethyl phosphate for cobalt). Rate ratios for Co:Rh:Ir at 25 °C vary a little with solvent, but approximate 90:40:1. Activation enthalpies and entropies have been determined in each case. For all solvents except water, the progressively slower rate constant from Co to Rh to Ir arises in the activation entropy term. For water, the principal variation is in the activation enthalpy, suggesting a mechanistic uniqueness for this solvent. The activation entropies are invariably negative, consistent with an associative (I$_a$) mechanism or a dissociative (I$_d$) mechanism with appreciable charge separation in the transition state with concomitant increase in solvent electrostriction. Various relationships of rate constant and solvent properties have been probed, and no simple uniparameter relationship exists, although multiparameter relationships may apply.

Introduction

Studies of reaction mechanisms in coordination chemistry have been extensive in recent decades.[1–4] Of factors that may affect rates and mechanisms of reaction, the role of the solvent has been one of the lesser studied, although not entirely neglected. Of those studies reported, mixed aqueous–organic solvent systems have predominated,[1,5–10] in part as a consequence of the solubility properties of ionic complexes.

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