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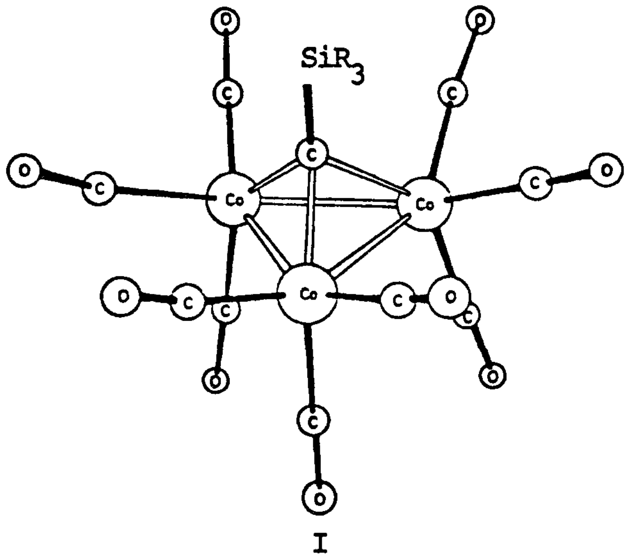
A General, High Yield Route to Novel Silicon-Functional Silylmethylidynetricobalt Nonacarbonyl Cluster Complexes[1]

Sir:

The generally applicable procedure for the preparation of alkylidynetricobalt nonacarbonyl complexes involves the reaction of an organic trihalide with dicobalt octacarbonyl.[2] We and others have used this reaction to prepare silyl-substituted methylidynetricobalt nonacarbonyls, I, including $Me_3SiCCo_3(CO)_9$,[3] $Me_2PhSiCCo_3(CO)_9$,[3] and other unspecified "$R_3SiCCo_3(CO)_9$" complexes.[4] This procedure has drawbacks in that it requires the preparation of the appropriate trihalomethyl silicon derivative. Furthermore, reactive functionality on silicon very likely would cause difficulties in this synthesis.



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We have developed a new route to silylmethylidynetricobalt nonacarbonyl complexes, which uses readily available starting materials, is easily effected and generally proceeds in high yield. Its principal advantage, however, is that it is compatible with a wide diversity of reactive functionality on silicon. This new procedure uses the reaction of methylidynetricobalt nonacarbonyl with silicon hydrides (eq 1).

$$\geqslant\mathrm{SiH} + \mathrm{HCCo_3(CO)_9} \xrightarrow[\text{30 min}]{\text{toluene,reflux}} \geqslant\mathrm{SiCCo_3(CO)_9} + \mathrm{H_2} \qquad (1)$$

These reactions were carried out under an atmosphere of carbon monoxide (to retard decomposition of the cluster complexes) using 1.0 g (2.26 mmol) of $HCCo_3(CO)_9$ and 5-12 mmol of the silane in 40 mL of dry toluene. The reaction mixture was stirred and heated at reflux (~105 °C) for 30 min. During this time, the originally purple color of the starting cluster changed to reddish purple. Upon completion of the reaction, the solvent was removed at reduced pressure and, in

Table I. $R_3SiCCo_3(CO)_9$ Compounds Prepared

Compd	R_3Si in $R_3SiCCo_3(CO)_9$[a]	Method of synthesis[b]	% yield	Mp, °C
1	Et_3Si	A	76	Softens above 70, dec
2	Me_2(i-Pr)Si	A	70	Softens above 110
3	n-Pr_3Si	A	81	85-86
4	Me_2PhSi	A	91	75[c]
5	$MePh_2Si$	A	60	84-85
6	Ph_3Si	A	39	139-140
7	$Me_2(EtO)Si$	A	48	120-122
8	Me_2ClSi	A	90	Apparent dec above 150
9	$Me_2(MeO)Si$	A/B	78	Dec at 140 without melting[d]
10	$Me_2(HO)Si$	A/B	76	Dec at 130 without melting[d]
11	$Me(MeO)_2Si$	A/B	73	Softens above 120
12	$Me(HO)_2Si$	A/B	81	Dec above 140 without melting
13	$(MeO)_3Si$	A/B	62	Softens above 120
14	$(HO)_3Si$	A/B	66	Dec above 150 without melting
15	Me_2FSi	C	93	205-206[d]
16	MeF_2Si	C	87	Softens above 170
17	F_3Si	C	85	Dec above 120
18	$Me_2(Me_3SiO)Si$	C	68	70-71
19	$Me(Me_3SiO)_2Si$	C	74	53-54
20	$(Me_3SiO)_3Si$	C	79	139-140

[a] All compounds listed have been characterized by combustion analysis and IR and NMR spectroscopy. [b] A: by reaction of $HCCo_3(CO)_9$ with the respective silicon hydride. A/B: by reaction of $HCCo_3(CO)_9$ with the respective chlorosilicon hydride followed by methanolysis or hydrolysis of the product. C: by further reaction of the respective hydroxysilane according to eq 2 or 3. [c] Reference 3. [d] M. O. Nestle, Ph.D. Thesis, Massachusetts Institute of Technology, 1977.

most cases, filtration chromatography was used to separate the product. Final purification was effected by sublimation at 50 °C in vacuo. This procedure served well in the synthesis of $R_3SiCCo_3(CO)_9$ compounds **1–7** shown in Table I. The same workup procedure could not be used for the isolation of chlorosilane-derived products since they were hydrolyzed on attempted chromatography on silicic acid. In the reaction of Me_2HSiCl with $HCCo_3(CO)_9$, $Me_2ClSiCCo_3(CO)_9$ was isolated in 90% yield as a black, crystalline solid in good purity simply by subliming away volatile impurities at 50 °C in vacuo. More usually, the products derived from reactions of $HCCo_3(CO)_9$ with $HSiCl_3$, $MeHSiCl_2$, and Me_2HSiCl were converted to the corresponding methoxy- or hydroxysilyl derivatives by dissolving the residue from solvent removal in benzene, adding 5 mL of methanol or water, and heating the resulting mixture at reflux under carbon monoxide for 30 min. These products are listed in Table I (compounds **9–14**). Further conversions of the silanols (**10, 12,** and **14**) which were carried out are shown in eq 2 and 3.

$$Me_n(HO)_{3-n}SiCCo_3(CO)_9 + BF_3 \cdot OEt_2 \xrightarrow[2h]{Et_2O,\ 25\ ^\circ C} Me_nF_{3-n}SiCCo_3(CO)_9 \quad (2)$$

$$Me_n(HO)_{3-n}SiCCo_3(CO)_9 + Me_3SiOSiMe_3 \xrightarrow[Et_2O]{concd\ H_2SO_4} Me_n(Me_3SiO)_{3-n}SiCCo_3(CO)_9 \quad (3)$$

$$n = 0\text{–}2$$

The products of these reactions are listed in Table I as compounds **15–20.** In the case of reaction 3, a reaction time of 2 h at room temperature sufficed in the trimethylsilylation of the silanol **10,** but these conditions gave incomplete conversion of the silanediol **12** to $Me_3SiO(HO)MeSiCCo_3(CO)_9$ (70% yield, mp 77–78 °C) and of the silanetriol **14** to $(Me_3SiO)_2(HO)SiCCo_3(CO)_9$ (68% yield, mp 51–52 °C). Reactions carried out in Et_2O/benzene at reflux (50 °C) for 3 and 10 h, respectively, gave the desired $(Me_3SiO)_2MeSiCCo_3(CO)_9$ and $(Me_3SiO)_3SiCCo_3(CO)_9$.

Very few silanetriols can be found in the literature, and these are very sensitive to condensation to siloxanes.[5] Thus the isolation of a stable, crystalline silanetriol, $(HO)_3SiCCo_3(CO)_9$, in the hydrolysis of $Cl_3SiCCo_3(CO)_9$, a reaction in which HCl which promotes silanol condensation[6,7] is formed, is very unusual. The compound had a correct combustion analysis (Calcd for $C_{10}H_3O_{12}SiCo_3$: C, 23.10; H, 0.58. Found: C, 22.97; H, 0.83.) and its observed molecular weight (vapor pressure osmometry in acetone) was 498 (calcd 520). Integration of a ^1H NMR spectrum of a 1:1 mixture of $(HO)_3SiCCo_3(CO)_9$ and $CH_3O_2CCCo_3(CO)_9$ showed the silicon compound to contain three hydrogen atoms. Silanol condensation is a bimolecular process and thus its rate is sensitive to steric factors.[8] (For instance, di-*tert*-butylsilanediol does not undergo homocondensation to a siloxane.[9]) That the substituent on the apical carbon atom of a methylidynetricobalt nonacarbonyl complex is in a highly hindered position was shown by Sutton and Dahl in their x-ray crystal structure determination of $CH_3CCo_3(CO)_9$.[10] It is likely that steric factors alone are sufficient to explain the remarkable stability of $(HO)_3SiCCo_3(CO)_9$. Smooth condensation of this compound and of the silanediol **12** to di- or polysiloxanes could not be effected by reaction with concentrated sulfuric acid in ether, a system which did permit their cocondensation with hexamethyldisiloxane (eq 3). IR studies (Nujol mull) showed the silanols **10, 12,** and **14** to be hydrogen bonded in the solid state. In addition to sharp bands at 3660, 3650, and 3640, respectively, there were strong, broad absorptions at 3400, 3390, and 3390, respectively, indicative of such interactions.

The ^{29}Si NMR shieldings of the silyl substituent on the $CCo_3(CO)_9$ cluster depend strongly on the other substituents on the silicon atom. Thus δ_{Si} for $Et_3SiCCo_3(CO)_9$ is found at +16.9 (downfield) from tetramethylsilane (TMS) (CCl_4 solution), for $(Me_3SiO)_2MeSiCCo_3(CO)_9$ at −38.5 (upfield) from TMS (neat liquid at 56 °C), and for $(HO)_3SiCCo_3(CO)_9$ at −51.8 ppm (acetone solution). The ^{13}C NMR apical carbon atom shieldings appear to be within the normal range,[11,12] at 301.3 for $(Me_3SiO)_2MeSiCCo_3(CO)_9$ and at 297.3 ppm for $(HO)_3SiCCo_3(CO)_9$.

The chemistry of these novel silicon-functional cobalt cluster complexes, especially of the silanols **10, 12,** and **14,** is under active investigation. Preliminary results indicate that these reactive substituents on silicon allow the incorporation of the methylidynetricobalt nonacarbonyl cluster into the side chains of various types of polymers, including polysiloxanes. In view of the known catalytic applications of $RCCo_3(CO)_9$ cluster complexes,[13] such anchoring of the $CCo_3(CO)_9$ to polymers may provide useful new catalysts.

That this element hydride/$HCCo_3(CO)_9$ reaction may find wider application is suggested by the preparation of $Ph_3GeCCo_3(CO)_9$, black crystals of mp 114–115 °C, in 33% yield by the reaction of Ph_3GeH with methylidynetricobalt nonacarbonyl.

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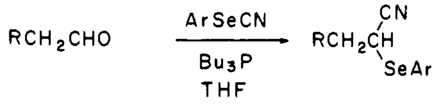
Aryl Selenocyanates: Useful Reagents for Cyanoselenenylation of Aldehydes

Sir:

Our continued interest in organoselenium chemistry[1] prompts us to report an exceptionally mild procedure for the direct cyanoselenenylation of aldehydes (eq 1). We have found that aryl selenocyanates (e.g., phenyl selenocyanate,[2a] *o*-ni-



$$RCH_2CHO \xrightarrow[Bu_3P \atop THF]{ArSeCN} RCH_2CH(CN)SeAr \quad (1)$$