The OPOPO impurity here produced 0.015 mmol of $(CF_3)_2P(O)Cl$.

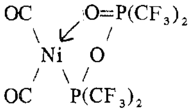
Similarly, 0.163 mmol of POPO and 0.183 mmol of HCl, in an NMR microtube, quickly showed the known ^{19}F doublet for $(CF_3)_2PCl$ at full intensity. The ^{19}F doublet for $(CF_3)_2POOH$ appeared at $\delta = 73.7$ ppm upfield of Cl_3CF ($J = 130.1\ s^{-1}$), and for ^{31}P, $\delta = -0.3$ (downfield of H_3PO_4) with $J = 129.8\ s^{-1}$ (septet not split by the proton). The proton spectrum of $(CF_3)_2POOH$ was a sharp singlet at $\delta = 13.63$ ppm (downfield of Me_4Si), probably not appreciably affected by the slight excess of HCl in the vapor phase. The HCl cleavage of either POPO or OPOPO is a relatively easy way to make a clean sample of this extremely strong acid.[9]

Potassium chloride also cleaves POPO, rapidly at 25 °C:

$$\text{POPO} + KCl \rightarrow KO_2P(CF_3)_2 + (CF_3)_2PCl\ (98\%)$$

This reaction was performed with excess KCl, finely powdered and vacuum-baked. The 2% by-product $(CF_3)_2P(O)Cl$ was due to OPOPO.

POPO as a Chelating Ligand. It was considered that the phosphine part of POPO might replace CO in nickel carbonyl, also perhaps liberating a second CO by chelation to form



The experiment employed 0.647 mmol each of $Ni(CO)_4$ and POPO, in a 25-mL reaction tube. Tiny bubbles appeared immediately at 25 °C. After 16 h, the CO was pumped off at −196 °C and measured to confirm the reaction

$$Ni(CO)_4 + \text{POPO} \rightarrow \text{POPO}\cdot Ni(CO)_3 + CO$$

The ^{19}F spectrum of the colorless liquid product showed the $(CF_3)_2P{=}O$ unit unchanged ($\delta = 72.6$ ppm and $J = 130.6\ s^{-1}$), whereas the doublet for the $(CF_3)_2P$ unit had moved upfield to $\delta = 70.0$ ppm with J increased to $101.3\ s^{-1}$, as a result of bonding P to Ni. During vacuum distillation, some CO was lost and the liquid turned green and then purple. Its ^{19}F NMR spectrum now showed (additionally) two overlapping second-order patterns, at $\delta = 53.2$ ppm with $J_1 + J_2 = 83.5\ s^{-1}$ and $\delta = 53.9$ with $J_1 + J_2 = 84.3\ s^{-1}$. It seemed that POPO had been reduced to POP (second-order spectra) in complexes wherein the transferred oxygen had either gone exclusively to nickel or oxidized some of the CO to formate. The whole reaction merits further study, including X-ray crystallography of the final purple solid.

Acknowledgment. The instruments used in this research were acquired with generous assistance by the National Science Foundation.

Registry No. POPO, 66792-50-5; POP, 2728-67-8; POPOPO, 34043-22-6; $P_2(CF_3)_4$, 2714-60-5; $(CF_3)_2PCl$, 650-52-2; $(CF_3)_2P(O)Cl$, 646-71-9; NO, 10102-43-9; $Ni(CO)_4$, 13463-39-3; $(CF_3)_2POOH$, 422-94-6; $POPO\cdot Ni(CO)_3$, 66792-56-1.

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Small-Ring Metallocycles Derived from Disiloxanes, Digermoxanes, or Bis(silyl)methanes and Transition-Metal Carbonyls

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Polymer-supported catalysts have been demonstrated to have many of the advantages possessed by both homogeneous and heterogeneous catalysts.[1-5] Cross-linked polystyrene beads, the most investigated support, are subjected to multistep modifications in order to bind transition-metal complexes to the polymer backbone.

Polymeric silicon hydrides, e.g., the commercially available Dow Corning 1107 Fluid, are potential polymer supports to which metal centers could be attached in a simple one-step reaction due to the reactivity of Si–H bonds toward low-valent metal complexes.[6-9] Furthermore, the hydridosilicone polymers may be cross-linked with, e.g., polybutadiene, to give a range of physical properties from solvent-swellable gums to brittle resins.

In order to better characterize the types of transition-metal compounds which might form with polymeric silicon hydrides, we investigated several reactions of tetramethyldisiloxane, $(Me_2SiH)_2O$ (TMDS), with transition-metal complexes since the HSiOSiH group is the simplest difunctional unit characteristic of the poly(hydridosiloxane). This work was expanded to include the behavior of tetramethyldigermoxane and bis(dimethylsilyl)methane toward metal carbonyl complexes.

Experimental Section

All air-sensitive materials were handled by standard Schlenk and/or high-vacuum techniques. Melting points were taken in sealed, evacuated capillaries. ^1H NMR spectra were recorded on a Varian A-60 spectrometer, mass spectra on an AEI 901 spectrometer, and IR spectra on a Perkin-Elmer 457 spectrometer. Photolyses were performed with a medium-pressure, 450-W Hanovia lamp. Tetramethyldisiloxane was a gift of the Dow Corning Corp.

Mass spectra were obtained on all new complexes. In all cases, the parent ion was observed, and the metallocycles had a fragmentation pattern showing $Me_4E_2XM_2(CO)_{8-n}^+$ ions. In addition, the germanium-containing complexes showed the correct isotope distributions.

1,3-Bis(tetracarbonylcobaltio)tetramethyldisiloxane, $[Me_2SiCo(CO)_4]_2O$. Tetramethyldisiloxane(0.75 g, 5.0 mmol) was added by syringe to 1.7 g (5.0 mmol) of dicobalt octacarbonyl dissolved in a minimum amount of petroleum ether (bp 30–60 °C). Gas evolution was immediate, and the solution was then allowed to stir at room temperature for 1 h, after which time the solvent was pumped away to give a brown oil. Repeated crystallization from petroleum ether at −78 °C gave the product as extremely thermolabile white crystals: ν(CO) 2080, 2020, 2000, 1960 (vw) cm^{-1}; NMR δ 0.6. Anal. Calcd for $C_{12}H_{12}Co_2O_9Si_2$: Si, 11.85; Co, 24.86. Found: Si, 11.42; Co, 24.08.

1,3-Bis(tetracarbonylcobaltio)tetramethyldigermoxane. This complex was prepared in the manner described for the disiloxane analogue above. Thus, 0.85 g (2.5 mmol) of $Co_2(CO)_8$ reacted with 0.56 g (2.4 mmol) of $(Me_2GeH)_2O$ to give the white crystalline product after low-temperature recrystallization. This compound is also extremely air-sensitive and thermolabile: ν(CO) 2090, 2040, 2020, 1985 (vw) cm^{-1}; ^1H NMR δ 1.0.

***cyclo*-1,3-(1,1,3,3-Tetramethyldisiloxanyl)octacarbonyldiiron-(*Fe–Fe*).** A solution consisting of 1.96 g (10.0 mmol) of iron pentacarbonyl and 0.67 g (5.0 mmol) of tetramethyldisiloxane in about 100 mL of pentane was photolyzed for 45 min in a jacketed, well-type reactor. The volatile material was then pumped away leaving a brown oil which was crystallized from a minimum volume of pentane at −20 °C to give the brown crystalline product, mp 84 °C, in 55% yield: ν(CO) (in hexane) 2080, 2040, 2020, 1980, 1960, 1950, 1940 cm^{-1}; ^1H NMR δ 0.55. Anal. Calcd for $C_{12}H_{12}Fe_2O_9Si_2$: C, 30.80; H, 2.59. Found: C, 30.59; H, 2.64.

cyclo-**1,3-(1,1,3,3-Tetramethyldisiloxanyl)octacarbonyldiruthenium(*Ru–Ru*).** This complex was prepared in the same manner as the iron analogue from 0.64 g (1.0 mmol) of $Ru_3(CO)_{12}$ and tetramethyldisiloxane (0.225 g, 1.5 mmol). After 90 min of photolysis, the Si–H stretch had disappeared from the IR spectrum. Removal of all volatiles gave a red oil which, when crystallized from pentane at −78 °C, gave the white crystalline product, mp 130 °C, in 50% yield. Anal. Calcd for $C_{12}H_{12}O_9Ru_2Si_2$: C, 25.81; H, 2.17. Found: C, 25.67; H, 2.09. ν(CO) (in hexane): 2090, 2060, 2030, 2010, 2000, 1990, 1940 cm^{-1}. ^{1}H NMR: δ 0.50.

cyclo-**1,3-(1,1,3,3-Tetramethyldigermoxanyl)octacarbonyldiiron(*Fe–Fe*).** This complex was prepared from iron pentacarbonyl (0.98 g, 5.0 mmol) and tetramethyldigermoxane (1.1 g, 5.0 mmol) in the manner described for the silicon analogue. After 60 min of photolysis, the volatiles were pumped off, leaving a light brown oil which afforded dark yellow crystals from pentane at −78 °C. ν(CO) (in hexane): 2080, 2040, 2020, 1980, 1960, 1950, 1940 cm^{-1}. ^{1}H NMR: δ 0.9.

cyclo-**2,4-(2,4-Dimethyl-2,4-disilapentanediyl)octacarbonyldiiron(*Fe–Fe*).** Iron pentacarbonyl (1.96 g, 10.0 mmol) and 0.66 g (5.0 mmol) of bis(dimethylsilyl)methane in ca. 100 mL of petroleum ether were photolyzed for 45 min. The volatiles were pumped off and the residue dissolved in a minimum quantity of ligroin. The mixture was then chromatographed over Florisil using deoxygenated petroleum ether as eluent. The product was crystallized from the major band to give yellow product, mp 78 °C, in 30% yield. Anal. Calcd for $C_{13}H_{14}Fe_2O_8Si_2$: C, 33.50; H, 3.03. Found: C, 33.64; H, 3.13. ν(CO) (in hexane): 2080, 2040, 2020, 1980, 1960, 1950, 1940 cm^{-1}. ^{1}H NMR: δ 0.35 (CH_3), 0.45 (CH_2).

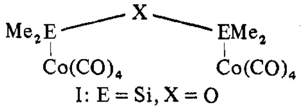
cyclo-**2,4-(2,4-Dimethyl-2,4-disilapentanediyl)octacarbonyldiruthenium(*Ru–Ru*).** Ruthenium dodecacarbonyl (0.64 g, 1.0 mmol) was dissolved in a solution of 0.20 g (1.5 mmol) of bis(dimethylsilyl)methane in ca. 100 mL of ligroin. This mixture was photolyzed for 90 min and the volatiles were then removed, leaving a red oil. The oil was dissolved in petroleum ether and chromatographed over Florisil under oxygen-free conditions. White crystals, mp 125 °C, were obtained when the major reddish orange eluate was cooled to −78 °C; yield 23%. Anal. Calcd for $C_{13}H_{14}O_8Ru_2Si_2$: C, 28.06; H, 2.54. Found: C, 28.20; H, 2.69. ν(CO) (hexane): 2090, 2060, 2030, 2010, 2000, 1990, 1940. ^{1}H NMR: δ 0.30 (CH_3), 0.40 (CH_2).

Metal–Polysiloxane Adducts. Dicobalt octacarbonyl (8.0 mmol) in petroleum ether was combined with Dow Corning 1107 Fluid (1.0 g, 16 mmol), also dissolved in petroleum ether. Hydrogen was immediately evolved. After 1 h of stirring, the solvent was removed, leaving a red oil which did not exhibit a Si–H stretch but did have a complex ν(CO) region centered around 2000 cm^{-1}. The ^{1}H NMR exhibited a singlet at δ 0.6. On standing under N_2, the red oil solidifies to an insoluble rubber (Si:Co = 1:1 by analysis). $Co_4(CO)_{12}$ may be washed out of the rubber.

Similarly, the 1107 Fluid reacts with $Fe(CO)_5$ under photolysis to give a brown, solvent-swellable resin with a Si:Fe ratio of 4:1. On standing in an inert atmosphere, the rubber hardens to a resin, and $Fe_3(CO)_{12}$ may be leached from the resin.

Results and Discussion

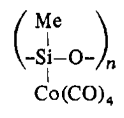
Dicobalt octacarbonyl reacts readily with tetramethyldisilane (TMDS), tetramethyldigermoxane (TMDG), or bis(dimethylsilyl)methane (BDSM) to yield the complexes I–III.



$$\underset{\displaystyle Co(CO)_4}{Me_2E}-X-\underset{\displaystyle Co(CO)_4}{EMe_2}$$

I: E = Si, X = O
II: E = Ge, X = O
III: E = Si, X = CH_2

These complexes are exceedingly thermolabile, decomposing slowly at −78 °C under a nitrogen atmoshere. The products of decomposition are $Co_4(CO)_{12}$ and unidentified polysiloxanes or polygermoxanes. This same type of instability was noted for polymeric silicone–cobalt tetracarbonyl,



$$\left(\underset{\displaystyle Co(CO)_4}{\overset{\displaystyle Me}{-Si}}-O-\right)_n$$

prepared from Dow Corning 1107 Fluid and dicobalt octacarbonyl and for various other silyl–cobalt complexes.[10-12] As these compounds appear to be much more thermolabile than mononuclear silylcobalt carbonyls,[13] the decreased stability may be due to the proximity of the two metallic centers.

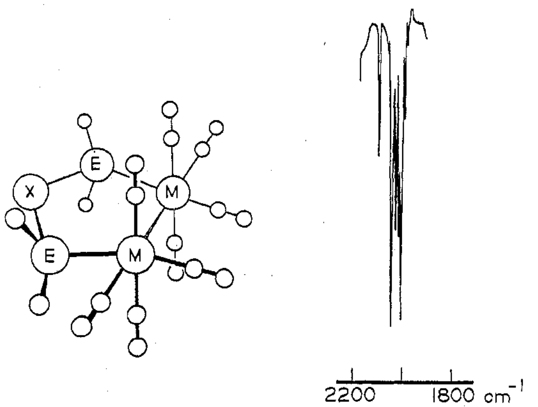
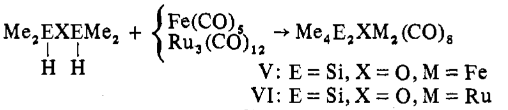


Figure 1. Proposed structure of $R_4E_2M_2(CO)_8X$ metallocycles and IR spectrum in carbonyl region of $Me_4Si_2Fe_2(CO)_8O$. The intensity pattern is typical of all five-membered metallocycles prepared in this study.

Under UV photolysis, TMDS, BDSM, and TMDG react with $Fe(CO)_5$ or $Ru_3(CO)_{12}$ to give five-membered metallocycles (eq 1). All of the complexes, V–IX, exhibited one



$$\underset{\displaystyle H\quad H}{Me_2EXEMe_2} + \left\{\begin{matrix}Fe(CO)_5\\ Ru_3(CO)_{12}\end{matrix}\right. \rightarrow Me_4E_2XM_2(CO)_8 \qquad (1)$$

V: E = Si, X = O, M = Fe
VI: E = Si, X = O, M = Ru
VII: E = Ge, X = O, M = Fe
VIII: E = Si, X = CH_2, M = Fe
IX: E = Si, X = CH_2, M = Ru

sharp singlet due to SiMe or GeMe in their ^{1}H NMR spectra, indicating the equivalence of all methyl groups, at least on the ^{1}H NMR time scale. The methylene-bridged complexes VIII and IX show in addition a singlet due to the methylene group in the correct area ratio.

The IR spectra in the carbonyl stretching region are consistent with C_{2v} symmetry for these complexes (see Figure 1). Seven bands are observed and seven bands (3 A_1 + B_1 + 3 B_2) are predicted to be IR active in C_{2v} symmetry. The diamagnetism and the preponderance of $R_4E_2XM_2(CO)_{8-n}$ ions in the mass spectra are consistent with the presence of a M–M bond. Finally, the proposed structure gives each M atom an 18-electron count. These complexes are the first examples of 1,3-disiloxanyl groups bridging M–M bonds, although other five-membered metallocycles have been reported.[12,14-16]

The reactivity of the metallocycles V–IX toward small molecules was investigated. Reactions of V with a variety of acetylenes gave only known iron–acetylene complexes[17] which contained no silicon. The ruthenium metallocycle VI failed to react with acetylenes. Both V and VI caused a moderately rapid isomerization of 1-hexene to internal hexenes, but upon attempted recovery of the catalyst, it was found that the metallocycles had decomposed to $Fe_3(CO)_{12}$ and $Ru_3(CO)_{12}$, respectively. Since both of these carbonyls are known to be isomerization catalysts for olefins, the observed isomerization was most likely due to the presence of these decomposition products.[18-20] The reaction of dimethyl disulfide with V gave only the known complex, $(\mu\text{-}Me_2S)_2Fe_2(CO)_6$.[21] No reaction was observed between V and hydrogen or sodium amalgam in THF. Inasmuch as the complexes prepared in this study serve as models, the poor stability and low reactivity observed for the siloxane–metal complexes suggest that direct attachment of metal centers to silicon in poly(methylsiloxanes) is not a feasible method of heterogenizing catalysts. However, some metals from four-membered *cyclo*-metallodisiloxanes which are active catalysts for the disproportionation of tetraalkyldisiloxanes to dialkylsilane and poly(dialkylsiloxanes).[22]

Acknowledgment. The authors thank the Dow Corning Corp. and the National Science Foundation for support of this research.

Registry No. I, 66515-89-7; II, 66515-90-0; V, 66515-91-1; VI, 66515-92-2; VII, 66515-93-3; VIII, 66515-94-4; IX, 66515-95-5; $Co_2(CO)_8$, 10210-68-1; $Fe(CO)_5$, 13463-40-6; $Ru_3(CO)_{12}$, 15243-33-1; TMDS, 3277-26-7; TMDG, 33129-30-5; BDSM, 18163-84-3.

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Thermal Decomposition of Hexachloroplatinic Acid

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The thermal decomposition of hexachloroplatinic acid has been the subject of two recent publications.[1,2] However, neither article identified the intermediate phase chemically and crystallographically and, therefore, failed to recognize some important implications of the chemistry of the intermediate.

Hexachloroplatinic acid, or chloroplatinic acid, is the most readily available compound of platinum. It is a hygroscopic material sold by the platinum assay. Anhydrous chloroplatinic acid has never been reported.[3] The commerical product is probably an oxonium salt of the hexachloroplatinate(IV) anion. Therefore, the correct formula is $[H_3O]_2[PtCl_6]\cdot xH_2O$ where x is variable; for a Pt assay of 40.0%, x is 2.32.[4]

Figure 1 shows a tracing of a thermogram of a sample of chloroplatinic acid obtained in He using a du Pont Model 950 thermogravimetric analyzer. The heating rate was 10°/min.

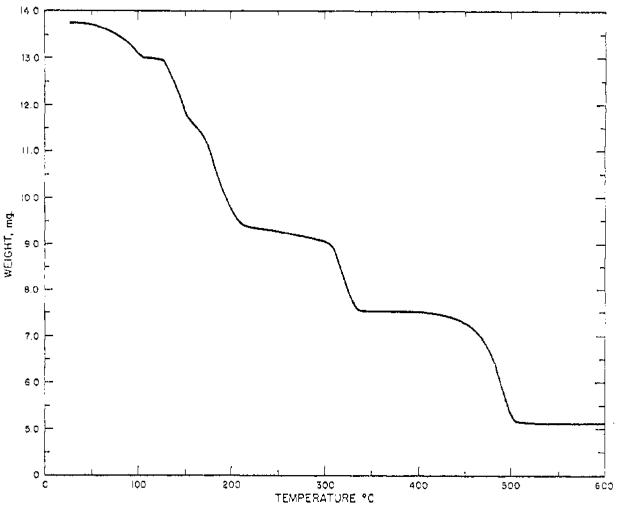

Figure 1.

Table I. Thermogravimetric Data of Chloroplatinic Acid

T, °C	sample wt, mg	% Pt obsd by anal. (H_2 reducn of separate samples)	compd present
25	13.61	40.42	$[H_3O]_2[PtCl_6]\cdot 2.04H_2O$
110–125	13.00		$[H_3O]_2[PtCl_6]\cdot 0.84H_2O$
at 220	9.35		approx $PtCl_4$
at 300	9.04		approx $PtCl_{3.5}$
350–415	7.50	73.5	$PtCl_2$[a]
above 510	5.11	100	Pt metal[b]

[a] For $PtCl_2$, theoretical % Pt = 73.32%. [b] For a 13.61-mg initial weight and 40.42% Pt, we calculate 5.50 mg of Pt at the end of the thermogram if no Pt is lost by volatilization of β-$PtCl_2$.

Identical thermograms were obtained in air or He at flow rates of 150 mL/min using either quartz or platinum sample pans. Thermograms in hydrogen gas all give elemental Pt below 100 °C. The starting material is very hygroscopic and hydrogen reduction to metal in the thermogravimetric balance was used for analysis. Also, intermediate compounds were all analyzed by hydrogen reduction to platinum. Table I shows actual weights of a typical thermogram under the stated conditions.

In air or He the final weight of metallic platinum is less than would be calculated from the initial weight of the sample and the platinum assay. When the thermogravimetric experiment at the composition shown between 350 and about 400 °C is interrupted and H_2 replaces the He purge at constant temperature, the reduction to metallic platinum occurs rapidly. The weight of platinum obtained then agrees with the platinum assay on the original sample. The formula weight of the solid in the temperature range of 350–400 °C (calculated using its weight relative to the weight of Pt metal obtained) corresponds to that of $PtCl_2$.

$PtCl_2$ is known in two different crystalline forms, α and β.[5,6] The structure of the α form has not been published. The β form contains discrete Pt_6Cl_{12} units and is volatile.[6,7] X-ray powder diffraction patterns of the $PtCl_2$ prepared by the thermogravimetric experiment were obtained using Cu Kα radiation both by photography and by use of a powder goniometer. We compared the diffractometer tracing to a powder pattern calculated from the structure of Broderson et al.[5,8] This shows that highly crystalline β-$PtCl_2$ is obtained thermogravimetrically; there was no evidence of the α form.

The weight loss above 375 °C must be due to the decomposition of $PtCl_2$ to Pt via

$$PtCl_2(s) \rightarrow Pt(s) + Cl_2(g)$$

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