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# Preparation and Derivatives of cis-$M(CO)_4(SiCl_3)_2$ (M = Fe, Ru, Os)

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The preparation of cis-$Ru(CO)_4(SiCl_3)_2$ by the ultraviolet irradiation of $Ru_3(CO)_{12}$ and excess $Cl_3SiH$ in hexane under carbon monoxide is described. The method is readily extended to the iron and previously unknown osmium analogues. Whereas cis-$Ru(CO)_4(SiCl_3)_2$ readily undergoes substitution at room temperature with ligands (L) to give mer-$Ru(CO)_3L(SiCl_3)_2$, the iron and osmium compounds require much more forcing conditions. Further substitution in the ruthenium derivatives to yield $Ru(CO)_2L_2(SiCl_3)_2$ could only be achieved when L had a small cone angle. However, it was verified that the remaining equatorial carbonyl ligand in $Ru(CO)_3(PPh_3)(SiCl_3)_2$ was still labile with the facile synthesis of $Ru(CO)_2(PPh_3)[P(OCH_3)_3](SiCl_3)_2$. The $^{31}P$ NMR spectra of the phosphorus derivatives and the isomerization (at 120 °C) of cis-$Os(CO)_4(SiCl_3)_2$ are also discussed.

## Introduction

The initial dissociation of CO is the most common rate-determining step in ligand substitution processes of octahedral metal carbonyls. Unlike square-planar complexes, cis labilization by the noncarbonyl substituent appears the most important factor in determining the rate of CO loss. Atwood and Brown have suggested that the labilization is mainly due to the stabilization of the transition state and have proposed a site-preference model to rationalize the experimental observations.[1]

The compound cis-$Ru(CO)_4(SiCl_3)_2$ is therefore remarkable in metal carbonyl chemistry in that the two carbonyls trans to the trichlorosilyl ligands undergo completely stereospecific exchange with $^{13}CO$ in heptane solution under mild conditions.[2] The peculiar mode of substitution has been interpreted by Atwood and Brown as being due to the high $\pi$-acceptor properties of the $SiCl_3$ group,[3] a possibility also suggested originally by Graham and co-workers.[2]

The nature of the intermediate in the exchange has been the subject of some discussion. Springer[4] has concluded that the simplest mechanisms consistent with the data for cis-$Ru(CO)_4(SiCl_3)_2$ were a rigid mechanism involving a square-pyramidal intermediate or a "nonrigid" mechanism involving a trigonal-bipyramidal intermediate. Graham and co-workers[2] favored the latter mechanism since such an intermediate also explained why trans-$Ru(CO)_4(SiCl_3)_2$ similarly gave, on ultraviolet irradiation under $^{13}CO$, the stereospecifically labeled cis compound as the first product. However, it may be that the thermal exchange of the cis molecule proceeds solely by a square-pyramidal intermediate and that, in the photochemical substitution of the trans isomer, the trigonal-bipyramidal intermediate is a high-energy form which quickly rearranges to the same square-pyramidal intermediate.

It was expected that substitution of the equatorial CO groups in cis-$Ru(CO)_4(SiCl_3)_2$ by ligands, to give the less common mer isomers, would readily occur. However, the study of this compound was hampered by the tedious separation (from the trans isomer) involved in the original method of preparation.[5] This paper describes a new synthesis of cis-$Ru(CO)_4(SiCl_3)_2$, free from the trans form, and its extension to the iron and previously unknown osmium analogues. The reaction of these compounds (especially cis-$Ru(CO)_4(SiCl_3)_2$) with ligands is also reported. Part of this work has appeared in a preliminary communication.[6]

## Experimental Section

**General Procedure.** Unless otherwise stated, reactions were carried out under a nitrogen atmosphere with use of standard Schlenk techniques. Many other manipulations such as removal of products from sublimation probes and preparation of the tetracarbonyl derivatives for microanalysis were carried out in the drybox (Vacuum Atmospheres). The ultraviolet irradiations were carried out with use of a Hanovia 200-W lamp inside a water-cooled, quartz jacket. The reactants in these reactions were contained in a cylindrical quartz tube (30 am × 3 cm diameter) fitted with a Teflon valve. The Carius tubes employed in this study were similar but were constructed of thick Pyrex glass. The high-pressure carbon monoxide investigations were performed in a 200-mL general-purpose bomb from Parr Instrument Co. Solvents were scrupulously dried, distilled, and stored under nitrogen before use. The carbonyls $Ru_3(CO)_{12}$ and $Os_3(CO)_{12}$ were prepared by literature methods.[7,8] Other reagents were available commericially. Most were used without further purification except $PPh_3$, which was recrystallized from $CH_2Cl_2$/hexane, and $P(OCH_3)_3$, which was distilled from sodium under nitrogen.

Infrared spectra (Table I) were recorded with a Perkin-Elmer 237 spectrometer fitted with an external recorder. The spectra (carbonyl region) were calibrated by using carbon monoxide. Phosphorus NMR spectra (Table II) were obtained on a Varian XL 100 instrument (operating in the Fourier-transform mode, with proton decoupling) with use of $CH_2Cl_2$ as solvent and $H_3PO_4$ (85%) as an external reference ($\delta = 0$, downfield negative). (Other NMR spectra were recorded on the same instrument.) Mass spectra were obtained on a Hitachi Perkin-Elmer RMU-6E double-focusing mass spectrometer using an ionization voltage of 80 eV. (Due to the fact that ruthenium and chlorine have more than one abundant isotope, the most intense peak, in the set of peaks corresponding to the parent ion, is usually 1 mass unit higher than that calculated from atomic weights.) Microanalyses (Table I) were performed by Mr. M. K. Yang of the microanalytical laboratory of Simon Fraser University. Melting points were determined in sealed capillaries by using a Gallenkamp apparatus; they are uncorrected.

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(2) Pomeroy, R. K.; Gay, R. S.; Evans, G. O.; Graham, W. A. G. *J. Am. Chem. Soc.* **1972**, *94*, 272.
(3) See ref 1, footnote 36.
(4) Springer, C. S. *J. Am. Chem. Soc.* **1973**, *95*, 1459.
(5) Pomeroy, R. K. Ph.D. Thesis, The University of Alberta, 1972.
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(7) Mantovani, A.; Cenini, S. *Inorg. Synth.* **1976**, *16*, 47.
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**Table I.** Analytical and Infrared Data

| compd | mp, °C | %C calcd | %C found | %H calcd | %H found | $\nu$(CO), cm$^{-1}$ | solvent |
|---|---|---|---|---|---|---|---|
| Fe(CO)$_4$(SiCl$_3$)$_2$[c] | 91–93 | 11.00 | 11.14 | 0.0 | 0.0 | 2125 m 2077 m 2069 vs 2061 s | a |
| d | 94–96 | | | | | 2125 2078 2071 2061 | a |
| cis-Ru(CO)$_4$(SiCl$_3$)$_2$[c] | 120–121 | 9.97 | 9.96 | 0.0 | 0.0 | 2150 w 2103 m 2094 m 2084 s | a |
| cis-Os(CO)$_4$(SiCl$_3$)$_2$[c] | 135–136 | 8.41 | 8.41 | 0.0 | 0.0 | 2153 w 2095 m 2080 vs | a |
| Fe(CO)$_3$(PPh$_3$)(SiCl$_3$)$_2$ | 220 | 37.59 | 37.71 | 2.25 | 2.23 | 2077 2035 2032 2017 | a |
| | | | | | | 2080 2037 2016 | b |
| Ru(CO)$_3$(PPh$_3$)(SiCl$_3$)$_2$ | 204–206 | 35.23 | 35.74 | 2.11 | 2.19 | 2113 2068 2047 | a |
| | | | | | | 2117 2075 2050 | b |
| Os(CO)$_3$(PPh$_3$)(SiCl$_3$)$_2$ | 214–215 | 31.32 | 31.41 | 1.89 | 1.89 | 2114 2056 2040 | a |
| | | | | | | 2118 2061 2042 | b |
| Ru(CO)$_3$[P(OCH$_3$)$_3$](SiCl$_3$)$_2$[c] | 111 | 12.47 | 12.88 | 1.57 | 1.59 | 2123 2082 2055 | a |
| Ru(CO)$_3$(PF$_3$)(SiCl$_3$)$_2$[c] | | 6.65 | 6.42 | 0.0 | 0.0 | 2140 2098 2082 | a |
| | | | | | | 2138 2096 2081 | b |
| Ru(CO)$_3$(ETPB)(SiCl$_3$)$_2$[g] | | 17.54 | 17.74 | 1.85 | 2.00 | 2133 2089 2068 | b |
| Ru(CO)$_3$[P(OC$_2$H$_5$)$_3$](SiCl$_3$)$_2$ | | 17.42 | 17.72 | 2.44 | 2.49 | 2122 2081 2054 | a |
| Ru(CO)$_3$[P(OPh)$_3$](SiCl$_3$)$_2$ | | 33.00 | 33.01 | 1.98 | 2.05 | 2124 2077 2064 | a |
| Ru(CO)$_3$[PPh(CH$_3$)$_2$](SiCl$_3$)$_2$ | | 22.31 | 22.75 | 1.87 | 1.97 | 2117 2075 2049 | b |
| Ru(CO)$_3$[PPh$_2$(CH$_3$)](SiCl$_3$)$_2$ | | 29.40 | 30.42 | 2.01 | 2.21 | 2115 2072 2046 | b |
| Ru(CO)$_3$[P[(o-C$_6$H$_4$(CH$_3$)]$_3$](SiCl$_3$)$_2$ | | 38.00 | 37.13 | 2.70 | 2.88 | 2111 2066 2041 | a |
| Ru(CO)$_3$[P(n-C$_4$H$_9$)$_3$](SiCl$_3$)$_2$ | | 27.45 | 27.30 | 4.15 | 4.04 | 2112 2062 2044 | a |
| Ru(CO)$_3$[P(C$_6$H$_{11}$)$_3$](SiCl$_3$)$_2$ | | 34.34 | 34.48 | 4.53 | 4.48 | 2106 2056 2037 | b |
| Ru(CO)$_3$(AsPh$_3$)(SiCl$_3$)$_2$ | | 33.18 | 33.46 | 1.99 | 2.03 | 2118 2072 2049 | b |
| Ru(CO)$_3$(SbPh$_3$)(SiCl$_3$)$_2$ | | 31.25 | 31.08 | 1.87 | 1.90 | 2114 2070 2047 | b |
| Ru(CO)$_3$[CNC(CH$_3$)$_3$](SiCl$_3$)$_2$[e] | | 17.89 | 17.59 | 1.69 | 1.89 | 2125 2078 2064 | a |
| Ru(CO)$_2$(PF$_3$)$_2$(SiCl$_3$)$_2$ | | 4.00 | 4.16 | 0.0 | 0.0 | 2079 | a |
| | | | | | | 2076 | b |
| Ru(CO)$_2$[P(OCH$_3$)$_3$]$_2$(SiCl$_3$)$_2$ | | 14.35 | 14.56 | 2.69 | 2.57 | 2026 | b |
| Ru(CO)$_2$(ETPB)$_2$(SiCl$_3$)$_2$·CH$_2$Cl$_2$[g] | | 21.60 | 21.33 | 2.90 | 2.98 | 2046 | b |
| Ru(CO)$_2$[P(OC$_2$H$_5$)$_3$]$_2$(SiCl$_3$)$_2$ | | 22.18 | 22.39 | 3.99 | 3.91 | 2023 | b |
| Ru(CO)$_2$[P(OPh)$_3$]$_2$(SiCl$_3$)$_2$ | | 43.61 | 44.42 | 2.89 | 2.81 | 2043 | b |
| Ru(CO)$_2$[PPh(CH$_3$)$_2$]$_2$(SiCl$_3$)$_2$ | | 30.78 | 30.73 | 3.16 | 3.22 | 2002 | b |
| Ru(CO)$_2$[PPh$_2$(CH$_3$)]$_2$(SiCl$_3$)$_2$·CH$_2$Cl$_2$ | | 37.72 | 37.85 | 3.06 | 3.08 | 2000 | b |
| Ru(CO)$_2$[P(n-C$_4$H$_9$)$_3$]$_2$(SiCl$_3$)$_2$ | | 37.60 | 37.78 | 6.55 | 6.52 | 1999 | b |
| Ru(CO)$_2$[P(OCH$_3$)$_3$](PPh$_3$)(SiCl$_3$)$_2$·CH$_2$Cl$_2$ | 162 | 32.13 | 32.44 | 2.92 | 2.97 | 2019 | b |
| Ru(CO)$_2$[P(OCH$_3$)$_3$](PPh$_3$)(SiCl$_3$)$_2$·C$_6$H$_6$ | 155 | 39.12 | 39.07 | 3.40 | 3.15 | 2019 | b |
| Ru(CO)$_2$[CNC(CH$_3$)$_3$]$_2$(SiCl$_3$)$_2$[f] | | 24.92 | 24.32 | 3.14 | 3.10 | 2043 | a |

[a] Hexane.  [b] CH$_2$Cl$_2$.  [c] Parent ion observed in the mass spectrum.  [d] Reference 30.  [e] % N: calcd, 2.60; found, 2.95.  [f] % N: calcd, 4.83; found, 4.74.  [g] ETPB = P(OCH$_2$)$_3$CC$_2$H$_5$.

**Preparation of cis-Ru(CO)$_4$(SiCl$_3$)$_2$.** A quartz tube containing Ru$_3$(CO)$_{12}$ (0.64 g, 1.0 mmol) and Cl$_3$SiH (3 mL, 30 mmol) in hexane (20 mL) was evacuated, degassed with one freeze–thaw cycle, and pressurized with carbon monoxide (2 atm). The stirred solution was irradiated with ultraviolet light (3 cm between the source and edge of solution) for at least 72 h. The colorless solution was then transferred to a Schlenk tube and cooled to –78 °C for 2 h. The hexane and excess Cl$_3$SiH were removed from the white crystals of cis-Ru-(CO)$_4$(SiCl$_3$)$_2$ (1.37 g, 95%) which were dried on the vacuum line. The compound at this stage is sufficiently pure for most purposes; however, it may be further purified by sublimation at 40 °C (0.02 mm) onto a probe at –78 °C. The compound is air sensitive, visibly yellowing in 1 h in humid air. It is, however, indefinitely stable under nitrogen or vacuum at room temperature.

It is essential in the preparation that the water jacket is kept clean during the synthesis and that the irradiation is continued for the full 72 h. If this is not done, the product is contaminated with the extremely air-sensitive cis-Ru(CO)$_4$(SiCl$_3$)(H) ($\nu$(CO) = 2147, 2089, 2074, 2071 cm$^{-1}$, in hexane solution).[6] The efficiency of the irradiation has been improved by surrounding the reaction vessel and UV lamp with aluminum foil. By recycling the mother solution, it is possible to obtain essentially quantiative yields of cis-Ru(CO)$_4$(SiCl$_3$)$_2$.

**Fe(CO)$_4$(SiCl$_3$)$_2$ and cis-Os(CO)$_4$(SiCl$_3$)$_2$.** The preparation of these compounds, in almost quantitative yield, was similar to that described for the ruthenium derivative with the following differences. The starting material for Fe(CO)$_4$(SiCl$_3$)$_2$ was Fe(CO)$_5$ (ca. 7 mmol). Since carbon monoxide is generated in the reaction, there was no need for the stabilizing atmosphere of carbon monoxide, and therefore the tube was evacuated at the start of the reaction. Since Os$_3$(CO)$_{12}$ is much less soluble in hexane, vigorous stirring (plus some mechanical shaking) was necessary to ensure all the yellow carbonyl had reacted. During the later stages of the reaction, cis-Os(CO)$_4$(SiCl$_3$)$_2$ precipitated from the solution. Warm hexane was used to facilitate the transfer of the product in the isolation stage. Although the iron

**Table II.** Phosphorus NMR Data for Ru(CO)$_3$L(SiCl$_3$)$_2$ and Ru(CO)$_2$L$_2$(SiCl$_3$)$_2$ Derivatives

| ligand | $\delta$ ligand | $\delta$ complex | $\Delta$CS[a] |
|---|---|---|---|
| Monosubstituted Derivatives | | | |
| P(OEt)$_3$ | –137.8 | –116.6 | +21.2 |
| P(OMe)$_3$ | –140.3 | –123.4 | +16.9 |
| P(OPh)$_3$ | –127.4 | –119.2 | +8.2 |
| ETPB | –92.5 | –119.7 | –27.2 |
| PPh$_3$ | +6.1 | –22.9 | –29.0 |
| PPh$_2$Me | +27.8 | –2.2 | –30.0 |
| PMe$_2$Ph | +46.4 | +14.2 | –32.2 |
| P(o-C$_6$H$_4$CH$_3$)$_3$ | +30.8 | +13.5 | –17.3 |
| P(C$_6$H$_{11}$)$_3$ | –10.2 | –37.9 | –27.7 |
| PF$_3$ | –97.0[b] | –126.9[c] | –29.9 |
| P(n-C$_4$H$_9$)$_3$ | +31.9 | +5.2 | –26.6 |
| Bissubstituted Derivatives | | | |
| P(OEt)$_3$ | –137.8 | –123.6 | +14.2 |
| P(OMe)$_3$ | –140.3 | –130.2 | +10.1 |
| P(OPh)$_3$ | –127.4 | –117.4 | +10.0 |
| ETPB | –92.5 | –125.3 | –32.8 |
| PPh$_2$M | +27.8 | –2.9 | –30.7 |
| PMe$_2$Ph | +46.4 | +9.4 | –37.0 |
| PF$_3$ | –97.0[b] | –129.6[c] | –32.6 |
| P(n-C$_4$H$_9$)$_3$ | +31.9 | 0.0 | –31.9 |

[a] $\Delta$CS is the coordination chemical shift, defined as $\delta$ complex – $\delta$ ligand, where $\delta$ complex and $\delta$ ligand are the chemical shifts of the complexed and free ligand, respectively.  [b] Taken from the literature.  [c] Fluorine decoupled.

derivative is at least as air sensitive as cis-Ru(CO)$_4$(SiCl$_3$)$_2$, the osmium analogue is more robust and can be handled for short periods in air with no apparent decomposition. Both compounds may be sublimed

(0.02 mm) at just above room temperature.

The $^{13}$C NMR spectrum of *cis*-Os(CO)$_4$(SiCl$_3$)$_2$ (CH$_2$Cl$_2$ solvent, –40 °C, Cr(acac)$_3$ relaxing agent) showed two peaks at 170.0 and 165.1 ppm downfield from Me$_4$Si ($^{13}$CH$_2$Cl$_2$ taken as $\delta$ = 54.0). These signals were assigned to the axial and equatorial carbonyl groups, respectively, on the basis of the previous $^{13}$C NMR study of these compounds.[9]

Attempts to obtain crystals of *cis*-Fe(CO)$_4$(SiCl$_3$)$_2$ apparently gave samples which were *trans*-Fe(CO)$_4$(SiCl$_3$)$_2$ in the solid state. Thus preliminary X-ray photographic data on crystals obtained from hexane solution at –15 °C indicated the space group $P2_1/n$ with unit cell dimensions $a$ = 9.0 Å, $b$ = 9.8 Å, $c$ = 8.3 Å, and $\beta$ = 96°, identical with those previously found for *trans*-Fe(CO)$_4$(SiCl$_3$)$_2$ ($a$ = 9.013 (6) Å, $b$ = 9.845 (7) Å, $c$ = 8.327 (4) Å, $\beta$ = 96.04 (4)°).[10] *trans*-Fe(CO)$_4$(SiCl$_3$)$_2$ is isostructural with *trans*-Ru(CO)$_4$(SiCl$_3$)$_2$; *cis*-Ru(CO)$_4$(GeCl$_3$)$_2$ adopts a different space group with very different cell parameters.[11] Crystals of Fe(CO)$_4$(SiCl$_3$)$_2$ obtained from solution at –78 °C had a solid-state Raman spectrum identical in pattern with those previously obtained[5] for *trans*-M(CO)$_4$(SiCl$_3$)$_2$ (M = Ru, Os), i.e.: for Fe(CO)$_4$(SiCl$_3$)$_2$ 2139 s, 2107 m, 2098 s; for *trans*-Ru-(CO)$_4$(SiCl$_3$)$_2$ 2173 s, 2143 m, 2137 s; for *trans*-Os(CO)$_4$(SiCl$_3$)$_2$ 2169 s, 2129 m, 2119 cm$^{-1}$. The infrared spectrum in solution, taken as soon as possible after dissolving solid Fe(CO)$_4$(SiCl$_3$)$_2$, was identical with that obtained if the solution had stood for some time (i.e., that given in Table I).

**Isomerization of *cis*-Os(CO)$_4$(SiCl$_3$)$_2$.** A solution of *cis*-Os-(CO)$_4$(SiCl$_3$)$_2$ (0.010 g) in heptane (20 mL) was heated to 110 °C for 12 h in an evacuated, sealed tube. An infrared spectrum of the cooled solution did not show any significant change from that of the original solution. (Since the carbonyl absorption in the infrared spectrum of *trans*-Os(CO)$_4$(SiCl$_3$)$_2$[5] is the same frequency as the strongest peak of the cis isomer (2080 cm$^{-1}$), it is hard to detect the presence of small amounts of the former compound in the presence of the latter.) The tube was reevacuated, sealed, and heated at 120 °C for 12 h. An infrared spectrum after this treatment indicated the product was mainly the trans isomer (a single strong absorption at 2080 cm$^{-1}$ in hexane), with a small amount of the cis form. Continued heating of the solution at 120 °C caused the infrared bands due to *cis*-Os(CO)$_4$(SiCl$_3$)$_2$ to decrease in intensity until they could barely be detected. Indeed, it is not certain that the bands attributed to the cis isomer were in fact not due to formally infrared-inactive modes of *trans*-Os(CO)$_4$(SiCl$_3$)$_2$. The bands in question were certainly far less intense than the band at 2048 cm$^{-1}$, attributed to *trans*-Ru-(CO)$_3$($^{13}$CO)(SiCl$_3$)$_2$ present in natural abundance.

The isomerization was not inhibited by carrying it out under 70 atm of carbon monoxide (and 120 °C). In this and other experiments involving carbon monoxide, bands in the infrared spectrum at 2023 and 2000 cm$^{-1}$ indicated the presence of trace amounts of Fe(CO)$_5$ in the carbon monoxide used (which was technical grade).

**Preparation of Ru(CO)$_3$(L)(SiCl$_3$)$_2$ Derivatives.** Except for the PF$_3$ derivative, these compounds were prepared by stirring together in hexane solution (25 mL) equimolar quantities of *cis*-Ru(CO)$_4$-(SiCl$_3$)$_2$ (ca. 1 mmol, 0.482 g) and the appropriate ligand (L) for at least 8 h. For the phosphines, a white precipitate of product began to form in the first hour of the reaction; the phosphite derivatives are more soluble in hexane. After the 8-h period, the precipitation was completed by storing it in the refrigerator at –15 °C for at least 2 h. The mother liquor was then removed and the product washed with cold hexane and dried on the vacuum line. The yield was at least 85% and in some cases almost quantitative. The analytical samples (as well-formed crystals) were obtained by recrystallization of the compounds from either CH$_2$Cl$_2$–hexane or benzene–hexane under carbon monoxide.

The SbPh$_3$ derivative was very pale yellow even after two recrystallizations, suggesting it is a property of the compound. All other compounds reported here are white. The reaction of BiPh$_3$ with *cis*-Ru(CO)$_4$(SiCl$_3$)$_2$ gave a product which appeared both thermally unstable and very air sensitive and was not investigated further.

$^1$H NMR: for Ru(CO)$_3$[P(OCH$_3$)$_3$](SiCl$_3$)$_2$, $\delta$ = 3.87 (d, $J_{P-H}$ = 12.0 Hz, CDCl$_3$ solution, with Me$_4$Si as internal standard); for Ru(CO)$_3$[CNC(CH$_3$)$_3$](SiCl$_3$)$_2$, $\delta$ = 1.60.

(9) Vancea, L.; Pomeroy, R. K.; Graham, W. A. G. *J. Am. Chem. Soc.* **1976**, *98*, 1407.
(10) Whitla, W. A.; Graham, W. A. G., unpublished results.
(11) Ball, R.; Bennett, M. *J. Inorg. Chem.* **1972**, *11*, 1806.

The P(*o*-tol)$_3$ derivative decomposes within seconds in air; the PPh$_3$ compound shows signs of decomposition after 1 h, whereas, for the P(OCH$_2$)$_3$CC$_2$H$_5$ analogue, decomposition is not apparent until after ca. 24 h.

There was no detectable conversion of Ru(CO)$_3$[P(OCH$_3$)$_3$](SiCl$_3$)$_2$ to Ru(CO)$_4$(SiCl$_3$)$_2$ after treatment with carbon monoxide (80 atm) in benzene solution at 100 °C for 12 h. However, similar treatment of Ru(CO)$_3$(PPh$_3$)(SiCl$_3$)$_2$ did give a small amount of Ru(CO)$_4$-(SiCl$_3$)$_2$ detected as the trans isomer ($\nu$(CO) = 2089 cm$^{-1}$, hexane solution) on sublimation of the solid product remaining after evaporation of the benzene.

The formation of Ru(CO)$_3$(PPh$_3$)(SiCl$_3$)$_2$ from *cis*-Ru(CO)$_4$-(SiCl$_3$)$_2$ and PPh$_3$ was considerably slowed when the reaction was carried out under 70 atm of carbon monoxide.

**Preparation of Ru(CO)$_3$(PF$_3$)(SiCl$_3$)$_2$.** A Carius tube containing a solution of *cis*-Ru(CO)$_4$(SiCl$_3$)$_2$ (0.20 g, 0.41 mmol) in hexane (15 mL) was cooled to –196 °C and evacuated. The solution was degassed with one freeze–thaw cycle. It was allowed to warm until it just melted, and then the tube was pressurized with PF$_3$ (ca. 2 atm). The solution was stirred at room temperature for 7 h. After approximately each 90-min period, the tube was cooled to –196 °C and the carbon monoxide was removed on the vacuum line. After the 7-h period, the clear solution was transferred to a Schlenk tube which was cooled to –78 °C for several hours. The supernatant liquid was removed from the white, crystalline Ru(CO)$_3$(PF$_3$)(SiCl$_3$)$_2$ (0.20 g, 89%) which was dried on the vacuum line. The analytical sample was obtained by subliming the product at room temperature (and 0.02 mm) onto a probe at –78 °C. Although it is very difficult to obtain Ru(C-O)$_3$(PF$_3$)(SiCl$_3$)$_2$ free of Ru(CO)$_4$(SiCl$_3$)$_2$ and Ru(CO)$_2$(PF$_3$)$_2$(SiCl$_3$)$_2$ because of their similar properties, the product, as isolated in the above procedure, appeared pure by infrared and $^{31}$P NMR spectroscopy (as well as chemical analysis).

There was no reaction of either Fe(CO)$_4$(SiCl$_3$)$_2$ or *cis*-Os-(CO)$_4$(SiCl$_3$)$_2$ with PF$_3$ under similar conditions even after several days.

**Preparation of Fe(CO)$_3$(PPh$_3$)(SiCl$_3$)$_2$.** (For reasons which are not clear, solutions of Fe(CO)$_4$(SiCl$_3$)$_2$ and PPh$_3$ are extremely oxygen sensitive.) A solution of Fe(CO)$_4$(SiCl$_3$)$_2$ (0.365 g, 0.84 mmol) and PPh$_3$ (0.22 g, 0.84 mmol) in heptane was heated at 110–120 °C in an evacuated sealed tube for 16 h. On cooling of the solution, the product Fe(CO)$_3$(PPh$_3$)(SiCl$_3$)$_2$ (0.53 g, 95%) deposited as pale yellow, almost colorless, crystals. The infrared spectrum in the carbonyl region of the compound as obtained showed a shoulder besides the three principal peaks (Table I). The infrared spectrum (and color) of the compound did not change after successive recrystallizations from CH$_2$Cl$_2$–hexane and benzene–hexane.

When equimolar quantities of Fe(CO)$_4$(SiCl$_3$)$_2$ and PPh$_3$ were heated together (in benzene) at 75 °C, an infrared spectrum after 2 days showed approximately equal quantities of Fe(CO)$_3$(PPh$_3$)-(SiCl$_3$)$_2$ and starting material. Even after a further 3 days of heating, Fe(CO)$_4$(SiCl$_3$)$_2$ could still be detected in the solution.

When Fe(CO)$_3$(PPh$_3$)(SiCl$_3$)$_2$ was heated in a sealed capillary to approximately 200 °C, it changed to a deeper yellow. The process seemed reversible, undergoing the color change several times with no apparent decomposition. (The compound melts above 220 °C with decomposition.)

**Preparation of Os(CO)$_3$(PPh$_3$)(SiCl$_3$)$_2$.** An evacuated Carius tube containing *cis*-Os(CO)$_4$(SiCl$_3$)$_2$ (0.285 g, 0.50 mmol) and PPh$_3$ (0.131 g, 0.50 mmol) in hexane (15 mL) was heated at 130–135 °C for 12 h. On cooling of the solution, white crystals of the product separated. After removal of the mother liquor and washing with hexane, the product was transferred to a Schlenk tube by using CH$_2$Cl$_2$ (3 × 5 mL). Removal of the CH$_2$Cl$_2$ on the vacuum line gave Os(CO)$_3$-(PPh$_3$)(SiCl$_3$)$_2$ (0.33 g, 82%). The analytical sample was obtained by recrystallization from benzene–hexane.

An infrared spectrum of the solution after a similar experiment, except that it was carried out at 100 °C, showed only the cis–trans mixture of Os(CO)$_4$(SiCl$_3$)$_2$ with perhaps a trace of Os(CO)$_3$-(PPh$_3$)(SiCl$_3$)$_2$. At 120 °C after 24 h the products were *trans*-Os-(CO)$_4$(SiCl$_3$)$_2$ and Os(CO)$_3$(PPh$_3$)(SiCl$_3$)$_2$; i.e., isomerization had occurred without incorporation of PPh$_3$.

Neither Os(CO)$_3$(PPh$_3$)(SiCl$_3$)$_2$ nor the iron analogue reacted with P(OCH$_3$)$_3$ when stirred in solution at room temperature with an excess of the phosphite.

**Preparation of Ru(CO)$_2$[P(OCH$_3$)$_3$]$_2$(SiCl$_3$)$_2$.** To *cis*-Ru(CO)$_4$-(SiCl$_3$)$_2$ (0.22 g, 0.46 mmol) in heptane (20 mL) was added P(OCH$_3$)$_3$

(0.135 g, 1.09 mmol) and the solution heated to 60–65 °C for 20 h. The solution was allowed to cool to room temperature and the heptane decanted from the white microcrystalline product, which was washed with hexane and dried on the vacuum line. The yield of Ru(CO)$_2$-[P(COH$_3$)$_3$]$_2$(SiCl$_3$)$_2$ was 88% (0.27 g). The analytical sample was obtained by recrystallization from benzene–hexane. $^1$H NMR: δ = 3.91, 3.72 (CDCl$_3$ solution) (main peaks of the H$_3$PP′H′$_3$ system).

The reaction did not go at a convenient rate at lower temperatures; e.g., there was no discernible formation of the bissubstituted product after Ru(CO)$_3$[P(OCH$_3$)$_3$](SiCl$_3$)$_2$ was stirred in solution with excess P(OCH$_3$)$_3$ for 24 h.

The compound showed no visible signs of decomposition after exposure to air for 24 h. Prolonged exposure did cause gradual yellowing.

Treatment of Ru(CO)$_2$[P(OCH$_3$)$_3$]$_2$(SiCl$_3$)$_2$ (in heptane solution) with carbon monoxide (70 atm) at 110 °C gave some Ru(CO)$_3$[P-(OCH$_3$)$_3$](SiCl$_3$)$_2$ (as detected by infrared spectroscopy) after 18 h. The amount of monosubstituted compound increased slightly with a further 24-h treatment with carbon monoxide under the same conditions.

Except for the two cases given below, the other Ru(CO)$_2$L$_2$(SiCl$_3$)$_2$ derivatives were prepared in a manner similar to the method given for Ru(CO)$_2$[P(OCH$_3$)$_3$]$_2$(SiCl$_3$)$_2$. The *tert*-butyl isocyanide derivative was however prepared at room temperature with a reaction time of 24 h. $^1$H NMR for Ru(CO)$_2$[CNC(CH$_3$)$_3$]$_2$(SiCl$_3$)$_2$: δ = 1.57 (CDCl$_3$ solution). This derivative appeared quite air sensitive. Some derivatives crystallized from CH$_2$Cl$_2$ retained a molecule of solvent.

It was verified that the bis PPh$_2$CH$_3$ and PPh(CH$_3$)$_2$ derivatives could be prepared from *trans*-Ru(CO)$_4$(SiCl$_3$)$_2$ and the appropriate phosphine by heating the two together in heptane at temperatures above 70 °C. There was no reaction below these temperatures. (Isomerization of the trans form occurs at a measurable rate above 70 °C.)

**Preparation of Ru(CO)$_2$(PF$_3$)$_2$(SiCl$_3$)$_2$.** The preparation of this compound was essentially the same as Ru(CO)$_3$(PF$_3$)(SiCl$_3$)$_2$ except that a time period of 4 days was used and the carbon monoxide was removed approximately every 8 h. The yield was almost quantitative. The above reaction may be reversed by using carbon monoxide in place of PF$_3$. Both PF$_3$ derivatives are air sensitive.

**Preparation of Ru(CO)$_2$[P(OPh)$_3$]$_2$(SiCl$_3$)$_2$.** (The reaction was carried out in a round-bottom flask, 80-mL total volume, fitted with a Teflon valve.) A hexane solution (25 mL) of Ru(CO)$_3$[P-(OPh)$_3$](SiCl$_3$)$_2$ (0.101 g, 0.132 mmol) and P(OPh)$_3$ (0.052 g, 0.17 mmol) was cooled to –196 °C and the vessel evacuated. The solution was degassed with two freeze–thaw cycles and then stirred for 40 h at 30 °C (the evacuation and degassing were repeated after 20 h). After the 40-h period the hexane and excess P(OPh)$_3$ were removed from the white, crystalline precipitate which was then washed with hexane and dried on the vacuum line (the yield was essentially quantitative). The analytical sample (as air-stable, white crystals) was obtained by recrystallization from benzene.

**Attempted Preparation of Ru(CO)$_2$(PPh$_3$)$_2$(SiCl$_3$)$_2$.** When a CH$_2$Cl$_2$ solution of Ru(CO)$_3$(PPh$_3$)(SiCl$_3$)$_2$ and excess PPh$_3$ were stirred together in a Schlenk tube to which a bubbler was fitted (i.e., an essentially static atmosphere), there was no detectable reaction even after 3 weeks. Similarly, when Ru(CO)$_3$(PPh$_3$)(SiCl$_3$)$_2$ and excess PPh$_3$ in benzene were heated in an evacuated sealed tube at 80 °C for 30 h, an infrared spectrum of the reaction solution showed only a very weak band at 1994 cm$^{-1}$ besides those bands due to the starting material. This indicated that if Ru(CO)$_2$(PPh$_3$)$_2$(SiCl$_3$)$_2$ was present, it was so in only trace amounts.

A solution of *cis*-Ru(CO)$_4$(SiCl$_3$)$_2$ (0.20 g, 0.41 mmol) and PPh$_3$ (0.52, 2.0 mmol) in CH$_2$Cl$_2$ (30 mL) was stirred under a slow stream of nitrogen. Over a period of 24 h (CH$_2$Cl$_2$ was added to replace evaporation losses), the solution became yellow and an absorption in the infrared spectrum at 1997 cm$^{-1}$ became more intense (with a concomitant decrease in those absorptions due to the monosubstituted derivatives). The infrared spectrum of the monosubstituted derivative could be restored by passing carbon monoxide over the solution instead of nitrogen. All attemps to precipitate the presumed Ru(CO)$_2$-(PPh$_3$)$_2$(SiCl$_3$)$_2$ from solution gave yellow products which had several absorptions in the carbonyl region of the infrared spectrum.

**Preparation of Ru(CO)$_2$(PPh$_3$)[P(OCH$_3$)$_3$](SiCl$_3$)$_2$.** A solution of *cis*-Ru(CO)$_4$(SiCl$_3$)$_2$ (0.20 g, 0.41 mmol) and PPh$_3$ (0.14, 0.53 mmol) in CH$_2$Cl$_2$ (20 mL) was stirred overnight. An infrared spectrum taken at this stage indicated only Ru(CO)$_3$(PPh$_3$)(SiCl$_3$)$_2$. To the solution

was added P(OCH$_3$)$_3$ (1.0 mL, 8.5 mmol), and the solution was stirred. The progress of the reaction was monitored by infrared spectroscopy which indicated that it was essentially complete after 6 h. After this period, an equal volume of hexane was added and the resulting solution cooled at –78 °C. The product Ru(CO)$_2$(PPh$_3$)[P(OCH$_3$)$_3$](SiCl$_3$)$_2$ (white crystals) was separated from the reaction solution, washed with hexane, and dried on the vacuum line. The analytical results (Table I) indicated solvent was associated with the compound, no matter if the compound was recrystallized from CH$_2$Cl$_2$–hexane or benzene–hexane. The presence of CH$_2$Cl$_2$ was confirmed by $^1$H NMR spectroscopy on the sample recrystallized from that solvent, i.e.: δ = 7.52–7.32 (aromatic protons), 5.29 (CH$_2$Cl$_2$), 3.53 (d, $J_{P-H}$ = 11.2 Hz, methyl protons); ratio of last two peaks 2:9 (CDCl$_3$ solvent, Me$_4$Si as internal standard). In both cases, the samples were well-formed crystals which appeared air stable.

A similar reaction of Ru(CO)$_3$(PPh$_3$)(SiCl$_3$)$_2$ with P(OCH$_3$)$_3$ was carried out only with the reagents in a mole ratio of 1:1.5. Infrared spectra taken at 1, 2.5, and 6 h were identical with those taken at the same stage for the reaction where the mole ratio was 1:21. (The yield of the product as Ru(CO)$_2$(PPh$_3$)[P(OCH$_3$)$_3$](SiCl$_3$)$_2$·CH$_2$Cl$_2$ was 97% in the latter reaction.)

**Preparation of Ru(CO)$_2$[P(OC$_2$H$_5$)$_3$]$_2$(SiCl$_3$)$_2$ from Ru(CO)$_3$-(PPh$_3$)(SiCl$_3$)$_2$.** A solution of Ru(CO)$_3$(PPh$_3$)(SiCl$_3$)$_2$ was first prepared by stirring *cis*-Ru(CO)$_4$(SiCl$_3$)$_2$ (0.280 g, 0.58 mmol) and PPh$_3$ (0.152, 0.58 mmol) in benzene (20 mL) for 16 h. To this solution was added P(OC$_2$H$_5$)$_3$ (0.87 g, 5.4 mmol), and the mixture was then heated to 65–70 °C for 4 h. After this period the solution was cooled to room temperature, hexane (15 mL) was added, and the resulting mixture was placed in the refrigerator at –12 °C overnight. Solvent and excess phosphite were removed from the white crystalline product, Ru(CO)$_2$[P(OC$_2$H$_5$)$_3$]$_2$(SiCl$_3$)$_2$ (0.36 g, 82%), which was washed with hexane and dried on the vacuum line. The analytical sample was obtained by recrystallization from CH$_2$Cl$_2$–hexane. The product was identified by its carbonyl infrared spectrum (2022 cm$^{-1}$, CH$_2$Cl$_2$ solution) and C/H analysis. Anal. Calcd: C, 22.18; H, 3.99. Found: C, 22.45; H, 4.02.

A similar reaction was carried out by using P(OCH$_3$)$_3$ in place of P(OC$_2$H$_5$)$_3$. The product Ru(CO)$_2$[P(OCH$_3$)$_3$]$_2$(SiCl$_3$)$_2$ was identified by its infrared spectrum (2026 cm$^{-1}$, CH$_2$Cl$_2$ solution) and $^1$H NMR spectrum.

## Results and Discussion

Ultraviolet irradiation of Ru$_3$(CO)$_{12}$ in hexane with excess Cl$_3$SiH under 2 atm of carbon monoxide gives, after 3 days, a virtually quantitative yield of *cis*-Ru(CO)$_4$(SiCl$_3$)$_2$. It is essential that the irradiation is carried out in quartz apparatus. This method may be contrasted to the reaction of Ru$_3$(CO)$_{12}$ and Cl$_3$SiH at 180 °C under carbon monoxide pressure to give a mixture of *cis*- and *trans*-Ru(CO)$_4$(SiCl$_3$)$_2$ in an approximate ratio of 1:3.[2,5]

An intermediate, *cis*-Ru(CO)$_4$(SiCl$_3$)(H), can be isolated from the reaction involving ultraviolet irradiation.[12] The hydride does not react with further Cl$_3$SiH unless irradiated, even though the molecule has a labile carbonyl group trans to the SiCl$_3$ ligand. This suggests the reaction of the hydride to give the bis(trichlorosilyl) derivative may go via a radical mechanism; Cl$_3$SiH is known to produce radicals under the ultraviolet irradiation.[13]

The iron and previously unknown osmium analogues of Ru(CO)$_4$(SiCl$_3$)$_2$ may be prepared by a similar procedure.[14] The cis configuration for the latter compound[16] is readily deduced from the two $^{13}$C signals in the $^{13}$C NMR spectrum due to the axial and equatorial carbonyl groups and also from the three carbonyl absorptions the compound exhibits in the

(12) The isolation and chemistry of *cis*-Ru(CO)$_4$(SiCl$_3$)(H) will be the subject of a separate paper. A preliminary account is given in ref 6.
(13) Sharp, K. G.; Sutor, P. A.; Farrar, T. C.; Ishibitsu, K. *J. Am. Chem. Soc.* **1975**, *97*, 5612.
(14) It has been found previously that ultraviolet irradiation of Fe(CO)$_5$ and Cl$_3$SiH gives *cis*-Fe(CO)$_4$(SiCl$_3$)(H) as a first product.[15]
(15) Jetz, W.; Graham, W. A. G. *Inorg. Chem.* **1971**, *10*, 4.
(16) The trans isomer may be prepared by the reaction of Os$_3$(CO)$_{12}$ with Cl$_3$SiH at 180 °C under 80 atm of carbon monoxide.[5]

solution infrared spectrum (Table I). It is assumed that two absorptions are degenerate[17] (at 2080 cm$^{-1}$) since four infra-red-active carbonyl stretches are expected for a M(CO)$_4$L$_2$ molecule of $C_{2v}$ symmetry. The iron compound has been shown by $^{13}$C NMR spectroscopy to consist of a mixture of cis and trans isomers (in the ratio of 4:1) in dynamic equilibrium at room temperature.[9] From a comparison of the pattern and position of the carbonyl bands in the infrared spectra of *cis-* and *trans*-M(CO)$_4$(SiCl$_3$)$_2$ (M = Ru, Os), it is probable that the absorption at 2069 cm$^{-1}$ in the spectrum of the iron derivative can be assigned to that due to the trans isomer. The absorption may be coincident with a band of the cis molecule.

Heating *cis*-Os(CO)$_4$(SiCl$_3$)$_2$ in solution to above 120 °C causes almost complete isomerization to the known trans isomer (which has a single carbonyl absorption at 2080 cm$^{-1}$ in the infrared spectrum).[16] The temperature of isomerization may be compared to the iron case and *cis*-Ru(CO)$_4$(SiCl$_3$)$_2$; the latter undergoes observable isomerization above 70 °C to give an equilibrium mixture having a cis to trans ratio of 1:2.2.[18]

The success of the present method in giving the thermo-dynamically less favored cis isomers (for the ruthenium and osmium compounds) almost certainly can be explained in terms of the preferred geometry adopted by the five-coordinate intermediate M(CO)$_3$(SiCl$_3$)$_2$ (M = Ru or Os). As stated in the Introduction, ultraviolet irradiation of *trans*-Ru(CO)$_4$-(SiCl$_3$)$_2$ under carbon monoxide gives the cis isomer.

The complete isomerization of *cis*-Os(CO)$_4$(SiCl$_3$)$_2$ to the trans form illustrates the trend that, for this type of complex, as one goes down the periodic table, the trans form is increasingly more favored.[9] This has been rationalized[19] for *cis*-Fe(CO)$_4$(SnCl$_3$)$_2$ and *trans*-Ru(CO)$_4$(SnCl$_3$)$_2$; in the latter case the π-acceptor capability of the SnCl$_3$ ligand (when bonded to ruthenium) is assumed comparable to that of carbon monoxide, and therefore the cis and trans forms would be equally preferred from an electronic standpoint and steric factors determine the adoption of the trans arrangement. Applying these arguments to the M(CO)$_4$(SiCl$_3$)$_2$ series of compounds, one can see (Table I) that the CO stretching frequencies of the ruthenium and osmium compounds (which are similar) are significantly higher than those of the iron derivative, which could be taken as indicating there is less π bonding between the heavier metals and CO and hence more to the SiCl$_3$ group. Why the trans isomer is more favored for osmium than for ruthenium is even less clear. If the SiCl$_3$ ligand were a better π acceptor than carbon monoxide, in, e.g., *cis*-Ru(CO)$_4$(SiCl$_3$)$_2$, then one would expect the cis geometry to again be preferred, since such a configuration would avoid as far as possible the two SiCl$_3$ groups competing for the same π-electron density on the metal atom. It is apparent that the most stable geometry adopted is a subtle balance of steric and electronic factors which are difficult to rationalize with any degree of confidence. Certainly the very high CO stretching frequencies of these compounds and the fact that in *cis*-Ru-(CO)$_4$(SiCl$_3$)$_2$ the equatorial carbonyl groups are labilized are consistent with the SiCl$_3$ ligand having exceptionally high π acceptor properties in these derivatives. It should also be pointed out that the trans bond-weakening effects of CO and GeCl$_3$ were adjudged the same from the crystal structures of *cis-* and *trans*-Ru(CO)$_4$(GeCl$_3$)$_2$.[11]

The structure of *cis*-Ru(CO)$_4$(GeCl$_3$)$_2$ showed it to have almost regular octahedral coordination with very little inter-

action between the GeCl$_3$ ligands. However, in *cis*-Fe-(CO)$_4$[Si(CH$_3$)$_3$]$_2$[20] and *cis*-Fe(CO)$_4$(SnPh$_3$)$_2$[21] there is significant distortion from octahedral geometry. Although the crystal structure of *trans*-Fe(CO)$_4$(SiCl$_3$)$_2$ is essentially a regular octahedral configuration,[10] bond lengths and angles taken from this molecule predict that, in the cis molecule, some of the chlorine atoms on opposite SiCl$_3$ groups would approach each other at a distance which is less than the sum of their van der Waals radii, and therefore distortion might occur. Attempts at preparing crystals of *cis*-Fe(CO)$_4$(SiCl$_3$)$_2$, for reasons which are discussed later, were unsuccessful.

The group of molecules M(CO)$_4$(SiCl$_3$)$_2$ (M = Fe, Ru, Os) belongs to the more general class of molecules M(CO)$_4$(ER$_3$)$_2$ (E = Si, Ge, Sn, Pb; R = organic group or chlorine), many of which undergo cis–trans isomerization[22] observable on the NMR time scale.[9] The barrier to the rearrangement for analogous complexes was found to be in the order Fe ≪ Ru ~ Os which is consistent with the result found here for Os-(CO)$_4$(SiCl$_3$)$_2$. The available evidence indicates that, when R = organic group (e.g., methyl), the rearrangement is a nondissociative process. Kinetic and labeling studies[18] suggest that the isomerization of *cis*-Ru(CO)$_4$(SiCl$_3$)$_2$ is also a non-dissociative process, even though this molecule readily loses CO in solution. As pointed out, it appears that, if the five-coordinate species Ru(CO)$_3$(SiCl$_3$)$_2$ is formed, the cis molecule results. That both Fe(CO)$_4$(SiCl$_3$)$_2$ and Os(CO)$_4$(SiCl$_3$)$_2$ undergo isomerization in the presence of PPh$_3$ without incorporation of the phosphine ligand and that isomerization of the osmium derivative is not inhibited by carbon monoxide pressure support the idea that the isomerization in these molecules also proceeds by a nondissociative pathway.

Attempts at obtaining crystals of *cis*-Fe(CO)$_4$(SiCl$_3$)$_2$ gave only the trans isomer. Thus preliminary X-ray data on samples of Fe(CO)$_4$(SiCl$_3$)$_2$ obtained by recrystallization at –15 °C indicated the same cell parameters and space group as those previously found for *trans*-Fe(CO)$_4$(SiCl$_3$)$_2$ (obtained by sublimation of Fe(CO)$_4$(SiCl$_3$)$_2$).[10] Even recrystallization at –78 °C produced a product whose Raman spectrum in the solid state was identical in pattern with the spectra observed for *trans*-M(CO)$_4$(SiCl$_3$)$_2$ (M = Ru, Os). This suggests that the dynamic cis–trans equilibrium is displaced in favor of the less soluble trans isomer on precipitation or sublimation of Fe(CO)$_4$(SiCl$_3$)$_2$.

**Comparison of the Reactivity of the M(CO)$_4$(SiCl$_3$)$_2$ Molecules.** Not unexpectedly, *cis*-Ru(CO)$_4$(SiCl$_3$)$_2$ reacts at room temperature with PPh$_3$ in hexane to give an essentially quantitative yield of *mer*-Ru(CO)$_3$(PPh$_3$)(SiCl$_3$)$_2$ after approximately 8 h. In contrast, the iron and osmium compounds require much more vigorous conditions to effect substitution. A temperature above 100 °C is required before Fe(CO)$_4$-(SiCl$_3$)$_2$ reacts at a convenient rate with PPh$_3$. Similarly, a temperature of 135 °C is required to bring about the same reaction for Os(CO)$_4$(SiCl$_3$)$_2$.

Except for a minor peak in the case of the iron compound, all three compounds of the formula M(CO)$_3$(PPh$_3$)(SiCl$_3$)$_2$ have the same pattern in the infrared spectrum (carbonyl region). It is probable that they all have the same geometry, namely, a meridional arrangement of the noncarbonyl ligands with the SiCl$_3$ groups mutually cis. A meridional configuration with the SiCl$_3$ ligands trans cannot be completely ruled out for the iron and osmium cases since the trans isomer is present under the conditions of synthesis. However, it is thought

(17) It is of interest that *cis*-Ru(CO)$_4$(GeCl$_3$)$_2$ also shows only three carbonyl absorptions.[5] The structure of this compound has been established by X-ray crystallography.[11]
(18) Ng, T. W.; Pomeroy, R. K.; Graham, W. A. G., unpublished results.
(19) Pomeroy, R. K.; Elder, M.; Hall, D.; Graham, W. A. G. *J. Chem. Soc. D* **1969**, 381.

(20) Vancea, L.; Bennett, M. J.; Jones, C. E.; Smith, R. A.; Graham, W. A. G. *Inorg. Chem.* **1977**, *16*, 897.
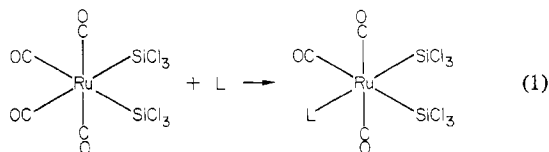(21) Pomeroy, R. K.; Vancea, L.; Calhoun, H. P.; Graham, W. A. G. *Inorg. Chem.* **1977**, *16*, 1508.
(22) The trans isomer of the iron derivatives cannot be detected in most cases. However, rapid exchange of the axial and equatorial carbonyl groups in the cis compound occurs, presumably via a trans intermediate.

unlikely in view of the fact that *trans*-Ru(CO)$_4$(SiCl$_3$)$_2$ does not react with PPh$_3$ below isomerization temperatures and that M(CO)$_3$(SiCl$_3$)$_2$, the intermediate by which the reaction probably proceeds, would most likely have the SiCl$_3$ groups cis, as indicated by the $^{13}$CO-exchange studies on Ru(CO)$_4$-(SiCl$_3$)$_2$.[2] The small additional carbonyl peak in the infrared spectrum of the iron derivative may indicate the presence of another isomer of Fe(CO)$_3$(PPh$_3$)(SiCl$_3$)$_2$, where isomerization has occurred after coordination of the phosphine. It has been found previously that the barrier to cis–trans isomerization is considerably raised when a carbonyl group in Os(CO)$_4$-[Si(CH$_3$)$_3$]$_2$ is replaced by PPh$_3$.[5] However, because that barrier to rearrangement is much lower in the iron derivatives, it is not unreasonable to assume that isomerization could take place at reaction temperatures (ca. 110 °C) for Fe(CO)$_3$-(PPh$_3$)(SiCl$_3$)$_2$.

A similar trend in reactivity is observed in the reaction of the M(CO)$_4$(SiCl$_3$)$_2$ compounds with mesitylene.[6] The reasons for this trend are not clear. It is often observed among organo–transition-metal compounds that the derivative having the second-row transition metal is the most reactive. There is nothing in the CO stretching frequencies or the $^{13}$C NMR resonances of these derivatives to indicate that cis-Ru-(CO)$_4$(SiCl$_3$)$_2$ should possess labile equatorial carbonyl groups. This may mean that, as with cis labilization,[1,23] it is not a ground-state property but the ease in which the five-coordinated, 16-electron intermediate is formed which is responsible for the increased reactivity in the case of *cis*-Ru(CO)$_4$(SiCl$_3$)$_2$.

**Substitution in *cis*-Ru(CO)$_4$(SiCl$_3$)$_2$. Monosubstituted Derivatives.** The replacement of one of the equatorial carbonyl groups (i.e., those trans to SiCl$_3$) in *cis*-Ru(CO)$_4$(SiCl$_3$)$_2$ by a two-electron-donor ligand (L) proceeds smoothly in solution at room temperature (eq 1).

$$\text{OC} \underset{\underset{\text{C}}{\overset{\text{O}}{|}}}{\overset{\text{O}}{\overset{\text{C}}{|}}}\text{Ru} \begin{matrix}\text{SiCl}_3 \\ \text{SiCl}_3\end{matrix} + \text{L} \longrightarrow \text{OC} \underset{\underset{\text{C}}{\overset{\text{O}}{|}}}{\overset{\text{O}}{\overset{\text{C}}{|}}}\text{Ru}\begin{matrix}\text{SiCl}_3 \\ \text{L} \qquad \text{SiCl}_3\end{matrix} \qquad (1)$$

As seen from Table I a number of derivatives with ligands having a variety of donor atoms have been prepared. Although the rate of substitution has not yet been measured accurately, the rate appeared independent of the nature of the ligand and approximately equal to the rate of exchange of the compound with $^{13}$CO.[2]

The *mer*-Ru(CO)$_3$L(SiCl$_3$)$_2$ derivatives are white solids slightly soluble in hexane and more so in CH$_2$Cl$_2$. They all show a three-band infrared spectrum in the carbonyl region (Figure 1). They are of varying air sensitivity. The air sensitivity of these and related derivatives (Fe(CO)$_4$(SiCl$_3$)$_2$ is an exception) appears to be related to the lability of the remaining equatorial carbonyl group (vide infra). For example, the P(o-tol)$_3$ derivative is extremely air sensitive, the PPh$_3$ compound is of intermediate sensitivity showing signs of decomposition after 1 h of exposure (which is similar to the case of the parent compound, *cis*-Ru(CO)$_4$(SiCl$_3$)$_2$), and Ru(C-O)$_3$[P(OCH$_3$)$_3$](SiCl$_3$)$_2$ is still more robust. Bissubstituted compounds such as Ru(CO)$_2$[P(OCH$_3$)$_3$]$_2$(SiCl$_3$)$_2$ and Ru-(CO)$_2$(PPh$_3$)[P(OCH$_3$)$_3$](SiCl$_3$)$_2$ do not show any signs of decomposition after exposure to air for 24 h.

Also related to the lability of the equatorial carbonyl group was the observation that satisfactory chemical analyses could not be obtained for compounds such as Ru(CO)$_3$(PPh$_3$)-(SiCl$_3$)$_2$ unless they were recrystallized under a atmosphere of carbon monoxide.
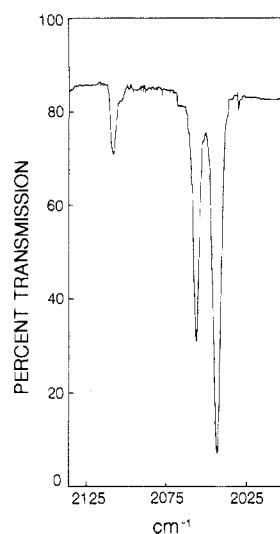


**Figure 1.** Carbonyl stretching region of the infrared spectrum of Ru(CO)$_3$[P(n-C$_4$H$_9$)$_3$](SiCl$_3$)$_2$ in hexane solution.

Once formed, the Ru–P bond in these derivatives was quite resistant to replacement by carbon monoxide. Treatment of a solution of Ru(CO)$_3$[P(OCH$_3$)$_3$](SiCl$_3$)$_2$ with carbon monoxide (80 atm) at 100 °C for 12 h did not produce any Ru(CO)$_4$(SiCl$_3$)$_2$. However, similar treatment of Ru(CO)$_3$-(PPh$_3$)(SiCl$_3$)$_2$ did give traces of Ru(CO)$_4$(SiCl$_3$)$_2$ (detected as the trans isomer).

**Bissubstituted Derivatives.** The substitution of the remaining carbonyl group in the Ru(CO)$_3$L(SiCl$_3$)$_2$ derivatives follows two patterns. If the cone angle[24] of L is small (e.g., P-(OCH$_3$)$_3$), the bissubstituted derivative Ru(CO)$_2$L$_2$(SiCl$_3$)$_2$ can be prepared. The conditions needed to affect the second substitution were usually more vigorous than those needed to prepare the monosubstituted derivative. For example, the preparation of Ru(CO)$_2$[P(OCH$_3$)$_3$]$_2$(SiCl$_3$)$_2$ required temperatures above 50 °C to carry out the synthesis at a convenient rate. The bis (CH$_3$)$_3$CNC and PF$_3$ compounds, however, can be prepared at room temperature.

If the cone angle of L is large (e.g., PPh$_3$, P(o-tol)$_3$), the bissubstituted derivative cannot be prepared. This is not to say that the remaining equatorial carbonyl group is not labile since Ru(CO)$_3$(PPh$_3$)(SiCl$_3$)$_2$ readily reacts (at a rate comparable to that of *cis*-Ru(CO)$_4$(SiCl$_3$)$_2$) with P(OCH$_3$)$_3$ to give the mixed substituted derivative Ru(CO)$_2$(PPh$_3$)[P-(OCH$_3$)$_3$](SiCl$_3$)$_2$. Indeed a kinetic study[25] has shown that the rates of reaction of Ru(CO)$_3$(PPh$_3$)(SiCl$_3$)$_2$ with a ligand L are identical for ligands having a cone angle of less than approximately 125° (e.g., P(OCH$_2$)$_3$CC$_2$H$_5$, P(OC$_2$H$_5$)$_3$, P(CH$_3$)$_2$Ph). For P(OPh)$_3$ (cone angle = 128°), the reaction is significantly slowed, and for PPh$_3$ (cone angle = 145°), the reaction does not proceed to any measurable extent. It is assumed in the latter case that the five-coordinate intermediate Ru(CO)$_2$(PPh$_3$)(SiCl$_3$)$_2$ recombines with the carbon monoxide which initially dissociated. When Ru(CO)$_3$(PPh$_3$)(SiCl$_3$)$_2$ was stirred in CH$_2$Cl$_2$ with excess PPh$_3$ under a slow stream of nitrogen to remove carbon monoxide, an absorption in the carbonyl region of the infrared spectrum of the solution appeared in the position expected for Ru(CO)$_2$(PPh$_3$)$_2$(SiCl$_3$)$_2$.[26] However, attempts to isolate the product were unsuccessful. Passing carbon monoxide through solutions of "Ru(CO)$_2$-

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(26) This may be compared with Ru[PPh$_3$]$_4$Cl$_2$ which is completely dissociated into Ru[PPh$_3$]$_3$Cl$_2$ and PPh$_3$ in solution.[27]
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(PPh₃)₂(SiCl₃)₂" caused conversion to Ru(CO)₃(PPh₃)(SiCl₃)₂.

Currently a kinetic study is under way to investigate the cis effect of the ligand L on the rate of substitution by P(OCH₃)₃ of the remaining equatorial carbonyl group in compounds of the type Ru(CO)₃L(SiCl₃)₂.[25] Initial results (and the results here) indicate the rate of substitution increases with the cone angle of L. There are some obvious exceptions (i.e., L = PF₃, CO). Although cis effects appear to be of dominant importance in the substitution reactions of most transition-metal carbonyl compounds, it should not be forgotten that it is the trans effect of the SiCl₃ groups in Ru(CO)₃L(SiCl₃)₂ derivatives which is mainly responsible for the carbonyl lability and this is modulated by the cis effect of the ligand L.

Again, it should be pointed out that there is no indication from the carbonyl stretching frequencies of these or other derivatives reported here of the lability of the carbonyl groups of the respective compound, even though such stretching frequencies are usually taken as being inversely proportional to the metal–carbon bond strength. This, as stated before, is taken to mean that the lability is due to the ease of formation of the intermediate.

At temperatures above 50 °C, Ru(CO)₃(PPh₃)(SiCl₃)₂ reacts with excess P(OCH₃)₃ to give Ru(CO)₂[P(OCH₃)₃]₂⁻ (SiCl₃)₂. Also treatment of Ru(CO)₂[P(OCH₃)₃]₂(SiCl₃)₂ in solution with 80 atm of carbon monoxide at 100 °C gives some Ru(CO)₃[P(OCH₃)₃](SiCl₃)₂ on cooling. As in "Ru(CO)₂⁻ (PPh₃)₂(SiCl₃)₂" the increased lability of the Ru–P bond in the bissubstituted derivatives, compared to that in the monosubstituted compounds, is probably due to the mutual cis effect of the two phosphorus ligands.

**Phosphorus NMR Data.** The ³¹P NMR data for the phosphorus derivatives are reported along with the chemical shift difference between the resonance of the phosphorus in the coordinated and uncomplexed ligand ($\Delta_{CS}$). The factors contributing to $\Delta_{CS}$ are not well understood.[28] In these compounds the donor–acceptor properties of the ligand appear to be unimportant in influencing $\Delta_{CS}$. For example, the PF₃ and P(n-C₄H₉)₃ derivatives show very similar downfield chemical shifts on coordination to the ruthenium, yet Tolman[29]

has adjudged these ligands, using CO stretching frequencies, at opposite ends of a scale based on electron donor–acceptor properties. Phosphites which are intermediate on the scale show upfield shifts on coordination except for P(OCH₂)₃C-C₂H₅, which exhibits a downfield shift comparable to phosphines. This last observation adds some support to the suggestion that the changes in the interligand angles on coordination have a marked effect on $\Delta_{CS}$. These changes can be related to the s character in the phosphorus–transition-metal bond.[28]

**Registry No.** Fe(CO)₄(SiCl₃)₂, 15306-36-2; *cis*-Ru(CO)₄(SiCl₃)₂, 36570-60-2; *cis*-Os(CO)₄(SiCl₃)₂, 36570-61-3; Fe(CO)₃(PPh₃)(SiCl₃)₂, 75030-80-7; Ru(CO)₃(PPh₃)(SiCl₃)₂, 71893-44-2; Os(CO)₃- (PPh₃)(SiCl₃)₂, 75030-81-8; Ru(CO)₃[P(OCH₃)₃](SiCl₃)₂, 75030- 82-9; Ru(CO)₃(PF₃)(SiCl₃)₂, 75030-83-0; Ru(CO)₃(ETPB)(SiCl₃)₂, 75030-84-1; Ru(CO)₃[P(OC₂H₅)₃](SiCl₃)₂, 75030-85-2; Ru(CO)₃- [P(OPh)₃](SiCl₃)₂, 75030-86-3; Ru(CO)₃[PPh(CH₃)₂](SiCl₃)₂, 75030-87-4; Ru(CO)₃[PPh₂(CH₃)](SiCl₃)₂, 75045-84-0; Ru(CO)₃- {P[o-C₆H₄(CH₃)]₃}(SiCl₃)₂, 75030-88-5; Ru(CO)₃[P(n-C₄H₉)₃]- (SiCl₃)₂, 75030-89-6; Ru(CO)₃[P(C₆H₄)₃](SiCl₃)₂, 75030-90-9; Ru(CO)₃(AsPh₃)(SiCl₃)₂, 75030-91-0; Ru(CO)₃(SbPh₃)(SiCl₃)₂, 75030-92-1; Ru(CO)₃[CNC(CH₃)](SiCl₃)₂, 75030-93-2; Ru(C- O)₂(PF₃)₂(SiCl₃)₂, 75030-94-3; Ru(CO)₂[P(OCH₃)₃]₂(SiCl₃)₂, 75030-95-4; Ru(CO)₂(ETPB)₂(SiCl₃)₂, 75030-96-5; Ru(CO)₂[P(O-C₂H₅)₃]₂(SiCl₃)₂, 75030-97-6; Ru(CO)₂[P(OPh)₃]₂(SiCl₃)₂, 75030-98-7; Ru(CO)₂[PPh(CH₃)₂]₂(SiCl₃)₂, 75030-99-8; Ru(CO)₂[PPh₂- (CH₃)]₂(SiCl₃)₂, 75031-00-4; Ru(CO)₂[P(n-C₄H₉)₃]₂(SiCl₃)₂, 75031-01-5; Ru(CO)₂[P(OCH₃)₃](PPh₃)(SiCl₃)₂, 71852-83-0; Ru-(CO)₂[P(C₆H₁₁)₃]₂(SiCl₃)₂, 75031-02-6; Ru(CO)₂[CNC(CH₃)₃]₂⁻ (SiCl₃)₂, 75031-03-7; Ru₃(CO)₁₂, 15243-33-1; Fe(CO)₅, 13463-40-6; Os₃(CO)₁₂, 15696-40-9; Cl₃SiH, 10025-78-2; *trans*-Os(CO)₄(SiCl₃)₂, 58957-82-7.

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# Superoxide Reactions with (Isonicotinamide)pentaammineruthenium(II) and -(III)

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The reactions of superoxide with [Ru(NH₃)₅isn]²⁺ and [Ru(NH₃)₅isn]³⁺ have been investigated in aqueous solution ($\mu$ = 0.1 M (formate buffer) at 23 ± 2 °C with use of pulse radiolysis). The radical HO₂ oxidizes Ru(II) with a rate constant of $9.07 \times 10^6$ M⁻¹ s⁻¹, and O₂⁻ reduces Ru(III) with a rate constant of $2.18 \times 10^8$ M⁻¹ s⁻¹. These values are in good agreement with those deduced from a study of the reaction of O₂ with [Ru(NH₃)₅isn]²⁺, and this agreement confirms many of the conclusions about the reaction mechanism arrived at from the latter study. Outer-sphere reductions of HO₂ to HO₂⁻ are shown to be anomalous from the perspective of the Marcus theory. Approximate values have also been obtained for the specific rates governing the reactions of Ru(III) with OH, H, $e_{aq}^-$, CO₂⁻, and HC(OH)₂ and of Ru(II) with OH.

## Introduction

As a part of a continuing study of the mechanisms of reduction of O₂ in aqueous solution, we recently published a

report of the autoxidation of a series of ruthenium(II) ammines.[1] One conclusion reached in that work was that the mechanism involves outer-sphere reduction of O₂ to O₂⁻ (superoxide); this was supported in part by a good correlation, using Marcus theory, of the rate and equilibrium constants.

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