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METHYLIDYNE TRICOBALT NONACARBONYL CLUSTERS; OPTICALLY ACTIVE SILICON AND GERMANIUM DERIVATIVES, AND SUBSTITUTIONS AT SILICON

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Summary

The preparation and alcoholysis of chiral chlorosilanes containing the nonacarbonyltricobaltcarbon cluster, $RR'Si(Cl)CCo_3(CO)_9$, is described. The alkoxy derivatives react with $i\text{-}Bu_2AlH$ or $BF_3 \cdot Et_2O$ to give the corresponding silicon hydride or fluoride. Reaction of methylidynetricobalt nonacarbonyl with optically active silanes of germane gave the optically active cluster complexes $R^1R^2R^3M^*CCo_3(CO)_9$ (M^* = Si, Ge). These compounds react with phosphine to give the monosubstituted $R^1R^2R^3M^*CCo_3(CO)_8(PR_3)$ (M^* = Si, Ge). The diastereomers have been resolved in the case of the MePhSi (Obornyl) $CCo_3(CO)_9$ complex.

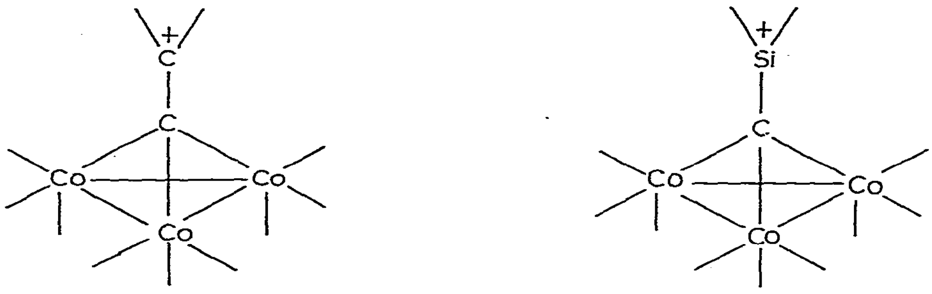
Introduction

In a programme of research on nonacarbonyltricobaltcarbon-substituted silicon derivatives, we wished to prepare optically active silicon complexes and study the influence of the cluster on the chemistry and stereochemistry of nucleophilic substitution at silicon. We were also interested in the observation by Seyferth et al. [1] that an α-nonacarbonyltricobaltcarbon substituent stabilized a carbonium ion (Fig. 1, a) and thought that the presence of the cluster might permit isolation of the siliconium ion (Fig. 1, b).

Results and discussion

1) Synthesis and reactivity of $RPhSi(Cl)CCo_3(CO)_9$

a) Preparation of $RPhSi(Cl)CCo_3(CO)_9$ and alkoxy derivatives. We prepared the silicon and germanium derivatives of methylidynetricobalt nonacarbonyl



(a) (b)

Fig. 1.

by the method described by Seyferth et al. [2,3] (eq. 1).

$$R_3MH + HCCo_3(CO)_9 \xrightarrow[110^\circ C]{\text{Toluene}} R_3MCCo_3(CO)_9 + H_2 \qquad (1)$$

M = Si; R_3 = Me_3, Ph_3, Me_2Cl etc...

M = Ge; R_3 = Ph_3, Et_3, Ph_2Cl, Et_2Cl etc...

Chiral chlorosilanes which would react with alcohols were prepared according to eqs. 2 and 3.

$$MePhSi(H)Cl + HCCo_3(CO)_9 \rightarrow MePhSi(Cl)CCo_3(CO)_9 \qquad (2)$$

$$MePhSi(Cl)CCo_3(CO)_9 \xrightarrow{R'OH} MePhSi(OR')CCo_3(CO)_9 \qquad (3)$$

The alcoholysis was performed in refluxing benzene in presence of an amine and the results are summarized in Table 1. The ester $[PhCH(OMe)COO]$-$SiMePhCCo_3(CO)_9$ was prepared by reaction of the chlorosilane with the ammonium salt $PhCH(OMe)COONH_3C_6H_{11}$.

The best yield of the alkoxy derivatives was obtained with methanol but the reaction works reasonably well with (—)menthol, (+)$Ph\overset{*}{C}H(Et)CH_2OH$, (—)$Ph\overset{*}{C}H(OMe)CH_2OH$ and (—)borneol. Ephedrine also was tried but gave a mixture of products which was not further investigated.

b) Reactions of $MePhSi(OMe)CCo_3(CO)_9$. We first studied the reactions of the most readily available and most reactive complex obtained, MePhSi(OMe)-

TABLE 1

ALCOHOLYSIS OF $MePhSi(Cl)CCo_3(CO)_9$

Alcohol	$MePhSi(OR)CCo_3(CO)_9$ yield (%)
MeOH	70
Isopropanol	32
(—)Menthol	54
(+)$Ph\overset{*}{C}H(Et)CH_2OH$	30
(—)$Ph\overset{*}{C}H(OMe)CH_2OH$	32
(—)Borneol	55

TABLE 2

REACTIONS OF $MePhSi(OMe)CCo_3(CO)_9$

Reagent	Product	Yield (%)
$i\text{-}Bu_2AlH$/hexane	$MePhSi(H)CCo_3(CO)_9$	68
$i\text{-}Bu_2AlH$/THF	no reaction	
$BF_3 \cdot Et_2O$	$MePhSi(F)CCo_3(CO)_9$	54
SbF_5/C	$MePhSi(F)CCo_3(CO)_9$	—
HCl	$MePhSi(OH)CCo_3(CO)_9$	90
Li AlH_4 — 40°C	no reaction	
Li AlH_4	decomposition of the cluster	
Li AlH_4 + 2 CuI≡AlH_2I		
3 $LiAlH_4$ + $AlCl_3$=AlH_3		
MeMgBr	decomposition	

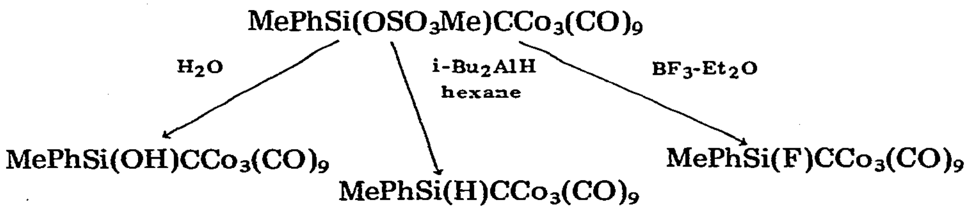
$CCo_3(CO)_9$. The results are summarized in Table 2. DIBAH (diisobutylaluminium hydride) reacted with the methoxy complex in hexane but not in THF. Fluorination occurred with $BF_3\text{-}Et_2O$ or SbF_5 in graphite, and hydrochloric acid gave $MePhSi(OH)CCo_3(CO)_9$ [6], as expected. This silanol was also obtained by treatment of $MePhSi[OCOCH(OMe)Ph]CCo_3(CO)_9$ with DIBAH in hexane. These reactions were extended to alkoxy complexes of another primary alcohol, $MePhSi(OH)CCo_3(CO)_9$ being obtained by reduction of $MePhSi[OCH_2CHPh(OMe)]CCo_3(CO)_9$ with DIBAH; this alkoxide reacted with $BF_3\text{-}Et_2O$ to give the expected fluorosilane. Other reducing agents such as $LiAlH_4$, "AlH_3" (3 $LiAlH_4$ + $AlCl_3$) [4] and "AlH_2I" ($LiAlH_4$ + 2 CuI) [5] caused decomposition of the methylidynetricobalt nonacarbonyl cluster. Decomposition was also observed when $MePhSi(OMe)CCo_3(CO)_9$ was treated with MeMgBr in large excess.

Treatment of a methylidynetricobalt nonacarbonyl-substituted alkoxysilane with $ClSO_3SiMe_3$ (cf. ref. 6) in benzene at room temperature gave two products (which were separated by TLC) as shown in eq. 4.

$$ClSO_3SiMe_3 + MePhSi(OMe)CCo_3(CO)_9 \rightarrow$$
$$Me_3SiCl + MePhSi(OSO_3Me)CCo_3(CO)_9 + MePhSi(OSiMe_3)CCo_3(CO)_9 \qquad (4)$$

The proportions of the two products depend on the conditions; the siloxane is favored by use of an excess of trimethylsilyl chlorosulfonate and a long reaction time (41% isolated with 2 equivalents $ClSO_3SiMe_3$ and 4 days reaction). It seems that $MePhSi(OSiMe_3)CCo_3(CO)_9$ is formed from the initial products, presumably by reaction of Me_3SiCl with $MePhSi(OSO_3Me)CCo_3(CO)_9$. The latter compound was not obtained pure, but was characterized by IR and NMR spectroscopy and by its reactions (scheme 1).

SCHEME 1



Hydrolysis and fluorination of the sulfonate took place readily, but DIBAH gave only a small amount of the expected silane.

We also attempted the synthesis of a silicon complex containing two nonacarbonyltricobaltcarbon substituents, $Me_2Si[CCo_3(CO)_9]_2$ (eq. 5,6).

$$Me_2Si(Cl)CCo_3(CO)_9 \xrightarrow[2)\ i\text{-}Bu_2AlH]{1)\ MeOH} Me_2Si(H)CCo_3(CO)_9 \tag{5}$$

$$Me_2Si(H)CCo_3(CO)_9 + HCCo_3(CO)_9 \not\rightarrow Me_2Si[CCo_3(CO)_9]_2 \tag{6}$$

However, in the second reaction (eq. 6) $HCCo_3(CO)_9$ was recovered and the only product identified was the siloxane $[Me_2SiCCo_3(CO)_9]_2O$, which was formed in low yield.

2) Preparation and substitution reactions of bifunctional silicon cluster complexes

Optically active bifunctional silicon derivatives can be obtained by two main methods: (i) preparation of a prochiral dichlorosilane and reaction with an optically active alcohol to give a chloroalkoxysilane [7], and (ii) synthesis of a prochiral dihydrogenosilane and catalysed reaction with an optically active alcohol to give a hydrogenoalkoxysilane [8]. We tried to prepare bifunctional silicon cluster derivatives by both routes.

$MeSi(Cl)_2CCo_3(CO)_9$ was prepared by reaction of $MeSiHCl_2$ with $HCCo_3(CO)_9$. The reaction of the dichlorosilane with one equivalent of alcohol (methanol or (—)borneol) gave a mixture of three major products: $MeSi(Cl)_2CCo_3(CO)_9$, $MeSi(OR')(Cl)CCo_3(CO)_9$ and $MeSi(OR')_2CCo_3(CO)_9$, along with $MeSi(OR')(OH)CCo_3(CO)_9$ and $MeSi(OH)_2CCo_3(CO)_9$ in the case of R' = bornyl. Column or TLC did not give any significant separation of the products.

The ready reduction of $MePhSi(OMe)CCo_3(CO)_9$ with DIBAH suggested that preparation of dihydrogeno complexes, $RSi(H)_2CCo_3(CO)_9$ would be easy. The dimethoxysilane complex was prepared according to eq. 7.

$$MeSi(Cl)_2CCo_3(CO)_9 \xrightarrow{MeOH} MeSi(OMe)_2CCo_3(CO)_9 \tag{7}$$

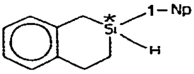
It reacted with BF_3-Et_2O to give the corresponding difluorosilane but no reaction was observed with DIBAH in hexane or THF, or with NaH. The dichlorosilane itself, $MeSi(Cl)_2CCo_3(CO)_9$, did not react with DIBAH. In the light of these results, attempts to prepare optically active bifunctional silicon cluster complexes were abandoned.

3) Synthesis of optically active silicon and germanium derivatives

a) Formation of Si—cluster and Ge—cluster bonds. The reaction depicted in eq. 1 was applied to optically active silicon and germanium compounds, with the results shown in Table 3. The stereochemistry of this reaction has not been established, but it is reasonable to expect retention of configuration at silicon, since this is the usual stereochemistry for Si—H bond rupture [9]. The germane MePh-1-NpGeH is known to racemize thermally [10], but in our hands it reacted with $HCCo_3(CO)_9$ in refluxing toluene to give an optically active methylidynetricobalt nonacarbonyl derivative. The O.R.D. curves of these com-

TABLE 3

PREPARATION OF OPTICALLY ACTIVE SILICON AND GERMANIUM DERIVATIVES

R_3M^*H $[\alpha]_D^{25}$ (°)	$R_3M^*CCo_3(CO)_9$		
	Colour, m.p. (°C)	Yield (%)	$[\alpha]_D^{25}$ (°)
MePh1-Np$\overset{*}{\text{Si}}$H +35.7	black 117—120, I	30	+550
 —21.6	black 130—132, II	64	+170
MePh1-NpGe*H —24.5 +24	black 96 III	30	—120 +85

plexes are nearly linear between 589 nm and 436 nm, the sign of rotation changing between 436 and 546 nm.

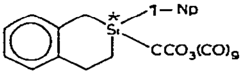
b) Exchange of ligands. Robinson and his coworkers have replaced 1,2 or 3 carbon monoxide ligands of $RCCo_3(CO)_9$ (R = organic group) by phosphines, arsines and phosphites [11]. The replacement of one CO by PPh_3 or PMe_2Ph took place readily at room temperature with our optically active compounds (eq. 8), and the results are summarized in Table 4.

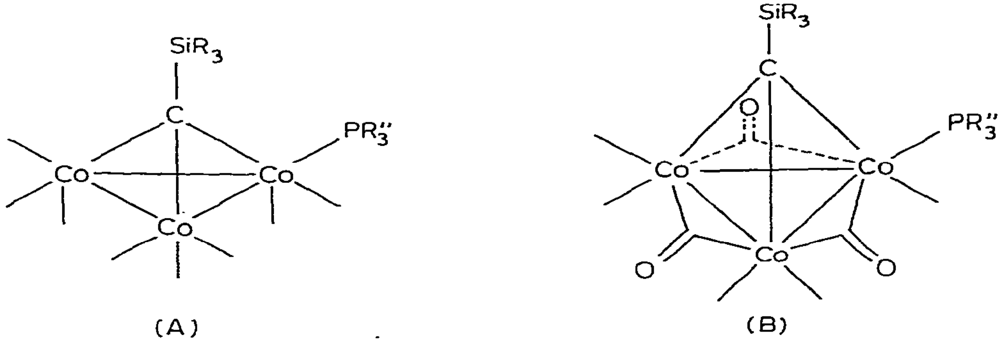
$$\text{MePh-1-NpSiCCo}_3\text{(CO)}_9 \xrightarrow[\text{hexane}]{\text{PMe}_2\text{Ph}} \text{MePh-1-NpSiCCo}_3\text{(CO)}_8\text{PMe}_2\text{Ph} \qquad (8)$$

We were unable to replace more than one carbon monoxide ligand. Use of higher temperature or of Me_3NO, which is known to cause activation in carbon monoxide substitutions [12], still gave only the monosubstituted product. This

TABLE 4

PHOSPHINE-SUBSTITUTED SILICON AND GERMANIUM DERIVATIVES

$R_3M^*CCo_3(CO)_9$ $[\alpha]_D^{25}$ (°)	$R_3\overset{*}{M}CCo_3(CO)_9(PMe_2Ph)$			
	Colour m.p. (°C)	Yield (%)	$[\alpha]_D^{25}$ (°)	Structure
MePh1-NpSi*CCo3(CO)9 +550, I	red—brown 138—142 (dec.), IV	20	+32	B
 +170, II	green-black 150—152, V	73	+100	A
MePh1-NpGe*CCo3(CO)9 —120, III	brick-red 142—145 (dec.), VI	—	—17	B
MePh1-NpSiCCo3(CO)9	$R_3MCCo_3(CO)_8(PPh_3)$			
	red-brown 135—140 (dec.), VII			B



(A) (B)

Fig. 2.

behaviour ruled out useful reaction with diphos ($Ph_2PCH_2CH_2PPh_2$) or arphos ($Ph_2PCH_2CH_2AsPh_2$). The phosphine-substituted complexes are of two types: complexes IV, VI and VII show C=O bridging frequencies in the IR spectra (1900w, 1879s, 1850s) while compound V shows frequencies similar to those from starting material II; this implies that, at least in solution, the acyclic complexes IV, VI and VII have structure B (Fig. 2) while V has structure A (Fig. 2) [11b].

4) *Preparation of MePhSi(Obornyl)CCo$_3$(CO)$_9$*

We have seen that prepartion of optically active bifunctional silicon cluster complexes was not possible, but that alcohols reacted with the chiral chlorosilane, $MePhSi(Cl)CCo_3(CO)_9$ to give alkoxy derivatives (Table 1). Use of optically active alcohols gave mixtures of diastereoisomers, which we tried to separate by fractional crystallization. Reactions with optically active alcohols (Table 1) mainly gave oily products, but with (—)borneol a solid product was obtained. We were able to enrich the diastereomeric mixture by crystallization in hexane at —20° C and, starting from a crude product with $[\alpha]^{25}_D = +80°$, we obtained a rotation of $[\alpha]^{25}_D = +170°$. This optically active complex is under investigation, and we plan to prepare $MePhSi^*(X)CCo_3(CO)_9$ compounds with X = H, Cl or OR.

Experimental

General

Infrared spectra were recorded on a Perkin-Elmer 457 spectrophotometer with CaF_2 cells in various solvents. Proton NMR spectra were recorded on a Varian EM 360 spectrometer with tetramethylsilane as internal standard. Phosphorus NMR spectra were recorded on a Fourier transform Brucker WP 80 spectrometer with H_3PO_4 as external standard (negative shifts to high field). Rotations of optically active compounds were measured with a Perkin-Elmer 141 polarimeter (*C* in g/100 ml) (1 cm cell); all the prepared clusters absorbed at 346 nm; the uncertainty in the rotation values is ca. ±10%. Melting points were determined using a Büchi circulating oil apparatus and are uncorrected.

Products were purified by crystallization or column chromatography on silicic acid with hexane/toluene as eluent. In some cases preparative TLC (Kiselgel 60 PF 254 purchased from Merck) was used with the same eluent. All solvents were dried and degassed before use. Published methods were used for the preparation of MePh-1-Np$\overset{*}{\mathrm{Si}}$H [13], 2-(1-naphthyl)-2-hydrogeno-2-sila-1,2,3,4-tetrahydronaphthalene [14], MePh-1-Np$\overset{*}{\mathrm{Ge}}$H [15], Ph-1-NpSi(H)Cl [7] and $HCCo_3(CO)_9$ [16]. MePhSiHCl was prepared by the reaction of PhMgBr with $MeSi(H)Cl_2$. $Co_2(CO)_8$ was purchased from Strem Chemicals and the solution of i-Bu_2AlH('DIBAH) (1 *M* in hexane) from Aldrich.

Resolution of phenylethylacetic acid [17] followed by reduction with $LiAlH_4$ [18] gave the optically active 1-phenyl-2-ethylethanol $[\alpha]_D^{25} = +26°$ ($C = 1.20$, EtOH). Resolution of phenylmethoxyacetic acid [19] (prepared from mandelic acid [10]), followed by reduction with $LiAlH_4$ [18] gave the optically active 2-phenyl-2-methoxyethanol $[\alpha]_D^{25} = -123°$ ($C = 0.225$, MeOH).

1) Synthesis of nonacarbonyltricobaltcarbon-substituted silanes

The general procedure corresponded with Seyferth's [2], but we used a slight excess of $HCCo_3(CO)_9$ (1.1 to 1.3 equivalents).

a) MePhSi(Cl)$CCo_3(CO)_9$. 2.06 g (4.6 mmol $HCCo_3(CO)_9$ and 1.46 g (12.6 mmol) MePhSiHCl were refluxed in 80 ml of toluene for 30 min to give 2.09 (3.5 mmol) of the title compound. Yield 75%. M.p.: 92°C. NMR: $\delta = 7.9$ (s, 2H), 7.5 (s, 3H) and 1.0 ppm (s, 3H). IR (CCl_4): 2110m, 2070s, 2050s and 2035m cm^{-1}.

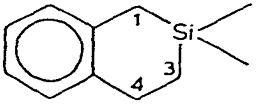
b) Ph-1-Np-Si(Cl)$CCo_3(CO)_9$. 564 mg (2.1 mmol) Ph-1-NpSiHCl and 1.06 g (2.4 mmol) $HCCo_3(CO)_9$ were refluxed for 35 min in 20 ml toluene to give 476 mg (0.67 mmol) of the title compound. Yield: 32%. M.p.: 115°C. NMR: aromatic only: $\delta = 8.35$, 7.95 and 7.45 ppm.

c) Reaction of $Me_2Si(H)CCo_3(CO)_9$ with $HCCo_3(CO)_9$. A solution of 770 mg (1.5 mmol) $Me_2Si(H)CCo_3(CO)_9$ and 750 mg (1.7 mmol) $HCCo_3(CO)_9$ in 30 ml toluene was refluxed for 3.5 hours. Nearly all the $HCCo_3(CO)_9$ (740 mg) was recovered by column chromatography but some $[Me_2Si(CCo_3(CO)_9)]_2O$ is also formed. NMR: $\delta = 0.4$ ppm (2 peaks, 4 Hz). IR: 2100m, 2055s, 2040s and 2020m cm^{-1}. Found: C, 28.36; H, 0.82. Calcd. for $C_{24}H_{12}Co_6O_{19}Si_2$: C, 28.42; H, 1.19%. Mass spectrum: *m/e* 844, 816, 788, 760, 732, 704, 676, 648, 620, 592, 564, 536, 508, 480, 452 ($[Me_2SiCCo_3(CO)_7]_2O^+$ and successive loss of 14 CO).

d) MePh-1-NpSi$CCo_3(CO)_9$ (I). MePh-1-NpSiH $[\alpha]_D^{25} = +35°$. 7 gave the title compound in 30% yield. $[\alpha]^{25} = +550°$ (589 nm), +290° (578 nm), +250° (546 nm) and −770° (436 nm). ($C = 0.0648$, hexane). M.p.: 80—85°C (racemic, 112—115°C). IR: 2090m, 2050s, 2030s and 2010m cm^{-1}. NMR: $\delta = 1.05$ (s, 3H) and 7.6 ppm (m, 12H). Found: C, 46.90; H, 2.30; Co, 24.75, Calcd. for $C_{27}H_{15}Co_3O_9Si$: C, 47.16; H, 2.20; Co, 25.6%.

e) MePh-1-NpGe$CCo_3(CO)_9$ (III). MePh-1-NpGeH, $[\alpha]_D^{25} = +24°$, gave the title compound in 30% yield. $[\alpha]^{25} = +85°$ (589 nm), +85° (578 nm), +24° (546 nm) and −360° (436 nm). ($C = 0.0818$, hexane). M.p.: 91°C, IR: 2090m, 2050s, 2030s and 2010m cm^{-1}. NMR: $\delta = 1.15$ (s, 3H) and 7.7 ppm (m, 12H). Found: C, 44.17; H, 2.11; Co, 23.83. Calcd. for $C_{27}H_{15}Co_3GeO_9$: C, 44.25; H, 2.06; Co, 24.12%. Mass spectrum: *m/e* 734, 706, 678, 650, 622, 594, 566, 538, 510, 482 (MePh-1-$NpGe^{74}CCo_3(CO)_9^+$ and successive loss of 9 CO).

f) 2-(1-Naphthyl)-2-nonacarbonyltricobaltcarbon-2-sila-1,3,4-trihydronaphthalene (II). 2-(1-Naphthyl)-2-sila-1,2,3,4-tetrahydronaphthalene, $[\alpha]_D^{25} = -9.5$ ($[\alpha]_D^{25}$ max = $-21.6°$) reacted with $HCCo_3(CO)_9$ to give 64% of the title compound $[\alpha]^{25} = +170°$ (579 nm), +170° (578 nm), +85° (546 nm) and −230° (436 nm) (after correction) ($C = 0.0792$, hexane). M.p.: 130—132°C. IR: 2090m, 2050s, 2030s and 2010m cm^{-1}. NMR: $\delta = 1.45$ (m, 2H, H3)), 2.85 (6 peaks, 4H, H(1) + H(4)) and 7.5 ppm (11H). Found: C, 47.57; H, 2.36; Co, 24.91. Calcd. for $C_{29}H_{17}Co_3O_9Si$: C, 48.77; H, 2.40; Co, 24.75%.



2) Phosphine substitutions

The following example is given as typical. Reactions are nearly quantitative but crystallization gave poor yield in some cases.

a) $MePh$-1-$NpSiCCo_3(CO)_8(PMe_2Ph)$ (IV). A solution of 200 mg (0.29 mmol) MePh-1-$NpSiCCo_3(CO)_9$ in 20 ml hexane was cooled at 0°C and 100 μl PMe_2Ph were added from a syringe. The solution turned red and chromatography filtration on silicic acid with toluene gave an orange residue, which was crystallized with difficulty at −20°C in 90/10 hexane/toluene. M.p.: 138—140°C (dec.). IR (Nujol): 2060m, 2030ms, 2025ms, 2000s, 1990s, 1980s, 1900w, 1870m and 1850ms cm^{-1}. NMR: $\delta = 0.9$ (s, 3H), 1.2 (d, 6H, $J(P-H) = 9$ Hz) and 7.5 ppm (m, 17H). ^{31}P NMR $\delta = +26.8$ ppm. Found: C, 51.26; H, 3.29; Co, 22.19. Calcd. for $C_{34}H_{26}Co_3O_8PSi$: C, 51.15; H, 3.28; Co, 22.14%.

Optically active compound: MePh-1-$NpSiCCo_3(CO)_9$ $[\alpha]_D^{25} = 550°$ gave the substituted product IV $[\alpha]_D^{25} = +32°$ ($C = 0.068$, hexane). (10 cm cell). M.p.: 138—142°C (dec.).

b) $MePh$-1-$NpGeCCo_3(CO)_8(PMe_2Ph)$ (VI). MePh-1-$NpGeCCo_3(CO)_9$ $[\alpha]_D^{25} = -120°$ gave VI$[\alpha]_D^{25} = -17°$ ($C = 0.0684$, cyclohexane) (10 cm cell). M.p.: 144—148°C (dec.). NMR: $\delta = 7.5$ (m, 17H), 1.2 (d, 6H, $J(P-H) = 9$ Hz) and 1.0 ppm (s, 3H). ^{31}P NMR $\delta = +26.5$ ppm. IR: 2060m, 2045ms, 2040ms, 2020s, 1990s, 1980s, 1900w, 1865m and 1850ms cm^{-1}. Found: C, 48.48; H, 3.36; Co, 1944. Calcd. for $C_{34}H_{26}Co_3GeO_8P$: C, 48.44; H, 3.11; Co, 20.97%.

c) 2-(1-Naphthyl)-2-[(dimethylphenylphosphine)octacarbonyltricobaltcarbon]-2-sila-1,3,4-trihydronaphthalene (V). With II $[\alpha]_D^{25} = +170°$ we obtained V as a green-black solid, $[\alpha]_D^{25} = +100°$ ($C = 0.0894$, cyclohexane), in 75% yield. M.p.: 150—152°C. NMR: $\delta = 7.7$ (br, m, 16H), 2.9 (br, m, 4H), 1.45 (br, m, 2H) and 1.35 ppm (d, 6H, $J(P-H) = 8$ Hz). IR (CCl_4): 2090s, 2070w, 2040vs, 2050vs, 2035vs, 2000w and 1980w cm^{-1}. Found: C, 52.20; H, 3.42; Co, 21.44. Calcd. for $C_{36}H_{28}Co_3O_8PSi$: C, 52.44; H, 3.40; Co, 21.36%.

d) $MePh$-1-$NpSiCCo_3(CO)_8(PPh_3)$ (VII). A solution of 188 mg (0.27 mmol) of MePh-1-$NpSiCCo_3(CO)_9$ and 71.6 mg (0.27 mmol) PPh_3 was refluxed in hexane for 30 min. The solvent was partially pumped off to leave an orange solid, which was washed with hexane to give 120 mg (0.13 mmol) of the title compound. Yield: 48%. M.p.: 143—145°C (dec). NMR: $\delta = 7.5$ (m, 27H) and 1.05 ppm (s, 3H). Found: C, 56.75; H, 3.42; Co, 19.0. Calcd. for $C_{44}H_{30}Co_3O_8PSi$: C, 57.29; H, 3.28; Co, 19.16%.

3) Alcoholysis reactions

Reactions were performed in refluxing degassed benzene under nitrogen, using an alcohol/amine mixture. The progress of the reaction was followed by TLC. Reaction times varied between 1 and 7 hours depending of the alcohol. Benzene was removed, and the products purified by column chromatography on silicic acid with 95/5 or 90/10 petroleum ether/toluene as eluent.

a) MePhSi(OMe)CCo$_3$(CO)$_9$. A solution of 915 mg (1.53 mmol) MePhSi(Cl)-CCo$_3$(CO)$_9$ in 3 ml benzene was heated with 3 ml MeOH for 1 hour to give 660 mg (1.1 mmol) of the title compound. Yield: 73%. M.p.: 60°C (dec.). NMR: δ = 7.5 (m, 5H), 3.67 (s, 3H) and 0.73 ppm (s,3H). Found: C, 37.15; H, 1.99; calcd. for $C_{18}H_{11}Co_3O_{10}Si$: C, 36.51; H, 1.87%.

b) MePhSi(O-i-Pr)CCo$_3$(CO)$_9$. 428 mg (0.72 mmol) MePhSi(Cl)CCo$_3$(CO)$_9$ was refluxed for 1 hour in a mixture of 3 ml isopropanol and 5 ml benzene to give 143 mg (0.23 mmol) of the title compound as an oil. Yield: 32%. NMR: δ = 7.53 (5H), 4.27 (m, 1H), 1.27 (d, 6H) and 0.73 ppm (s, 3H).

c) MePh[Ph(Et)CHCH$_2$O]SiCCo$_3$(CO)$_9$. 530 mg (0.89 mmol) MePhSi(Cl)-CCo$_3$(CO)$_9$, 267 mg (1.78 mmol) 2-phenyl-2-ethylethanol, $[\alpha]_D^{25}$ = +26° (C = 1.2, EtOH) [17,18], and 89 mg (0.89 mmol) cyclohexylamine were refluxed in 10 ml benzene for 3 hours to give 190 mg (0.27 mmol) of the title compound as a sticky solid. Yield 30%. NMR: δ = 7.33 (10H), 3.92 (d, 2H), 2.73 (m, 1H) and 2.23—0.55 ppm (m, 8H). No crystallization occurred in hexane at various concentrations, at room temperature or —20°C.

d) MePhSi[Ph(OMe)CHCH$_2$O]CCo$_3$(CO)$_9$. 500 mg (0.84 mmol) MePhSi(Cl)-CCo$_3$(CO)$_9$, 255 mg (1.68 mmol) 2-phenyl-2-methoxyethanol, $[\alpha]_D^{25}$ = —123° (C = 0.225, methanol) [18,20], and 83 mg (0.84 mmol) cyclohexylamine were refluxed in 10 ml benzene for 3 hours to give 190 mg (0.27 mmol) of the title compound as a sticky solid. Yield 32%. NMR: δ = 7.50 (10H), 4.20 (br. m, 1H), 3.80 (br. m, 2H), 3.10 (2 peaks, 3H) and 0.60 ppm (2 peaks, 3H). The mixture of diastereomers was 50/50 as indicated by the relative areas of the two peaks observed for -OMe (10 Hz) and -Me (6 Hz) groups. $[\alpha]_D^{25}$ = 0 (C = 0.574, hexane). No crystallization occurred in hexane at various concentrations at room temperature or —20°C.

e) MePhSi(OMen)CCo$_3$(CO)$_9$. 442 mg (0.74 mmol) MePhSi(Cl)CCo$_3$(CO)$_9$, 235 mg (1.5 mmol) (—)menthol and 150 mg (1.5 mmol) cyclohexylamine were refluxed in 10 ml benzene for 7 hours to give 172 mg (0.24 mmol) of the title compound as an oil. $[\alpha]_D^{25}$ = 350° (C = 0.106, hexane). Yield 32% (once 54%). NMR: δ = 7.5 (m, 5H), 3.63 (1H) and methoxy group between 1.67 and 0.47 ppm. No crystallization occurred in hexane at various concentrations, at room temperature or —20°C.

f) MePhSi(Obornyl)CCo$_3$(CO)$_9$. 745 mg (1.25 mmol) MePhSi(Cl)CCo$_3$(CO)$_9$, 385 mg (2.5 mmol) (—)borneol, $[\alpha]_D^{25}$ = —23°, and 124 mg (1.25 mmol) cyclohexylamine were refluxed in 10 ml benzene for 7 hours to give 533 mg (0.75 mmol) of the title compound as an oil. Yield 60%. Crude product: $[\alpha]_D^{25}$ = +80° (C = 0.084, hexane). NMR: δ = 7.53 (m, 5H), 4.13 (m, 1H), 0.72 (s, 3H) and 2.50—0.63 ppm (bornyl group). Found: C, 45.61; H, 3.73. Calcd. for $C_{27}H_{25}Co_3O_{10}Si$: C, 45.39; H, 3.53%. Mass spectrum: m/e 714, 686, 658, 630, 602, 574, 546, 518, 490, 462 (MePhSi(Obornyl)CCo$_3$(CO)$_9^+$ and successive loss of 9 CO).

g) MePh[Ph(OMe)CHCOO]SiCCo$_3$(CO)$_9$. PhCH(OMe)COONH$_3$C$_6$H$_{11}$ was prepared by mixing slowly cyclohexane solutions of 720 mg (4.0 mmol) (MeO)PhCHCOOH [20] and 430 mg (4.3 mmol) C$_6$H$_{11}$NH$_2$. The product separated out as a solid, which was filtered off and dried under vacuo.

870 mg (1.46 mmol) MePhSi(Cl)CCo$_3$(CO)$_9$ and 600 mg (2.26 mmol) Ph(OMe)CHCOONH$_3$C$_6$H$_{11}$ were heated at 60°C in 15 ml chloroform for 3 hours. After filtration, the solvent was removed and the residue crystallized from hexane at $-20°$C. Yield 30%. M.p.: 81°C (dec.). NMR: δ = 7.33 (m, 10H), 4.77 (s, 1H), 3.40 (s, 3H) and 0.93 ppm (s, 3H). Found: C, 43.03; H, 2.50; Co, 24.30. Calcd. for $C_{27}H_{17}Co_3O_{12}Si$: C, 42.99; H, 2.36; Co, 24.34%.

h) MePhSi(OH)CCo$_3$(CO)$_9$. 380 mg (0.64 mmol) MePhSi(Cl)CCo$_3$(CO)$_9$ were refluxed in 3 ml benzene and 1 ml H$_2$O. 280 mg (0.49 mmol) of silanol was obtained after chromatographic filtration through silicic acid with 50/50 toluene-hexane as eluent. Yield: 77%. M.p.: 78°C dec. NMR: δ = 7.66 (m, 5H), 2.33 (s, 1H) and 0.77 ppm (s, 3H). Found: C, 35.25; H, 1.66. Calcd. for $C_{17}H_9Co_3O_{10}Si$: C, 35.53; H, 1.57%.

4) Reactions of MePhSi(OMe)CCo$_3$(CO)$_9$

a) Reduction with DIBAH. 0.9 ml of a solution of DIBAH (1 *M* in hexane) was added to 328 mg (0.55 mmol) of MePhSi(OMe)CCo$_3$(CO)$_9$ dissolved in 2 ml hexane and the mixture was stirred for 3 hours. Hydrolysis with HCl (4 *N*), and extraction with hexane followed by column chromatography on silicic acid with the same solvent gave 210 mg (0.37 mmol) of MePhSi(H)CCo$_3$(CO)$_9$. Yield: 68%. M.p.: 49—50°C dec. NMR: δ = 7.40 (5H), 5.32 (q, 1H) and 0.75 ppm (d, 3H). Found: C, 37.21; H, 1.32. Calcd. for $C_{17}H_9Co_3O_9Si$: C, 36.32; H, 1.61%.

In THF with 1.5 equivalents DIBAH and after 4 hours at 50°C we observed partial decomposition but no hydrogenosilane.

b) Fluorination. BF$_3$ · Et$_2$O: 0.2 ml (1.6 mmol) BF$_3$ · Et$_2$O were added from a syringe to 370 mg (0,62 mmol) of MePhSi(OMe)CCo$_3$(CO)$_9$ in 5 ml benzene and the mixture was heated for 8 hours at 80°C to give 194 mg (0.34 mmol) of MePhSi(F)CCo$_3$(CO)$_9$ after purification on TLC. Yield 54%. M.p.: 72°C dec. NMR: δ = 7.53 (5H) and 0.80 ppm (d, 3H, ^3J(F—H) = 10 Hz). Found: C, 35.43; H, 1.46; Co, 30.37. Calcd. for $C_{17}H_8Co_3FO_9Si$: C, 35.20; H, 1.39; Co, 30.48%.

SbF$_5$/C [23]: 327 mg (0.55 mmol) MePhSi(OMe)CCo$_3$(CO)$_9$ and 0.27 mmol SbF$_5$ in graphite were refluxed in 5 ml toluene for 4 hours. Reaction was incomplete and the NMR spectrum showed that a mixture of MePhSi(F)-CCo$_3$(CO)$_9$ and starting material were obtained even after preparative TLC.

c) Reaction with HCl. 10 ml of a solution of HCl in THF (0.6 *M*) was added to 307 mg (0.52 mmol) MePhSi(OMe)CCo$_3$(CO)$_9$ and the mixture was stirred for 40 hours at room temperature. Purification on TLC gave 270 mg (0.47 mmol) MePhSi(OH)CCo$_3$(CO)$_9$. Yield: 90%. M.p.: 78°C dec. NMR: δ = 7.63 (5H), 2.37 (s, 1H) and 0.75 ppm (s, 3H). Mass spectrum: *m/e* 578, 550, 522, 494, 466, 438, 410, 382, 354, 326 (MePhSi(OH)CCo$_3$(CO)$_9^+$ and successive loss of 9 CO).

d) Reaction with miscellaneous hydrides. LiAlH$_4$ at $-40°$C: A mixture of MePhSi(OMe)CCo$_3$(CO)$_9$/LiAlH$_4$ (1/1.2) in ether was stirred at $-40°$C for 1 hour. No reaction was observed.

$LiAlH_4$ at room temperature: When $LiAlH_4$ was added to a solution of $MePhSi(OMe)CCo_3(CO)_9$ in ether, gas evolution occurred and the characteristic cluster colour disappeared. Cluster decomposition also occurred when $Ph_3SiCCo_3(CO)_9$ was used.

"AlH_3": This reagent was prepared according to the following equation [4]:

$$AlCl_3 + 3\ LiAlH_4 \xrightarrow{Et_2O} 4\ AlH_3 + 3\ LiCl$$

and the solution was titrated using Felkin's method [21].

0.4 mmol "AlH_3" in ether was added to a solution of 210 mg (0.35 mmol) $MePhSi(OMe)CCo_3(CO)_9$ in 2 ml ether and refluxed for 3 hours; complete decomposition of the cluster occurred.

"AlH_2I": This reagent was prepared according to the following equation [5]:

$$LiAlH_4 + 2\ CuI \xrightarrow{THF} AlH_2I + LiI + Cu^0 + H_2$$

1.48 mmol "AlH_2I" was added to 245 mg (0.41 mmol) of $MePhSi(OMe)CCo_3(CO)_9$ in 3 ml hexane. Decomposition of the cluster occurred after stirring for several hours at room temperature.

e) Reactions with Grignard reagent. 5 equivalents MeMgBr were added to a solution of 140 mg (0.24 mmol) $MePhSi(OMe)CCo_3(CO)_9$ in 3 ml ether; evolution of gas and discolouration indicated that decomposition had occurred.

5) Preparation of $Me_2Si(H)CCo_3(CO)_9$.

8 mmol DIBAH were added to 1.95 g (3.68 mmol) $Me_2Si(OMe)CCo_3(CO)_9$ in 15 ml hexane and the mixture stirred at room temperature for 18 hours to give 950 mg (1.9 mmol) of the title compound after hydrolysis with a solution of HCl (4 *M*), extraction with pentane and chromatographic filtration through silicic acid. Yield 52%. M.p.: 116°C dec. NMR: $\delta = 0.45$ (d, 6H, $^3J = 4$ Hz) and 4.90 ppm (hept, 1H, $^3J = 4$ Hz).

6) Reaction of $MeSi(OMe)_2CCo_3(CO)_9$

a) Reaction with $BF_3 \cdot Et_2O$. 0.4 ml (3 mmol) $BF_3 \cdot Et_2O$ was added to a solution of $MeSi(OMe)_2CCo_3(CO)_9$ in 5 ml benzene and the mixture was refluxed for 4 hours. Filtration and evaporation of the solvent left a residue which was heated at 50°C under vacuo to remove excess $BF_3 \cdot Et_2O$ and methylborates. The remaining oil was $MeSi(F)_2CCo_3(CO)_9$. NMR: = 0.6 ppm (tr, $^3J(F—H) = 6$ Hz).

b) Attempts with DIBAH. 4 ml (4 mmol) of a solution of DIBAH (1 *M*) in hexane were added to 500 mg (0.92 mmol) $MeSi(OMe)_2CCo_3(CO)_9$ in 5 ml hexane and the mixture was stirred at room temperature for 24 hours; no reduction occurred and column chromatography gave 200 mg of starting material.

The same mixture was refluxed in hexane for 27 hours or in THF for 15 hours to give complete or partial decomposition, respectively.

c) Attempt with NaH. NaH(dispersion in oil) was washed several times with DME before use. 336 mg (0.62 mmol) $MeSi(OMe)_2CCo_3(CO)_9$ in 10 ml DME were added to a suspension of 75 mg (3 mmol) NaH in DME and stirred for 3 days at room temperature; partial decomposition occurred but after hydrolysis and extraction with ether starting material only is recovered, as proved by TLC, IR and NMR.

6) Preparation and reaction of MePhSi(OSO₃Me)CCo₃(CO)₉

$ClSO_3SiMe_3$ was prepared from Me_3SiCl and $ClSO_3H$ [22].

a) Preparation of $MePhSi(OSO_3Me)CCo_3(CO)_9$. 0.15 ml (0.97 mmol) $ClSO_3SiMe_3$ was added from a syringe to 510 mg (0.86 mmol) $MePhSi(OMe)CCo_3(CO)_9$ in 4 ml hexane. The reaction was monitored by TLC and was complete after 4 hours at room temperature. This crude solution was used for further reactions. The solvent was removed under vacuo and the residue characterized by NMR, IR and by its reactions. IR (hexane): $\nu(OSO_3)$: 1390(br), 1360(br) and 1195s cm^{-1}. NMR (CCl_4): δ = 7.3—8.0 (m, 5H), 4.0 (s, 3H) and 1.1 ppm (s, 3H).

This reaction gave also $MePhSi(OSiMe_3)CCo_3(CO)_9$; the NMR spectra indicated 9% and 16% siloxane after 40 min and 4 hours reaction, respectively. A 2 : 1 ratio of $ClSO_3SiMe_3$ and $MePhSi(OMe)CCo_3(CO)_9$ was stirred for 4 days in hexane and gave a 41% yield of siloxane after column chromatography (90/10 petroleum ether/toluene). NMR: δ = 7.3—8.0 (m, 5H), 0.7 (s, 3H) and 0.13 ppm (s, 9H). IR $\nu(SiOSi)$: 1040 cm^{-1}. Found: C, 36.44; H, 2.65. Calcd. for $C_{20}H_{17}Co_3O_{10}Si_2$: C, 36.94; H, 2.64%. Mass spectrum: *m/e* 650, 622, 594, 566, 538, 510, 484, 454, 426, 398 ($MePhSi(OSiMe_3)CCo_3(CO)_9^+$ and successive loss of 9 CO).

b) Reaction with $BF_3 \cdot Et_2O$. 0.125 ml (1 mmol) $BF_3 \cdot Et_2O$ was added from a syringe to a solution of $MePhSi(OSO_3Me)CCo_3(CO)_9$ (prepared with 0.36 mmol $MePhSi(OMe)CCo_3(CO)_9$) in hexane and the mixture was stirred for 3 days; preparative TLC gave 127 mg (0.22 mmol) $MePhSi(F)CCo_3(CO)_9$. Yield 61%. M.p.: 73°C dec. NMR and m.p. are identical to those of an authentic sample (reaction of $MePhSi(OMe)CCo_3(CO)_9$ with $BF_3 \cdot Et_2O$).

c) Reaction with H_2O. A solution of $MePhSi(OSO_3Me)CCo_3(CO)_9$ (prepared with 0.35 mmol $MePhSi(OMe)CCo_3(CO)_9$) was stirred overnight at room temperature in a mixture of hexane and water to give 187 mg (0.32 mmol) $MePhSi(OH)CCo_3(CO)_9$ after column chromatography on silicic acid. Yield 91%. M.p.: 76°C dec. M.p. and NMR are identical to those of an authentic sample (reaction of $MePhSi(OMe)CCo_3(CO)_9$ with HCl).

d) Reaction with DIBAH. 0.66 mmol DIBAH was added to a solution of $MePhSi(OSO_3Me)CCo_3(CO)_9$ (prepared with 0.63 mmol $MePhSi(OMe)CCo_3(CO)_9$) in 10 ml hexane and the mixture was stirred overnight. Hydrolysis and column chromatography on silicic acid gave 137 mg of a mixture of $MePhSi(H)CCo_3(CO)_9$ and $MePhSi(OSiMe_3)CCo_3(CO)_9$, characterized by NMR spectroscopy. The yield of silane was about 30%.

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