# Transition-Metal (Phosphinoalkyl)silanols: Ligand Functionality Designed for Surface Attachment. Chemistry of P-Coordinated ((Diphenylphosphino)alkyl)dimethylsilanol Complexes of Ruthenium, Rhodium, and Iridium

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*Received February 25, 1993**

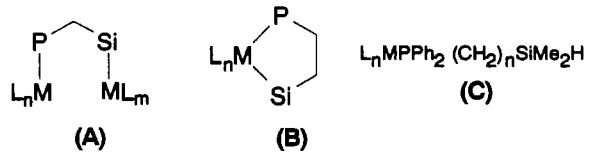
The Si–C bond in the phosphinomethysilane $Ph_2PCH_2SiMe_2H$ (**1**) is very sensitive to cleavage by $H_2O$, MeOH, or HCl, affording $(Me_2SiO)_2O$, $SiHMe_2(OMe)$, or $SiHMe_2Cl$ respectively, together with $PPh_2Me$. By contrast, the ethyl congener $Ph_2PCH_2CH_2SiMe_2H$ (**2**) of **1**, which is unaffected by $H_2O$ or MeOH, gives $Ph_2PCH_2CH_2SiMe_2Cl$ on treatment with HCl. The phosphonium salts $[Ph_2P(Me)(CH_2)_nSiMe_2H][I]$ (**3**, $n = 1$; **4**, $n = 2$) are formed quantitatively on treatment of **1** or **2** with MeI. A number of transition metal complexes react with silanes **1** and **2** to yield products in which the Si–H bond remains intact: thus $[Ru(\eta^6\text{-arene})(\mu\text{-Cl})Cl]_2$ with **1** or **2** gives $[Ru(\eta^6\text{-arene})Cl_2(L)]$ (arene = *p*-cym [cym = cymene, *i.e.* isopropyltoluene], **5**, L = **1**; arene = *p*-cym, **6**, L = **2**; arene = $C_6Me_6$, **7**, L = **2**; arene = $C_6H_6$, **8**, L = **2**), $[RuCpCl(PPh_3)_2]$ (Cp = $\eta^5$-$C_5H_5$) gives $[RuCpCl(PPh_3)(L)]$ (**9**, L = **1**; **10**, L = **2**), $[Ru_2Cp_2(C_2Ph_2)(CO)_3]$ with **2** gives $[Ru_2Cp_2(CO)_3(PPh_2CH_2CH_2SiMe_2H)]$ (**11**), and $[M(\eta^5\text{-}C_5Me_5)(\mu\text{-Cl})Cl]_2$ with **2** gives $[M(\eta^5\text{-}C_5Me_5)Cl_2(PPh_2CH_2CH_2SiMe_2H)]$ (**12**, M = Rh; **13**, M = Ir). The Si–H bonds in complexes **6** and **12** are sensitive to hydrolysis that effects transformation of the monodentate phosphinoalkylsilane into a "dangling" silanol, *i.e.* $[Rh(\eta^5\text{-}C_5Me_5)Cl_2(PPh_2CH_2CH_2SiMe_2OH)]$ (**14**) (from **12**), for which the X-ray crystal structure is described, and $[Ru(\eta^6\text{-cym})Cl_2(PPh_2CH_2CH_2SiMe_2OH)]$ (**15**) (from **6**). Nucleophilic displacement at Si in compounds **5** and **6** is general so that treatment of **5** with HX gives $[Ru(\eta^6\text{-cym})Cl_2(PPh_2CH_2SiMe_2X)]$ (**16**, X = Cl; **18**, X = OMe; **21**, X = $O(CH_2)_{13}CH_3$) while the products $[Ru(\eta^6\text{-cym})Cl_2(PPh_2CH_2CH_2SiMe_2X)]$ (**17**, X = Cl; **19**, X = OMe; **20**, X = OEt; **22**, X = $OCH_2CH_2C(Me)=CH_2$; **23**, X = $OC_{11}H_{17}$) are formed from **6**. The unusual reactivity of the Si–H bond in this family of complexes is further illustrated by the isolation of $[Ru(\eta^6\text{-cym})Cl(PPh_2CH_2CH_2SiMe_2F)_2]$ $[PF_6]$ (**24**) from a reaction in which the only source of F is the classically unreactive $PF_6^-$ ion.

## Introduction

Phosphinoalkylsilanes are bifunctional ligand precursors in which a reactive silane center is connected to one or more organophosphine donor sites through a backbone of methylene units.[1,2] Two prototypal members of this now extensive[1-3] family of related compounds are ((diphenylphosphino)methyl)dimethylsilane (**1**) and its phosphinoethyl congener **2** [i.e., $Ph_2P(CH_2)_nSiMe_2H$; $n = 1$ or 2, respectively]. Oxidative addition of the Si–H bond in such silanes to low valent transition metal centers leads to (phosphinoalkyl)silyl ("PSi") ligands bound in either bridged binuclear[4] ($n = 1$, **A**) or mononuclear[5] chelate ($n = 2$, **B**) configurations.

We have drawn attention[6] to the existence of a fundamental difference in reactivity between compounds **1** and **2**: the first (i.e. $n = 1$) has been found to be extremely sensitive to protodesilylation (effecting Si–C bond-cleavage at the carbon $\alpha$ to P) under conditions that have no such effect on the congener **2** ($n = 2$). This characteristic of **1** is, however, entirely suppressed[6] when the phosphorus is coordinated to a metal, so that the complexes $[Ru(\eta^6\text{-cym})(L)Cl_2]$ (cym = *p*-cymene; L = **1** or **2** attached at Ru as a monofunctional phosphine ligand) show no differences in reactivity of the coordinated PSi ligand L. In either system, nucleophilic substitution for Y in the $[RuPPh_2(CH_2)_n\text{-}SiMe_2Y]$ chain is unusually facile (i.e. for $n = 1$ or 2) and provides a versatile and convenient methodology for adapting the terminal functionality in the "dangling"[6] phosphinoalkylsilane ligand.

The monodentate, P-bound mode of attachment[6] of **1** or **2**, *i.e.* geometry **C**, provides a model for prior coordination through P as the first step in "chelate-assisted" hydrosilylation that leads[7]




ultimately to configuration **B**. The stability of the complexes $[Ru(\eta^6\text{-cym})(L)Cl_2]$ (L = **1** or **2**) implies that a vacant site is needed at the metal center for formation of such a chelate structure via Si–H bond activation. Specifically, when such behavior is centered on an octahedral site like $Ir^{III}$ (*e.g.* in the reaction[8] of $[IrH(CO)(Cl)(PPh_3)(chel)]$ (chelH = **2**) with excess **2**/$NEt_3$), reductive elimination (*e.g.* of HCl) must occur to make room for Si–H addition. The latter will thus be channeled through the $Ir^I$ state in order to generate the product $[IrH(CO)(chel)_2]$. As we report below, in circumstances that disfavor this sequence, no chelate adduction is observed; in the mononuclear $M^{III}$ complexes $[M(Cp^*)Cl_2(L)]$, (M = Rh or Ir; $Cp^* = \eta^5\text{-}C_5Me_5$; L = **2**) that are formed on addition of silane **2** to the dimers $[M(Cp^*)Cl(\mu\text{-Cl})]_2$, the "dangling" L (=**2**) cannot be brought into chelation by addition of $NEt_3$. Thus the latter reagent fails to induce

* Abstract published in *Advance ACS Abstracts*, October 1, 1993.

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0020-1669/93/1332-5195$04.00/0 

intramolecular elimination that is not metal-centered (i.e., that involves sites remote from one another within the framework of a coordinatively saturated metal atom). Instead, substitution (OH for H) at Si (when M = Rh) occurs to give a product that has been characterized crystallographically as the monodentate (phosphinoethyl)silanol complex $[Rh(Cp^*)Cl_2(PPh_2CH_2CH_2SiMe_2OH)]$. More significantly, we have also found that further similar substitution of such silanols is facile and can be used to assemble realistic models for attachment of a platinum group metal PSi complex to chiral frameworks, to organic polymers or their monomer precursors, or onto silicaceous supports (polysiloxane or oxide surfaces).

## Experimental Section

All manipulations were carried out under an inert atmosphere of dry dinitrogen gas using standard Schlenk techniques. Solvents were dried and distilled prior to use. The phosphinoalkylsilanes $Ph_2PCH_2SiMe_2H$ (**1**) and $Ph_2PCH_2CH_2SiMe_2H$ (**2**), as well as $[Ru(\eta^6\text{-p-cym})(\mu\text{-Cl})Cl]_2$, $[Ru(\eta^6\text{-}C_6Me_6)(\mu\text{-Cl})Cl]_2$, $[Ru(\eta^6\text{-}C_6H_6)(\mu\text{-Cl})Cl]_2$, $[Ru(\eta^5\text{-}C_5H_5)(Cl)(PPh_3)_2]$, $[Rh(\eta^5\text{-}C_5Me_5)(\mu\text{-Cl})Cl]_2$, and $[Ru_2(\eta^5\text{-}C_5H_5)_2(\mu\text{-CO})(CO)_2(PhCCPh]$, were prepared by literature methods.[1,9-12] Satisfactory microanalytical data were obtained for all new compounds, supplied either by Canadian Microanalytical Services Ltd., Vancouver, Canada, or from Atlantic Microanalytical Services, Atlanta, GA, and are listed in Table S1. IR spectra were measured by using Perkin-Elmer 283 or 983 spectrometers and mass spectral data with a VG Analytical 707E FAB mass spectrometer. The $^1H$, $^{13}C$, or $^{31}P$ NMR spectra were recorded by using either Bruker WM250 (operating at 250.1, 101.3, or 62.9 MHz field equivalent, respectively) or Bruker WM400 (400.1, 162.1, or 100.6 MHz) instruments; the $^{19}F$ NMR spectra were obtained at 338.8 MHz using a Bruker WM360 spectrometer.

**A. Reactions of Ligands. (i) $Ph_2PCH_2SiMe_2H$ (1) with $H_2O$.** A solution of compound **1** (50 mg, 0.2 mmol) in $CDCl_3$ (0.5 mL) was treated with $H_2O$ (0.1 mL) in a 5-mm NMR tube which was sealed *in vacuo*. The subsequent reaction was followed by $^{31}P$ and $^1H$ NMR spectroscopy and showed complete conversion to $PPh_2Me$ and $(SiMe_2H)_2O$ after 1 week. $^{31}P\{^1H\}$ NMR ($CDCl_3$): $\delta$ −26.6 (s). $^1H$ NMR ($CDCl_3$): $\delta$ 0.29 (d, $^3J_{HH}$ = 3Hz, 6H), 1.63 (d, $^2J_{HP}$ = 13 Hz, 3H), 4.71 (m, $^3J_{HH}$ = 3 Hz, 1H), 7.3–7.9 (m, 10H). An otherwise identical reaction with $D_2O$ produced $Ph_2P(CH_2D)$ and $(Me_2SiH)_2O$, (D = $^2H$).

**(ii) $Ph_2PCH_2SiMe_2H$ (1) with MeOH.** In a similar procedure to that in part i above, a solution of **1** was converted to $Ph_2PMe$ and $Me_2SiH(OMe)$ as the sole *products* after 10 d through treatment with MeOH. $^{31}P\{^1H\}$ NMR ($CDCl_3$): $\delta$ −26.7 (s). $^1H$ NMR ($CDCl_3$): $\delta$ 0.20 (d, $^3J_{HH}$ = 3 Hz, 6H), 1.63 (d, $^2J_{HP}$ = 13 Hz, 3H), 3.48 (s, 3H), 4.71 (m, $^3J_{HH}$ = 3 Hz, 1H), 7.3–7.9 (m, 10H).

**(iii) $Ph_2PCH_2SiMe_2H$ (1) with HCl.** A 5-mm NMR tube was charged with a solution of **1** (50 mg, 0.2 mmol) in $CDCl_3$ (0.5 mL). Gaseous hydrogen chloride was bubbled through the solution (15 s) and then the tube was sealed. Conversion to the *products* $PPh_2Me$ and $SiMe_2(Cl)H$ was complete after 1 h as revealed by $^{31}P$ and $^1H$ NMR spectroscopy. $^{31}P\{^1H\}$ NMR ($CDCl_3$): $\delta$ −26.6 (s). $^1H$ NMR ($CDCl_3$): $\delta$ 0.54 (d, $^3J_{HH}$ = 3 Hz, 6H), 1.63 (d, $^2J_{HP}$ = 13 Hz, 3H), 4.92 (m, $^3J_{HH}$ = 3 Hz, 1H), 7.3–7.9 (m, 10H).

**(iv) $[Ph_2P(Me)CH_2SiMe_2][I]$ (3).** To a stirred solution of compound **1** (0.2 g, 0.8 mmol) in benzene (5 mL) was added MeI (0.15 mL, 0.8 mmol). After 1 h the solution was evaporated to dryness, yielding the *product* as a white crystalline solid (0.29 g, 95%).

**(v) $Ph_2PCH_2CH_2SiMe_2H$ (2) with $H_2O$ and MeOH.** Examination of sealed NMR tubes containing solutions of compound **2** in $CDCl_3$ with $H_2O$ or MeOH as described in procedures i and ii above led to observation of signals attributable only to the starting materials.

**(vi) $Ph_2PCH_2CH_2SiMe_2H$ (2) with HCl.** In a parallel procedure to that described in procedure iii above, a solution of $PPh_2PCH_2CH_2SiMe_2H$ (**2**) was converted to the *product* $PPh_2PCH_2CH_2SiMe_2Cl$ in 10 min. $^{31}P\{^1H\}$ NMR ($CDCl_3$): $\delta$ −9.2 (s). $^1H$ NMR ($CDCl_3$): $\delta$ 0.38 (s, 6H), 0.82 (m, 2H), 2.12 (m, 2H), 7.0–8.1 (m, 10H).

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**Table I.** Crystallographic Data for Compound **14**

| | |
|---|---|
| $C_{26}H_{36}RhCl_2PSiO$ | space group: $P2_12_12_1$ |
| fw = 598.14 | $T$ = 22 °C |
| $a$ = 17.345(4) Å | $\rho_{obsd}$ = 1.42 g cm$^{-3}$ |
| $b$ = 15.624(6) Å | $\rho_{calcd}$ = 1.43 g cm$^{-3}$ |
| $c$ = 10.274(6) Å | $\mu$ = 8.31 cm$^{-1}$ |
| $V$ = 2771(3) Å$^3$ | $R^a$ = 0.0606 |
| $Z$ = 4 | $R_w{}^b$ = 0.0616 |

$^a$ $R = \sum(|F_o| - (|F_d|)/\sum(|F_o|)$. $^b$ $R_w = [\sum w(|F_o| - (|F_d|)^2/\sum(F_o^2)]^{1/2}$.

**(vii) $[Ph_2P(Me)CH_2CH_2SiMe_2H][I]$ (4).** Paralleling the procedure described in part iv above, a sample of compound **2** was converted to the white crystalline *product* (0.30 g, 98%).

**B. Synthesis of Monodentate Complexes. (i) $[Ru(\eta^6\text{-p-cym})Cl_2(PPh_2CH_2SiMe_2H)]$ (5) and $[Ru(\eta^6\text{-p-cym})Cl_2(PPh_2CH_2CH_2SiMe_2H)]$ (6).** Treatment of a suspension of $[Ru(\eta^6\text{-p-cym})(\mu\text{-Cl})Cl]_2$ (0.92 g, 1.5 mmol) in THF (10 mL) dropwise with either a solution of compound **1** (0.78 g, 3.0 mmol) or compound **2** (0.82 g, 3.0 mmol) in THF (5 mL) was followed by stirring (20 min) the reaction mixture and then removal of the precipitates by filtration. Each of the solid residues was washed with hexane (3 × 5 mL) and dried *in vacuo*, to yield the orange, solid *products* **5** (1.24 g, 73%) and **6** (1.53 g, 88%), respectively.

**(ii) $[Ru(\eta^6\text{-}C_6Me_6)Cl_2(PPh_2CH_2CH_2SiMe_2H)]$ (7).** A solution of compound **2** (0.33 g, 1.20 mmol) in THF (2 mL) was added to a stirred suspension of $[Ru(\eta^6\text{-}C_6Me_6)(\mu\text{-Cl})Cl]_2$ (0.40 g, 0.60 mmol) in THF (15 mL). The solution clarified instantly and was stirred (15 min) after which the solvent was removed *in vacuo*. The resulting red oil was stirred (1 h) with hexane (10 mL), affording the *product* as a red powder (0.55 g, 76%).

**(iii) $[Ru(\eta^6\text{-}C_6H_6)Cl_2(PPh_2CH_2CH_2SiMe_2H)]$ (8).** A solution of compound **2** (0.44 g, 1.6 mmol) in benzene (3 mL) was added to a refluxing solution of $[Ru(\eta^6\text{-}C_6H_6)(\mu\text{-Cl})Cl]_2$ (0.40 g, 0.8 mmol) in benzene (40 mL). After 4 h the reaction mixture was filtered (hot), and then all volatiles were removed *in vacuo*. The remaining red oil was washed with hexane (15 mL), which led to the deposition of the *product* as an orange solid (0.59 g, 70%).

**(iv) $[Ru(\eta^5\text{-}C_5H_5)(Cl)(PPh_3)(PPh_2CH_2SiMe_2H)]$ (9) and $[Ru(\eta^5\text{-}C_5H_5)(Cl)(PPh_3)(PPh_2CH_2CH_2SiMe_2H)]$ (10).** A stirred solution of $[Ru(\eta^5\text{-}C_5H_5)(Cl)(PPh_3)_2]$ (0.20 g, 0.28 mmol) in THF (30 mL) was treated with a solution of compound **1** (0.071 g, 0.28 mmol) in THF (2 mL). The resulting mixture was heated under reflux (4 h), then the solvent was removed *in vacuo*. The yellow residue was washed with hexane (10 mL) yielding the *product* **9** as a yellow solid (0.16 g, 82%). Parallel chemistry using compound **2** in place of **1** in the procedure described above gave compound **10** as a yellow solid (0.18 g, 82%).

**(v) $[Ru_2(\eta^5\text{-}C_5H_5)(\mu\text{-CO})_2(CO)(PPh_2CH_2CH_2SiMe_2H)]$ (11).** A refluxing solution of $[Ru_2(\eta^5\text{-}C_5H_5)_2(\mu\text{-CO})(CO)_2(PhCCPh)]$ (0.20 g, 0.34 mmol) in toluene (40 mL) was treated with a solution of compound **2** (0.092 g, 0.34 mmol) in toluene (2 mL). After reflux (15 min) the mixture was filtered, and then volatiles were removed *in vacuo*. The resulting orange oil was agitated with hexane (1 h), resulting in the deposition of the *product* as an orange solid (0.14 g, 70%).

**(vi) $[Rh(\eta^5\text{-}C_5Me_5)Cl_2(PPh_2CH_2CH_2SiMe_2H)]$ (12) and $[Ir(\eta^5\text{-}(C_5Me_5)Cl_2(PPh_2CH_2CH_2SiMe_2H)]$ (13).** A solution of compound **1** (0.088 g, 0.32 mmol) in THF (2 mL) was added slowly to a stirred solution of $[Rh(\eta^5\text{-}C_5Me_5)(\mu\text{-Cl})Cl]_2$ (0.1 g, 0.16 mmol). The resulting mixture was stirred (30 min), and then the solvent was removed *in vacuo*, giving the *product* **12** as a pale red solid (0.17 g, 88%). Complex **13** was obtained in 73% yield when the iridium compound was used instead of its rhodium analogue.

**(vii) $[Rh(\eta^5\text{-}C_5Me_5)Cl_2(PPh_2CH_2CH_2SiMe_2OH)]$ (14).** A stirred solution of complex **12** (0.10 g, 0.17 mmol) in THF (25 mL) was treated with $H_2O$ (0.5 mL). After 5 min, evolution of gas had ceased; all volatiles were then removed *in vacuo*. The residual red oil was dissolved in $Et_2O$ (5 mL) and layered with hexane (8 mL); the *product* was deposited as deep red crystals over 3 d (0.132 g, 68%).

**C. X-ray Structure Determination for Complex 14.** Crystallographic data are collected in Table I. The lattice parameters were determined from a least-squares refinement of 25 reflections ($2\theta > 30°$).

Data were collected using the $\omega$–$2\theta$ method for the range $1.0 < 2\theta < 45°$, on a crystal 0.3 × 0.1 × 0.025 mm, using an Enraf-Nonius CAD-4 diffractometer, with Mo K$\alpha$ radiation ($\lambda$ = 0.71069 A) and $\mu$ = 8.31 cm$^{-1}$. A total of 1401 unique reflections were considered observed [$I \geq 4\sigma(I)$] out of a total of 1488 collected. The intensities were corrected for Lorentz and polarization effects and for absorption using EMPABS.[13]

The structure was solved with the use of standard Patterson and Fourier techniques using the SHELX series of programs.[14] Atomic scattering factors and anomalous dispersion terms were taken from the usual tabulations.[15,16] Several cycles of full-matrix least-squares refinement with isotropic temperature factors, followed by more cycles with anisotropic thermal parameters, led to final values of $R = \Sigma(|F_o| - (|F_d|)/\Sigma(|F_d|) = 0.0606$ and $R_w = [\Sigma w(|F_o| - (|F_d|)^2/\Sigma(F_o^2)]^{1/2} = 0.0616$. Unit weights were used at all stages. The largest parameter shifts in the final cycle were less than 0.002 of their estimated standard deviations.

**D. Nucleophilic Displacements Reactions at Silicon. (i) [Ru($\eta^6$-p-cym)Cl$_2$(PPh$_2$CH$_2$CH$_2$SiMe$_2$OH)] (15).** A stirred solution of complex **6** (0.10 g, 0.17 mmol) in THF (15 mL) was treated with $H_2O$ (0.1 mL). After 4 h the volatiles were removed *in vacuo* and the residual red oil was washed with hexane (2 × 10 mL), depositing the *product* as a red solid (0.08 g, 78%).

**(ii) [Ru($\eta^6$-p-cym)Cl$_2$(PPh$_2$CH$_2$SiMe$_2$Cl)] (16).** Hydrogen chloride was bubbled through a solution of complex **5** (0.10 g, 0.18 mmol) in THF/$CH_2Cl_2$ (5 mL/5mL) for 15 min. The solvent was removed *in vacuo*, and then the residual red oil was washed with hexane (2 × 10 mL) deposited the *product* as a red solid (0.08 g, 78%).

**(iii) [Ru($\eta^6$-p-cym)Cl$_2$(PPh$_2$CH$_2$CH$_2$SiMe$_2$Cl)] (17).** In a similar procedure to that given in part D(ii) above, treatment of a solution of complex **6** in THF (5 mL) with HCl led to the isolation of the *product* as a red solid (87%).

**(iv) [Ru($\eta^6$-p-cym)Cl$_2$(PPh$_2$CH$_2$SiMe$_2$OMe)] (18).** A stirred solution of complex **5** (0.10 g, 0.18 mmol) in $CH_2Cl_2$ (10 mL) was treated with MeOH (2 mL). After 4 h the volatiles were removed *in vacuo*, and then the resulting red oil was washed with hexane (2 × 10 mL) to yield the *product* as a red solid (0.07 g, 65%).

**(v) [Ru($\eta^6$-p-cym)Cl$_2$(PPh$_2$CH$_2$CH$_2$SiMe$_2$OMe)] (19).** In a procedure similar to that given in part D(iv) above, treatment of a solution of complex **6** with MeOH resulted in the isolation of the *product* as a red solid (75%).

**(vi) [Ru($\eta^6$-p-cym)Cl$_2$(PPh$_2$CH$_2$CH$_2$SiMe$_2$OEt)] (20).** In a further procedure similar to that given in part D(iv) above, treatment of a solution of complex **6** with EtOH for 8 h resulted the isolation of the *product* as a red solid (67%).

**(vii) [Ru($\eta^6$-p-cym)Cl$_2$(PPh$_2$CH$_2$SiMe$_2$O(CH$_2$)$_{13}$CH$_3$)] (21).** The alcohol $CH_3(CH_2)_{13}OH$ (0.038 g, 0.18 mmol) was added to a stirred solution of complex **6** (0.10 g, 0.18 mmol) in $CH_2Cl_2$ (10 mL). The reactants were stirred (15 h), after which time the volatiles were removed *in vacuo*. The resulting red oil was washed with hexane (2 × 10 mL), allowing the *product* to be recovered as a red orange powder (0.10 g, 74%).

**(viii) [Ru($\eta^6$-p-cym)Cl$_2$(PPh$_2$CH$_2$CH$_2$SiMe$_2$OCH$_2$CH$_2$C(Me)=CH$_2$)] (22).** In a procedure similar to that outlined in part D(vii) above, a solution of compound **6** was treated with isoprenyl alcohol to afford the *product* as a red powder (75%).

**(ix) [Ru($\eta^6$-p-cym)Cl$_2$(PPh$_2$CH$_2$CH$_2$SiMe$_2$OC$_{11}$H$_{17}$)] (23).** In a procedure similar to that outlined in part D(vii) above, a solution of compound **6** was treated with nopol (with vigorous stirring of the reactants over 36 h) to afford the *product* as a red brown powder (65%).

**(x) [Ru($\eta^6$-p-cym)Cl(PPh$_2$CH$_2$CH$_2$SiMe$_2$F)$_2$][PF$_6$] (24).** A solution of [RuCl$_2$($\eta^6$-cym)]$_2$ (200 mg, 0.32 mmol) and $NH_4PF_6$ (100 mg, 0.61 mmol) in methanol (50 mL) was stirred (24 h), resulting in a yellow-brown solution. The solvent was removed *in vacuo* and the solid dissolved in $CH_2Cl_2$ (5 mL) and filtered through a plug of Celite. Diethyl ether (20 mL) was layered on the top of the solution, resulting in the deposition of the known diruthenium complex [Ru$_2$($\mu$-Cl)$_3$($\eta^6$-p-cym)$_2$][PF$_6$] as brown crystals (210 mg, 90%). Anal. Calcd for $C_{20}H_{28}Ru_2Cl_3PF_6$: C, 33.28; H, 3.91. Found: C, 33.16; H, 3.95. $^1$H NMR ($CDCl_3$): 1.29 (d, $^3J_{HH}$ = 7 Hz, 6H), 2.21 (s, 3H), 2.77 (m, 1H), 5.46 (m, 2H), 5.65 (m, 2H). A solution of compound **2** (237 mg, 0.87 mmol) in THF (15 mL) was treated with [Ru$_2$($\mu$-Cl)$_3$($\eta^6$-p-cym)$_2$][PF$_6$] (157 mg, 0.22 mmol) and stirred (10 min). Solid $NH_4PF_6$ (100 mg, 0.61 mmol) was added, and then the solution was refluxed (3 h). After cooling, the solvent was removed *in vacuo* and then the residue was extracted with $CH_2Cl_2$ (10 mL), filtered through Celite, and layered with diethyl ether, finally affording the *product* as a yellow powder (370 mg, 85%).

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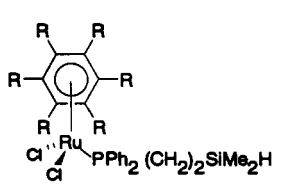
## Results

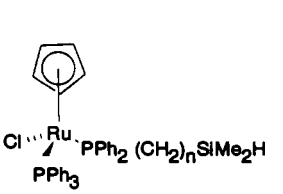
**A. Chemistry of ((Diphenylphosphino)methyl)dimethylsilane: Si–C Bond Cleavage $\alpha$ to Phosphorus.** Synthesis of the air-sensitive silane PPh$_2$CH$_2$SiMe$_2$H (**1**) according to the published method[1] uses as its starting point the lithiation of methyldiphenylphosphine, PPhMe. The presence of the latter in laboratory samples of **1**, as well as in mixtures recovered from reactions of **1** with transition element species, was initially dismissed as the result of ineffective purification procedures; more careful handling showed, however, that PPh$_2$Me was being generated from **1** even under ostensibly inert atmosphere conditions. The condition of a sealed sample of neat liquid **1** was therefore monitored by $^{31}$P NMR spectroscopy; no change was detectable over 2 weeks. By contrast, after water (*ca.* 25 molar equiv) was added to a solution of **1** in $CDCl_3$, conversion to PPh$_2$Me could be followed by $^1$H NMR to completion within 1 week; during the same period, a new dimethylsilyl pattern emerged which was attributable to[17] the disiloxane (Me$_2$SiH)$_2$O. In a parallel experiment using $^2H_2O$, identical spectral changes occurred except that the Me signal of PPh$_2$Me ($\delta$ 1.63, $^2J$ = 13 Hz) was found to be broadened and reduced in relative intensity by one-third (to 2 vs. 3), i.e. characteristic of the isotopomer PPh$_2$CH$_2$$^2$H. Methanolysis (*ca.* 20 molar equiv of methanol) of compound **1**, which was monitored similarly in dilute $CDCl_3$ solution, afforded PPh$_2$Me and SiMe$_2$(OMe)H (showing[18] $\delta$(OC$H_3$) = 3.48 ppm) as sole products. By contrast, with PPh$_2$CH$_2$CH$_2$SiMe$_2$H (**2**) there was no sign of any spectral change during a 2-week exposure to degassed water or methanol in sealed evacuated NMR tubes.

Compounds **1** and **2** each reacted rapidly with HCl gas, but in quite different ways: thus PPh$_2$Me was again formed from **1**, together with SiMe$_2$HCl, while **2** afforded the known[1] PPh$_2$(CH$_2$)$_2$SiMe$_2$Cl as the only product in solution. Conversely, the two compounds reacted identically with MeI in benzene solution: white, crystalline materials were obtained that were identified conclusively as the phosphonium salts [PPh$_2$Me(CH$_2$)$_n$SiMe$_2$H]I (**3**, $n$ = 1; **4**, $n$ = 2), formed essentially quantitatively and showing $^{31}$P resonances shifted by over 40 ppm vs the precursors.

**B. Formation of Transition Metal Complexes: Monodentate Coordination of 1 or 2 at Ru and of 2 at Rh or Ir.** Addition to a suspension in THF of the chloro-bridged arene–ruthenium dimer[9] [Ru(*p*-cym)($\mu$-Cl)Cl]$_2$ of either silane (i.e. **1** or **2**) led to rapid formation of orange solids that were subsequently characterized by microanalysis, IR, NMR, and mass spectrometry (see Tables II–IV) as the Ru(II)–phosphine adducts [Ru(*p*-cym)Cl$_2$(L)], (*p*-cym = $\eta^6$-*p*-cymene; **5**, L = **1**; **6**, L = **2**) formed in >70% yield. In both these products, the retention of an intact Si–H bond was confirmed by observation of the characteristic pattern in the $^1$H NMR due to the –SiHMe$_2$ group, and by IR absorption near 2120 cm$^{-1}$ ($\nu_{SiH}$), while $\delta$($^{31}$P) was shifted by about 50 ppm to high frequency (i.e. deshielded) vs **1** or **2**. A similar approach was used to prepare analogues **7** and **8** of complex **6** from the (phosphinoethyl)silane (**2**) in which the $\eta^6$-arene ligand at Ru is hexamethylbenzene or simply benzene.




(**7**; R = Me)
(**8**; R = H)




(**9**; n = 1)
(**10**; n = 2)

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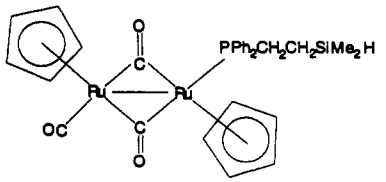
**Table II.** Selected Infrared and Mass Spectral Data

| compd | IR[a] $cm^{-1}$ | MS,[b] *m/e* |
|---|---|---|
| **3** | 2112 s[c] | 273 (273.4) |
| **4** | 2108 s[c] | 287 (287.4) |
| **5** | 2121 s[c] | 528 (528.1) |
| **6** | 2118 m[d] | 579 (578.6) |
| **7** | 2108 m[c] | |
| **8** | 2112 m[c] | |
| **9** | 2122 m[c] | 722 (722.3) |
| **10** | 2120 m[c] | 736 (736.3) |
| **11** | 2118 m[c], 1940 s, 1718 s[d,e] | 690 (689.8) |
| **12** | 2114 m[c] | 582 (581.4) |
| **13** | 2114 m[c] | |
| **14** | 3400 br[e,f] | |
| **15** | 3320 br[e,f] | |
| **16** | 459 m[g] | |
| **17** | 452 m[g] | |
| **18** | 1080 s[h] | |
| **19** | 1090 s[h] | |
| **20** | 1085 s[h], 910 m[e,i] | |
| **21** | 1076 s,[h] 910 s[e,i] | 776 (776.9) |
| **24** | 840 s[j] | |

[a] KBr disk unless marked. [b] Calculated molecular mass shown in parentheses; phospinoalkylsilane cation obtained by fast atom bombardment for compounds **3** and **4**; tabulated *M* for compound **5** corresponds to loss of HCl. [c] $\nu$(SiH). [d] $\nu$(C=O). [e] $CH_2Cl_2$ solution. [f] $\nu$(OH). [g] $\nu$(SiCl). [h] $\nu$(C—O). [i] $\nu$(Si—O). [j] $\nu$(P—F).

Displacement by **1** or **2** of one phosphine ligand from the labile mononuclear Ru(II) complex[10] $[RuCpCl(PPh_3)_2]$ (Cp = $\eta^5$-$C_5H_5$) was observed to occur in THF solution, to yield the products $[RuCpCl(PPh_3)(L)]$ (**9**, L = **1**; **10**, L = **2**), which were again shown to be the P-bonded, (phosphinoalkyl)silane complexes. In particular the $^{31}P$ NMR spectra consisted of *ab* multiplets: $\delta$ 44.8, 37.5 ppm, $^2J$ = 43 Hz (**9**); $\delta$ 44.0, 43.5 ppm, $^2J$ = 41 Hz (**10**) (see Table III), i.e. characteristic of a cis arrangement of inequivalent P centers. Features in the IR and $^1H$ NMR confirmed the presence of an unmodified $-SiHMe_2$ fragment, in which the two Me groups are diastereotopic ($\Delta\delta$ = 0.62 ppm for **9**, 0.02 ppm for **10**, Table III). The effect of replacement by **2** of the labile[12] alkyne ligand in the dimer $[Ru_2Cp_2(C_2Ph_2)(CO)_3]$ was also investigated, but led only to formation of a more elaborate example of the "dangling" silane geometry. Thus the product **11**, for which microanalytical data were consistent with formulation as the diruthenium species $[Ru_2Cp_2(CO)_3(PPh_2CH_2CH_2SiMe_2H)]$, showed IR absorption at 2118, 1940, and 1718 $cm^{-1}$, assigned respectively to stretching of Si–H and terminal and bridging CO bonds, and two NMR resonances ($^1H$ or $^{13}C$) due to nonequivalent Cp ligands.

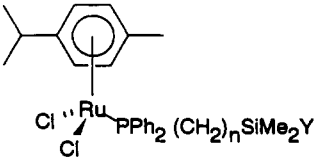



**(11)**

Addition of the (phosphinoethyl)silane **2** to the binuclear M(III) compounds $[M(\eta^5\text{-}C_5Me_5)(\mu\text{-}Cl)Cl]_2$ (M = Rh or Ir) occurred under mild conditions to afford products that were respectively pale red or yellow. Spectroscopic data included IR absorption at 2114 $cm^{-1}$ and septet resonances in $^1H$ NMR spectra (at $\delta$ 3.70, $^3J$ = 3 Hz; or $\delta$ 3.72, $^3J$ = 4 Hz), features that confirm the presence of unreacted Si–H bonds and were otherwise fully consistent with a formulation $[M(\eta^5\text{-}C_5Me_5)Cl_2(L)]$ (**12**, M = Rh; **13**, Ir; L = **2**) that is a direct relative of the ruthenium(II) configuration represented by **9** and **10**. Attempts at cyclization by abstraction of HCl were completely unsuccessful: thus addition of $NMe_3$ to **13** produced no effect whatever, while under the same conditions gas evolution was noted from solutions of **12**, after which addition of hexane led to deposition of deep red crystals of a further complex **14**. The latter exhibited no spectroscopic properties attributable to Si–H bonds, but instead showed a broad IR band centered at 3450 $cm^{-1}$, and a broad $^1H$ NMR signal at $\delta$ 3.3 ppm that disappeared on shaking with $^2H_2O$. This compound was therefore identified as a "dangling" silanol complex, $[Rh(\eta^5\text{-}C_5Me_5)Cl_2(PPh_2CH_2CH_2SiMe_2OH)]$, a conclusion verified by the results of an X-ray crystal structure determination (see below). We have described elsewhere[6] the crystal structure of a closely related ruthenium(II) silanol complex, derived from silane **1** via formation of complex **5**, and in accordance with the generality of such chemistry, addition of water to a solution in THF of complex **6** yielded a further red product identified as $[Ru(\eta^6\text{-cym})Cl_2(PPh_2CH_2CH_2SiMe_2OH)]$ (**15**).

**C. X-ray Crystal and Molecular Structure of Compound 14. "Dangling" Silanol Geometry.** The molecular structure of the rhodium(III) ((diphenylphosphino)ethyl)dimethylsilanol complex **14** is illustrated in Figure 1; selected bond lengths and angles are collected in Table V and the fractional atomic coordinates and temperature parameters are given in Table VI. The arrangement about the rhodium center is pseudooctahedral as expected, with the $C_5Me_5$ framework lying across one face and the opposing facial sites occupied by the three unidentate ligands. The "dangling" Si–OH function shows no evidence for intramolecular association and is remote from the metal center. The conformation of the P-bound silanol chain zigzags between the chloride ligands to end with the silanol oxygen rotated toward the phenyls attached to phosphorus. The Rh–C distances to the cyclopentadienyl system are slightly shorter trans to Cl than are those opposite the P center (in accord with the relative trans influences of these two ligands), thereby imposing a slight tilt to the ring in the direction of the diphenylphosphino group. The overall structure is thus strikingly similar to that of $[Ru(\eta^6\text{-cym})Cl_2(L)]$ (L = **1**), which has been illustrated elsewhere.[6]

**D. Nucleophilic Displacement of the Silanol OH Group in Complexes 5 and 6. Formation of (Phosphinoalkyl)siloxy Complexes and Unanticipated Fluorination at Si.** Complexes **5** and **6** each reacted immediately with gaseous hydrogen chloride; this was accompanied by the disappearance from IR and NMR spectra of features due to a Si–H linkage, and microanalysis was consistent with formulation of these products as chlorosilyl complexes $[Ru(\eta^6\text{-cym})Cl_2(PPh_2(CH_2)_nSiMe_2Cl)]$ (**16**, *n* = 1; **17**, *n* = 2). There was no evidence for P–C bond cleavage during conversion of **5** to **16**. Similarly, addition of methanol to a solution of **5** in $CH_2Cl_2$ afforded another red compound, which was identified as the alkoxysilane complex $[Ru(\eta^6\text{-cym})Cl_2(PPh_2CH_2SiMe_2OMe)]$ (**18**); the doublet $SiCH_3$ resonance in the $^1H$ NMR spectrum of **5** (i.e., coupling to Si–*H*) was replaced in that of **18** by a singlet at $\delta$ –0.39 and a new signal was present at $\delta$ 2.91 ppm, assigned to $OCH_3$ protons. Complex **6** underwent solvolysis by methanol in the same fashion, affording the phosphinoethyl analogue $[Ru(\eta^6\text{-cym})Cl_2(PPh_2CH_2CH_2SiMe_2$-




(**5**; n = 1, Y = H)
(**6**; n = 2, Y = H)
(**15**; n = 2, Y = OH)
(**16**; n = 1, Y = Cl)
(**17**; n = 2, Y = Cl)
(**18**; n = 1, Y = OMe)
(**19**; n = 2, Y = OMe)
(**20**; n = 2, Y = OEt)
(**21**; n = 1, Y = $O(CH_2)_{13}Me$)
(**22**; n = 2, Y = $OCH_2CH_2C(Me){:}CH_2$)
(**23**; n = 2, Y = $OCH_2$–C$_6$H$_5$)

**Table III.** Selected $^{31}P$ and $^{1}H$ NMR Data

| compd | $\delta(^{31}P)$,[a] ppm | $\delta(^{1}H)$,[b] ppm: SiMe | SiH | $CH_2$ and others |
|---|---|---|---|---|
| **3** | 20.6 | −0.05 (d)[c] | 3.87 (m) | 2.69 (m) | 2.54 (d)[d] |
| **4** | 27.0 | 0.18 (d)[c] | 3.95 (m) | 0.77 (m), 2.83 (m) | 2.83 (d)[d] |
| **5** | 24.0[e] | −0.43 (d)[c] | 3.45 (m) | 1.91 (dd) | 0.70 (d),[g] 1.83 (s), 2.50 (m), 5.03 (d),[h] 5.25 (d)[h] |
| **6** | 29.0[e] | −0.13 (d)[c] | 3.65 (m) | 0.22 (m)[i] | 0.74 (d),[g] 1.84 (s), 2.50 (m),[i] 5.03 (d),[h] 5.25 (d)[h] |
| **7** | 29.7 | −0.11 (d)[c] | 3.43 (m) | 0.34 (m), 2.60 (m) | 1.68 (s) |
| **8**[k] | 29.1 | −0.06 (d)[c] | 3.70 (m) | 0.36 (m), 2.61 (m) | 5.32 (s) |
| **9** | 44.8,[o] 37.5[o] | −0.92 (d),[c] −0.30 (d)[c] | 3.29 (m) | 1.84 (m) | 4.06 (s)[p] |
| **10** | 44.0,[q] 43.5[q] | 0.12 (d),[c] 0.14 (d)[c] | 3.51 (m) | 0.09 (m), 0.91 (m), 1.60 (m), 2.42 (m) | 4.06 (s)[p] |
| **11** | 51.3 | −0.08 (d)[c] | 3.66 (m) | 0.27 (m), 1.66 (m) | 4.73 (s),[p] 5.20 (s)[p] |
| **12**[k] | 34.5[r] | −0.06 (d)[c] | 3.70 (m) | 0.42 (m), 2.81 (m) | 1.31 (s)[s] |
| **13**[k] | 0.0 | −0.04 (d)[c] | 3.72 (m) | 0.046 (m), 2.82 (m) | 1.31 (s)[s] |
| **14**[k] | 33.0[x] | −0.06 (s) | | 0.39 (m), 2.75 (m) | 3.30 (br), 1.29 (s)[y] |
| **15** | 27.9 | −0.03 (s) | | *i* | 3.56 (br), 0.78 (d),[g] 1.84 (s), 2.50 (m),[i] 5.06 (d),[h] 5.24 (d)[h] |
| **16**[k] | 23.0[e] | −0.08 (s) | | 2.31 (d)[i] | 0.81 (d),[g] 1.81 (s), 2.55 (m),[i] 5.09 (d),[h] 5.25 (d)[h] |
| **17**[k] | 28.0 | 0.28 (s) | | *i* | 0.83 (d),[g] 1.89 (s), 2.55 (m),[i] 5.29 (d),[h] 6.08 (d)[h] |
| **18** | 21.3[b] | −0.39 (s) | | *i* | 2.91 (s), 0.77 (d),[g] 1.81 (s), 2.50 (m),[i] 5.28 (d),[h] 6.08 (d)[h] |
| **19** | 28.4[b] | 0.05 (s) | | 0.37 (m)[i] | 3.22 (s), 0.78 (d),[g] 1.86 (s), 2.50 (m),[i] 5.05 (d),[h] 5.22 (d)[h] |
| **20** | 28.5 | −0.05 (s) | | 0.27 (m) | 0.78 (d),[g] 1.04 (t),[m] 1.85 (s), 2.40 (m),[i] 3.46 (q), 5.04 (d),[h] 5.22 (d)[h] |
| **21** | 21.0 | −0.32 (s) | | 0.27 (m) | 0.86 (5),[g] 0.95 (d), 1.55 (br),[n] 1.83 (s), 2.50 (m),[i] 5.08 (d),[h] 5.22 (d)[h] |
| **22** | 29.4 | −0.06 (s) | | 0.24 (m), 2.51 (m), 2.06 (t),[t] 3.48 (t)[t] | 0.74 (d),[g] 1.62 (s),[u] 1.85 (s), 2.51 (m),[i] 4.62 (d),[v] 5.04 (d),[h] 5.22 (d)[h] |
| **23** | 29.4 | −0.06 (s) | | 0.23 (m), 2.50 (m), 2.02 (m),[g] 3.34 (m)[t] | 0.71 (s),[w] 0.75 (d),[g] 1.03 (d), 1.18 (s), 1.86 (s), 1.89 (m), 2.10 (m), 2.14 (m), 2.23 (m), 2.50 (m),[i] 5.03 (d),[h] 5.11 (m), 5.23 (d)[h] |
| **24** | 27.1, −143.0[z] | 0.13 (d), 0.14 (d)[aa] | | 0.25 (m), 2.18 (m), 2.95 (m) | 0.89 (s), 1.26 (d),[g] 2.79 (m), 5.51 (d),[h] 5.98 (m)[h] |

[a] THF solution unless stated otherwise. [b] $CDCl_3$ solution unless stated otherwise. [c] $^{3}J(HH) = 4$ Hz. [d] P–$CH_3$; $^{2}J(PH) = 13$ Hz. [e] $CH_2Cl_2$ solution. [f] $^{2}J(HP) = 14$ Hz, $^{3}J(HH) = 3$ Hz. [g] –$CH(CH_3)_2$, $^{3}J(HH) = 7$ Hz. [h] AA′BB′ spin system of the aromatic hydrogens on the *p*-cymene ligand, $^{3}J(HH) = 6$ Hz. [i] Signal obscured by other resonances. [j] –$CH(CH_3)_2$. [k] $CD_2Cl_2$ solution. [l] $^{2}J(HP) = 15$ Hz. [m] $^{3}J(HH) = 7$ Hz, O–$CH_2CH_3$. [n] $CH_2$ groups. [o] Doublet, $^{2}J(PP) = 43$ Hz. [p] $C_5H_5$. [q] Doublet, $^{2}J(PP) = 41$ Hz. [r] Doublet, $^{2}J(PRh) = 141$ Hz. [s] O–$CH_2CH_2$–. [t] O–$CH_2CH_2$–. [u] –$CH_2C(CH_2)CH_3$, $^{3}J(HH) = 7$ Hz. [v] –$CH_2C(CH_2)CH_3$. [w] See text for assignment of nopol resonances. [x] Doublet, $^{2}J(PRh) = 140$ Hz. [y] $C_5Me_5$. [z] $PF_6$, $^{1}J(PF) = 700$ Hz. [aa] $^{3}J(HF) = 7$ Hz.

**Table IV.** Selected $^{13}C$ NMR Data[a]

| compd | SiMe | $CH_2$ | others |
|---|---|---|---|
| **3** | −3.2 (s) | 8.8 (d)[b] | 11.0 (d)[c] |
| **4** | −4.2 (s) | 5.8 (d),[d] 19.2 (d)[b] | 7.7 (d)[c] |
| **5** | −3.0 (s) | 8.3 (d)[e] | 17.2 (s),[f] 21.2 (s),[g] 30.0 (s)[h] |
| **6** | −4.9 (s) | 6.8 (d),[i] 18.0 (d)[e] | 17.2 (s),[f] 21.2 (s),[g] 29.9 (s)[h] |
| **7**[j] | −4.9 (s) | 7.7 (d),[k] 23.0 (d)[e] | 15.0 (s), 95.8 (s) |
| **8**[j] | −4.2 (s) | 7.5 (d),[k] 18.9 (d)[e] | 88.9 (s) |
| **9** | −3.4 (s), −1.0 (s) | 7.0 (d)[l] | 81.4 (s) |
| **10** | −4.0 (s), −3.9 (s) | 8.5 (d),[m] 16.3 (d)[n] | 81.4 (s) |
| **11** | −4.2 (s) | 8.9 (d),[k] 24.3 (d)[l] | 89.9 (s), 90.5 (s) |
| **12** | −4.1 (s) | 8.5 (d),[k] 23.8 (d)[e] | 9.3 (s), 99.1 (s) |
| **13** | −4.0 (s) | 8.1 (d),[k] 22.5 (d)[o] | 8.9 (s), 90.5 (s) |
| **22** | 0.1 (s) | 12.0 (d),[l] 23.3 (d)[p] | 8.9 (s), 99.2 (s) |

[a] $CDCl_3$ solution unless stated otherwise. [b] $^{1}J(PC) = 44$ Hz. [c] P*C*$H_3$, $^{1}J(PC) = 58$ Hz. [d] $^{2}J(PC) = 7$ Hz. [e] $^{1}J(PC) = 25$ Hz. [f] *C*$H_3C_6H_4CH(CH_3)_2$. [g] $CH_3C_6H_4CH(CH_3)_2$. [h] $CH_3C_6H_4CH(CH_3)_2$. [i] $^{2}J(PC) = 10$ Hz. [j] $CD_2Cl_2$ solution. [k] $^{2}J(PC) = 9$ Hz. [l] $^{2}J(PC) = 16$ Hz. [m] $^{2}J(PC) = 11$ Hz. [n] $^{1}J(PC) = 15$ Hz. [o] $^{1}J(PC) = 30$ Hz. [p] $^{1}J(PC) = 23$ Hz.

OMe)] **19** of **18**. It was found that this type of displacement also occurred readily at Si with a range of alcoholic substrates: red or orange analytically pure solids were obtained through reaction of **6** with ethanol (giving compound **20**), **5** with tetradecanol (giving **21**), and **6** with either isoprene alcohol (i.e., 3-methyl-3-buten-1-ol) or nopol (i.e., 6,6-di-methyl-1-{1-hydroxy-2-ethyl}-1-heptene) to give **22** or **23** respectively. Reaction with hexamethyldisilazane, $NH(SiMe_3)_2$ resulted in O-silylation i.e. modification of the –$SiMe_2OH$ group to –$SiMe_2OSiMe_3$.

Abstraction of chloride by silver ions was investigated as a method for developing a vacant site at Ru in complex **6**, in an attempt to induce intramolecular Si–H bond addition. It was found, however, that instead of chelate formation by the PSi unit, addition of $AgBF_4$ yielded isolable materials only on addition of external ligand L including $PPh_3$, $PEt_3$, or $P(OEt)_3$. The nature of these products remained unclear until $^{19}F$ and $^{31}P$ NMR as well as 2D-NMR spectroscopy provided unambiguous proof for coordination as unidentate ligands at a single Ru($\eta^6$-cym) fragment of both $PPh_3$ and $PPh_2(CH_2)_2SiMe_2F$ ($\delta_P$ 24.6, 23.5 ppm, $^{2}J_{PP} = 51$ Hz; $\delta_F$ 13.7 ppm, septet, $^{3}J_{FMe} = 8$ Hz). The only source of fluorine in these reactions was the $BF_4^-$ counterion;

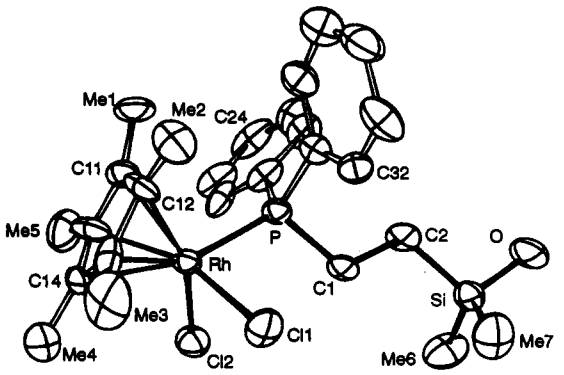



**Figure 1.** Molecular geometry of [Rh($\eta^5$-$C_5Me_5$)$Cl_2$($PPh_2CH_2CH_2SiMe_2OH$)] (**14**).

**Table V.** Selected Bond Lengths (Å) and Bond Angles (deg) in Complex **14**

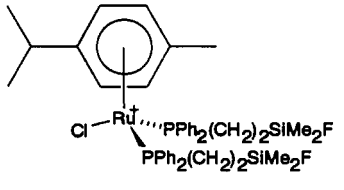
| | | | |
|---|---|---|---|
| **Bond Lengths** | | | |
| Rh–C(11) | 2.171(18) | Rh–C(12) | 2.154(16) |
| Rh–C(13) | 2.201(18) | Rh–C(14) | 2.229(17) |
| Rh–C(15) | 2.139(20) | C(1)–C(2) | 1.553(25) |
| Rh–Cl(1) | 2.399(5) | Rh–Cl(2) | 2.411(5) |
| Rh–P | 2.327(5) | P–C(1) | 1.849(18) |
| Si–C(2) | 1.869(19) | Si–Me(6) | 1.836(21) |
| Si–Me(7) | 1.855(22) | Si–O | 1.653(13) |
| **Bond Angles** | | | |
| P–Rh–Cl(1) | 87.7(2) | P–Rh–Cl(2) | 91.1(2) |
| Cl(1)–Rh–Cl(2) | 90.7(1) | Rh–P–C(1) | 113.2(5) |
| P–C(1)–C(2) | 115.6(12) | C(1)–C(2)–Si | 110.9(11) |
| C(2)–Si–O | 103.8(7) | Me(6)–Si–O | 112.2(10) |
| Me(7)–Si–O | 109.3(9) | | |

**Table VI.** Fractional Atomic Coordinates and Temperature Parameters for Compound **14**[a]

| atom | x/a | y/b | z/c | $U_{eq}$, Å$^2$ |
|---|---|---|---|---|
| Rh | 44482(7) | 27116(9) | 9690(0) | 323(5) |
| Cl(1) | 4580(3) | 1301(3) | 1863(5) | 56(2) |
| Cl(2) | 3126(3) | 2776(4) | 1685(5) | 53(2) |
| P | 4080(2) | 2071(3) | -979(5) | 33(1) |
| Si | 2663(3) | -345(3) | -1588(5) | 44(2) |
| C(11) | 5148(11) | 3725(13) | 138(16) | 40(7) |
| C(12) | 5635(9) | 3081(13) | 708(16) | 45(7) |
| C(13) | 5441(11) | 3124(12) | 2147(21) | 53(8) |
| C(14) | 4846(11) | 3725(13) | 2340(17) | 46(7) |
| C(15) | 4624(9) | 4065(13) | 1072(17) | 47(7) |
| Me(1) | 5214(13) | 4008(14) | -1277(18) | 63(8) |
| Me(2) | 6286(10) | 2586(14) | 202(20) | 61(8) |
| Me(3) | 5862(15) | 2608(15) | 3187(23) | 88(10) |
| Me(4) | 4498(16) | 3952(16) | 3565(22) | 92(11) |
| Me(5) | 4079(12) | 4780(12) | 877(25) | 70(8) |
| C(21) | 3554(10) | 2723(13) | -2189(18) | 44(7) |
| C(22) | 3128(11) | 3397(12) | -1704(23) | 54(8) |
| C(23) | 2652(12) | 3851(14) | -2564(22) | 65(9) |
| C(24) | 2643(13) | 3655(17) | -3879(26) | 80(10) |
| C(25) | 3087(14) | 2977(17) | -4299(26) | 72(10) |
| C(26) | 3553(12) | 2500(12) | -3513(18) | 53(8) |
| C(31) | 4893(10) | 1600(11) | -1810(14) | 34(6) |
| C(32) | 5236(11) | 859(12) | -1301(17) | 46(7) |
| C(33) | 5942(13) | 535(14) | -1715(21) | 61(8) |
| C(34) | 6348(12) | 995(15) | -2729(22) | 64(9) |
| C(35) | 6031(13) | 1716(15) | -3279(24) | 70(9) |
| C(36) | 5299(10) | 2031(12) | -2843(19) | 51(7) |
| C(1) | 3409(10) | 1164(11) | -751(15) | 42(6) |
| C(2) | 3209(11) | 650(12) | -2000(16) | 48(7) |
| Me(6) | 1704(11) | -99(15) | -929(27) | 75(9) |
| O | 2615(8) | -867(9) | -2985(11) | 68(5) |
| Me(7) | 3244(14) | -976(14) | -413(23) | 74(8) |

[a] Estimated Standard deviations are given in parentheses. Coordinates $\times 10^n$, where $n$ = 5, 4, 4, 4, 4, 4 for Rh, Cl, P, Si, O, C. Temperature Parameters $\times 10^n$, where $n$ = 4, 3, 3, 3, 3, 3 for Rh, Cl, P, Si, O, C. $U_{eq} = {}^1/_3\sum_i\sum U_{ij}a_i^*a_j^*(a_i a_j)$. $T = \exp(8\pi^2 U_{iso}\sin^2\theta/\lambda^2)$.

however, in spite of NMR evidence for the latter, as well as for a cation of the type $[Ru(\eta^6\text{-cym})(PPh_3)(PPh_2CH_2CH_2SiMe_2F)(X)]^+$, none of the solids produced could be satisfactorily characterized by elemental analysis. To try to clarify these observations, and in a search for a way of attaching two (phosphinoalkyl)silane ligands at a single Ru center, the binuclear cation $[Ru_2(\eta^6\text{-cym})_2(\mu\text{-Cl})_3]^+$ (obtained as its $PF_6$ salt by a new route which eliminates the need for $AgPF_6$ and results in a superior yield to literature[19] methods) was treated with **2** (4 molar equiv) and then $NH_4PF_6$. This procedure afforded in 85% yield a yellow, crystalline salt $[Ru(\eta^6\text{-cym})Cl(PPh_2CH_2CH_2SiMe_2F)_2]PF_6$ (**24**) that was fully characterized by microanalysis as well as by multinuclear NMR spectroscopy. A crystallographic study which was taken far enough to confirm the gross features of the cation structure in **24** could not be completed due to anion disorder.




(24; $BF_4^-$ salt)

## Discussion

The extreme sensitivity of the (phosphinomethyl)silane **1** to reagents that can protonate at P and introduce a nucleophilic fragment at Si is directly related to the sequential solvolytic cleavage of silyl groups from the phosphine $Ph_2PC(SiMe_3)_3$ observed by Eaborn et al.[20] Intermediacy of an ylidic arrangement that rapidly tautomerizes by proton transfer to $C_\alpha$, from which the silyl can act as a leaving group, has been suggested. Such a pathway is removed when either the silyl-substituted carbon is not $\alpha$ to P or lone-pair density is not available at P, and this accounts for the stability to Si–C bond cleavage both of the ethyl congener (**2**) of **1** and of metal complexes of the latter.

Ligands **1** or **2**, when reacted with chloro-bridged diruthenium precursors, act as monodentate phosphines preserving the Si–H functionality. The same type of arrangement at Ru is accessible by displacement of $PPh_3$ (in accordance with the more basic character of **1** or **2**) or a labile alkyne, the former providing access to complexes (**9** or **10**) that are chiral at the Ru center. Solvolysis of the Si–H bond in **5** ($n$ = 1) by even traces of water affords a (phosphinoalkyl)silanol complex of Ru(II), as was highlighted earlier,[6] and this also occurs when $n$ = 2. Even under strictly neutral conditions, facile alcoholysis of the same Si–H linkage appears to be quite general. This is remarkable since related reactions of simple organosilanes (*e.g.* of the type $R_3SiH$) invariably require acid or base catalysis. The products **21–23** formed in this way define a novel strategy for the attachment of a ruthenium-centered unit to a surfactant or polymer, to a polymerizable fragment, or to an optically active framework.

In a final related context, substitution of H by F at Si was apparent in systems in which the only source of fluorine was a classically unreactive, noncoordinating perfluoroanion, either $BF_4^-$ or $PF_6^-$. This terminated our attempts to develop a bis((phosphinoalkyl)silanol)ruthenium(II) geometry (for bipodal immobilization) at a bis((diphenylphosphino)methyl)(dimethyl)fluorosilane analogue (**24**). Similar fluorination at P by $BF_4^-$, which was reported recently,[21] is said to be hitherto very rare. Solvolysis of $PF_6^-$ to $PO_2F_2^-$ in rhodium dimers has also been reported.[22]

**Acknowledgment.** We thank the NSERC, Canada, and the University of Victoria for financial support and Ms. K. Beveridge for crystallographic assistance.

**Supplementary Material Available:** A table of analytical data for **3–24** and tables of anisotropic thermal parameters, bond distances, and bond angles for compound **14** (4 pages). Ordering information is given on any current masthead page.

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