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.

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

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

$$n = 0–2$$

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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Dietmar Seyferth,* Cynthia L. Nivert
Department of Chemistry
Massachusetts Institute of Technology
Cambridge, Massachusetts 02139

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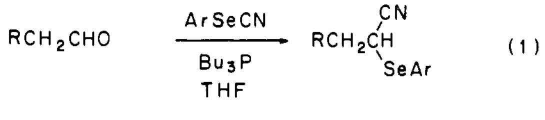
Aryl Selenocyanates: Useful Reagents for Cyanoselenenylation of Aldehydes

Sir:

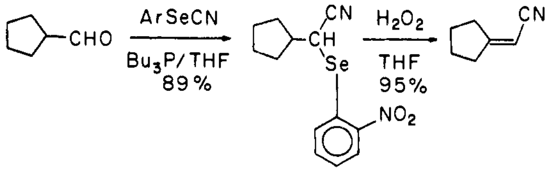
Our continued interest in organoselenium chemistry[1] prompts us to report an exceptionally mild procedure for the direct cyanoselenenylation of aldehydes (eq 1). We have found that aryl selenocyanates (e.g., phenyl selenocyanate,[2a] *o*-ni-



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

trophenyl selenocyanate[2b]) react rapidly at room temperature with aldehydes in the presence of tri-*n*-butylphosphine to give cyano selenides, **1**, in excellent yields (Table I).

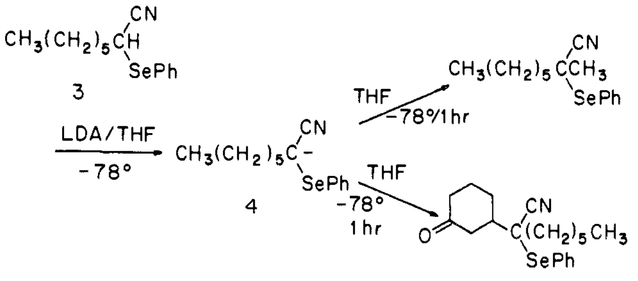
The one-carbon homologation of an aldehyde to a nitrile possessing an α-arylseleno substituent represents a synthetically useful reaction which permits a variety of synthetic transformations.[3] For example, cyclopentylmethanal was converted directly (eq 2) into the α,β-unsaturated nitrile **2** in



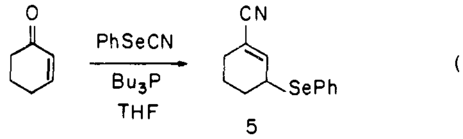
(2)

high overall yield. Similarly dodecanal was converted to a 55:45 (trans:cis) mixture of its corresponding α,β-unsaturated nitrile in 84% overall yield.

The cyanoselenenylation of *n*-heptanal with phenyl selenocyanate provided **3** in high yield which when treated with 1.2 equiv of lithium diisopropylamide in tetrahydrofuran at −78 °C generated anion **4**. Anion **4** undergoes (a) smooth alkylation with methyl iodide (87%) and (b) Michael addition to cyclohexenone in 91% yield.



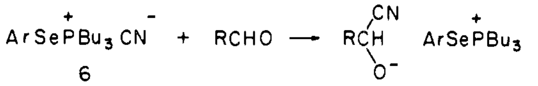
In contrast to aldehydes ketones do not undergo cyanoselenenylation but rather give rise to cyanohydrin formation. However, cyclohexenone does undergo reaction with phenyl selenocyanate in the presence of tributylphosphine giving rise to the rearranged product **5** in 50% yield (eq 3). Other α,β-unsaturated ketones (e.g., methyl vinyl ketone, cyclopentenone) gave similar results in only modest yield.



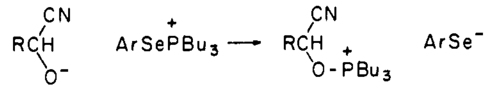
5

(3)

As illustrated in Table I, aldehydes require ~2.5 h for complete conversion to cyano selenide. If, however, the reaction is worked up after 10–15 min, the corresponding cyanohydrin contaminated with ~10% cyanoselenenylated product can be isolated in very high yield. The formation of the observed products is believed to involve, upon mixing tributylphosphine and the aryl selenocyanate, instantaneous formation of selenophosphonium cyanide **6** which rapidly reacts with the aldehyde as indicated in eq 4. The resulting species gives rise to the products by oxaphosphonium salt formation (eq 5) followed



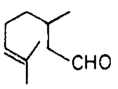
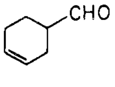
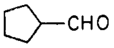
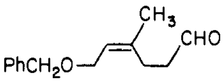
$$\underset{\mathbf{6}}{\overset{+}{\mathrm{ArSePBu_3}}\,\overset{-}{\mathrm{CN}}} + \mathrm{RCHO} \longrightarrow \mathrm{R}\underset{\mathrm{O^-}}{\overset{\mathrm{CN}}{\mathrm{C}}}\mathrm{H} \quad \overset{+}{\mathrm{ArSePBu_3}} \qquad (4)$$



$$\mathrm{R}\underset{\mathrm{O^-}}{\overset{\mathrm{CN}}{\mathrm{C}}}\mathrm{H} \quad \overset{+}{\mathrm{ArSePBu_3}} \longrightarrow \mathrm{R}\underset{\mathrm{O-PBu_3}}{\overset{\mathrm{CN}}{\mathrm{C}}}\mathrm{H}^{+} \quad \mathrm{ArSe^-} \qquad (5)$$

by aryl selenide displacement of tributylphosphine oxide which produces the cyanoselenenylated product. The mechanism of this reaction is very similar to the mechanism involved in the direct conversion of alcohols to aryl alkyl selenides with aryl selenocyanates and tributylphosphine.[4]

Table I. Cyanoselenenylation of Aldehydes Using *o*-Nitrophenyl Selenocyanate

Aldehyde	% yield of product[a-c]
dodecanal	93
heptanal	94
	96
	99
	89
	76

[a] All compounds were fully characterized by spectral methods. [b] Yields reported are for isolated, chromatographically pure substances. [c] All reactions were performed at room temperature over 2.5 h in tetrahydrofuran using 1.5 equiv of aryl selenocyanate and 1.5 equiv of tri-*n*-butylphosphine.

The following general procedure indicates the simplicity of the method. A solution of aldehyde in tetrahydrofuran containing 1.5 equiv of aryl selenocyanate at room temperature is treated with a solution of 1.5 equiv of tri-*n*-butylphosphine in tetrahydrofuran. After the addition is complete, the reaction is allowed to stir for 2.5 h. Evaporation of the solvent gives the crude product which is filtered through silica gel to remove tributylphosphine oxide and minor impurities.

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(5) Fellow of the Alfred P. Sloan Foundation.

Paul A. Grieco,*[5] **Yuusaku Yokoyama**
Department of Chemistry, University of Pittsburgh
Pittsburgh, Pennsylvania 15260

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Preparation of Optically Active Benzyl-α-*d* Alcohol via Reduction by *B*-3α-Pinanyl-9-borabicyclo[3.3.1]nonane. A New Highly Effective Chiral Reducing Agent

Sir:

B-3α-Pinanyl-9-borabicyclo[3.3.1]nonane, readily prepared by hydroboration of (+)-α-pinene with 9-borobicy-