the latter reaction were not established.

The reaction of mercury(II) with organochromium(III) complexes is believed to occur by a bimolecular electrophilic substitution of Hg^{2+} on the carbon coordinated to chromium(III).[36] This is consistent with the second-order kinetics and decreasing rate constant with more electron-withdrawing substituents on the organic ligand.[15,37] The reactivity of $(H_2O)_5CrCH_2CN^{2+}$ and $(NH_3)_5CoNCCH_2Cr(OH_2)_5^{5+}$ fits into this pattern.

An unusual feature of the $(NH_3)_5CoNCCH_2Cr(OH_2)_5^{5+} + Hg^{2+}$ reaction is the inverse hydrogen ion term in the rate law. Since this is not normally observed[15,37] for these reactions, the simplest explanation seems to involve ionization of a water coordinated to chromium(III), as suggested in eq 11. The presence of the $(NH_3)_5CoNCCH_2^{2+}$ ligand may enhance the acidity of a coordinated water enough to make the inverse hydrogen ion path detectable.

The chromium(II) reduction of $(NH_3)_5CoNCCH_2Cr(OH_2)_5^{5+}$ presents a special problem in that it is not clear which metal center is reduced first. The fact that the rate constant (2.39×10^{-3} M^{-1} s^{-1}) is less than that for $Cr^{2+} + (H_2O)_5CrCH_2CN$ (1.73×10^{-2} M^{-1} s^{-1}) is consistent with the earlier argument that chromium(II) coordinates at the nitrile nitrogen in the latter system. Then the chromium(III) end of $(NH_3)_5CoNCCH_2Cr(OH_2)_5^{5+}$ would show normal, i.e., very low, reactivity toward chromium(II). The absence of an $[H^+]^{-1}$ term in the rate law for this reaction is consistent also with no reactivity at chromium(III). These observations indicate that the cobalt(III) is reduced first by an outer-sphere mechanism.

$$(NH_3)_5CoNCCH_2Cr(OH_2)_5^{5+} + Cr^{2+} \xrightarrow{H^+} Co^{2+} + 5NH_4^+ + NCCH_2Cr(OH_2)_5^{2+} + Cr(OH_2)_6^{3+} \quad (15)$$

$$(H_2O)_5CrCH_2CN^{2+} + Cr^{2+} \xrightarrow{H^+} Cr^{2+} + Cr(OH_2)_6^{3+} + NCCH_3 \quad (16)$$

The second reaction is much faster than the first (see Table I) so that monophasic kinetics are observed.

An unusual feature of the results is that $(NH_3)_5CoNCCH_2I^{3+}$ reacts essentially quantitatively with chromium(II) to produce the cobalt(III)–organochromium(III) dimer, and no cobalt(II) is detected. This indicates that intramolecular electron transfer within the $(NH_3)_5CoNCCH_2^{3+}$ radical is slow compared to reaction with chromium(II).

$$(NH_3)_5CoNCCH_2^{3+} \xrightarrow[\text{detected}]{\text{not}} Co^{2+} + 5NH_4^+ + NCCH_2^+ \rightarrow \text{products} \quad (17)$$

This seems surprising in view of ESR studies, which show considerable unpaired spin density on nitrogen in the $\cdot CH_2CN$ radical.[38,39] The thermodynamic instability of the carbonium ion $NCCH_2^+$ may explain the apparent absence of intramolecular electron transfer. That the carbonium ion is unstable can be judged from the fact that the ionization potential of $\cdot CH_2CN$ is 61 kcal mol^{-1} higher than that of $\cdot CH_2OH$.[40,41] The latter radical does reduce $Co(NH_3)_6^{3+}$.[42]

It is possible to estimate an upper limit for the rate of reaction 17. If the rate constant for $(NH_3)_5CoNCCH_2^{3+}\cdot + Cr^{2+}$ is $\sim 1 \times 10^7$ M^{-1} s^{-1},[8] then a consideration of our cobalt(II) detectability limits for experiments in which essentially equivalent amounts of $(NH_3)_5CoNCCH_2I^{3+}$ and Cr^{2+} were mixed indicates that reaction 17 has a rate constant $\leq 3.5 \times 10^3$ s^{-1}.

Acknowledgment. We thank the Natural Science and Engineering Research Council of Canada for financial support for this work and for fellowship support to W.C.K.

Registry No. $[(NH_3)_5CoNCCH_2I](ClO_4)_3$, 88157-86-2; $[(NH_3)_5CoNCCH_2Cl](ClO_4)_3$, 88157-88-4; $[(NH_3)_5CoNCCH_2Hg(OH_2)](ClO_4)_4$, 88157-90-8; CH_2CN, 624-75-9; $ClCH_2CN$, 107-14-2; Cr^{2+}, 22541-79-3; $(H_2O)_5CrCH_2CN^{2+}$, 76068-68-3; $(NH_3)_5CoNCCH_2Cr(OH_2)_5^{5+}$, 88157-91-9; Hg^{2+}, 14302-87-5.

Supplementary Material Available: Tables of appropriate concentrations and rate constants (8 pages). Ordering information is given on any current masthead page.

---

(36) Abraham, M. H. "Comprehensive Chemical Kinetics"; Bamford, C. H. Tipper, C. H. F., Eds.; Elsevier: Amsterdam, 1973; Vol. 12, Chapter 3.

(37) Leslie, J. P., II; Espenson, J. H. *J. Am. Chem. Soc.* **1976**, *98*, 4839.

(38) Smith, P.; Kaba, R. A.; Smith, T. C.; Pearson, J. T.; Wood, P. B. *J. Magn. Reson.* **1975**, *18*, 254.

(39) Kaba, R. A.; Ingold, K. U. *J. Am. Chem. Soc.* **1976**, *98*, 523.

(40) Pottie, R. F.; Lossing, F. P. *J. Am. Chem. Soc.* **1961**, *83*, 4737.

(41) Vendeneyev, V. I.; Gurvich, L. V.; Kondrat'yev, V. N.; Medvedev, V. A.; Frankevich, Y. E. "Bond Energies, Ionization Potentials, and Electron Affinities"; St. Martin's Press: New York, 1966; p 176.

(42) Cohen, H.; Meyerstein, D. *J. Am. Chem. Soc.* **1972**, *94*, 6944.

Direct Observation of the Intermediates in the Photochemical Reaction of $R_3SiCo(CO)_4$ with R'_3SiH and Establishment of the Mechanism for $R'_3SiCo(CO)_4$ Formation

F. Ruth Anderson and Mark S. Wrighton*

Contribution from the Department of Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139. *Received May 9, 1983*

Abstract: Irradiation of $R_3SiCo(CO)_4$ in the presence of R'_3SiH yields $R'_3SiCo(CO)_4$ and R_3SiH at 298 K in an alkane solvent. The mechanism for this reaction has been established by irradiation at low temperature in alkane media. At 77 K in a rigid alkane medium, irradiation of $R_3SiCo(CO)_4$ (R = Me, Et, Ph) yields dissociative loss of CO to give a 16 e^- complex, $R_3SiCo(CO)_3$, as determined by infrared spectroscopy. If the matrix contains a sufficiently high concentration of R_3SiH (R = Et) the light-induced loss of CO occurs, but the metal carbonyl product is $(R_3Si)(R'_3Si)Co(CO)_3H$. This species can also be formed photochemically at 196 K in fluid solution. The $(Et_3Si)_2Co(CO)_3H$ is sufficiently inert that the Co–hydride resonance in the ^1H NMR can be observed at δ −9.8. Warmup of the $(R_3Si)(R'_3Si)Co(CO)_3H$ to 298 K results in generation of both $R_3SiCo(CO)_4$ and $R'_3SiCo(CO)_4$. The low-temperature photochemistry thus provides direct evidence for both the 16 e^- primary photoproduct and the Co(III) oxidative addition product in the exchange mechanism.

We wish to report spectroscopic detection of intermediates, $R_3SiCo(CO)_3$ and $(R_3Si)(R'_3Si)Co(CO)_3H$, in the photochemical exchange process represented by eq 1.[1] These results establish the mechanism for the exchange process in (1) to be as represented

0002-7863/84/1506-0995$01.50/0 © 1984 American Chemical Society

$$R_3SiCo(CO)_4 + R'_3SiH \xrightarrow{h\nu,\ 298\ K} R'_3SiCo(CO)_4 + R_3SiH \quad (1)$$

by eq 2–5. To detect the intermediates we have exploited the

$$R_3SiCo(CO)_4 \underset{\Delta}{\overset{h\nu}{\rightleftharpoons}} R_3SiCo(CO)_3 + CO \quad (2)$$

$$R_3SiCo(CO)_3 + R'_3SiH \underset{\Delta}{\overset{\Delta}{\rightleftharpoons}} (R_3Si)(R'_3Si)Co(CO)_3H \quad (3)$$

$$(R_3Si)(R'_3Si)Co(CO)_3H \underset{\Delta}{\overset{\Delta}{\rightleftharpoons}} R'_3SiCo(CO)_3 + R_3SiH \quad (4)$$

$$R'_3SiCo(CO)_3 + CO \underset{h\nu}{\overset{\Delta}{\rightleftharpoons}} R'_3SiCo(CO)_4 \quad (5)$$

principle that the excited-state loss of CO can occur at a sufficiently low temperature (77 K) that the $R_3SiCo(CO)_3$ can be accumulated in a rigid matrix. We find that oxidative addition of R'_3SiH occurs readily at low temperature (even 77 K) to yield $(R_3Si)(R'_3Si)Co(CO)_3H$ that is sufficiently thermally inert to be observed spectroscopically at 196 K. The low-temperature irradiation followed by warmup allows us to unravel the mechanism of a bimolecular reaction. Oxidative addition of H_2 is known to occur to photogenerated, coordinatively unsaturated $Fe(CO)_4$[2] or $HCo(CO)_3$[3] at low temperatures, providing precedence for the low-temperature oxidative addition reactivity reported here.

The observation of the $(R_3Si)(R'_3Si)Co(CO)_3H$ and the 16 e^- $R_3SiCo(CO)_3$ provides direct support for the intermediates proposed in the thermally activated exchange process corresponding to eq 1.[4] The delineation of the mechanism for the exchange process is of significance in part because the cobalt–carbonyl systems are known to be low-temperature hydrosilation catalysts.[4a] Additionally, our data establish that the oxidative addition–reductive elimination mechanism, eq 3 and 4, can account for the facile exchange; direct evidence for such exchange mechanisms is important in establishing the mechanism of a variety of significant catalytic reactions. Other mechanisms for such exchange processes, not involving oxidative addition, have been discussed.[5]

Experimental Section

Instruments. IR spectra were recorded by using a Nicolet 7199 Fourier transform spectrometer. NMR spectra were recorded by using a JEOL FX90Q, a Bruker 250, or a Bruker 270-MHz Fourier transform spectrometer. Generally, all manipulations of the organometallic complexes were carried out under N_2 by using a Vacuum Atmospheres drybox, an N_2 purged glovebag, or conventional Schlenk line techniques. However, $Ph_3SiCo(CO)_4$ is relatively air stable in the dark, and can be handled in air.

Chemicals. Hexane and toluene were reagent grade and freshly distilled from CaH_2 under N_2. Methylcyclohexane was reagent grade and deoxygenated before use. The following compounds were used as received: Me_3SiH and Ph_3SiH (Petrarch), $P(OPh)_3$ (Aldrich), and $Co_2(CO)_8$ (Aldrich). Et_3SiH (Petrarch) was distilled from molecular sieves prior to use. Et_3SiD was available from previous work.[6] Perdeuterated methylcyclohexane (Cambridge Isotopes) was distilled prior to use.

The literature procedure was used to prepare and purify $Ph_3SiCo(CO)_4$ and $Et_3SiCo(CO)_4$.[7] The literature preparation[7b] of $Me_3SiCo(CO)_4$ was modified by condensing the Me_3SiH onto $Co_2(CO)_8$ at −78 °C and allowing the flask to warm to room temperature.

Irradiations. Two General Electric Blacklight bulbs (355 ± 20 nm, $\sim 2 \times 10^{-6}$ einstein/min) or a Bausch and Lomb SP 250 high-pressure Hg lamp were used for irradiation. When the high pressure Hg lamp was used, a 10-cm water filter with Pyrex windows was also used to filter out IR and deep-UV irradiation.

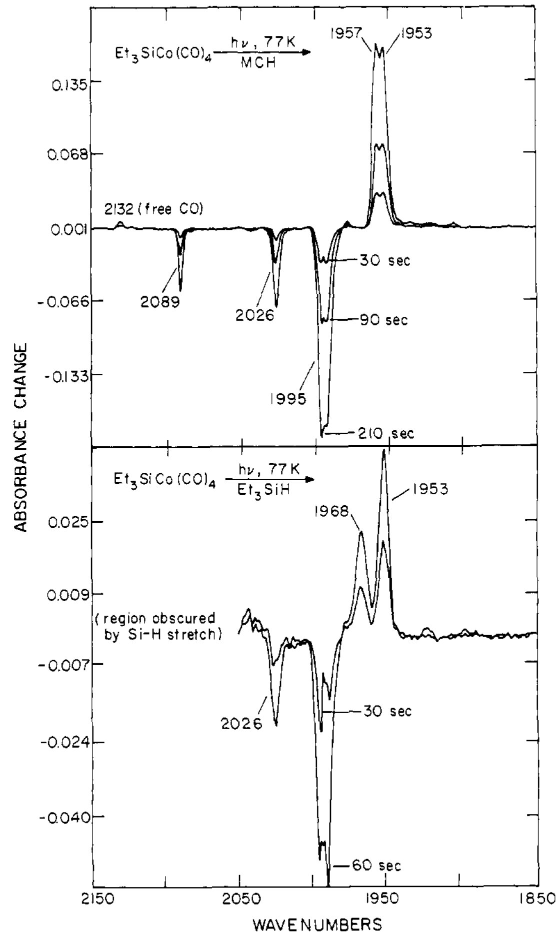


Figure 1. (a, top) IR difference spectra upon irradiation of 5 mM $Et_3SiCo(CO)_4$ at 77 K in methylcyclohexane. Curves are for (1) 30 s, (2) 90 s, and (3) 210 s of irradiation to give ~50% consumption of the $Et_3SiCo(CO)_4$ at 210 s. (b, bottom) IR difference spectra upon irradiation of 5 mM $Et_3SiCo(CO)_4$ in Et_3SiH at 77 K. The Si–H stretch of the Et_3SiH obscures both the free CO absorption and the highest energy absorption of $Et_3SiCo(CO)_4$.

Low-Temperature Spectra. Low-temperature IR and UV–vis spectra were obtained by using a Precision Cell, Inc., Model P/N 21.000 variable-temperature cell with CaF_2 outer windows using liquid N_2 or dry ice/acetone as the coolant. A small hole drilled into the metal portion of the sample cell accommodates the junction end of a copper-constantan thermocouple. Temperatures are considered accurate to ±2 °C at fixed temperatures and ±10 °C while the sample is being warmed or cooled.

Low-temperature NMR spectra were obtained by irradiating the sample in an NMR tube immersed in a quartz Dewar containing either liquid N_2 or dry ice/acetone as coolant, followed by immediate removal to the cooled probe of the NMR spectrometer.

Results and Discussion

a. Irradiation of $R_3SiCo(CO)_4$ at 77 K in Alkane Matrices. Near-UV photolysis of $R_3SiCo(CO)_4$ (R = Me, Et) at 77 K in a rigid methylcyclohexane matrix results in rapid IR spectral changes in the CO stretching region (Figure 1). Band positions for relevant compounds are given in Table I. The feature that grows in at 2132 cm^{-1} is attributable to the ejected CO and the split band, 1957, 1953 cm^{-1}, is assigned to $R_3SiCo(CO)_3$. The amount of CO generated compared to the amount of $R_3SiCo(CO)_4$ consumed is consistent with the loss of one molecule of CO per $R_3SiCo(CO)_4$.[8] We find no evidence for the photogeneration of $Co(CO)_4$ from Si–Co homolysis. It is possible that Co–Si homolysis occurs, but the efficiency for cage escape may be negligible,

---

[1] Reichel, C. L.; Wrighton, M. S. *Inorg. Chem.* **1980**, *19*, 3858; *J. Am. Chem. Soc.* **1981**, *103*, 7180.

[2] Sweany, R. L. *J. Am. Chem. Soc.* **1981**, *103*, 2410.

[3] Sweany, R. L. *J. Am. Chem. Soc.* **1982**, *104*, 3739.

[4] (a) Harrod, J. F.; Chalk, A. J., In "Organic Syntheses via Metal Carbonyls"; Wiley: New York, 1977; Vol. 2, pp 687–690 and references therein. (b) Sommer, L. H.; Lyons, J. E.; Fujimoto, H. *J. Am. Chem. Soc.* **1969**, *91*, 7051.

[5] (a) Brintzinger, H. H. *J. Organomet. Chem.* **1979**, *171*, 337. (b) Watson, P. L. *J. Am. Chem. Soc.* **1983**, *105*, 6491.

[6] Reichel, C. L., Ph.D. Thesis, Massachusetts Institute of Technology, 1981.

[7] (a) Chalk, A. J.; Harrod, J. F. *J. Am. Chem. Soc.* **1967**, *89*, 1640. (b) Baay, Y. L.; MacDiarmid, A. G. *Inorg. Nucl. Chem. Lett.* **1967**, *3*, 159.

[8] The absorptivity of free CO in the alkane matrices used here has been determined to be ~350 M^{-1} cm^{-1}. The details will be published elsewhere.

Table I. IR Band Positions for Relevant Compounds[a]

compound	temp, K	band maxima, cm^{-1} (ϵ, M^{-1} cm^{-1}, or relative absorbance)
Et_3SiH	298	2102 (250)
Ph_3SiH	298	2125 (250)
$Et_3SiCo(CO)_4$	298	2089 (2700), 2026 (3400), 1995 (8600)
$Et_3SiCo(CO)_3P(OPh)_3$	298	1965
$Et_3SiCo(CO)_3$	77	1957 (1.00), 1953 (1.00)
$Me_3SiCo(CO)_4$	77	2090 (0.25), 2026 (0.58), 1995 (1.00)
$Me_3SiCo(CO)_3$	77	1956 (0.91), 1953 (1.00)
$Ph_3SiCo(CO)_4$	298	2093 (2200), 2032 (2400), 2004 (9900)
$Ph_3SiCo(CO)_3$, C_s isomer	77	2046 (0.68), 1984 (0.60), 1953 (1.00)
C_{3v} isomer	77	1967 (0.86), 1964 (1.00)
$(Et_3Si)_2Co(CO)_3H$	196	1968 (0.52), 1954 (1.00)
	77[b]	1968 (0.65), 1953 (1.00)
$(Et_3Si)(Me_3Si)Co(CO)_3H$	196	1966 (0.52), 1955 (1.00)
$(Et_3Si)(Ph_3Si)Co(CO)_3H$[c]	196	1976, 1971, 1966

[a] All spectral data are for methylcyclohexane unless noted otherwise. [b] In pure Et_3SiH. [c] Cf. Figure 3 for relative absorbances.

yielding no net homolysis.[9] The homolysis of Co–H in $HCo(CO)_4$ to photogenerate $Co(CO)_4$ is inefficient compared to CO loss.[10]

The 16 e^- $R_3SiCo(CO)_3$ is the intermediate proposed in the photochemical reaction represented by eq 6. Consistent with this

$$R_3SiCo(CO)_4 \xrightarrow[P(OPh)_3]{h\nu,\ 298\ K} R_3SiCo(CO)_3P(OPh)_3 + CO \quad (6)$$

conclusion, warmup of a matrix containing photogenerated $Et_3SiCo(CO)_3$ and 0.1 M $P(OPh)_3$ leads to the formation of $Et_3SiCo(CO)_3P(OPh)_3$. In the absence of an added ligand, warmup leads to back reaction to regenerate the $R_3SiCo(CO)_4$. Some decomposition (<15%) is also found in such warmup experiments, and $Co_2(CO)_8$ can be detected as a product.

The low-temperature/rigid-matrix photoreaction of $R_3SiCo(CO)_4$ shows that loss of CO is the only detectable chemical result of excited-state decay. This is consistent with earlier findings in fluid solution at 298 K.[1] Thus, despite the fact that the excited species should have a weakened Co–Si bond, we do not find cleavage of this bond. The loss of CO does occur, and the appearance of the bands at 1957, 1953 cm^{-1} suggests a structure for the $R_3SiCo(CO)_3$ that is C_{3v} as found in the photogenerated $LFe(CO)_3$ species that are isoelectronic.[11] For $Ph_3SiCo(CO)_3$ it appears that both a C_{3v} and a C_s isomer are formed (vide infra), as for certain $LFe(CO)_3$ species.[11]

b. Irradiation of $R_3SiCo(CO)_4$ in the Presence of Et_3SiH. Irradiation of $R_3SiCo(CO)_4$ in the presence of R'_3SiH at 298 K can result in the exchange process represented by eq 1.[1] At 77 K, irradiation of $Et_3SiCo(CO)_4$ in pure Et_3SiH results in the IR spectral changes included in Figure 1. As can be seen in Figure 1, the bands in the CO stretching region for the photoproduct are very different from those for $Et_3SiCo(CO)_3$ formed in an alkane matrix. Irradiation of $R_3SiCo(CO)_4$ (R = Me, Et) in a 77 K methylcyclohexane matrix containing 0.1 M Et_3SiH gives only the bands for $R_3SiCo(CO)_3$. However, the slightest warmup of the $R_3SiCo(CO)_3$/0.1 M Et_3SiH system leads to disappearance of the 1957, 1953 cm^{-1} features attributable to $R_3SiCo(CO)_3$. Concomitantly, bands at 1968, 1954 cm^{-1} grow. These product bands are at nearly the same position and relative intensity as the bands for the product from irradiation of $Et_3SiCo(CO)_4$ in pure Et_3SiH at 77 K. Further, the disappearance of $R_3SiCo(CO)_3$ is accompanied by decline in the 2102-cm^{-1} absorption associated with the Si–H stretch of the Et_3SiH. Thus, it appears that photogenerated $R_3SiCo(CO)_3$ can react thermally with Et_3SiH at very low temperature.

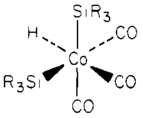
The two-band pattern, 1968, 1954 cm^{-1}, in the methylcyclohexane/0.1 M Et_3SiH medium persists up to ~230 K; at higher temperatures there is significant regeneration of $R_3SiCo(CO)_4$ (>85%) and some formation of $Co_2(CO)_8$. Indeed, the same 1968, 1954 cm^{-1} bands appear upon irradiation of $R_3SiCo(CO)_4$ (R = Me, Et) in methylcyclohexane/0.1 M Et_3SiH at 196 K (Table I). In addition, small bands at ~1950 and 1936 cm^{-1} appear that seem to be associated with the decomposition to $Co_2(CO)_8$. The same ~1950, 1936 cm^{-1} bands appear when $Et_3SiCo(CO)_4$ is irradiated in the absence of Et_3SiH in methylcyclohexane at 196 K. In the absence of Et_3SiH the 1968, 1954 cm^{-1} bands do not appear. Higher concentrations of Et_3SiH lead to smaller amounts of this side product relative to the product associated with the 1968, 1954 cm^{-1} bands. The broad, relatively weak 2102-cm^{-1} absorption of Et_3SiH can be monitored quantitatively, and the ratio of $R_3SiCo(CO)_4$ to Et_3SiH consumed is determined to be ~1.1 to 1.0 at 0.1 M Et_3SiH. To confirm this the irradiation was carried out in the presence of Et_3SiD; the changes in the vicinity of 2102 cm^{-1} are not observed. Unfortunately, the Si–D stretch is obscured by solvent. The results are consistent with a product that comes from the oxidative addition of Et_3SiH to $Et_3SiCo(CO)_3$, eq 7.

$$R_3SiCo(CO)_3 + Et_3SiH \xrightarrow{\Delta} (R_3Si)(Et_3Si)Co(CO)_3H \quad (7)$$

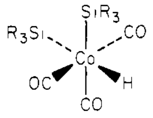
This process is analogous to the oxidation addition of H_2 to photogenerated $HCo(CO)_3$.[3] The detection of the Co–H by IR has not been possible, presumably because the absorption is too weak.

The photoreaction of 0.01 M $Et_3SiCo(CO)_4$ in perdeuteriomethylcyclohexane/0.02 M Et_3SiH at 196 K has been monitored by ^1H NMR. The key result is that the silicon hydride resonance declines and a new resonance grows in at δ −9.8, consistent with the formation of a cobalt hydride. Integration shows that the amount of cobalt hydride formed is at least 80% of the amount of silicon hydride consumed. Thus, the IR and NMR data taken together lead to the conclusion that the 1968, 1954 cm^{-1} peaks in the IR and the −9.8 ppm resonance in the NMR are due to the $(Et_3Si)_2Co(CO)_3H$ formed via oxidative addition of the Et_3SiH to the photogenerated $Et_3SiCo(CO)_3$. Higher nuclearity cobalt hydrides are ruled out as possible products, since the irradiation of $Et_3SiCo(CO)_4$ at 77 K in rigid Et_3SiH yields the same compound. Given the electronic similarity of Me_3Si- and Et_3Si- it is not surprising that the IR spectra of $(Et_3Si)(Me_3Si)Co(CO)_3H$ from $Me_3SiCo(CO)_4/Et_3SiH$ has nearly the same IR spectrum in the CO stretching region as $(Et_3Si)_2Co(CO)_3H$ (Table I).

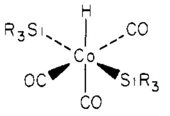
The $(R_3Si)_2Co(CO)_3H$ species could exist as isomers:



facial



meridional



meridional

Our data do not allow an unambiguous assignment, but we favor the facial structure. The facial arrangement is the only one in which there are no H- or R_3Si- (σ-donor only) ligands trans to each other, allowing each H- or R_3Si-ligand to be trans to a π-back bonding CO ligand.

c. Observation of Intermediates in the Productive R_3Si- Exchange in $R_3SiCo(CO)_4$. The fact that warmup of $(Et_3Si)_2Co(CO)_3H$ in the presence of the ejected CO yields regeneration of $Et_3SiCo(CO)_4$ suggests that it should be possible to observe productive exchange by irradiating $Et_3SiCo(CO)_4$ in the presence of a silicon hydride other than Et_3SiH. Irradiation of $Et_3SiCo(CO)_4$ in methylcyclohexane containing 0.1 M Ph_3SiH at 77 K results in the formation of the $Et_3SiCo(CO)_3$, as determined by the IR spectral changes. Warmup to ~175 K yields a new set of IR absorptions in the vicinity of 1970 cm^{-1} at the expense of the 1957, 1953 cm^{-1} features for $Et_3SiCo(CO)_3$. Further warming to 298 K regenerates a tetracarbonyl compound, but it is $Ph_3SiCo(CO)_4$. Apparently, the absorptions in the vicinity of 1970

---

(9) van Leeuwen, P. W. N. M.; van der Heijden, H.; Roobeek, C. F.; Frijns, J. H. G. *J. Organomet. Chem.* **1981**, *209*, 169.

(10) Sweany, R. L. *Inorg. Chem.* **1982**, *22*, 752.

(11) Boxhoorn, G.; Cerfontain, M. B.; Stufkens, D. J.; Oskam, A. *J. Chem. Soc., Dalton Trans.* **1980**, 1336.

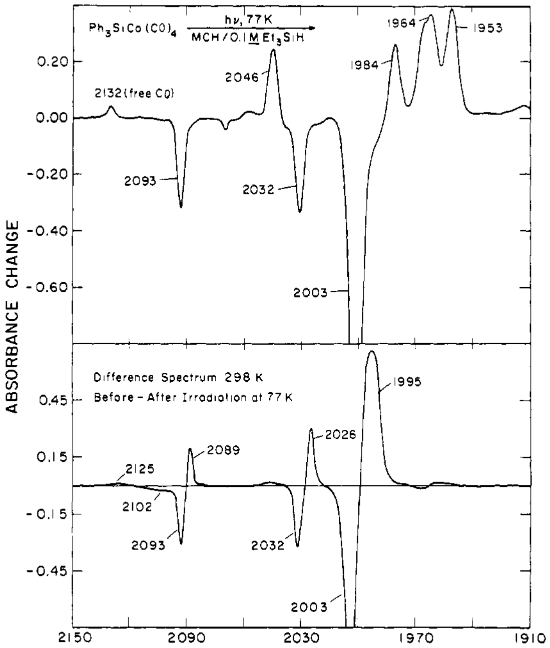


Figure 2. (Top) IR difference spectrum at 77 K upon photolysis of 0.01 M $Ph_3SiCo(CO)_4$ in methylcyclohexane/0.1 M Et_3SiH. The spectrum is for ~50% conversion of $Ph_3SiCo(CO)_4$ to the C_{3v} (~1964 cm^{-1}) and C_s (2046, 1984, 1953 cm^{-1}) isomers of $Ph_3SiCo(CO)_3$. (Bottom) IR difference spectrum at 298 K of the same sample before and after the 77 K irradiation. The product peak at 2125 cm^{-1} is Ph_3SiH and those at 2089, 2026, 1995 cm^{-1} are due to $Et_3SiCo(CO)_4$ that appear at the expense of Et_3SiH (2102 cm^{-1}) and $Ph_3SiCo(CO)_4$ (2093, 2032, 2003 cm^{-1}), respectively.

cm^{-1} are due to the oxidative addition product generated according to eq 8. The ultimate formation of $Ph_3SiCo(CO)_4$ must then come about from the reductive elimination of Et_3SiH, eq 9, and followed by reaction with CO, eq 10.

$$Et_3SiCo(CO)_3 + Ph_3SiH \xrightarrow{\Delta} (Et_3Si)(Ph_3Si)Co(CO)_3H \qquad (8)$$

$$(Et_3Si)(Ph_3Si)Co(CO)_3H \underset{\Delta}{\overset{\Delta}{\rightleftharpoons}} Ph_3SiCo(CO)_3 + Et_3SiH \qquad (9)$$

$$Ph_3SiCo(CO)_3 + CO \underset{h\nu}{\overset{\Delta}{\rightleftharpoons}} Ph_3SiCo(CO)_4 \qquad (10)$$

If the mechanism for the generation of $Ph_3SiCo(CO)_4$ is correct, the reaction of $Ph_3SiCo(CO)_4$ with Et_3SiH should yield the same oxidative addition product as in 8. Accordingly, we have examined the photochemistry of $Ph_3SiCo(CO)_4$. At 77 K in an alkane matrix the irradiation of $Ph_3SiCo(CO)_4$ yields loss of one CO per molecule consumed just as for $R_3SiCo(CO)_4$ (M = Me, Et) (Figure 1), but the $Ph_3SiCo(CO)_3$ appears to exist as a mixture of a C_s and a C_{3v} isomer as does $LFe(CO)_3$ generated by light-induced loss of CO from $Fe(CO)_4L$.[11] At very low extent conversion it appears that the C_{3v} structure (1968, 1964 cm^{-1}) dominates, but as the irradiation is continued the C_s structure, having three IR bands in the CO stretching region, (2046, 1984, 1953 cm^{-1}), becomes a significant fraction of the mixture (Figure 2).

Warmup to ~175 K of a 77 K matrix containing $Ph_3SiCo(CO)_3$ and 0.1 M Et_3SiH yields the IR spectral changes shown in Figure 3. The features at 1966, 1971, and 1976 cm^{-1} are in the same positions as for $(Et_3Si)(Ph_3Si)Co(CO)_3H$ generated from the irradiation of $Et_3SiCo(CO)_4$ in the presence of Ph_3SiH at the same temperature. Thus, the same species is generated from $Et_3SiCo(CO)_4$ and $Ph_3SiCo(CO)_4$ by irradiating in the presence of Ph_3SiH and Et_3SiH, respectively.

Warming the $(Et_3Si)(Ph_3Si)Co(CO)_3H$/0.1 M Et_3SiH further, to ~230 K, yields the appearance of a significant quantity of $Et_3SiCo(CO)_4$ and the features at 1968, 1954 cm^{-1} attributable to $(Et_3Si)_2Co(CO)_3H$ (Figure 3). Finally, warming to 298 K cleanly yields the loss of the $(Et_3Si)_2Co(CO)_3H$ and the additional growth of $Et_3SiCo(CO)_4$. As seen in Figure 3, there is virtually no regeneration of the $Ph_3SiCo(CO)_4$; rather the intermediates appear to lead to the formation of $Et_3SiCo(CO)_4$. This fact is consistent with the presence of excess Et_3SiH. Thus, when the temperature is sufficiently high, the reductive elimination of Ph_3SiH occurs, reversibly (eq 11), but the $Et_3SiCo(CO)_3$ is scavenged by excess Et_3SiH to give $(Et_3Si)_2Co(CO)_3H$. Competitively, the $Et_3SiCo(CO)_3$ can be scavenged by CO initially ejected in the primary photochemical step to give the exchange product $Et_3SiCo(CO)_4$.

$$(Et_3Si)(Ph_3Si)Co(CO)_3H \underset{\Delta}{\overset{\Delta}{\rightleftharpoons}} Et_3SiCo(CO)_3 + Ph_3SiH \qquad (11)$$

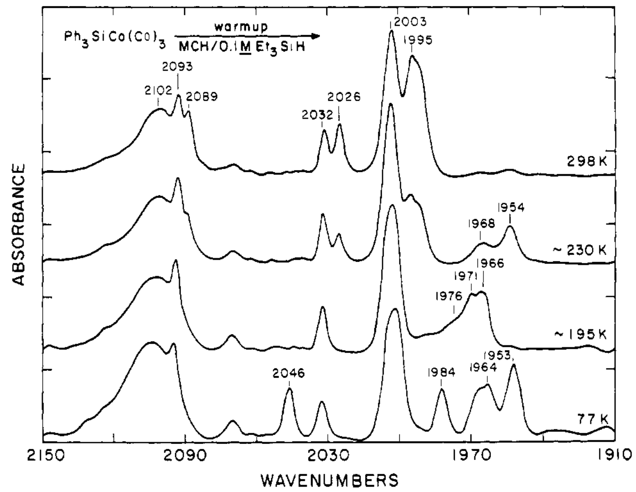


Figure 3. IR absorption spectra of irradiated solution characterized by the difference spectra in Figure 2 showing the spectral changes that occur in warming the photogenerated $Ph_3SiCo(CO)_3$ from 77 to 298 K. Temperatures for the intermediate spectra are approximate.

Figure 2 shows the difference in the 298 K IR absorption spectrum of the 0.01 M $Ph_3SiCo(CO)_4$/0.1 M Et_3SiH before the irradiation/warmup experiment and after the irradiation/warmup. The clean changes for consumption of $Ph_3SiCo(CO)_4$ and growth of $Et_3SiCo(CO)_4$ are unambiguous. Further, there is also direct evidence in the difference spectrum for the consumption of Et_3SiH, ν_{Si-H} = 2102 cm^{-1}, and the growth of the Ph_3SiH, ν_{Si-H} = 2125 cm^{-1}. Experiments paralleling those summarized in Figures 2 and 3 have also been carried out starting with $Et_3SiCo(CO)_4$ and Ph_3SiH. In such cases, the appearance of $Ph_3SiCo(CO)_4$ and Et_3SiH is observed at the expense of $Et_3SiCo(CO)_4$ and Ph_3SiH. Thus, the 16 e^- intermediates $R_3SiCo(CO)_3$ and the oxidative addition products $(R_3Si)(R'_3Si)Co(CO)_3H$ have been observed in the $R_3SiCo(CO)_4 \rightarrow R'_3SiCo(CO)_4$ exchange process. Interestingly, we have not observed the reductive elimination of $R_3Si-SiR'_3$ from $(R_3Si)(R'_3Si)Co(CO)_3H$. Further experiments to characterize the reactivity of $(R_3Si)(R'_3Si)Co(CO)_3H$ at carefully controlled temperatures are in progress.

Conclusion

Our results establish the mechanism for the light-induced reaction:[1]

$$R_3SiCo(CO)_4 + R'_3SiH \rightleftharpoons R'_3SiCo(CO)_4 + R_3SiH$$

Further, the observation of $R_3SiCo(CO)_3$ and $(R_3Si)(R'_3Si)Co(CO)_3H$ lends strong support for the mechanistic proposal for the analogous thermal process.[4,7a] In particular, we have provided direct evidence for the intermediates as well as for each of the elementary steps in the mechanism represented by eq 2–5 in the text. The rate-determining step in the thermal exchange is presumably loss of CO, inasmuch as oxidative addition of R_3SiH to $R'_3SiCo(CO)_3$ can occur thermally at very low temperature (as low as ~77 K) and reductive elimination of R_3SiH from $(R_3Si)(R'_3Si)Co(CO)_3H$ occurs well below 298 K. The elementary steps can be observed in the light-activated exchange reaction, because dissociative loss of CO from the lowest excited state occurs with a sufficiently low thermal activation barrier that the intermediates not observed at 298 K can be accumulated and characterized at low temperatures.

Acknowledgment. We thank the National Science Foundation for support of this research.

Registry No. Et_3SiH, 617-86-7; Ph_3SiH, 789-25-3; $Et_3SiCo(CO)_4$, 14049-72-0; $Et_3SiCo(CO)_3P(OPh)_3$, 75030-69-2; $Et_3SiCo(CO)_3$, 88179-98-0; $Me_3SiCo(CO)_4$, 15693-82-0; $Me_3SiCo(CO)_3$, 88179-99-1; $Ph_3SiCo(CO)_4$, 14095-19-3; $Ph_3SiCo(CO)_3$, 88180-00-1; $(Et_3Si)_2Co(CO)_3H$, 88180-01-2; $(Et_3Si)(Me_3Si)Co(CO)_3H$, 88180-02-3; $(Et_3Si)(Ph_3Si)Co(CO)_3H$, 88180-03-4; Et_3SiO, 1631-33-0.

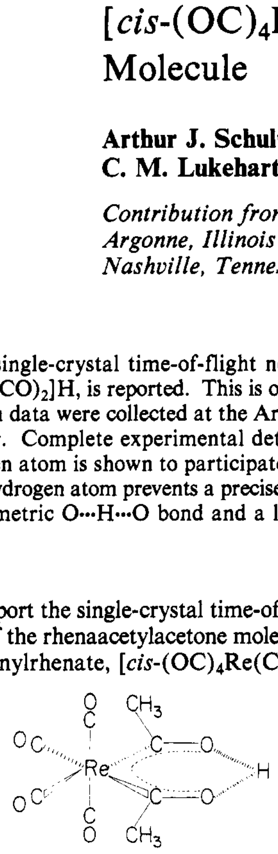
Single-Crystal Time-of-Flight Neutron Diffraction Structure of Hydrogen *cis*-Diacetyltetracarbonylrhenate, [*cis*-$(OC)_4Re(CH_3CO)_2$]H: A Metallaacetylacetone Molecule

Arthur J. Schultz,*[1a] K. Srinivasan,[1b] Raymond G. Teller,[1a] Jack M. Williams,[1a] and C. M. Lukehart*[1b]

Contribution from the Chemistry Division, Argonne National Laboratory, Argonne, Illinois 60439, and the Department of Chemistry, Vanderbilt University, Nashville, Tennessee 37235. *Received May 11, 1983*

Abstract: A single-crystal time-of-flight neutron diffraction structure of hydrogen *cis*-diacetyltetracarbonylrhenate, [*cis*-$(OC)_4Re(CH_3CO)_2$]H, is reported. This is one of the first successful structure determinations reported by using this technique. The diffraction data were collected at the Argonne Intense Pulsed Neutron Source with the unique time-of-flight single-crystal diffractometer. Complete experimental details are provided. The positions of all hydrogen atoms are determined, and the enolic hydrogen atom is shown to participate in an intramolecular O···H···O hydrogen bond. Although large thermal motion of the enolic hydrogen atom prevents a precise definition of the symmetry of this hydrogen bond, most of the results are consistent with an asymmetric O···H···O bond and a localized π-electron system within the rhena chelate ring.

In this paper, we report the single-crystal time-of-flight neutron diffraction structure of the rhenaacetylacetone molecule, hydrogen *cis*-diacetyltetracarbonylrhenate, [*cis*-$(OC)_4Re(CH_3CO)_2$]H, **1**.



1

This investigation was undertaken to unambiguously locate the position of the enolic hydrogen atom and to confirm the presence of O···H···O intramolecular hydrogen bonding. Although the enolic hydrogen atom was not located in a previous X-ray diffraction study of **1**, the molecular structure is consistent with a symmetrical or nearly symmetrical O···H···O enolic hyrogen bond.[2] Furthermore, the low-field ^1H NMR resonance at δ 21.79 (in CS_2 solution) for the enolic hydrogen atom of **1** and the O···H···O vibrational stretching frequency of 1658 cm^{-1} (in C_6H_{12} solution) for **1** indicate that extensive O···H···O hydrogen bonding is probably present. Vibrational stretching frequencies near 1650 cm^{-1} for O···H···O bonds have been proposed by others to indicate symmetrical or nearly symmetrical hydrogen bonding.[3]

Because this is one of the first reports[4] of a molecular structure derived from single-crystal time-of-flight neutron diffraction data, we believe a short description of the technique is desirable. The driving force to develop pulsed neutron sources and the instrumentation to utilize them for a wide variety of condensed-matter research[5] is the need for higher neutron flux and shorter data collection times than presently exist at steady-state reactor sources, for which the technical problem of heat removal is the major limiting factor in increasing their flux. Pulsed neutron sources have the advantage that they produce heat for only a small percentage of the time, whereas heat removal is continuous, and therefore the potential exists to produce fluxes orders of magnitude greater than those from reactor sources.[6]

At the Argonne Intense Pulsed Neutron Source (IPNS),[7] neutrons are generated by a pulsed spallation process in which short bursts of high-energy (500-MeV) protons are used to bombard a target of heavy nuclei (e.g., depleted uranium) 30 times per second (see Figure 1). The high-energy neutrons emanating from the target are thermalized by a hydrogen-containing moderator (e.g., polyethylene or liquid methane). Beam lines for each of the IPNS instruments are grouped radially around each of the four moderators. At a distance l from the moderator, the wavelength λ of a neutron is determined by the de Broglie equation:

$$\lambda = \frac{h}{mv} = \left(\frac{h}{m}\right)\left(\frac{t}{l}\right)$$

where h is Planck's constant, m is the neutron mass, v is the velocity of the neutron, and t is the time-of-flight for flight path,

---

(1) (a) Argonne National Laboratory. (b) Vanderbilt University.

(2) Lukehart, C. M.; Zeile, J. V. *J. Am. Chem. Soc.* **1976**, *98*, 2365-2367.

(3) (a) Ratajczak, H.; Orville-Thomas, W. J. *J. Mol. Struct.* **1967**, *1*, 449-461. (b) Joesten, M. D.; Schaad, L. J. In"Hydrogen Bonding"; Marcel Dekker: New York, 1974.

(4) Schultz, A. J.; Teller, R. G.; Beno, M. A.; Williams, J. M.; Brookhart, M.; Lamanna, W; Humphrey, M. B. *Science (Washington D.C.)* **1983**, *220*, 197-199.

(5) For a complete description of pulsed neutron sources and instrumentation see: Windsor, C. G. "Pulsed Neutron Scattering"; Halsted Press: New York, 1981.

(6) Carpenter, J. M. *Nucl. Instrum. Methods* **1977**, *145*, 91-113.

(7) Carpenter, J. M.; Price, D. L.; Swanson, N. J. "IPNS-A National Facility for Condensed Matter Research", Report No. ANL-78-88; Argonne National Laboratory; Argonne, IL, 1978.