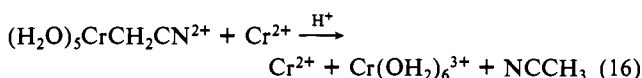
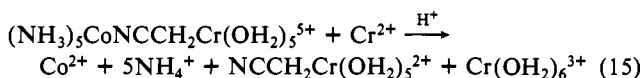


the latter reaction were not established.

The reaction of mercury(II) with organochromium(III) complexes is believed to occur by a bimolecular electrophilic substitution of  $\text{Hg}^{2+}$  on the carbon coordinated to chromium(III).<sup>36</sup> This is consistent with the second-order kinetics and decreasing rate constant with more electron-withdrawing substituents on the organic ligand.<sup>15,37</sup> The reactivity of  $(\text{H}_2\text{O})_5\text{CrCH}_2\text{CN}^{2+}$  and  $(\text{NH}_3)_5\text{CoNCCH}_2\text{Cr}(\text{OH}_2)_5^{5+}$  fits into this pattern.

An unusual feature of the  $(\text{NH}_3)_5\text{CoNCCH}_2\text{Cr}(\text{OH}_2)_5^{5+} + \text{Hg}^{2+}$  reaction is the inverse hydrogen ion term in the rate law. Since this is not normally observed<sup>15,37</sup> 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  $(\text{NH}_3)_5\text{CoNCCH}_2^{2+}$  ligand may enhance the acidity of a coordinated water enough to make the inverse hydrogen ion path detectable.

The chromium(II) reduction of  $(\text{NH}_3)_5\text{CoNCCH}_2\text{Cr}(\text{OH}_2)_5^{5+}$  presents a special problem in that it is not clear which metal center is reduced first. The fact that the rate constant ( $2.39 \times 10^{-3} \text{ M}^{-1} \text{ s}^{-1}$ ) is less than that for  $\text{Cr}^{2+} + (\text{H}_2\text{O})_5\text{CrCH}_2\text{CN}$  ( $1.73 \times 10^{-2} \text{ M}^{-1} \text{ s}^{-1}$ ) is consistent with the earlier argument that chromium(II) coordinates at the nitrile nitrogen in the latter system. Then the chromium(III) end of  $(\text{NH}_3)_5\text{CoNCCH}_2\text{Cr}(\text{OH}_2)_5^{5+}$  would show normal, i.e., very low, reactivity toward chromium(II). The absence of an  $[\text{H}^+]^{-1}$  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.

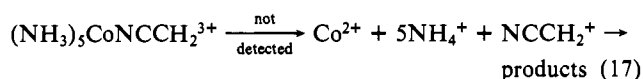


The second reaction is much faster than the first (see Table I) so that monophasic kinetics are observed.

An unusual feature of the results is that  $(\text{NH}_3)_5\text{CoNCCH}_2\text{I}^{3+}$  reacts essentially quantitatively with chromium(II) to produce

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the cobalt(III)-organochromium(III) dimer, and no cobalt(II) is detected. This indicates that intramolecular electron transfer within the  $(\text{NH}_3)_5\text{CoNCCH}_2^{3+}$  radical is slow compared to reaction with chromium(II).



This seems surprising in view of ESR studies, which show considerable unpaired spin density on nitrogen in the  $\cdot\text{CH}_2\text{CN}$  radical.<sup>38,39</sup> The thermodynamic instability of the carbonium ion  $\text{NCCH}_2^+$  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  $\cdot\text{CH}_2\text{CN}$  is 61 kcal mol<sup>-1</sup> higher than that of  $\cdot\text{CH}_2\text{OH}$ .<sup>40,41</sup> The latter radical does reduce  $\text{Co}(\text{NH}_3)_6^{3+}$ .<sup>42</sup>

It is possible to estimate an upper limit for the rate of reaction 17. If the rate constant for  $(\text{NH}_3)_5\text{CoNCCH}_2^{3+} + \text{Cr}^{2+}$  is  $\sim 1 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$ ,<sup>8</sup> then a consideration of our cobalt(II) detectability limits for experiments in which essentially equivalent amounts of  $(\text{NH}_3)_5\text{CoNCCH}_2\text{I}^{3+}$  and  $\text{Cr}^{2+}$  were mixed indicates that reaction 17 has a rate constant  $\leq 3.5 \times 10^3 \text{ s}^{-1}$ .

**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.**  $[(\text{NH}_3)_5\text{CoNCCH}_2\text{I}](\text{ClO}_4)_3$ , 88157-86-2;  $[(\text{NH}_3)_5\text{CoNCCH}_2\text{Cl}](\text{ClO}_4)_3$ , 88157-88-4;  $[(\text{NH}_3)_5\text{CoNCCH}_2\text{Hg}(\text{OH}_2)](\text{ClO}_4)_4$ , 88157-90-8;  $\text{CH}_2\text{CN}$ , 624-75-9;  $\text{ClCH}_2\text{CN}$ , 107-14-2;  $\text{Cr}^{2+}$ , 22541-79-3;  $(\text{H}_2\text{O})_5\text{CrCH}_2\text{CN}^{2+}$ , 76068-68-3;  $(\text{NH}_3)_5\text{CoNCCH}_2\text{Cr}(\text{OH}_2)_5^{5+}$ , 88157-91-9;  $\text{Hg}^{2+}$ , 14302-87-5.

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

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## Direct Observation of the Intermediates in the Photochemical Reaction of $\text{R}_3\text{SiCo}(\text{CO})_4$ with $\text{R}'_3\text{SiH}$ and Establishment of the Mechanism for $\text{R}'_3\text{SiCo}(\text{CO})_4$ Formation

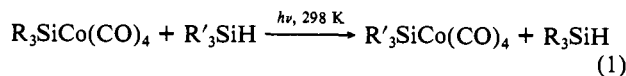
F. Ruth Anderson and Mark S. Wrighton\*

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

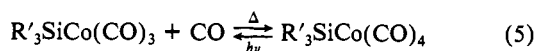
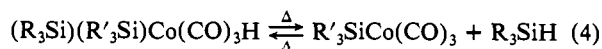
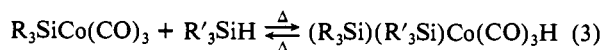
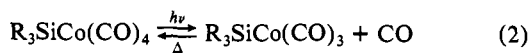
**Abstract:** Irradiation of  $\text{R}_3\text{SiCo}(\text{CO})_4$  in the presence of  $\text{R}'_3\text{SiH}$  yields  $\text{R}'_3\text{SiCo}(\text{CO})_4$  and  $\text{R}_3\text{SiH}$  at 298 K in an alkane solvent. The mechanism for this reaction has been established by irradiation at low temperature in alkane media. At 77 K in a rigid alkane medium, irradiation of  $\text{R}_3\text{SiCo}(\text{CO})_4$  ( $\text{R} = \text{Me}, \text{Et}, \text{Ph}$ ) yields dissociative loss of CO to give a 16 e<sup>-</sup> complex,  $\text{R}_3\text{SiCo}(\text{CO})_3$ , as determined by infrared spectroscopy. If the matrix contains a sufficiently high concentration of  $\text{R}_3\text{SiH}$  ( $\text{R} = \text{Et}$ ) the light-induced loss of CO occurs, but the metal carbonyl product is  $(\text{R}_3\text{Si})(\text{R}'_3\text{Si})\text{Co}(\text{CO})_3\text{H}$ . This species can also be formed photochemically at 196 K in fluid solution. The  $(\text{Et}_3\text{Si})_2\text{Co}(\text{CO})_3\text{H}$  is sufficiently inert that the Co-hydride resonance in the <sup>1</sup>H NMR can be observed at  $\delta -9.8$ . Warmup of the  $(\text{R}_3\text{Si})(\text{R}'_3\text{Si})\text{Co}(\text{CO})_3\text{H}$  to 298 K results in generation of both  $\text{R}_3\text{SiCo}(\text{CO})_4$  and  $\text{R}'_3\text{SiCo}(\text{CO})_4$ . The low-temperature photochemistry thus provides direct evidence for both the 16 e<sup>-</sup> primary photoproduct and the Co(III) oxidative addition product in the exchange mechanism.

We wish to report spectroscopic detection of intermediates,  $\text{R}_3\text{SiCo}(\text{CO})_3$  and  $(\text{R}_3\text{Si})(\text{R}'_3\text{Si})\text{Co}(\text{CO})_3\text{H}$ , in the photochemical

exchange process represented by eq 1.<sup>1</sup> These results establish the mechanism for the exchange process in (1) to be as represented



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



principle that the excited-state loss of CO can occur at a sufficiently low temperature (77 K) that the  $\text{R}_3\text{SiCo}(\text{CO})_3$  can be accumulated in a rigid matrix. We find that oxidative addition of  $\text{R}'_3\text{SiH}$  occurs readily at low temperature (even 77 K) to yield  $(\text{R}_3\text{Si})(\text{R}'_3\text{Si})\text{Co}(\text{CO})_3\text{H}$  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  $\text{H}_2$  is known to occur to photogenerated, coordinatively unsaturated  $\text{Fe}(\text{CO})_4^2$  or  $\text{HCo}(\text{CO})_3^3$  at low temperatures, providing precedence for the low-temperature oxidative addition reactivity reported here.

The observation of the  $(\text{R}_3\text{Si})(\text{R}'_3\text{Si})\text{Co}(\text{CO})_3\text{H}$  and the  $16 e^-$   $\text{R}_3\text{SiCo}(\text{CO})_3$  provides direct support for the intermediates proposed in the thermally activated exchange process corresponding to eq 1.<sup>4</sup> 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 hydrosilylation catalysts.<sup>4a</sup> 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.<sup>5</sup>

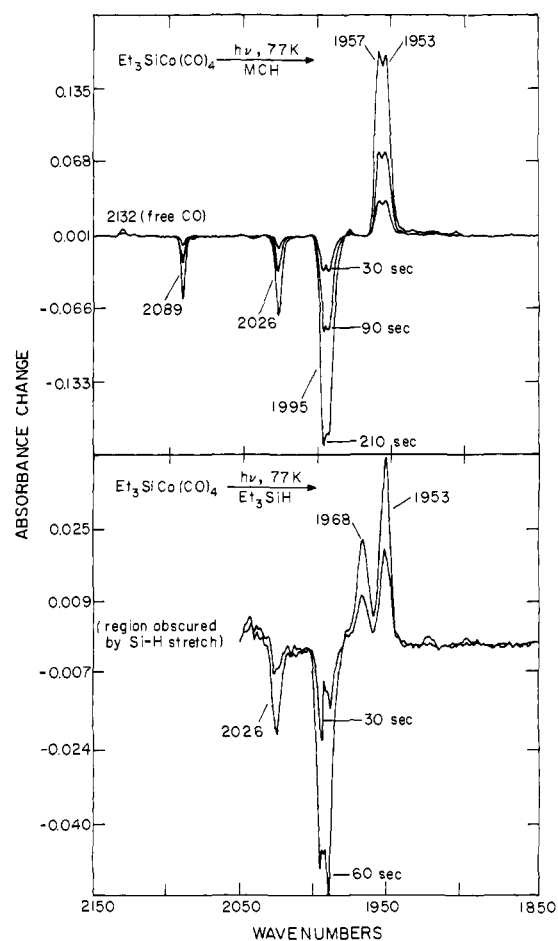
## Experimental Section

**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  $\text{N}_2$  by using a Vacuum Atmospheres dry-box, an  $\text{N}_2$  purged glovebag, or conventional Schlenk line techniques. However,  $\text{Ph}_3\text{SiCo}(\text{CO})_4$  is relatively air stable in the dark, and can be handled in air.

**Chemicals.** Hexane and toluene were reagent grade and freshly distilled from  $\text{CaH}_2$  under  $\text{N}_2$ . Methylcyclohexane was reagent grade and deoxygenated before use. The following compounds were used as received:  $\text{Me}_3\text{SiH}$  and  $\text{Ph}_3\text{SiH}$  (Petrarch),  $\text{P}(\text{OPh})_3$  (Aldrich), and  $\text{Co}_2(\text{CO})_8$  (Aldrich).  $\text{Et}_3\text{SiH}$  (Petrarch) was distilled from molecular sieves prior to use.  $\text{Et}_3\text{SiD}$  was available from previous work.<sup>6</sup> Perdeuterated methylcyclohexane (Cambridge Isotopes) was distilled prior to use.

The literature procedure was used to prepare and purify  $\text{Ph}_3\text{SiCo}(\text{CO})_4$  and  $\text{Et}_3\text{SiCo}(\text{CO})_4$ .<sup>7</sup> The literature preparation<sup>7b</sup> of  $\text{Me}_3\text{SiCo}(\text{CO})_4$  was modified by condensing the  $\text{Me}_3\text{SiH}$  onto  $\text{Co}_2(\text{CO})_8$  at  $-78^\circ\text{C}$  and allowing the flask to warm to room temperature.

**Irradiations.** Two General Electric Blacklight bulbs ( $35 \pm 20 \text{ nm}$ ,  $\sim 2 \times 10^{-6} \text{ einstein/min}$ ) or a Bausch and Lomb SP 250 high-pressure



**Figure 1.** (a, top) IR difference spectra upon irradiation of 5 mM  $\text{Et}_3\text{SiCo}(\text{CO})_4$  at 77 K in methylcyclohexane. Curves are for (1) 30 s, (2) 90 s, and (3) 210 s of irradiation to give  $\sim 50\%$  consumption of the  $\text{Et}_3\text{SiCo}(\text{CO})_4$  at 210 s. (b, bottom) IR difference spectra upon irradiation of 5 mM  $\text{Et}_3\text{SiCo}(\text{CO})_4$  in  $\text{Et}_3\text{SiH}$  at 77 K. The Si-H stretch of the  $\text{Et}_3\text{SiH}$  obscures both the free CO absorption and the highest energy absorption of  $\text{Et}_3\text{SiCo}(\text{CO})_4$ .

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.

**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  $\text{CaF}_2$  outer windows using liquid  $\text{N}_2$  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  $\pm 2^\circ\text{C}$  at fixed temperatures and  $\pm 10^\circ\text{C}$  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  $\text{N}_2$  or dry ice/acetone as coolant, followed by immediate removal to the cooled probe of the NMR spectrometer.

## Results and Discussion

### a. Irradiation of $\text{R}_3\text{SiCo}(\text{CO})_4$ at 77 K in Alkane Matrices.

Near-UV photolysis of  $\text{R}_3\text{SiCo}(\text{CO})_4$  ( $\text{R} = \text{Me}, \text{Et}$ ) 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  $2132 \text{ cm}^{-1}$  is attributable to the ejected CO and the split band,  $1957, 1953 \text{ cm}^{-1}$ , is assigned to  $\text{R}_3\text{SiCo}(\text{CO})_3$ . The amount of CO generated compared to the amount of  $\text{R}_3\text{SiCo}(\text{CO})_4$  consumed is consistent with the loss of one molecule of CO per  $\text{R}_3\text{SiCo}(\text{CO})_4$ .<sup>8</sup> We find no evidence for the photogeneration of  $\text{Co}(\text{CO})_4$  from Si-Co homolysis. It is possible that Co-Si homolysis occurs, but the efficiency for cage escape may be negligible,

(8) The absorptivity of free CO in the alkane matrices used here has been determined to be  $\sim 350 \text{ M}^{-1} \text{ cm}^{-1}$ . The details will be published elsewhere.

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Table I. IR Band Positions for Relevant Compounds<sup>a</sup>

compound	temp, K	band maxima, $cm^{-1}$ ( $\epsilon$ , $M^{-1} cm^{-1}$ , 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 <sup>b</sup>	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

<sup>a</sup> All spectral data are for methylcyclohexane unless noted otherwise. <sup>b</sup> In pure  $Et_3SiH$ . <sup>c</sup> Cf. Figure 3 for relative absorbances.

yielding no net homolysis.<sup>9</sup> The homolysis of Co-H in  $HCo(CO)_4$  to photogenerate  $Co(CO)_4$  is inefficient compared to CO loss.<sup>10</sup>

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



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.

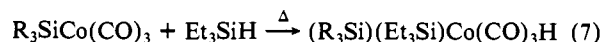
The low-temperature/rigid-matrix photoreaction of  $R_3SiCo(CO)_4$  shows that loss of CO is the only detectable chemical result of excited-state decay. This is consistent with earlier findings in fluid solution at 298 K.<sup>1</sup> Thus, despite the fact that the excited species should have a weakened 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  $LFc(CO)_3$  species that are isoelectronic.<sup>11</sup> For  $Ph_3SiCo(CO)_3$  it appears that both a  $C_{3v}$  and a  $C_s$  isomer are formed (vide infra), as for certain  $LFc(CO)_3$  species.<sup>11</sup>

#### 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.<sup>1</sup> 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.

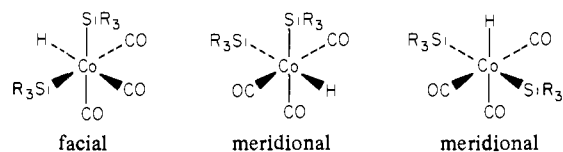
The two-band pattern, 1968, 1954  $cm^{-1}$ , in the methylcyclohexane/0.1 M  $Et_3SiH$  medium persists up to  $\sim 230$  K; at higher temperatures there is significant regeneration of  $R_3SiCo(CO)_4$  (>85%) and some formation of  $Co_2(CO)_8$ . Indeed, the same 1968, 1954  $cm^{-1}$  bands appear 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  $\sim 1950$  and 1936  $cm^{-1}$  appear that seem to be associated with the decomposition to  $Co_2(CO)_8$ . The same  $\sim 1950, 1936 cm^{-1}$  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  $\sim 1.1$  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.



This process is analogous to the oxidation addition of  $H_2$  to photogenerated  $HCo(CO)_3$ .<sup>3</sup> 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 perdeuterio-methylcyclohexane/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  $\delta -9.8$ , 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:



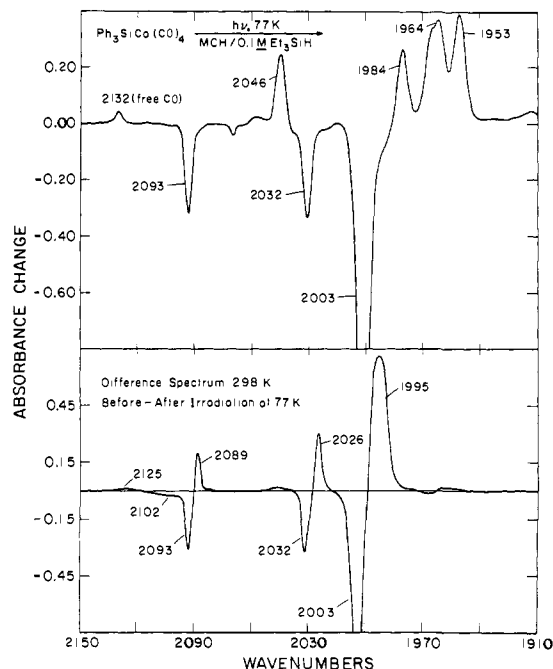
Our data do not allow an unambiguous assignment, but we favor the facial structure. The facial arrangement is the only one in which there are no H- or  $R_3Si-$  ( $\sigma$ -donor only) ligands trans to each other, allowing each H- or  $R_3Si$ -ligand to be trans to a  $\pi$ -back bonding CO ligand.

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  $\sim 175$  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

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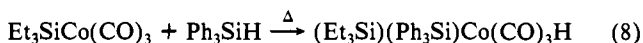
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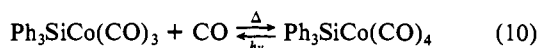
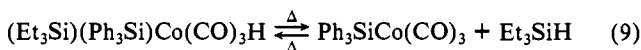


**Figure 2.** (Top) IR difference spectrum at 77 K upon photolysis of 0.01 M  $\text{Ph}_3\text{SiCo}(\text{CO})_4$  in methylcyclohexane/0.1 M  $\text{Et}_3\text{SiH}$ . The spectrum is for  $\sim 50\%$  conversion of  $\text{Ph}_3\text{SiCo}(\text{CO})_4$  to the  $C_{3v}$  ( $\sim 1964 \text{ cm}^{-1}$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

$\text{cm}^{-1}$  are due to the oxidative addition product generated according to eq 8. The ultimate formation of  $\text{Ph}_3\text{SiCo}(\text{CO})_4$  must then come



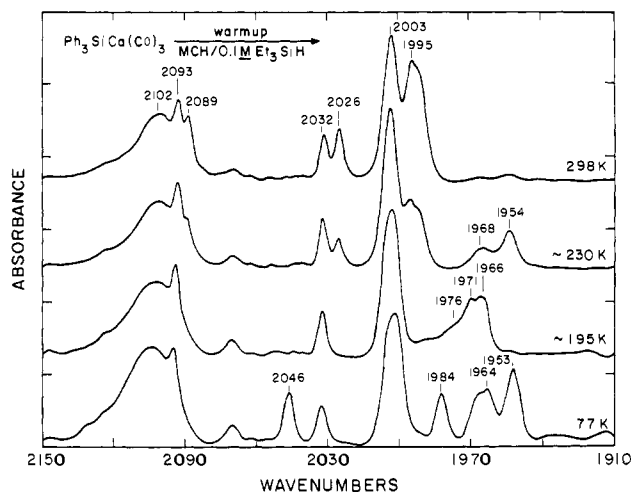
about from the reductive elimination of  $\text{Et}_3\text{SiH}$ , eq 9, and followed by reaction with CO, eq 10.



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

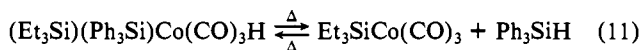
Warmup to  $\sim 175 \text{ K}$  of a 77 K matrix containing  $\text{Ph}_3\text{SiCo}(\text{CO})_3$  and 0.1 M  $\text{Et}_3\text{SiH}$  yields the IR spectral changes shown in Figure 3. The features at 1966, 1971, and  $1976 \text{ cm}^{-1}$  are in the same positions as for  $(\text{Et}_3\text{Si})(\text{Ph}_3\text{Si})\text{Co}(\text{CO})_3\text{H}$  generated from the irradiation of  $\text{Et}_3\text{SiCo}(\text{CO})_4$  in the presence of  $\text{Ph}_3\text{SiH}$  at the same temperature. Thus, the same species is generated from  $\text{Et}_3\text{SiCo}(\text{CO})_4$  and  $\text{Ph}_3\text{SiCo}(\text{CO})_4$  by irradiating in the presence of  $\text{Ph}_3\text{SiH}$  and  $\text{Et}_3\text{SiH}$ , respectively.

Warming the  $(\text{Et}_3\text{Si})(\text{Ph}_3\text{Si})\text{Co}(\text{CO})_3\text{H}/0.1 \text{ M Et}_3\text{SiH}$  further, to  $\sim 230 \text{ K}$ , yields the appearance of a significant quantity of  $\text{Et}_3\text{SiCo}(\text{CO})_4$  and the features at  $1968, 1954 \text{ cm}^{-1}$  attributable to  $(\text{Et}_3\text{Si})_2\text{Co}(\text{CO})_3\text{H}$  (Figure 3). Finally, warming to 298 K cleanly yields the loss of the  $(\text{Et}_3\text{Si})_2\text{Co}(\text{CO})_3\text{H}$  and the additional



**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  $\text{Ph}_3\text{SiCo}(\text{CO})_3$  from 77 to 298 K. Temperatures for the intermediate spectra are approximate.

growth of  $\text{Et}_3\text{SiCo}(\text{CO})_4$ . As seen in Figure 3, there is virtually no regeneration of the  $\text{Ph}_3\text{SiCo}(\text{CO})_4$ ; rather the intermediates appear to lead to the formation of  $\text{Et}_3\text{SiCo}(\text{CO})_4$ . This fact is consistent with the presence of excess  $\text{Et}_3\text{SiH}$ . Thus, when the temperature is sufficiently high, the reductive elimination of  $\text{Ph}_3\text{SiH}$  occurs, reversibly (eq 11), but the  $\text{Et}_3\text{SiCo}(\text{CO})_3$  is sca-

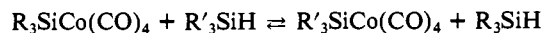


venaged by excess  $\text{Et}_3\text{SiH}$  to give  $(\text{Et}_3\text{Si})_2\text{Co}(\text{CO})_3\text{H}$ . Competitively, the  $\text{Et}_3\text{SiCo}(\text{CO})_3$  can be scavenged by CO initially ejected in the primary photochemical step to give the exchange product  $\text{Et}_3\text{SiCo}(\text{CO})_4$ .

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

## Conclusion

Our results establish the mechanism for the light-induced reaction:<sup>1</sup>



Further, the observation of  $\text{R}_3\text{SiCo}(\text{CO})_3$  and  $(\text{R}_3\text{Si})(\text{R}'_3\text{Si})\text{Co}(\text{CO})_3\text{H}$  lends strong support for the mechanistic proposal for the analogous thermal process.<sup>4,7a</sup> 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  $\text{R}_3\text{SiH}$  to  $\text{R}'_3\text{SiCo}(\text{CO})_3$  can occur thermally at very low temperature (as low as  $\sim 77 \text{ K}$ ) and reductive elimination of  $\text{R}_3\text{SiH}$  from  $(\text{R}_3\text{Si})(\text{R}'_3\text{Si})\text{Co}(\text{CO})_3\text{H}$  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.

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**Registry No.** Et<sub>3</sub>SiH, 617-86-7; Ph<sub>3</sub>SiH, 789-25-3; Et<sub>3</sub>SiCo(CO)<sub>4</sub>, 14049-72-0; Et<sub>3</sub>SiCo(CO)<sub>3</sub>P(OPh)<sub>3</sub>, 75030-69-2; Et<sub>3</sub>SiCo(CO)<sub>3</sub>, 88179-98-0; Me<sub>3</sub>SiCo(CO)<sub>4</sub>, 15693-82-0; Me<sub>3</sub>SiCo(CO)<sub>3</sub>, 88179-99-1; Ph<sub>3</sub>SiCo(CO)<sub>4</sub>, 14095-19-3; Ph<sub>3</sub>SiCo(CO)<sub>3</sub>, 88180-00-1; (Et<sub>3</sub>Si)<sub>2</sub>Co(CO)<sub>3</sub>H, 88180-01-2; (Et<sub>3</sub>Si)(Me<sub>3</sub>Si)Co(CO)<sub>3</sub>H, 88180-02-3; (Et<sub>3</sub>Si)(Ph<sub>3</sub>Si)Co(CO)<sub>3</sub>H, 88180-03-4; Et<sub>3</sub>SiO, 1631-33-0.

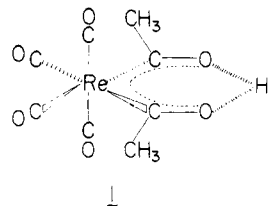
## Single-Crystal Time-of-Flight Neutron Diffraction Structure of Hydrogen *cis*-Diacyltetracarbonylrhenate, [*cis*-(OC)<sub>4</sub>Re(CH<sub>3</sub>CO)<sub>2</sub>]H: A Metallacetylacetonone Molecule

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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*-diacyltetracarbonylrhenate, [*cis*-(OC)<sub>4</sub>Re(CH<sub>3</sub>CO)<sub>2</sub>]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  $\pi$ -electron system within the rhenate chelate ring.

In this paper, we report the single-crystal time-of-flight neutron diffraction structure of the rhenacetylacetonone molecule, hydrogen *cis*-diacyltetracarbonylrhenate, [*cis*-(OC)<sub>4</sub>Re(CH<sub>3</sub>CO)<sub>2</sub>]H, **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 hydrogen bond.<sup>2</sup> Furthermore, the low-field <sup>1</sup>H NMR resonance at  $\delta$  21.79 (in CS<sub>2</sub> solution) for the enolic hydrogen atom of **1** and the O...H...O vibrational stretching frequency of 1658 cm<sup>-1</sup> (in C<sub>6</sub>H<sub>12</sub> solution) for **1** indicate that extensive O...H...O hydrogen bonding is probably present. Vibrational stretching frequencies near 1650 cm<sup>-1</sup> for O...H...O bonds have been proposed by others to indicate symmetrical or nearly symmetrical hydrogen bonding.<sup>3</sup>

Because this is one of the first reports<sup>4</sup> 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<sup>5</sup> 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.<sup>6</sup>

At the Argonne Intense Pulsed Neutron Source (IPNS),<sup>7</sup> 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  $\lambda$  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,

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