

Acknowledgments. The authors are grateful to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for a postdoctoral fellowship to H. L. C. and for support of this research. We are also appreciative to the Research Corp. for a Cottrell Research Grant to D. J. Darensbourg and M. Y. D. for the purchase of a Perkin-Elmer 521 infrared spectrophotometer. We

(24) We would suggest that the most negative site in the acylate complex is the acyl oxygen which is ion paired with, in our studies, Li^+ . Such ion pairing has been invoked to explain HMPA (hexamethylphosphoramide) inhibition of the cation-assisted alkyl to carbonyl migration reaction of the $\text{RFe}(\text{CO})_4^-$ conversion to $\text{LFe}(\text{CO})_3-\text{C}(\text{O})\text{R}^-$.⁹ Only the very strong alkylating agents Et_3O^+ and THF-Me^+ are capable of displacing the Li^+ , forming the carbene complexes. Softer or weaker alkylating agents, MeI or MeOSO_2F , react at the next most negative site, either the iron, the acyl carbon, or most likely the iron-acyl carbon-acyl oxygen electron sink, centering at acyl carbon.

wish to acknowledge the helpful suggestions of D. J. Darensbourg and E. J. Panek of Tulane University.

Registry No. *trans*- $\text{Ph}_3\text{PFe}(\text{CO})_3\text{C}(\text{OLi})\text{Ph}$, 49655-04-1; *trans*-(*n*-Bu) $_3\text{PFe}(\text{CO})_3\text{C}(\text{OLi})\text{Ph}$, 49655-05-2; *trans*-(PhO) $_3\text{PFe}(\text{CO})_3\text{C}(\text{OLi})\text{Ph}$, 49655-06-3; *trans*- $\text{Fe}(\text{CO})_4\text{C}(\text{OLi})\text{Ph}$, 49655-07-4; *trans*- $\text{Ph}_3\text{PFe}(\text{CO})_3\text{C}(\text{OLi})\text{Me}$, 49655-08-5; *trans*-(*n*-Bu) $_3\text{PFe}(\text{CO})_3\text{C}(\text{OLi})\text{Me}$, 49655-09-6; *trans*- $\text{Ph}_3\text{PFe}(\text{CO})_3\text{C}(\text{OEt})\text{Ph}$, 42947-52-4; *trans*- $\text{Ph}_3\text{PFe}(\text{CO})_3\text{C}(\text{OEt})\text{Me}$, 42947-54-6; *trans*- $\text{Ph}_3\text{PFe}(\text{CO})_3\text{C}(\text{OMe})\text{Ph}$, 49634-48-2; *trans*-(*n*-Bu) $_3\text{PFe}(\text{CO})_3\text{C}(\text{OEt})\text{Ph}$, 49634-49-3; *trans*-(*n*-Bu) $_3\text{PFe}(\text{CO})_3\text{C}(\text{OEt})\text{Me}$, 42947-57-9; *trans*-(PhO) $_3\text{PFe}(\text{CO})_3\text{C}(\text{OEt})\text{Ph}$, 42947-53-5; *trans*-(PhO) $_3\text{PFe}(\text{CO})_3\text{C}(\text{OEt})\text{Me}$, 42947-55-7; *trans*- $\text{Fe}(\text{CO})_4\text{C}(\text{OEt})\text{Ph}$, 49634-53-9; *trans*- $\text{Ph}_3\text{PFe}(\text{CO})_4$, 49655-10-9; *trans*-(Ph $_3\text{P}$) $_2\text{Fe}(\text{CO})_3$, 49655-11-0; *trans*- $\text{Ph}_3\text{PFe}(\text{CO})_3\text{P}(\text{OPh})_3$, 49655-12-1; *trans*-(*n*-Bu) $_3\text{PFe}(\text{CO})_4$, 49655-13-2; *trans*-[(*n*-Bu) $_3\text{P}$] $_2\text{Fe}(\text{CO})_3$, 49655-14-3; *trans*-(PhO) $_3\text{PFe}(\text{CO})_4$, 49655-15-4; *trans*-(PhO) $_3\text{P}$] $_2\text{Fe}(\text{CO})_3$, 49655-16-5; *trans*- $\text{Fe}(\text{CO})_5$, 13463-40-6; MeOSO_2F , 421-20-5; $\text{Et}_3\text{O}^+\text{BF}_4^-$, 368-39-8; MeI , 74-88-4; $\text{THFMe}^+\text{SO}_3\text{F}^-$, 49655-17-6; (*n*-Bu) $_3\text{P}$, 998-40-3; (PhO) $_3\text{P}$, 101-02-0; *trans*-(PhO) $_3\text{PFe}(\text{CO})_3\text{C}(\text{OLi})\text{Me}$, 49655-18-7; Ph_3P , 603-35-0.

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Silicon-Transition Metal Chemistry. VII.¹ Metal Carbonyl Derivatives of 1,2-Bis(dimethylsilyl)ethane

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Received July 18, 1973

The reaction of 1,2-bis(dimethylsilyl)ethane with $\text{Fe}(\text{CO})_5$, $\text{Ru}_3(\text{CO})_{12}$, or $\text{Os}_3(\text{CO})_{12}$ affords the chelate compounds $(\text{OC})_4-\text{MSiMe}_2\text{CH}_2\text{CH}_2\text{SiMe}_2$ [M = Fe (I), Ru (II), and Os (III)]. The product with $\text{Co}_2(\text{CO})_8$ is $(\text{OC})_4\text{CoSiMe}_2\text{CH}_2\text{CH}_2\text{Me}_2\text{SiCo}(\text{CO})_4$, IV. Carbonyl stretching frequencies and proton and carbon-13 magnetic resonance spectra are reported.

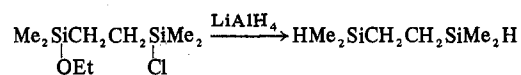
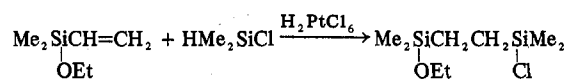
Introduction

Recent reports from this laboratory have described the remarkable stereospecific carbon monoxide exchange that takes place in *cis*- $\text{Ru}(\text{CO})_4(\text{SiCl}_3)_2$ ^{2a} and the nonrigid character of $\text{Os}(\text{CO})_4(\text{SiMe}_3)_2$,^{2b,3} for which *cis* and *trans* isomers interconvert rapidly in a nondissociative process. To further our understanding of such systems, it was of interest to prepare analogs in which the silyl groups were linked so that they would be constrained to *cis* positions. In such chelated derivatives, for example, the possibility of interchange of axial and equatorial carbonyls without passing through a *trans*-octahedral form could be investigated.

The reaction of silicon-hydrogen bonds with metal carbonyls has proven to be of great utility,⁴ and it was accordingly decided to utilize the silane $\text{HMe}_2\text{SiCH}_2\text{CH}_2\text{SiMe}_2\text{H}$ as a starting material. This paper describes a convenient synthesis of this useful ligand and its reactions with $\text{Fe}(\text{CO})_5$, $\text{Ru}_3(\text{CO})_{12}$, $\text{Os}_3(\text{CO})_{12}$, and $\text{Co}_2(\text{CO})_8$.

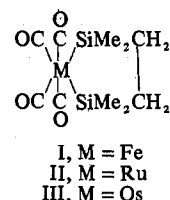
Results and Discussion

The silane starting material has been prepared in an overall yield of 56% from commercially available organosilicon compounds using the sequence of reactions



The intermediate in this preparation, 1-(dimethylethoxy)silyl-2-(dimethylchlorosilyl)ethane, was not isolated, but was reduced directly with LiAlH_4 to yield 1,2-bis(dimethylsilyl)ethane. This silane has been prepared before by the LiAlH_4 reduction⁵ of the somewhat less readily available 1,2-bis(dimethylchlorosilyl)ethane.⁶

In general, the silane reacted either with heat or with ultraviolet irradiation with carbonyls of the iron group to produce the anticipated chelate complexes I-III. These have been fully characterized by analysis, mass spectrometry, and in-



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frared and nmr spectroscopy (^1H and ^{13}C).

Compound I was prepared by reaction of $\text{Fe}(\text{CO})_5$ with the silane under ultraviolet irradiation; it is a yellow, air-sensitive compound, decomposing slowly in solution or on storage to form $\text{Fe}_3(\text{CO})_{12}$ and $\text{Fe}_2(\text{CO})_9$.

The much more stable ruthenium and osmium derivatives II and III were prepared in a nearly quantitative reaction of the silane with $\text{M}_3(\text{CO})_{12}$ at 175° and 1000 psi of CO. They are white waxy solids. Solutions of II or III in *n*-heptane showed no change in infrared spectra after a 24-hr exposure to the atmosphere.

Complexes I-III have C_2 symmetry, taking into account the nonplanar character of the five-membered chelate ring. Four carbonyl stretching bands are expected and observed in I and II (*cf.* Table I); three bands are observed in III, no doubt owing to accidental degeneracy. A fuller discussion of the infrared spectra of these compounds will be given in connection with a study of exchange reactions with ^{13}CO .⁷

Reaction of cobalt carbonyl with excess silane at room temperature produced white, crystalline $(\text{OC})_4\text{CoSiMe}_2\text{CH}_2\text{-CH}_2\text{Me}_2\text{SiCo}(\text{CO})_4$ (IV), a rather unstable compound particularly in solution. Formation of this nonchelated compound indicates an alternative reaction pathway for the silane. The reaction presumably proceeds *via* $\text{HSiMe}_2\text{CH}_2\text{-CH}_2\text{Me}_2\text{SiCo}(\text{CO})_4$, although this intermediate was not observed; reaction of the second silicon-hydrogen bond with another molecule of $\text{Co}_2(\text{CO})_8$ [or $\text{HCo}(\text{CO})_4$] must then be preferred to chelation, since the latter would be expected to form a rather improbable cobalt(III) complex.

The infrared spectrum of IV is as expected for noninteracting cobalt tetracarbonyl groups. The E mode is not split since the threefold symmetry is not sufficiently perturbed by the rather similar methyl and methylene substituents on silicon. The appearance of a weak shoulder on the higher energy side of the 2089-cm^{-1} band is unusual; we can offer no explanation but believe that it is genuine.

An iron complex closely related to IV, $[\text{C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{SiMe}_2\text{CH}_2]_2$, has recently been prepared by reaction of the metal carbonyl anion with 1,2-bis(dimethylchlorosilyl)ethane.⁹ The iron compound appears to be more stable.

Nmr Spectra. Proton nmr spectra of all compounds (Table I) show singlets for the methylene and methyl protons of the silane ligand. In the chelate compounds I-III, this indicates that the expected rapid ring inversion is taking place resulting in a time-averaged C_{2v} symmetry.

Carbon-13 nmr data for compounds I-III are shown in Table II. The chemical shifts of the carbonyl carbons move to higher field along the series Fe, Ru, Os. This trend parallels that observed in the hexacarbonyls of Cr, Mo, and W.¹⁰ A second important trend is the increasing separation between axial and equatorial ^{13}C shifts along the Fe, Ru, Os series. No trend of this kind seems to have been noted previously for carbonyls of any periodic group. The results reported here are the first ^{13}C nmr study of an osmium compound.

In Table II, the ^{13}C resonance at lower field is assigned as axial. Previously, assignment of carbonyl resonances in *cis*- $\text{L}_2\text{M}(\text{CO})_4$ complexes has not been possible.¹¹ We base

Table I. Infrared and ^1H Nmr Data

| Compd | Carbonyl stretching bands ^a | ^1H nmr spectrum ^c | |
|-------|---|--|---------------|
| | | CH_2 | CH_3 |
| I | 2068 (6.7), 2003 (7.0), 2000 (3.6), ^b 1978 (10) | 9.00 | 9.44 |
| II | 2091 (4.4), 2032 (6.3), 2024 (8.3), 2010 (10) | 9.12 | 9.55 |
| III | 2096 (2.3), 2028 (4.8), 2012 (10) | 9.12 | 9.42 |
| IV | 2091 (4.0), ^b 2089 (7.6), 2028 (8.5), 1995 (10) | 8.87 | 9.38 |

^a In *n*-heptane solution; band positions in cm^{-1} with intensities in parentheses relative to the strongest band as 10, using a per cent transmission scale. ^b Shoulder. ^c Values on τ scale; CDCl_3 solution.

Table II. Carbon-13 Nmr Data^a

| Compd | Chem shifts | | | | |
|-----------------|-------------------------|-------------------------|---------------|---------------|---|
| | CO_{ax} | CO_{eq} | CH_2 | CH_3 | $\delta_{\text{ax}} - \delta_{\text{eq}}$ |
| I | 208.89 | 207.86 | 17.54 | 8.37 | 1.03 |
| II ^b | 198.18 | 193.58 | 17.95 | 4.70 | 4.60 |
| III | 181.00 | 175.50 | 17.92 | 3.89 | 5.50 |

^a Chemical shifts in toluene- d_6 on the δ scale relative to tetramethylsilane. Axial and equatorial CO groups defined so that the central metal atom and the two silicon ligands lie in the equatorial plane, as shown in text. ^b In CDCl_3 .

our assignments in this work on a study of $\text{H}_2\text{Os}(\text{CO})_4$,⁷ in which the proton-coupled ^{13}C spectrum unambiguously identifies the two carbonyl resonances as axial (A_2X) and equatorial ($\text{AA}'\text{X}$).

The ^{13}C nmr spectra clearly establish that compounds I-III are stereochemically rigid on the nmr time scale at ambient temperature. As noted above, it was of interest to examine the possibility of axial-equatorial carbonyl exchange in these compounds, where the chelate ligand eliminates the possibility that such interchange could occur *via* a trans isomer.^{2b} The compounds were therefore examined at higher temperatures (80° for I, 160° for II, and 90° for III) and found to be rigid at these temperatures also. Higher temperatures resulted in decomposition. This finding enables a very crude lower limit of about 20 kcal mol^{-1} to be assigned to ΔG^\ddagger for the exchange process.¹² Actually, one would expect the barrier for such an exchange in an octahedral complex to be a great deal higher.¹³

The usual problem in an nmr study of fluxional or non-rigid processes is to obtain the low-temperature limiting spectra; the large chemical shift differences characteristic of ^{13}C nmr will aid in the solution of this problem. However, in the present case, where the barrier to exchange is expected to be reasonably high, large shift differences are disadvantageous since higher temperatures will then be required for coalescence.

Experimental Section

Reactions were carried out under an atmosphere of dry, oxygen-free nitrogen. Solvents were distilled from LiAlH_4 and saturated with nitrogen. Carbonyls of ruthenium¹⁴ and osmium¹⁵ were prepared by literature methods. All other starting materials were commercially available and were used as received except for $\text{Co}_2(\text{CO})_8$, which was sublimed.

Infrared spectra in the carbonyl region were scanned at $39\text{ cm}^{-1}\text{ min}^{-1}$ using a Perkin-Elmer Model 337 grating spectrometer fitted

(12) Given the low-temperature limiting axial-equatorial ^{13}C shift difference of 104 Hz for compound II, the value of ΔG^\ddagger quoted here is that which would result in coalescence at 160° .

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with an external recorder. Spectra were referenced with gaseous CO, and reported bands are considered accurate to $\pm 1 \text{ cm}^{-1}$.

Mass spectra were taken with Associated Electrical Industries MS-9 or modified MS-2 instruments. Samples were introduced by direct evaporation or sublimation, at temperatures just sufficient to produce the spectrum. All compounds showed the expected molecular ions with consecutive loss of CO and CH_3 as the dominant feature.

Proton nmr spectra were measured on Varian A-60 and HA-100 spectrometers. Natural-abundance ^{13}C nmr spectra were recorded on a Bruker HFX-90 spectrometer operating at 22.6 MHz and using the pulse Fourier transform technique. Toluene- d_6 or CDCl_3 solutions (0.7–0.8 M) in 10-mm o.d. tubes were employed to obtain the spectra at temperatures below 100° ; a spectrum of II at 160° was measured in *o*-dichlorobenzene. The number of scans was usually 1K, the number of data points was 8K, the pulse length was 50 μsec , and the delay time was 70 μsec . Spectra were assigned using the off-resonance technique. The ^{13}C chemical shifts were converted to the external TMS scale using as reference CDCl_3 or the quaternary carbon from toluene- d_6 , whose chemical shifts, on the TMS scale, were taken as 77.09 and 137.46 ppm, respectively. The error in chemical shifts is believed to be ± 0.04 ppm.

The melting points are uncorrected and were determined on a Minimet Thomas-Hoover apparatus or with a Kofler hot-stage.

Microanalyses were performed by the Alfred Bernhardt Microanalytische Laboratorium, Bonn, West Germany, and by the microanalytical laboratory of this department.

See Table III for analytical data.

Preparation of 1,2-Bis(dimethylsilyl)ethane. A mixture of 110.6 g (0.85 mol) of dimethylvinylethoxysilane and 2 drops of hexachloroplatinic acid in 2-propanol (0.1 M) was heated at 75° and 88.5 g (1.10 mol) of dimethylchlorosilane was added in dropwise fashion with stirring. The rate of addition was adjusted so that the temperature of the reaction mixture did not exceed 90° . After the addition was complete, the mixture was refluxed for 3 hr. The resulting 1-(dimethylethoxysilyl)-2-(dimethylchlorosilyl)ethane was added dropwise to a slurry of 90 g (2.37 mol) of LiAlH_4 in 1000 ml of anhydrous ether and refluxed for 8 hr. The ether was then replaced by 1.5 l. of petroleum ether (bp $50\text{--}80^\circ$), and the LiAlH_4 residue removed by filtration. The mixture was fractionally distilled, affording 69.4 g of 1,2-bis(dimethylsilyl)ethane (bp $115\text{--}20^\circ$ (704 mm), yield 55.8%).

Preparation of 1,2-Bis(dimethylsilyl)ethanetetra-carbonyliron, I. A mixture of 2.01 g (10.3 mmol) of $\text{Fe}(\text{CO})_5$ and 1.815 g (12.4 mmol) of the silane in 215 ml of petroleum ether (bp $50\text{--}80^\circ$) was irradiated for 45 min using a 450-W uv lamp inside a water-cooled quartz jacket with the solution in the annular space outside the jacket. The solvent was evaporated under vacuum (10 mm). An infrared spectrum showed bands of an impurity, presumably a hydrido species, in addition to the main product. Room-temperature sublimation of the resulting black oil yielded 1.64 g (51.2%) of the product as a waxy yellow solid. No further sublimation took place, but

Table III. Elemental Analysis, Melting Points, and Molecular Weights^a

| Compd | Calcd | | | Found | | | Mp, $^\circ\text{C}$ |
|-------|--------|-------|------|--------|-------|------|----------------------|
| | Mol wt | % C | % H | Mol wt | % C | % H | |
| I | 312 | 38.47 | 5.16 | 312 | 37.54 | 5.41 | 58–60 |
| II | 358 | 33.60 | 4.51 | 358 | 33.20 | 4.79 | 91–92 |
| III | 448 | 26.89 | 3.61 | 448 | 26.49 | 3.82 | 98–100 |
| IV | 486 | 34.58 | 3.32 | 486 | 34.37 | 3.56 | 128–130 dec |

^a Determined by mass spectrometer. Values quoted refer to the most intense peak of the isotopic multiplet due to the particular ion.

the residue underwent extensive decomposition to $\text{Fe}_3(\text{CO})_{12}$ and $\text{Fe}_2(\text{CO})_9$.

Preparation of 1,2-Bis(dimethylsilyl)ethanetetra-carbonylruthenium, II. A sample of $\text{Ru}_3(\text{CO})_{12}$ (1.400 g, 2.2 mmol), the silane (1.45 g, 9.9 mmol), and $50\text{--}80^\circ$ petroleum ether (30 ml) were placed into a 200-ml Parr autoclave which was pressurized with CO to 1000 psi. The autoclave was heated, with stirring, at 175° for 20 hr, and cooled, and then the gases were vented. The solvent was evaporated at reduced pressure (10 mm) and the remaining solid material was sublimed onto a water-cooled probe at 0.005 mm and room temperature, to give 2.085 g (88.8%) of colorless waxy solid.

Preparation of 1,2-Bis(dimethylsilyl)ethanetetra-carbonylsmium, III. Triosmium dodecacarbonyl (0.50 g, 0.55 mmol) and the silane (0.637 g, 4.35 mmol) were brought to reaction and worked up exactly as just described. The sublimation afforded 0.66 g (89.3%) of colorless waxy product.

Preparation of 1,2-Bis(tetra-carbonylcobaltdimethylsilyl)ethane, IV. A sample of $\text{Co}_2(\text{CO})_8$ (1.95 g, 5.7 mmol) and 1,2-bis(dimethylsilyl)ethane (2.5 g, 17.1 mmol) were placed in a Schlenk tube and stirred under nitrogen for 1.5 hr. A vigorous evolution of hydrogen was observed during the first 15 min of reaction. Addition of *n*-pentane (20 ml) to the brown paste precipitated the product as a white, crystalline material. Filtration at 0° gave 1.0 g of IV, yield 36.1%. The analytical sample was recrystallized from CH_2Cl_2 . Compound IV can be handled in air for short periods but decomposes rapidly in solution to give $\text{Co}(\text{CO})_8$.

Acknowledgment. We thank the Institute for Chemical and Pharmaceutical Research, Cluj, Romania, for a leave of absence to L. V., Dr. T. Nakashima for ^{13}C spectra, and the National Research Council of Canada for financial support.

Registry No. I, 43198-13-6; II, 43198-14-7; III, 43198-15-8; IV, 43198-16-9; $\text{HMe}_2\text{SiCH}_2\text{CH}_2\text{SiMe}_2\text{H}$, 20152-11-8; $\text{Fe}(\text{CO})_5$, 13463-40-6; $\text{Ru}_3(\text{CO})_{12}$, 15243-33-1; $\text{Os}_3(\text{CO})_{12}$, 15696-40-9; $\text{Co}_2(\text{CO})_8$, 10210-68-1.