Table IV. Bond Distances (Å) and Bond Angles (deg) in $Fe(CO)(C_5H_5)C_4H_6N(C_3H_7)_2$ (24b)

Bond Distances			
Fe(1)-C	1.700 (5)	Fe(1)-C(2)	1.927 (4)
Fe(1)-C(5)	2.044 (5)	Fe(1)-C(10)	2.117 (7)
Fe(1)-C(11)	2.103 (7)	Fe(1)-C(12)	2.085 (5)
Fe(1)-C(13)	2.091 (5)	Fe(1)-C(14)	2.119 (6)
C-O	1.167 (6)	C(2)-C(3)	1.507 (7)
C(2)-N(6)	1.317 (6)	C(3)-C(4)	1.512 (8)
C(4)-C(5)	1.487 (8)	N(6)-C(7)	1.487 (6)
N(6)-C(8)	1.509 (6)	C(7)-C(71)	1.515 (7)
C(7)-C(72)	1.503 (7)	C(8)-C(81)	1.506 (7)
C(8)-C(82)	1.509 (7)	C(10)-C(11)	1.420 (10)
C(10)-C(14)	1.350 (10)	C(11)-C(12)	1.373 (9)
C(12)-C(13)	1.347 (9)	C(13)-C(14)	1.399 (8)
Bond Angles			
C-Fe(1)-C(2)	91.9 (2)	C-Fe(1)-C(5)	89.4 (2)
C(2)-Fe(1)-C(5)	84.1 (2)	Fe(1)-C-O	178.0 (4)
Fe(1)-C(2)-C(3)	111.8 (3)	Fe(1)-C(2)-N(6)	129.4 (4)
C(3)-C(2)-N(6)	118.8 (4)	C(2)-C(3)-C(4)	104.3 (4)
C(3)-C(4)-C(5)	108.2 (4)	Fe(1)-C(5)-C(4)	108.3 (4)
C(2)-N(6)-C(7)	120.2 (4)	C(2)-N(6)-C(8)	126.4 (4)
C(7)-N(6)-C(8)	113.3 (3)	N(6)-C(7)-C(71)	111.7 (4)
N(6)-C(7)-C(72)	111.5 (4)	C(71)-C(7)-C(72)	112.6 (4)
N(6)-C(8)-C(81)	112.8 (4)	N(6)-C(8)-C(82)	113.6 (4)
C(81)-C(8)-C(82)	114.0 (4)	C(11)-C(10)-C(14)	108.3 (6)
C(10)-C(11)-C(12)	105.9 (6)	C(11)-C(12)-C(13)	110.0 (6)
C(12)-C(13)-C(14)	107.9 (5)	C(10)-C(14)-C(13)	108.0 (6)

are given in Table III, with the distances and angles given in Table IV. The molecule is shown in Figure 1, with the atomic numbering used and the final thermal ellipsoids. All calculations were carried out on a Model 30 Desktop Eclipse, using the programs and data in the Nicolet-SHELXTL package.[32]

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Registry No. **5**, 99495-03-1; **8**, 110078-09-6; **14** (isomer 1), 110078-10-9; **14** (isomer 2), 110169-81-8; **15**, 110078-11-0; **19**, 110078-12-1; **20** (isomer 1), 110078-13-2; **20** (isomer 2), 110169-82-9; **21**, 110078-14-3; **22**, 60337-37-3; **23a**, 110078-15-4; **23b**, 110078-17-6; **24a**, 110078-16-5; **24b**, 110078-18-7; **26**, 39723-01-8; **28**, 39723-03-0; KFp, 60039-75-0; Ph_3P, 603-35-0; Me_2NH, 124-40-3; *i*-Pr_2NH, 108-18-9; 1-methoxycyclobutanecarboxylic acid, 99495-07-5; 1-methoxycyclobutanecarbonyl chloride, 110046-66-7; 1-hydroxycyclopentanecarboxylic acid, 16841-19-3; 1-methoxycyclopentanecarboxylic acid, 17860-28-5; 1-methoxycyclopentanecarbonyl chloride, 73555-14-3; 1-hydroxynorbornylcarboxylic acid, 41248-20-8; *endo*-1-methoxynorbornylcarboxylic acid, 110046-67-8; *exo*-1-methoxynorbornylcarboxylic acid, 110046-68-9; 1-methoxynorbornylcarbonyl chloride, 110046-69-0; cyclobutanecarboxylic acid, 3721-95-7; 1-hydroxycyclobutanecarboxylic acid, 41248-13-9.

Supplementary Material Available: Tables of the hydrogen atom positions and the thermal parameters for the non-hydrogen atoms (2 pages); a listing of observed and calculated structure amplitudes (10 pages). Ordering information is given on any current masthead page.

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[32] Sheldrick, G. M. *DESKTOP SHELXTL*; Nicolet X-ray Instruments: Madison, WI, 1986.

Synthesis and Characterization of Polysilane Derivatives of Rhenium and Ruthenium[1]

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The preparation of the silane-metal derivatives LM-Si_n, LM = $(CO)_5Re$ or $(\eta^5\text{-}C_5H_5)Ru(CO)_2$ (Rp) and Si_n = Me_3Si, Me_5Si_2, Me_7Si_3, CH_2SiMe_3, or $CH_2Si_2Me_5$, is reported. Characterizations by ^{29}Si NMR and IR spectroscopy are included. In contrast to the related $(\eta^5\text{-}C_5H_5)Fe(CO)_2$– complexes, the new complexes of Re and Ru are not photolabile with respect to deoligomerization to monosilane metal derivatives. Base treatment of Rp-$SiMe_3$ results in migration of the silyl group from Ru to the cyclopentadienyl ring.

Introduction

There is considerable current interest in the chemistry of organopolysilane compounds.[2-4] These materials are of interest due to their potential as commercially useful photoresist materials[4] and also as dopable semiconductors.[3] We have previously shown that $(\eta^5\text{-}C_5H_5)Fe(CO)_2$– (Fp) substituents on short-chain polysilanes enhance their photochemical degradation relative to the completely permethylated analogues, eq 1.[5]

$$\text{Fp-SiMe}_2\text{SiPh}_3 \rightarrow \underset{8\%}{\text{Fp-SiMe}_2\text{Ph}} + \underset{85\%}{\text{Fp-SiMePh}_2} + \underset{7\%}{\text{Fp-SiPh}_3} \quad (1)$$

We are presently engaged in a program to enlarge the range of known polysilane metal derivatives, both in the field of high polymers and their lower homologues. In this paper we wish to report the synthesis and properties of new ruthenium and rhenium complexes.

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[1] Part 13 of "Organometalloidal Derivatives of the Transition Metals"; for part 12 see ref 5.

[2] West, R.; David, L. D.; Djurovich, P. I.; Stearly, K. L.; Srinivasan, K. S. U. Yu, H. *J. Am. Chem. Soc.* **1981**, *103*, 7352. Miller, R. D.; Hofer, D.; Rabolt, J.; Fickes, G. N. *J. Am. Chem. Soc.* **1985**, *107*, 2172.

[3] Wesson, J. P.; Williams, T. C. *J. Polym. Sci., Polym. Chem. Ed.* **1980**, *18*, 959.

[4] Hofer, D. C.; Miller, R. D.; Wilson, G. C. *SPIE* **1984**, *16*, 469. Zeigler, J. M.; Hurrah, L. A.; Johnson, *SPIE* **1985**, *166*, 539.

[5] Pannell, K. H.; Cervantes, J. C.; Hernandez, C.; Cassias, J.; Vincenti, S. *Organometallics* **1986**, *5*, 1086.

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Table I

complex[a,b]	ν(CO) cm^{-1}	anal. calcd (found)	
		C	H
Re–Me	2125, 2011, 1981	ref 22	ref 22
$ReCH_2SiMe_3$	2128 (m), 2052 (w), 2016 (s) 2012 (sh), 1980 (s)	26.62 (26.14)	2.82 (2.68)
Re–$CH_2Si_2Me_5$	2127 (m), 2052 (w), 2016 (s), 2012 (sh), 1980 (s)	28.06 (28.01)	3.58 (3.63)
Re–$SiMe_3$	2113 (mw), 2001 (s), 1968 (w)	ref 15	ref 15
Re–Si_2Me_5	2113 (mw), 2004 (s), 1969 (w), 1999 (sh)	26.17 (26.25)	3.46 (3.30)
Re–Si_3Me_7	2113 (mw), 2004 (s), 1969 (w), 1997 (sh)	27.96 (27.95)	4.16 (4.10)
Re–$SiMe(SiMe_3)_2$	2113 (mw), 2006 (s), 1970 (w), 1997 (s)	27.75 (27.95)	4.29 (4.10)
Rp–Me	2022, 1962	ref 13	ref 13
Rp–CH_2SiMe_3	2021, 1962	42.94 (42.70)	5.35 (5.21)
Rp–CH_2SiMe_5	2021, 1962	42.39 (42.48)	6.09 (6.03)
Rp–$SiMe_3$	2014, 1955		
Rp–Si_2Me_5	2014, 1956	40.77 (41.12)	5.70 (6.14)
Rp–Si_3Me_7	2014, 1957	40.85 (41.00)	6.37 (6.47)
Rp–$SiMe(SiMe_3)_2$	2016, 1959		

[a] Re = $(CO)_5Re$, Rp = $(\eta^5\text{-}C_5H_5)Ru(CO)_2$; infrared spectra run in hexane. [b] All complexes are oils with the exception of $ReCH_2Si_2Me_5$, mp 78–79.5 °C, and $ReSiMe(SiMe_3)_2$, mp 122–124 °C.

Experimental Section

All reactions were performed under inert N_2 or argon atmospheres in oven-dried glassware. All solvents were used dry and oxygen free; Me_3SiCl, Me_6Si_2, and $ClCH_2SiMe_3$ were obtained from Petrarch Systems Inc., Bristol, PA. The silanes Me_5Si_2Cl,[6] $ClCH_2Me_5Si_2$,[7] $ClSiMe_2SiMe_2SiMe_3$,[8] and $(Me_3Si)_2SiMeCl$[8] were prepared according to published procedures as was $[(\eta^5\text{-}C_5H_5)Ru(CO)_2]_2$,[9] by using $RuCl_3{\cdot}nH_2O$ purchased from Alfa. K(*sec*-Bu)$_3$BH (1.0 M in THF) and *n*-BuLi (2.5 M in hexane) were purchased from the Aldrich Chemical Co.

Infrared spectra were recorded on a Perkin-Elmer 580B spectrometer and the NMR spectra on an IBM NR/200 FTNMR spectrometer. All analysis were performed by Galbraith Laboratories Inc., Knoxville, TN.

Preparation of $[(\eta^5\text{-}C_5H_5)Ru(CO)_2]^-K^+$. Into a 100-mL Schlenk flask equipped with a magnetic stirring bar and septum was placed 0.5 g (1.0 mmol) of $[(\eta^5\text{-}C_5H_5)Ru(CO)_2]_2$ dissolved in 25 mL of THF. To this was added 6.7 mL of K-selectride (6.7 mmol) during 1 min. With mild heating (40 °C), maximum anion formation was obtained after 2.5 h as determined by infrared monitoring of the anion CO stretching frequencies at 1894 and 1811 cm^{-1}.

General Procedure for Synthesis of Rp–Si Complexes. The carbonylate solution prepared as above was cooled to −78 °C and a 2-fold excess of the corresponding chlorosilane compound added with stirring during 1 min. The solution was stirred at this temperature for 30 min, allowed to warm to room temperature, and stirred for an additional 3 h. The solvent was removed under vacuum and the residue dissolved in hexane and, subsequent to filtration and concentration, placed upon a 2 × 18 cm silica gel column. Elution with hexane yielded between 20 and 40% of the desired Rp–silyl complex.

The following were obtained in this manner: Rp–$SiMe_3$; Rp–$SiMe_2SiMe_3$; Rp–$SiMe_2SiMe_2SiMe_3$; Rp–$SiMe(SiMe_3)_2$; Rp–$CH_2SiMe_2SiMe_3$; Rp–CH_2SiMe_3.

Spectral and elemental analysis data on these complexes are presented in Tables I–III.

Synthesis of $(CO)_5Re$–$SiMe_2SiMe_3$. A 100-mL Schlenk tube fitted with a septum and a magnetic stirring bar was charged with 40 g of a 1% Na/Hg amalgam and 50 mL of THF. To this was added 1.06 g (1.62 mmol) of $Re_2(CO)_{10}$. The mixture was stirred for 1–2 h at which time infrared monitoring indicated that the starting material had been transformed into the required carbonylate salt $[(CO)_5Re]^-Na^+$, ν(CO) 1909 and 1862 cm^{-1}, along with some $[Re_2(CO)_9]^{2-}(Na^+)_2$.

After the carbonylate solution was cooled to −78 °C, 1.0 mL of $ClSi_2Me_5$ was added over 1 min. The solution was permitted to stir at the low temperature for 10 min, warmed gradually to room temperature for 30 min, and then stirred for 4 h. The solvent was removed and the residue extracted into hexane. Cooling this solution to −78 °C precipitated most of the unreacted $Re_2(CO)_{10}$. Chromatography of the resulting solution on a 2 × 25 cm silica gel column with hexane yielded 0.58 g (39%) of the title complex.

The following were synthesized by using the same technique: $(CO)_5Re$–$SiMe_3$ (37%); $(CO)_5Re$–$SiMe_2SiMe_2SiMe_3$ (13%); $(CO)_5Re$–$SiMe(SiMe_3)_2$ (50%). For the latter two complexes it was neccessary to extract the crude reaction mixture with hexane/H_2SO_4 prior to chromatography to remove siloxane impurities.

The complexes $(CO)_5Re$–CH_2SiMe_3 (8%) and $(CO)_5Re$–$CH_2SiMe_2SiMe_3$ (12%) were synthesized by the same procedure, except that is was neccessary to reflux the carbonylate/chloromethylsilane mixture for 12 h to ensure formation of the complexes.

Base Treatment of Rp–$SiMe_3$. To a cooled (−78 °C) solution of the title complex (0.1 g, 0.34 mmol) was added 1.0 mL (2.5 mmol) of *n*-BuLi. An infrared spectrum recorded after 1 h indicated the CO stretching frequencies of the title complex had disappeared and two new bands at ≃1900 and 1822 cm^{-1} were observed. To this solution was added an excess of CH_3I (0.5 g, 3.5 mmol), and the mixture was allowed to warm to room temperature (30 min). After the solution was stirred for an extra hour, the solvent was removed and the residue extracted with hexane and placed upon a 2.5 × 10 cm silica gel column. Elution with hexane produced 30 mg (28%) of $[(\eta^5\text{-}Me_3SiC_5H_4)Ru(CO)_2CH_3]$; IR (hexane ν(CO) 2022, 1960 cm^{-1}. NMR spectral data are recorded in the tables.

Photochemical Treatment of LM–Si$_n$ Complexes. Typical experiments involved irradiating THF or benzene solutions of the new complexes in quartz flasks with a 500-W Hanovia low-pressure mercury lamp for periods up to 48 h. Under these conditions the related Fp–Si$_n$ complexes would have deoligomerized to monsilane complexes. Analysis of the experiments performed in this study by using NMR techniques, ^{29}Si, ^{13}C, and ^{1}H, showed that no such deoligomerizations occurred.

Results and Discussion

Synthesis. Synthesis of new Re and Ru complexes containing a Si–Si bond has been successfully accomplished via well-established salt elimination reactions, eq 2.[10–12]

$$[LM]^-M_a^+ + R_3SiX \rightarrow R_3SiML + M_aCl \qquad (2)$$

LM = $(CO)_5Re$, $(\eta^5\text{-}C_5H_5)Ru(CO)_2$;
M_a = Na, K; R_3SiX = Me_3Si, Me_5Si_2,
Me_7Si_3 (both isomers), CH_2SiMe_3, $CH_2Si_2Me_5$

In the case of the Ru complex it was found that formation of the carbonylate anion via Na/Hg reductive cleavage of the dimer $[(\eta^5\text{-}C_5H_5)Ru(CO)_2]_2$, $[Rp]_2$, led to extremely low yields of the desired complex, with significant ruthenocene formation.[13] We therefore opted for

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(6) Kumada, M.; Ishikawa, M.; Sajiro, M. *J. Organomet. Chem.* **1964**, *2*, 478.

(7) Sakurai, H.; Tominaga, K.; Watanabe, T.; Kumada, M. *Tetrahedron Lett.* **1966**, *8*, 5493.

(8) Kumada, M.; Ishikawa, M.; Maeda, S. *J. Organomet. Chem.* **1964**, *2*, 478.

(9) Gibson, D. H.; Hsu, W. L.; Steinmetz, A. L. *J. Organomet. Chem.* **1981**, *208*, 89.

(10) King, R. B.; Pannell, K. H.; Bennett, C. R.; Ishaq, *J. Organomet. Chem.* **1969**, *19*, 327.

(11) Nicholson, B. K.; Simpson, J. *J. Organomet. Chem.* **1971**, *32*, C29.

(12) Malisch, W. *J. Organomet. Chem.* **1971**, *31*, C28.

(13) Others have observed this same problem, e.g.: (a) Jacobsen, S. E.; Wojcicki, A. *J. Organomet. Chem.* **1974**, *72*, 113. (b) Joseph, M. F.; Page, J. A.; Baird, M. C. *Inorg. Chim. Acta* **1982**, *64*, L121.

Table II. NMR Data for New Complexes

complex[a]	^{1}H	^{13}C	^{29}Si
Re–SiMe$_3$	0.53	187.9, 6.5	−13.4
Re–Si$_2$Me$_5$	0.62, 0.18	187.9, 181.2, 0.88, −1.6	−43.9, −9.9
Re–Si$_3$Me$_7$	0.7, 0.23, 0.18	188.2, 182.4, 2.4, 0.75, −6.1	−38.8, −36.7, −14.6
Re–SiMe(SiMe$_3$)$_2$	0.60, 0.26	187.6, 181.5, 0.75, −6.12	−88.4, −7.5
Re–CH$_2$SiMe$_3$	0.14, −0.66	185.4, 180.6, 2.1, −28.6	9.8
Re–CH$_2$Si$_2$Me$_5$	0.2, 0.17, −0.46	185.5, 180.4, 0.2, −1.8, −31.4	−5.0, −19.3
Rp–SiMe$_3$	4.55, 0.51	202.5, 87.0, 8.5	27.1
Rp–Si$_2$Me$_5$	4.64, 0.55, 0.18	202.2, 86.6, 3.7, −0.7	2.5, −12.2
Rp–Si$_3$Me$_7$	4.68, 0.67, 0.28, 0.26	202.1, 86.7, 5.0, −1, −4.5	6.2, −37.5, −15.1
Rp–SiMe(SiMe$_3$)$_2$	4.70, 0.62, 0.25	202.3, 86.2, 1.0, −4.1	−37.6, −9.2
Rp–CH$_2$SiMe$_3$	4.60, 0.19, 0.04	202.6, 88.0, 2.2, −29.1	9.1
Rp–CH$_2$Si$_2$Me$_5$	4.58, 0.25, 0.22	202.6, 87.9, −0.1, −1.6, −31.2	−6.9, −19.8
(C$_5$H$_4$SiMe$_3$)Ru(CO)$_2$Me	4.79, 4.68, 0.53, 0.10	202.8, 96.2, 89.8, −0.2, −32.0	−5.0

[a] Re = (CO)$_5$Re, Rp = CpRu(CO)$_2$; NMR spectra run in C$_6$D$_6$.

Table III. Δ[δ(LM^{29}Si) − δ(Me^{29}Si)]

complex	Si$^\alpha$	Si$_\beta$	Si$_\gamma$
Rp–SiMe$_3$	27.1		
Rp–SiMe$_2$SiMe$_3$	22.1	7.4	
Rp–SiMe$_2$SiMe$_2$SiMe$_3$	22.1	11.0	0.8
Rp–SiMe(SiMe$_3$)$_2$	10.9	6.7	
Rp–CH$_2$SiMe$_3$		7.2	
Rp–CH$_2$SiMe$_2$SiMe$_3$		12.7	−0.3
Re–SiMe$_3$	−13.4		
Re–SiMe$_2$SiMe$_3$	−24.4	9.6	
Re–SiMe$_2$SiMe$_2$SiMe$_3$	−22.9	12.7	1.3
Re–SiMe(SiMe$_3$)$_2$	−39.0	8.4	
Re–CH$_2$SiMe$_3$		9.8	
Re–CH$_2$SiMe$_2$SiMe$_3$		14.5	0.2

the alternative reaction sequence to obtain the desired salt, developed by Gladysz et al.,[14] namely, the reduction of [Rp]$_2$ with potassium selectride, K(*sec*-Bu)$_3$BH. This route has been successfully used to produce moderate to good yields of related Rp–alkyl complexes.[13b] The exact mechanism of this reduction is not clear, but infrared monitoring indicated the initial reaction involves formation of a formyl group exhibiting a strong ν(CO) at 1694 cm^{-1}.[14] After 2 h of mild heating at 40 °C this band disappears and two strong bands at 1894 and 1811 cm^{-1} appear which are due to the desired carbonylate anion [Rp]$^-$. With this route moderate yields of the corresponding Rp–silyl complexes were obtained.

Most reported examples of (CO)$_5$Re–silyl complexes have been synthesized by using the hydrogen elimination route (3).[15,16]

$$2R_3SiH + Re_2(CO)_{10} \rightarrow 2R_3SiRe(CO)_5 + H_2 \quad (3)$$

Such a thermal reaction involving Me$_5$Si$_2$H has been reported to produce extremely low yields of what may be Me$_5$Si$_2$Re(CO)$_5$, 2%;[17] thus the route used in this study providing between 25% and 50% yields is far preferable. However, a major side reaction occurs with the Na/Hg reduction method, namely, the formation of polynuclear carbonylate [Re$_2$(CO)$_9$]$^{2-}$.[18] This impurity, which is always formed, does not react with the various chlorosilanes and chloromethylsilanes we have used, and thus no significant separation problems were associated with the isolation and characterization of the desired products. In general the [(CO)$_5$Re]$^-$ salt reacts more rapidly with the chlorosilanes than with the chloromethylsilanes, a result of the greater susceptibility to nucleophilic substitution of the Si–Cl bond, cf. the C–Cl bond.

Spectral Properties. The use of ^{29}Si NMR for elucidating structure, bonding, and molecular dynamics of transition-metal silicon compounds has been demonstrated, and we have applied this technique to the complexes reported in this article.[19,20] The chemical shifts of the complexes are recorded in Table II, but as previously noted it is far more significant to compare the differences in chemical shift of the various complexes with those of the related permethylated organosilicon compounds, i.e. Δδ = [δ(LMSiR$_3$) − δ(MeSiR$_3$)], as recorded in Table III. Several features are apparent subsequent to this treatment.

For both the Ru and Re series of complexes the Si atom directly bonded to the metal atom (Si$_\alpha$) exhibits the greatest chemical shift difference. The Rp complexes parallel the related Fp, (η^5-C$_5$H$_5$)Fe(CO)$_2$–, complexes with shifts of the Si$_\alpha$ atom to *lower* field; however, the shifts of the Rp complexes are ≃20 ppm whereas those for Fp complexes are ≃40 ppm. In the case of the Re complexes the Si$_\alpha$ Δδ is to *higher* field with individual values ranging from −13 ppm for (CO)$_5$Re*Si*Me$_3$ to −39 ppm for (CO)$_5$Re*Si*Me(SiMe$_3$)$_2$. For both the Re and Ru complexes, was with the previously reported Fp complexes, the Si$_\beta$ atom is shifted to lower field with Δδ ≃ 10 ppm. This shift is irrespective of whether the atom attached directly to the transition-metal atom is C or Si. For all complexes thus far studied, the chemical shift of the Si$_\gamma$ atom is relatively unaffected, although the slight changes that are noted may be more definatively cataloged as more examples are synthesized.

Infrared spectral properties of silyl transition-metal carbonyls has also proven useful in determining some aspects of the metal–silicon bond characteristics.[21] The data from the complexes synthesized in this study are recorded in Table I. As with the related Fp–Si complexes, the stretching frequencies of the Rp–Si and Re–Si complexes are uniformly lower than those of the related LM–alkyl complexes. Thus, for example, whereas (CO)$_5$Re–Me has stretching frequencies at 2125, 2011, and 1981 cm^{-1},[22] the silyl complexes with direct Si–Re bonds are all some 10–13 cm^{-1} lower. Likewise ν(CO) for Rp–Me (2022, 1962 cm^{-1}) and Rp–CH$_2$SiMe$_3$ (2021, 1962 cm^{-1}) are ≃8 cm^{-1} higher than the Rp–Si complexes, e.g. Rp–SiMe$_3$ (2014, 1955 cm^{-1}). Such low-frequency shifts have been interpreted as indicating a significant σ donation of the silyl substit-

---

(14) Gladysz, J. A.; Williams, G. M.; Tam, W.; Johnson, D. L.; Parker, D. W.; Selover, J. C. *Inorg. Chem.* **1979**, *18*, 553.

(15) Burnham, R. A.; Stobart, S. R. *J. Chem. Soc., Dalton Trans.* **1977**, 1489.

(16) Dalton, J.; Smith, J. G.; Stone, F. G. A. *J. Chem. Soc. A* **1971**, 3469.

(17) Brookes, A.; Knox, S. A. R.; Stone, F. G. A. *J. Chem. Soc. A.* **1971**, 3469.

(18) Ellis, J. E.; Flom, E. A. *J. Organomet. Chem.* **1975**, *99*, 263.

(19) Pannell, K. H.; Bassindale, A. R. *J. Organomet. Chem.* **1982**, *229*, 1.

(20) Li, D. S.; Johnson, D. L.; Gladysz, J.; Servis, K. L. *J. Organomet. Chem.* **1979**, *166*, 317.

(21) Pannell, K. H.; Wu, C. C.; Long, G. J. *J. Organomet. Chem.* **1980**, *186*, 85.

(22) Wilford, J. B.; Stone, F. G. A. *Inorg. Chem.* **1965**, *4*, 389.

uent compared to that of the alkyl group. No data from such studies need to be interpreted in terms of any significant π bonding between the metal and silicon atoms.[21]

It is reported that for the Re–Me complex, no B_1 band and a single E mode band are observed due to the symmetric top nature of the Me group.[22] We note that no B mode band is observed for the disilyl and trisilyl groups, but the E mode band is split. The silylmethyl and disilylmethyl complexes exhibit both E mode splitting and the appearance of a B_1 mode band. In the case of the Rp complexes both the symmetric and antisymmetric bands are of equivalent intensity, indicating that the OC–Ru–CO bond angle is $\simeq$90° for all the complexes and that steric features of the varying $(Si)_n$ groups do not change the geometry at the metal center.

Reactivity. In contrast to the Fp–disilyl and –trisilyl complexes, irradiation of the Ru and Re polysilyl complexes with a 500-W Hanovia lamp gave no deoligomerization (<1%) after 48 h. In the case of the related Fp complexes, under identical conditions, irradiation for time periods as short as 2 h will give complete deoligomerization. It is not clear what is the root cause for such distinction between the Fp complexes and the two sets of complexes reported here. In the case of the Fp complexes, we have suggested that the initial step in the photochemical deoligomerization is the loss of a CO ligand to produce a reactive $16e^-$ system. It appears that the Ru and Re complexes are significantly resistant to CO expulsion under the conditions reported here.

Migrations of silyl groups from Fe to the cyclopentadienyl ring in Fp–SiR_3 complexes has been effected by base treatment, *n*-BuLi or Li(*i*-Pr)$_2$N.[5,23,24] These reactions involve initial deprotonation on the cyclopentadienyl ring, followed by migration of the silyl group to the ring with the formation of an Fe centered ion, which may be trapped by, inter alia, MeI. We have performed a similar reaction with Rp–$SiMe_3$ and find that an exactly analogous reaction takes place involving migration of the Me_3Si group from Ru to the cyclopentadienyl ring. The mechanism is presumably the same as that for the Fp complexes.

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Registry No. Rp–$SiMe_3$, 43184-26-5; Rp–$SiMe_2SiMe_3$, 109584-80-7; Rp–$SiMe_2SiMe_2SiMe_3$, 109584-81-8; Rp–SiMe($SiMe_3$)$_2$, 109584-82-9; Rp–$CH_2SiMe_2Me_3$, 109584-83-0; Rp–CH_2SiMe_3, 109584-84-1; LM–$SiMe_2SiMe_3$, 36632-62-9; RpK, 84332-45-6; $(Rp)_2$, 12132-87-5; $Re_2(CO)_{10}$, 14285-68-8; $Na_2[Re_2(CO)_9]$, 109584-85-2; $ClSi_2Me_5$, 1560-28-7; LM–$SiMe_3$, 55208-33-8; LM–$SiMe_2SiMe_2SiMe_3$, 109584-86-3; LM–SiMe($SiMe_3$)$_2$, 109584-87-4; LM–CH_2SiMe_3, 109584-88-5; LM–$CH_2SiMe_2SiMe_3$, 109584-89-6; $ClCH_2Me_5Si_2$, 5181-46-4; $ClSiMe_2SiMe_2SiMe_3$, 918-19-4; $(Me_3Si)_2SiMeCl$, 754-38-1; Me_3SiCl, 75-77-4; Me_6Si_2, 1450-14-2; $ClCH_2SiMe_3$, 2344-80-1; $(C_5H_4SiMe_3)Ru(CO)_2Me$, 109584-90-9; ^{29}Si, 14304-87-1.

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[23] Thum, G.; Riews, W.; Malisch, W.; *J. Organomet. Chem.* **1983**, *252*, C67.

[24] Berryhill, S. R.; Sharenow, B. *J. Organomet. Chem.* **1981**, *221*, 143. Berryhill, S. R.; Clevenger, G. L.; Burdurli, *Organometallics* **1985**, *4*, 1509.

Synthesis and Characterization of Mesitylgallium Chloride Compounds Including the Crystal and Molecular Structure of Dichloromesitylgallium(III), an Inorganic Polymer

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The mesitylgallium chloride compounds $GaMes_2Cl$ and $GaMesCl_2$ have been prepared and fully characterized by melting point data, elemental analyses, solubility properties, IR and ^1H and ^{13}C NMR spectroscopic data, and Lewis acidity studies. Cryoscopic molecular weight studies of $GaMes_2Cl$ in benzene solution are consistent with the presence of dimeric molecules. Lewis bases such as Et_2O and THF react with $(GaMes_2Cl)_2$ in benzene to establish two equilibria which are consistent with the presence of the dimer, a monochloride bridged 2:1 adduct $[(GaMes_2Cl)_2{\cdot}base]$, and the 1:1 adduct. The dichloro derivative $GaMesCl_2$ is an unusually high melting solid which is insoluble in hydrocarbon solvents and crystallizes in the centrosymmetric monoclinic space group $P2_1/m$ (C^2_{2h}; No. 11) with $a = 8.3989$ (21) Å, $b = 6.9976$ (19) Å, $c = 18.0347$ (57) Å, $\beta = 100.159$ (23)°, $V = 1043.3$ (5) Å^3, and $Z = 4$ (formula units). Diffraction data (Mo Kα, $2\theta = 5.0$–$45.0°$) were collected with a Syntex $P2_1$ diffractometer, and the structure was refined to $R_F = 6.2\%$ for all 1502 independent reflections. Dichloromesitylgallium(III) is a one-dimensional polymer in which planar GaMesCl (Mes = mesityl) units are linked by bridging chloride ligands. The correct formulation is $[Ga(C_6H_2Me_3)Cl(\mu\text{-}Cl)]_\infty$. Distances of interest include Ga···Ga = 3.781 (1) Å, Ga–Cl(terminal) = 2.150 (4)–2.164 (4) Å, Ga–Cl(bridging) = 2.363 (3)–2.369 (3) Å, and Ga–C(mesityl) = 1.943 (12)–1.970 (14) Å.

Introduction

The presence of bulky organic substituents on main-group elements leads to a variety of interesting and unusual chemical properties. Four mesityl (Mes) groups served to stabilize the first fully characterized compound with a silicon–silicon double bond,[1] Si_2Mes_4. In group 13 chemistry, the effects of bulky substituents are just beginning to be elucidated. In indium(I) chemistry, the bulky pen-

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[1] (a) West, R.; Fink, M. J.; Michl, J. *Science (Washington, D.C.)* **1981**, *214*, 1343. (b) Fink, M. J.; Michalczyk, M. J.; Haller, K. J.; West, R.; Michl, J. *Organometallics* **1984**, *3*, 793.

0276-7333/87/2306-2088$01.50/0