

ORGANOCOBALT CLUSTER COMPLEXES

XXXII *. THE PREPARATION OF GERMYLSUBSTITUTED METHYLIDYNETRICOBALT NONACARBONYL COMPLEXES

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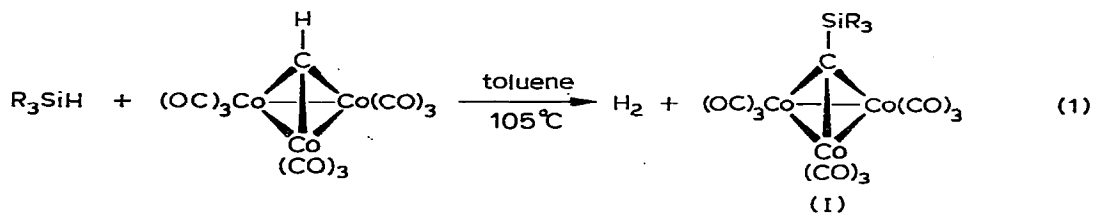
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Summary

The reaction of methylidyne tricobalt nonacarbonyl, $\text{HCCo}_3(\text{CO})_9$, with organogermanium hydrides, $\text{R}_n\text{Cl}_{3-n}\text{GeH}$ ($n = 2, 3$) in refluxing benzene solution under an atmosphere of carbon monoxide gave germlyl-substituted methylidyne tricobalt nonacarbonyl complexes of type $\text{R}_n\text{Cl}_{3-n}\text{GeCCo}_3(\text{CO})_9$.

Introduction

In a previous paper of this series [2] we described a general synthesis of silyl-substituted methylidyne tricobalt nonacarbonyl complexes of type I (eq. 1). Included in the examples of these reactions was the synthesis of $\text{Ph}_3\text{GeCCo}_3-$

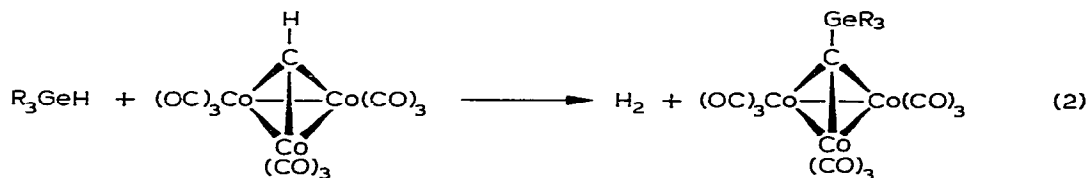


$(\text{CO})_9$, by the reaction of triphenylgermane with methylidyne tricobalt nonacarbonyl. We report here the extension of this reaction to the preparation of other germlyl-substituted methylidyne tricobalt nonacarbonyl complexes.

* Part XXXI: ref. 1.

Results and discussion

The reactions of triethyl-, tri-*n*-butyl-, chlorodiphenyl-, chlorodiethyl-, chloroethylphenyl- and chlorodibenzyl-germane with methylidyne tricobalt nonacarbonyl proceeded satisfactorily to give the respective germyl-substituted methylidyne tricobalt nonacarbonyl complexes in yields of 20–70% (eq. 2).



Reactions carried out using a twofold excess of $HCCo_3(CO)_9$ in refluxing benzene under an atmosphere of carbon monoxide gave best results. The silicon analogs, I, had been prepared in higher yield in refluxing toluene solution, but the germyl-substituted cluster complexes are less thermally stable. Table 1 presents the details of these preparations.

Attempts to prepare $Cl_3GeCCo_3(CO)_9$ were not successful. When $HGeCl_3 \cdot 2 Et_2O$ and $HCCo_3(CO)_9$ were heated in refluxing benzene solution for 3 h, the starting cobalt complex was completely consumed, but only intractable products formed.

The reactions of chlorosilicon hydrides with $HCCo_3(CO)_9$ gave the expected $R_nCl_{3-n}SiCCo_3(CO)_9$ products. These, however, could not be purified by column chromatography on silicic acid or alumina as such treatment converted them to the silanols, $R_n(HO)_{3-n}SiCCo_3(CO)_9$ [2]. The hydrolysis of chlorogermans is, in general, less facile than that of chlorosilanes [3], and it was found that such column chromatography did not affect the Ge–Cl bonds of $R_2ClGeCCo_3(CO)_9$ complexes.

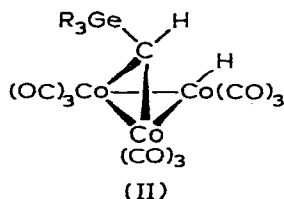
As in the case of the $R_3SiH/HCCo_3(CO)_9$ dehydrocondensation reaction, the mechanism of the $R_3GeH/HCCo_3(CO)_9$ reaction remains unknown. We suggest that here too an addition-elimination mechanism of the type proposed for the

TABLE I
DEHYDROCONDENSATION REACTIONS OF ORGANOGermanium HYDRIDES WITH METHYLIDYNETRICOBALT NONACARBONYL^a

Organogermanium hydride	$R_nCl_{3-n}GeCCo_3(CO)_9$ Product (% yield) ^c
Ph_3GeH	$Ph_3GeCCo_3(CO)_9$ (30) (ref. 2)
Et_3GeH	$Et_3GeCCo_3(CO)_9$ (30)
$n-Bu_3GeH$	$n-Bu_3GeCCo_3(CO)_9$ (44)
Ph_2ClGeH	$Ph_2ClGeCCo_3(CO)_9$ (57)
Et_2ClGeH	$Et_2ClGeCCo_3(CO)_9$ (19)
$EtPhClGeH$	$EtPhClGeCCo_3(CO)_9$ (71)
$(PhCH_2)_2ClGeH$	$(PhCH_2)_2ClGeCCo_3(CO)_9$ (49)
$(PhCH_2)_2ClGeH$	$(PhCH_2)_2ClGeCCo_3(CO)_9$ (46) ^b

^a In refluxing benzene solution. ^b In refluxing toluene solution for 0.6 h. A 6.5 h reaction time gave a 25% yield. ^c Yields are based on unrecovered $HCCo_3(CO)_9$.

$R_3SiH/HCCo_3(CO)_9$, reaction [2] should be considered, with an intermediate adduct of type II being formed in the initial interaction.



Experimental

General Comments

Infrared spectra were obtained using a Perkin-Elmer 457A grating infrared spectrophotometer with samples in carbon tetrachloride solution. Proton magnetic resonance spectra were recorded using either a Varian Associates T60 or a Hitachi-Perkin Elmer R24B spectrometer, both operating at 60 MHz. Chemical shifts are reported in δ units, ppm downfield from internal tetramethylsilane. Mass spectra were obtained on a Varian MAT-44 mass spectrometer operating at 70 eV. Melting points are uncorrected.

Organogermanium hydrides were obtained through the courtesy of Professor J. Stag e, Laboratoire des Organomin raux, Universit  Paul Sabatier, Toulouse. Methylidyne tricobalt nonacarbonyl was prepared by the reaction of bromoform with dicobalt octacarbonyl [4,5].

General procedure for $R_3GeH/HCCo_3(CO)_9$ reactions

All reactions were carried out in a standard apparatus which consisted of a 100 ml, three-necked, round-bottomed flask equipped with a reflux condenser topped with a gas inlet tube which also led to a Nujol bubbler, two no-air stoppers and a magnetic stir-bar. The apparatus was flame-dried under a brisk stream of nitrogen, then was flushed with carbon monoxide. The flask then was charged with the $HCCo_3(CO)_9$, and the appropriate solvent (benzene or toluene). A twofold excess of the cobalt complex was used, except in those cases where the $R_3GeCCo_3(CO)_9$ product and $HCCo_3(CO)_9$ could not be separated by column chromatography. Carbon monoxide (Matheson, research purity) was bubbled through the resulting solution at room temperature for 10 min. Then the germanium hydride was added and the reaction mixture was stirred and heated at reflux while carbon monoxide was bubbled slowly through the solution. Reactions carried out in refluxing benzene for 3–6 h gave the highest yields. During the heating period there was a just perceptible color change from purple to purple-brown.

Upon completion of the reaction, the mixture was cooled to room temperature and the solvent was removed at reduced pressure. Filtration chromatography through a pad of 100 mesh Mallinckrodt silicic acid was used to recover unconverted $HCCo_3(CO)_9$, and to isolate the desired product.

Dehydrocondensation reactions of germanium hydrides with methylidyne tricobalt nonacarbonyl

(a) *Triethylgermane*. A reaction was carried out between 0.88 g (2.0 mmol)

of the cobalt complex and 1.0 ml (6.2 mmol) of the germane in 40 ml of benzene at reflux for 15 h. Filtration chromatography using pentane as eluent and subsequent recrystallization from hexane at -30°C yielded 0.34 g (0.60 mmol, 30%) of black needles, $\text{Et}_3\text{GeCCo}_3(\text{CO})_9$, m.p. $177\text{--}179^{\circ}\text{C}$. (Anal. Found: C, 31.92; H, 2.56. $\text{C}_{16}\text{H}_{15}\text{O}_9\text{GeCo}_3$ calcd.: C, 31.99; H, 2.52%). IR (cm^{-1}): $\nu(\text{C}\equiv\text{O})$: 2097s, 2051vs, 2036vs, 2012s, 1973w.

(b) *Tri-n-butylgermane*. A reaction was carried out between 0.44 g (1.0 mmol) of $\text{HCCo}_3(\text{CO})_9$ and 1.0 ml (3.9 mmol) of the germane in 30 ml of benzene at reflux for 8 h. Filtration chromatography (pentane) and subsequent recrystallization from hexane at -30°C gave 0.30 g (0.44 mmol, 44%) of $(n\text{-C}_4\text{H}_9)_3\text{GeCCo}_3(\text{CO})_9$, black platelets with m.p. $65.5\text{--}67^{\circ}\text{C}$. (Anal. Found: C, 38.50; H, 4.05. $\text{C}_{22}\text{H}_{27}\text{O}_9\text{GeCo}_3$ calcd.: C, 38.58; H, 3.98%). IR (cm^{-1}): $\nu(\text{C}\equiv\text{O})$: 2098s, 2051vs, 2035vs, 2021s, 1972m.

(c) *Chlorodiphenylgermane*. A reaction between 0.88 g (2.0 mmol) of $\text{HCCo}_3(\text{CO})_9$ and 0.186 ml (1.0 mmol) of Ph_2ClGeH was carried out in 35 ml of benzene at reflux for 3.5 h. Filtration chromatography (pentane) separated unconverted $\text{HCCo}_3(\text{CO})_9$. Continued elution with dichloromethane, followed by recrystallization from hexane at -30°C , gave 0.30 g (0.4 mmol, 57% based on unrecovered cobalt complex) of $\text{Ph}_2\text{ClGeCCo}_3(\text{CO})_9$, black nuggets, m.p. $122\text{--}123^{\circ}\text{C}$. (Anal. Found: C, 37.71; H, 1.54. $\text{C}_{22}\text{H}_{10}\text{ClO}_9\text{GeCo}_3$ calcd.: C, 37.58; H, 1.44%). IR (cm^{-1}): $\nu(\text{C}\equiv\text{O})$: 2107s, 2062vs, 2047vs, 2030m, 1982w.

(d) *Chlorodiethylgermane*. A reaction was carried out between 0.88 g (2.0 mmol) of $\text{HCCo}_3(\text{CO})_9$ and 0.14 ml (1.0 mmol) of Et_2ClGeH in 30 ml of benzene at reflux for 5 h. Filtration chromatography was used to separate starting material from product. Elution with pentane gave 0.56 g (1.3 mmol) of $\text{HCCo}_3(\text{CO})_9$; with dichloromethane eluent, followed by recrystallization from pentane at -30°C , 0.08 g (0.14 mmol, 19%) of $\text{Et}_2\text{ClGeCCo}_3(\text{CO})_9$, black nuggets, m.p. $144\text{--}146^{\circ}\text{C}$, were obtained. (Anal. Found: C, 27.29; H, 1.88. $\text{C}_{14}\text{H}_{10}\text{ClO}_9\text{GeCo}_3$ calcd.: C, 27.70; H, 1.66%). IR (cm^{-1}): $\nu(\text{C}\equiv\text{O})$: 2101m, 2057vs, 2041vs, 2024w, 1937w. Mass spectrum: M^+ (0.2%) at m/e 608; fragment ions corresponding to successive loss of the nine CO ligands; $(M - 9\text{CO} - \text{C}_2\text{H}_5)^+$ (74.7%) at m/e 326.

(e) *Chloroethylphenylgermane*. A reaction was carried out between 1.33 g (3.0 mmol) of the cobalt complex and 0.28 ml (2.0 mmol) of the germanium hydride in 35 ml of benzene at reflux for 3 h. Filtration chromatography (95% pentane/5% dichloromethane) eluted 0.85 g (1.9 mmol) of $\text{HCCo}_3(\text{CO})_9$. Elution with dichloromethane, followed by recrystallization from pentane at -30°C , gave 0.50 g (0.76 mmol, 71%) of $\text{EtPhClGeCCo}_3(\text{CO})_9$, brown powder, m.p. $78\text{--}79.5^{\circ}\text{C}$. (Anal. Found: C, 32.79; H, 1.65. $\text{C}_{18}\text{H}_{10}\text{ClO}_9\text{GeCo}_3$ calcd.: C, 33.00; H, 1.54%). IR (cm^{-1}): $\nu(\text{C}\equiv\text{O})$: 2103m, 2060vs, 2042vs, 2023w, 1937w. Mass spectrum: fragment ions corresponding to successive loss of the nine CO ligands.

(f) *Chlorodibenzylgermane*. A reaction was carried out between 0.88 g (2.0 mmol) of the cobalt compound and 0.29 g (1.0 mmol) of the germane in 30 ml of benzene at reflux for 4 h. Filtration chromatography as in (e) gave 0.61 g (1.4 mmol) of $\text{HCCo}_3(\text{CO})_9$ and the germanium-containing product which was recrystallized from hexane at -10°C to give 0.22 g (0.30 mmol, 49%) of $(\text{PhCH}_2)_2\text{ClGeCCo}_3(\text{CO})_9$, black needles, m.p. $130\text{--}131.5^{\circ}\text{C}$. (Anal. Found: C,

39.56; H, 2.21. $C_{24}H_{14}ClO_9GeCo_3$ calcd.: C, 39.42; H, 1.93%. IR (cm^{-1}): $\nu(C\equiv O)$: 2104m, 2060vs, 2042vs, 2029w, 1940w. NMR ($CDCl_3$): δ 2.75 (s, 4H, CH_2) and 6.90–7.23 ppm (m, 10H, Ph).

Acknowledgments

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