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ORGANOCOBALT CLUSTER COMPLEXES

XIV*. THE REDUCTION OF FORMYL- AND ACYL-METHYLIDYNE-TRICOBALT NONACARBONYL COMPLEXES TO THE RESPECTIVE ALKYLIDYNE- AND HYDROXYALKYLIDYNE-TRICOBALT NONACARBONYLS BY TRIETHYLSILANE

DIETMAR SEYFERTH, GARY H. WILLIAMS, PAUL L.K. HUNG and
JOHN E. HALLGREN

Department of Chemistry, Massachusetts Institute of Technology,
Cambridge, Massachusetts 02139 (U.S.A.)

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Summary

The action of triethylsilane/trifluoroacetic acid in THF on $(OC)_9Co_3$-$CC(O)R$ (R = alkyl or aryl) resulted in reduction to the respective $(OC)_9Co_3$-CCH_2R complexes. Reduction of these ketones to the respective alcohol, $(OC)_9Co_3CCH(OH)R$, could be effected by treating them with triethylsilane in refluxing benzene and then pouring the reaction product into concentrated sulfuric acid and hydrolyzing the solution thus formed.

Introduction

In our further development of the organofunctional chemistry of alkylidynetricobalt nonacarbonyl cluster complexes [2—6], we became interested in investigating the chemistry of $(OC)_9Co_3C$-substituted alcohols, especially those where the OH group is α to the cluster substituent. While the direct reaction of dicobalt octacarbonyl with an organic tri- or di-halide serves well in the preparation of diversely substituted $(OC)_9Co_3CR$ compounds [2] [e.g., $R = CO_2R'$, $C(O)R'$, $C(O)NR'_2$, OCH_3, NMe_2, $P(O)(OR')_2$, $SiMe_3$, etc.], the application of this procedure to the synthesis of alcohols of type $(OC)_9Co_3CC(OH)RR'$ was very unsatisfactory. Other workers [7] who had studied the reactions of chloro- or bromo-alcohols, $CX_3CRR'OH$, with dicobalt octacarbonyl reported that these did not give the expected $(OC)_9Co_3CC(OH)RR'$ complexes. Instead, reduction occurred in some unexplained manner, and the respective $(OC)_9Co_3CCHRR'$ compounds were obtained, albeit in very low (3—9%) yields. In our hands [2], such reactions with 2,2,2-trichloroethanol did give the expected $(OC)_9Co_3CCH_2$-OH, but the yield of this product was only 0.8%. Protection of the OH group

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* For Part XIII see ref. 1.

by its conversion to the trimethylsilyl ether (e.g., $CCl_3CH_2OSiMe_3$ and $CBr_3CH_2OSiMe_3$) prior to reaction with $Co_2(CO)_8$ gave better yields (4—5%) of $(OC)_9Co_3CCH_2OH$ after hydrolysis of the $CX_3CH_2OSiMe_3/Co_2(CO)_8$ reaction mixture. However, a better preparative route to such $(OC)_9Co_3C$-substituted alcohols was required in order to facilitate an investigation of their chemistry.

We had found that the reaction of 1,1,1-trichloromethyl ketones with dicobalt octacarbonyl occurs readily, giving $(OC)_9Co_3CC(O)R$ compounds in quite acceptable yield [2], and we then turned our attention to the possibility of preparing secondary alcohols, $(OC)_9Co_3CCH(OH)R$, by their reduction. The precursor for the primary alcohol, the aldehyde $(OC)_9Co_3CCHO$, also was available for this study [4].

Results and discussion

Our initial attempts to reduce formylmethylidynetricobalt nonacarbonyl to $(OC)_9Co_3CCH_2OH$ were not successful. Treatment of this compound with sodium borohydride in tetrahydrofuran (THF) at reflux gave a mixture of $CH_3CCo_3(CO)_9$ and $HCCo_3(CO)_9$, while reaction with lithium aluminum hydride or sodium borohydride in benzene gave only $HCCo_3(CO)_9$.

Some functional alkylidynetricobalt nonacarbonyl complexes are quite stable toward strongly acidic media [3], and this prompted us to examine an acidic reducing system, triethylsilane in the presence of trifluoroacetic acid. This reducing system had been developed by Kursanov, Parnes and their coworkers [8] and had been the subject of further investigations by other workers [9,10]. It had been found to reduce aliphatic ketones to a mixture of the alcohol and its trifluoroacetate, but diaryl and aryl alkyl ketones directly to the hydrocarbon [10b,11]. The reaction course shown in Scheme 1 was proposed [8]. Aryl aldehydes also were reduced to the corresponding methylarenes [10b,12], but aliphatic aldehydes gave an ether ($RCHO \rightarrow RCH_2OCH_2R$) on treatment with this reducing system [12]. The entirely reasonable explanation given for this difference in reactivity when the carbonyl carbon atom bore aryl substituents involved the easier accessibility of the more stable arylcarbonium ions, $Ar\overset{+}{C}HR$ (R = H, alkyl, aryl) and their subsequent reduction by the silicon hydride. In most of these reactions a 1/2-2.5/2-10 molar ratio range of the carbonyl compound, triethylsilane and trifluoroacetic acid reactants, respectively, was used, and usually no organic diluent was added.

Application of the Et_3SiH/CF_3CO_2H reducing system to the reduction of organocobalt cluster carbonyl ketones, $(OC)_9Co_3CC(O)R$, resulted in their

SCHEME 1

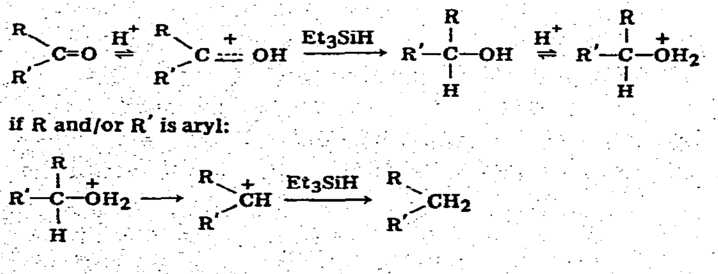
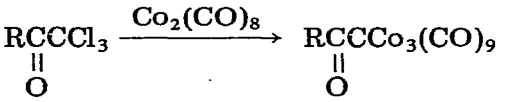


TABLE 1

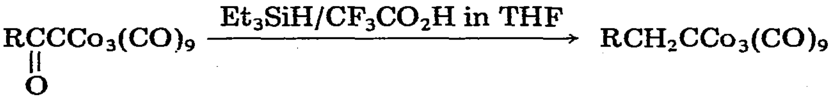
REDUCTION OF $RC(O)CCo_3(CO)_9$ TO $RCH_2CCo_3(CO)_9$ BY Et_3SiH/CF_3CO_2H

R in $RC(O)CCo_3(CO)_9$ (mmol)	Et_3SiH (mmol)	CF_3CO_2H (mmol)	$RCH_2CCo_3(CO)_9$ (% yield)
CH_3 (2.9)	7	6	$C_2H_5CCo_3(CO)_9$ (90)
C_2H_5 (3)	7	6	n-$C_3H_7CCo_3(CO)_9$ (92)
n-C_3H_7 (3)	7	6	n-$C_4H_9CCo_3(CO)_9$ (87)
n-C_4H_9 (3)	7	6	n-$C_5H_{11}CCo_3(CO)_9$ (80)
n-C_6H_{13} (3)	8	8	n-$C_7H_{15}CCo_3(CO)_9$ (85)
cyclo-C_6H_{11} (3)	8	9	cyclo-$C_6H_{11}CH_2CCo_3(CO)_9$ (75)
$(CH_3)_2CH$ (2)	5	6	$(CH_3)_2CHCH_2CCo_3(CO)_9$ (81)
C_6H_5 (2)	5	5	$C_6H_5CH_2CCo_3(CO)_9$ (82)
p-$CH_3C_6H_4$ (2)	5.2	6	p-$CH_3C_6H_4CH_2CCo_3(CO)_9$ (78)
p-BrC_6H_4 (2.9)	7	6	p-$BrC_6H_4CH_2CCo_3(CO)_9$ (67)

complete reduction to the alkyl derivatives, $(OC)_9Co_3CCH_2R$, even when the reaction medium was of relatively low acidity [e.g., reactions of 3 mmol of $(OC)_9Co_3CC(O)R$ with 7 mmol of Et_3SiH in the presence of 6 mmol of CF_3CO_2H in 50 ml of THF]. These reactions were easily effected and proceeded in high (75—92%) yield when R was a primary or secondary alkyl or an aryl group (Table 1). In fact, this reaction sequence (eqns. 1 and 2) represents one of the most effective procedures for the preparation of alkylidynetricobalt nonacarbonyl complexes of this type.



$$\mathrm{R\underset{\underset{O}{\|}}{C}CCl_3} \xrightarrow{Co_2(CO)_8} \mathrm{R\underset{\underset{O}{\|}}{C}CCo_3(CO)_9} \tag{1}$$



$$\mathrm{R\underset{\underset{O}{\|}}{C}CCo_3(CO)_9} \xrightarrow{Et_3SiH/CF_3CO_2H\text{ in THF}} \mathrm{RCH_2CCo_3(CO)_9} \tag{2}$$

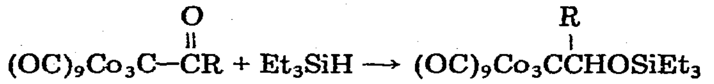
Attempted reduction of $(OC)_9Co_3CC(O)CMe_3$ and of $[(OC)_9Co_3C]_2CO$ by this procedure was not successful. Apparently, steric hindrance does become an important factor as the size of the substituent R in $RC(O)CCo_3(CO)_9$ increases.

The fact that the action of triethylsilane on the $(OC)_9Co_3CC(O)R$ ketones in a fairly dilute acid medium resulted in complete reduction suggested that the $(OC)_9Co_3\overset{+}{C}HR$ species which very likely were involved as intermediates (Scheme 1) are quite stable carbonium ions. Further work, which we have reported in preliminary communications [1,6], has provided ample confirmation of this idea.

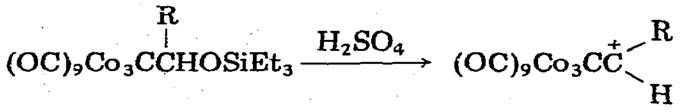
The conversion of the cluster-substituted ketones to the respective alcohols still was an unrealized goal. Since reduction with triethylsilane in the presence of trifluoroacetic acid went past the alcohol stage, presumably by the path shown in Scheme 1, we considered the possibility of carrying out such reductions with triethylsilane in the absence of trifluoroacetic acid. The reaction now sought was quite a different one: Si—H addition to the C=O bond of the ketone to give an alkoxysilane, whose solvolysis then would result in formation of the desired alcohol.

Silicon hydride addition to the C=O bonds of ketones and aldehydes had been described previously. Phenylsilanes had been shown to add to benzophenone, but reaction temperatures of 220—270° were required [13]. [Under these conditions the $(OC)_9Co_3C$-cluster complexes would undergo rapid thermal decomposition.] Triphenylsilane was known to add to aliphatic ketones when the reaction mixture was irradiated with ultraviolet light, but such C=O addition was not successful in the case of acetophenone or benzophenone [14]. Zinc chloride [15], chloroplatinic acid [16] and tris(triphenylphosphine)rhodium chloride [17] have been found to catalyze ketone and aldehyde hydrosilylation.

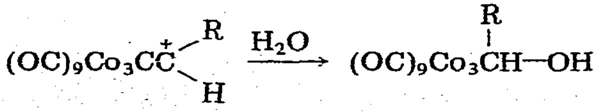
In the present investigation we found that hydrosilylation of the $(OC)_9Co_3C$-substituted ketones occurs under surprisingly mild conditions and in the absence of added catalyst. When approximately equimolar quantities of the ketone and triethylsilane were heated in refluxing benzene under an atmosphere of carbon monoxide for about 8 h, the initially dark brown solution underwent a gradual change to deep purple. In further processing, the solvent was evaporated and the residue was dissolved in concentrated sulfuric acid. The resulting solution was poured into an ice—water mixture to give, after extraction and purification, the expected alcohol, generally in high yield. The reactions occurring are summarized by eqns. (3—5). The maintainance of a protective atmosphere of carbon monoxide, rather than of nitrogen, appears to be essential in order to obtain good yields.



$$(OC)_9Co_3C{-}\overset{O}{\overset{\|}{C}}R + Et_3SiH \longrightarrow (OC)_9Co_3\overset{R}{\overset{|}{C}}HOSiEt_3 \qquad (3)$$



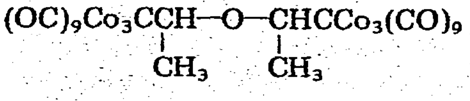
$$(OC)_9Co_3\overset{R}{\overset{|}{C}}HOSiEt_3 \xrightarrow{H_2SO_4} (OC)_9Co_3C\overset{+}{C}{<}^{R}_{H} \qquad (4)$$



$$(OC)_9Co_3C\overset{+}{C}{<}^{R}_{H} \xrightarrow{H_2O} (OC)_9Co_3\overset{R}{\overset{|}{C}}H{-}OH \qquad (5)$$

This procedure also served in the reduction of the formyl-substituted complex to the primary alcohol, $(OC)_9Co_3CCH_2OH$. The reductions carried out are summarized in Table 2.

To date our investigations of the chemistry of these alcohols have not been very comprehensive in scope. They serve excellently as starting materials for the synthesis of stable cluster-substituted carbonium ion salts of type $(OC)_9Co_3CCHR^+PF_6^-$ [6]. Attempted acetylation of $(OC)_9Co_3CCH(OH)CH_3$ with acetyl chloride in dichloromethane in the absence of a hydrogen chloride scavenger



$$(OC)_9Co_3C\underset{CH_3}{\underset{|}{C}}H{-}O{-}\underset{CH_3}{\underset{|}{C}}HCCo_3(CO)_9$$

(I)

gave the ether (I) in 75% yield, presumably via the reaction of the carbonium ion, $(OC)_9Co_3\overset{+}{C}HCH_3$, with the alcohol. A tosylate, p-$CH_3C_6H_4SO_2OCH(CH_3)$

TABLE 2

REDUCTION OF $RC(O)CCo_3(CO)_9$ TO $RCH(OH)CCo_3(CO)_9$

R in $RC(O)CCo_3(CO)_9$ (mmol)	Et_3SiH (mmol)	$RCH(OH)CCo_3(CO)_9$ (% yield)
CH_3 (16.0)	17.5	$CH_3CH(OH)CCo_3(CO)_9$ (84)
(19.7)	20.8	(90)
C_2H_5 (3)	3.2	$C_2H_5CH(OH)CCo_3(CO)_9$ (73)
n-C_3H_7 (3)	3.2	n-$C_3H_7CH(OH)CCo_3(CO)_9$ (75)
n-C_4H_9 (3)	3.4	n-$C_4H_9CH(OH)CCo_3(CO)_9$ (81)
n-C_6H_{13} (3)	3.4	n-$C_6H_{13}CH(OH)CCo_3(CO)_9$ (81)
$(CH_3)_2CH$ (3)	3.0	$(CH_3)_2CHCH(OH)CCo_3(CO)_9$ (80)
cyclo-C_6H_{11} (3)	3.4	cyclo-$C_6H_{11}CH(OH)CCo_3(CO)_9$ (52)
C_6H_5 (64.0)	87.5	$C_6H_5CH(OH)CCo_3(CO)_9$ (87)
p-$CH_3C_6H_4$ (3)	3.4	*p*-$CH_3C_6H_4CH(OH)CCo_3(CO)_9$ (70)
p-BrC_6H_4 (3)	3.4	*p*-$BrC_6H_4CH(OH)CCo_3(CO)_9$ (84)
H (10.6)	31.4	$HOCH_2CCo_3(CO)_9$ (46)

$CCo_3(CO)_9$, could be prepared by treatment of $(OC)_9Co_3CCH(OH)CH_3$ with *p*-toluenesulfonyl chloride in the presence of triethylamine. However, attempted conversion of the tosylate to the chloride, $(OC)_9Co_3CCHClCH_3$, by treatment with anhydrous lithium chloride in THF [18] resulted in complete decomposition of the cluster.

Further chemical transformations of these cluster-substituted alcohols are under investigation.

Experimental

General comments

All reactions were carried out in a flame-dried, three-necked flask of appropriate size equipped with a magnetic stirring unit, a reflux condenser topped with a nitrogen inlet tube and a thermometer ("standard apparatus"). Column chromatography was used extensively for separation of products. In general, a 40 × 600 mm column fitted with a fritted glass disc and a Teflon stopcock was used. Silicic acid (Mallinckrodt reagent, 100 mesh) served well in most separations. Thin layer chromatography (TLC) was used for monitoring the progress of reactions (Eastman Chromagram Sheet No. 6060). The cobalt-containing species are intensely colored and readily observed.

Infrared spectra were obtained using Perkin—Elmer 257 and 457A double beam grating infrared spectrophotometers. NMR spectra were obtained using Varian T60 or Perkin—Elmer R20 NMR spectrometers. Chemical shifts are reported in δ units, ppm downfield from internal tetramethylsilane. Tetrahydrofuran (THF) was distilled either from sodium benzophenone ketyl or lithium aluminum hydride immediately before use; benzene was distilled from potassium benzophenone ketyl and stored under nitrogen.

The $RC(O)CCo_3(CO)_9$ compounds were prepared as described in a previous paper of this series [2] by reaction of the appropriate $RC(O)CCl_3$ and dicobalt octacarbonyl (Strem Chemicals, Inc.). Two have not been reported previously:

n-$C_6H_{13}C(O)CCo_3(CO)_9$, a brown oil obtained in 41% yield. NMR (CCl_4):

δ 0.93 (m, 3H, CH_3); 1.1—2.0 (m, 8H); 2.80 ppm [t, J 7 Hz, 2H, C(O)$C\underline{H}_2$].

Cyclo-$C_6H_{11}C(O)CCo_3(CO)_9$, a purple-black solid, mp 86°, in 47% yield. (Found: C, 36.92; H, 2.08. $C_{17}H_{11}Co_3O_{10}$ calcd.: C, 36.98; H, 2.00%.) NMR (CCl_4): δ 1.2—2.1 (m, 10H); 2.85 ppm [m, 1H, C(O)CH].

Triethylsilane was purchased from PCR Chemicals, Inc.

Reaction of acylmethylidynetricobalt nonacarbonyl complexes with triethylsilane/trifluoroacetic acid in tetrahydrofuran

The reduction of $(OC)_9Co_3CC(O)CH_3$ is illustrative of the procedure used.

The standard apparatus (100 ml flask) was flame-dried, evacuated and refilled with dry nitrogen and then was charged with 1.40 g (2.9 mmol) of $(OC)_9Co_3CC(O)CH_3$ and 50 ml of dry THF. The mixture was stirred under nitrogen to effect solution and then 0.81 g (7 mmol) of triethylsilane and 0.82 g (6.0 mmol) of trifluoroacetic acid were added in succession by syringe. The mixture was heated at reflux for 6 h, cooled to room temperature and an equal volume of 10% hydrochloric acid was added. The aqueous layer was extracted three times with hexane. The combined organic phases were dried ($MgSO_4$) and filtered through a bed of silicic acid. The filtrate was evaporated at reduced pressure and the residue was sublimed in vacuo to give 1.22 g (90%) of C_2H_5-$CCo_3(CO)_9$.

In some of the other reductions (Table 1), the product was purified by recrystallization from hexane or by column chromatography (hexane eluent).

Preparation of $RCH(OH)CCo_3(CO)_9$ complexes

The preparation of $CH_3CH(OH)CCo_3(CO)_9$ is illustrative of the general procedure used.

The standard apparatus (1 liter flask) was flamed-dried, evacuated and refilled with dry nitrogen and then was charged with 9.54 g (19.7 mmol) of the cluster ketone, 500 ml of dry benzene and 2.41 g (20.8 mmol) of triethylsilane. A wide bore glass tube (flushed with carbon monoxide) was attached to the flask through a thermometer adapter and carbon monoxide was passed through the stirred solution for 10 min at room temperature, with stirring. The gas was vented out through the tube on the reflux condenser into the hood. The reaction mixture then was heated at reflux for 8 h while a continuous slow stream of carbon monoxide was passed through the solution. During this time the initially intensely brown solution underwent a gradual change to deep purple. Subsequently, the reaction mixture was cooled to room temperature, transferred to a one-necked flask and evaporated at reduced pressure. The reddish-purple oil which remained was diluted with hexane and filtered through a bed of neutral alumina (grade IV, ca. 200 cc). When all of the product had been washed from the filter bed with hexane, the solvent was removed and the remaining oil chilled to below 0°. The chilled oil was treated with 200 ml of concentrated sulfuric acid for 30 min. During this operation, the reddish color of the solution changed to a deep brown. The brown solution was poured slowly into a well-stirred ice/water mixture. The organic product was extracted with diethyl ether. The ether extracts were dried and evaporated at reduced pressure. The solid residue was recrystallized from pentane to give 8.59 g (90%) of red-purple $CH_3CH(OH)CCo_3(CO)_9$.

In other reactions (cf. Table 2), column chromatography occasionally was required to effect product purification. In the case of the preparation of $(OC)_9Co_3CCH_2OH$, the crude product, a red oil, was adsorbed on 200 cc of silicic acid in a sintered glass filter. Hexane eluted a blue impurity which was discarded and then chloroform was used to elute the desired alcohol.

Reaction of $CH_3CH(OH)CCo_3(CO)_9$ with acetyl chloride

The standard apparatus (100 ml flask) was charged with 1.46 g (3 mmol) of the cluster alcohol, 50 ml of dry dichloromethane and 0.25 g (3.2 mmol) of acetyl chloride. The mixture was heated at reflux under nitrogen for 5 h. The reaction mixture was evaporated at reduced pressure and the residue was chromatographed on the 40 × 200 mm column of silicic acid using hexane as eluent. A single fraction was eluted which was recrystallized from hexane to give 0.55 g (75%) of the ether $[(OC)_9Co_3CCH(CH_3)]_2O$, m.p. 172—173° (dec.), a light chocolate brown-colored solid. (Found: C, 30.57; H, 1.01. $C_{24}H_8Co_6O_{19}$ calcd.: C, 30.22; H, 0.85%.) NMR ($CDCl_3$): δ 1.67 (d, J 6 Hz, 3H) and 4.15 ppm (q, J 6 Hz, 1H). The IR spectrum (CCl_4) showed no band in the O—H region.

Preparation of $CH_3CH(OSO_2C_6H_4CH_3\text{-}p)CCo_3(CO)_9$

The standard apparatus (100 ml flask) was charged with 2.5 g (5.25 mmol) of $CH_3CH(OH)CCo_3(CO)_9$, 2.0 g of recrystallized *p*-toluenesulfonyl chloride, 50 ml of dry dichloromethane and 1.06 g (10.5 mmol) of freshly distilled triethylamine. The mixture was heated at reflux for 48 h while a continuous stream of carbon monoxide was passed slowly through the stirred reaction mixture. Subsequently, the mixture was evaporated under reduced pressure and the residue was chromatographed on a silicic acid column using hexane as eluent. The sole major band was collected and recrystallized from dry, degassed hexane (Schlenk apparatus) to give 1.41 g (42%) of slightly air-sensitive, chocolate-colored product, m.p. 139—140°. (Found: C, 36.21; H, 1.96. $C_{19}H_{11}Co_3O_{12}S$ calcd.: C, 35.64; H, 1.73%.) NMR ($CDCl_3$): δ 1.72 (d, J 7 Hz, $C\underline{H}_3CH$); 2.50 (s, $C\underline{H}_3C_6H_4$); 5.0 (q, J 7 Hz, $CH_3C\underline{H}$) and 7.33—7.98 ppm (A_2B_2 q, J 8 Hz, $C_6\underline{H}_4$).

A 1.28 g (2 mmol) sample of this product and 0.17 g of lithium chloride (dried overnight at 120°/0.1 mm) in 50 ml of dry THF were stirred at room temperature for 36 h under nitrogen. During this time, the solution turned green. TLC ($CHCl_3$) showed the presence of only trace quantities of a cobalt cluster complex.

New compounds

The new compounds prepared in these reduction reactions and their characterizing data are listed in Table 3. The IR spectrum of each compound was recorded. In general, all alkylidynetricobalt nonacarbonyl complexes show five bands in their IR spectrum in the region 2150—1950 cm^{-1} (terminal carbonyl region) with the intensity pattern: medium, very strong, strong, weak, very weak. This band structure serves to identify an $RCCo_3(CO)_9$ complex, but shifts in these bands with change in R are minimal. Thus for $CH_3CH_2CH_2CCo_3(CO)_9$ these absorptions were found (in CCl_4 solution) at 2102, 2053, 2040, 2020 and 1945 cm^{-1}; for $CH_3CH_2CH(OH)CCo_3(CO)_9$ they were observed at 2100, 2050, 2038, 2020 and 1950 cm^{-1}. All of the alcohols showed an absorption in the range 3595—3617 cm^{-1} due to the OH group.

TABLE 3

NEW $RCCo_3(CO)_9$ COMPOUNDS

R	M.p. (°C)	Color	Analysis, found (calcd.) (%)		NMR, δ (ppm)
			Carbon	Hydrogen	
C_2H_5	190—192	Purple-black	30.73 (30.66)	1.16 (1.07)	1.53 (t, *J* 8 Hz, 3H); 3.77 (q, *J* 8 Hz, 2H) ($CDCl_3$)
n-C_3H_7	121—123	Purple-black	32.45 (32.25)	1.57 (1.45)	1.2 (t, *J* 7 Hz, 3H); 1.95 (sextet, $CH_3C\underline{H}_2$, 2H); 3.77 (t, *J* 7 Hz, 2H) (CCl_4)
n-C_4H_9	74—75	Purple-black	34.05 (33.76)	2.06 (1.82)	1.05 (m, 3H); 1.3—2.3 (m, 4H); 3.77 (t, *J* 8 Hz, 2H, $Co_3CC\underline{H}_2$) (CCl_4)
n-C_7H_{15}	31	Dark violet	38.12 (37.80)	2.97 (2.79)	0.95 (m, 3H); 1.18—2.18 (m, 10H); 3.73 (t, *J* 7 Hz, 2H, $Co_3CC\underline{H}_2$) (CCl_4)
cyclo-$C_6H_{11}CH_2$	40	Purple-black	37.81 (37.94)	2.51 (2.43)	1.1—2.15 (m, 11H); 3.63 (d, *J* 3 Hz, 2H, $Co_3CC\underline{H}_2$) (CCl_4)
$(CH_3)_2CHCH_2$	112—113	Purple-black	33.97 (33.76)	2.11 (1.82)	1.28 (d, *J* 6 Hz, 6H); 2.16 (m, 1H); 3.75 (d, *J* 6 Hz, 2H, $Co_3CC\underline{H}_2$) (CCl_4)
p-$CH_3C_6H_4CH_2$	86—87	Purple-black	39.71 (39.59)	1.77 (1.66)	2.33 (s, 3H); 4.78 (s, 2H); 7.18 (s, 4H) (CCl_4)
p-$BrC_6H_4CH_2$	94—95	Purple-black	33.61 (33.42)	1.03 (0.99)	4.85 (s, 2H); 7.35 (A_2B_2 q, *J* 9 Hz, 4H) (CCl_4)
$CH_3CH(OH)$	162 (dec.)	Black (needles)	29.56 (29.60)	1.14 (1.03)	1.68 (d, *J* 6 Hz, 3H); 2.27 (d, *J* 5H, O$\underline{H}$); 5.35 (m, 1H) (CCl_4)
$C_2H_5CH(OH)$	137—138	Purple-black	31.28 (31.22)	1.57 (1.41)	1.22 (t, *J* 8 Hz, 3H); 1.4—2.2 (m, 2H); 2.37 (d, *J* 6 Hz, O$\underline{H}$); 4.97 (m, 1H) ($CDCl_3$)
n-$C_3H_7CH(OH)$	83	Black (needles)	32.78 (32.71)	1.88 (1.76)	1.03 (t, *J* 6 Hz, 3H); 1.27—2.13 (m, 4H); 2.38 (d, *J* 6 Hz, O$\underline{H}$); 5.05 (m, 1H) ($CDCl_3$)
n-$C_4H_9CH(OH)$	73.5—74	Dark violet	34.06 (34.11)	2.20 (2.10)	0.97 (m, 3H); 1.17—2.23 (m, 6H); 2.30 (m, O$\underline{H}$); 5.05 (m, 1H) ($CDCl_3$)
n-$C_6H_{13}CH(OH)$	44—45	Purple-black	36.55 (36.72)	2.67 (2.71)	0.51—2.18 (m, 13H); 2.30 (m, O$\underline{H}$); 5.05 (m, 1H) ($CDCl_3$)
$(CH_3)_2CHCH(OH)$	114—116	Black	32.71 (32.71)	1.82 (1.76)	1.18 (t, *J* 6 Hz, 6H); 2.07 (m, 1H, $Me_2C\underline{H}$); 2.30 (d, *J* 6 Hz, O$\underline{H}$); 4.97 (m, 1H) ($CDCl_3$)

(continued)

TABLE 3 (continued)

R	M.p. (°C)	Color	Analysis, found (calcd.) (%)		NMR, δ (ppm)
			Carbon	Hydrogen	
cyclo-$C_6H_{11}CH(OH)$	55	Purple-black	36.95 (36.84)	2.44 (2.36)	0.8—1.8 (m, 11H); 2.33 (m, $\mathrm{O\underline{H}}$); 4.9 (m, 1H) ($CDCl_3$)
$C_6H_5CH(OH)$	89—91	Black (needles)	37.20 (37.26)	1.31 (1.29)	2.72 (d, J 4 Hz, $\mathrm{O\underline{H}}$); 6.20 (d, J 4Hz, 1H); 7.42 (m, 5H) (CCl_4)
p-$CH_3C_6H_4CH(OH)$	98—99	Purple-black	38.64 (38.46)	1.82 (1.61)	2.30 (s, 3H); 2.72 (d, J 2 Hz, $\mathrm{O\underline{H}}$); 6.12 (d, J 2 Hz, 1H); 7.28 (A_2B_2 q, J 8 Hz, 4H) ($CDCl_3$)
p-$BrC_6H_4CH(OH)$	129—130	Black	32.58 (32.56)	1.04 (0.96)	2.78 (d, J 3 Hz, $\mathrm{O\underline{H}}$); 6.15 (d, J 3 Hz, 1H); 7.45 (s, 4H) ($CDCl_3$)

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References

1 D. Seyferth, G.H. Williams and D.D. Traficante, J. Amer. Chem. Soc., 96 (1974) 604.
2 D. Seyferth, J.E. Hallgren and P.L.K. Hung, J. Organometal. Chem., 50 (1973) 265.
3 J.E. Hallgren, C.S. Eschbach and D. Seyferth, J. Amer. Chem. Soc., 94 (1972) 2547.
4 D. Seyferth and G.H. Williams, J. Organometal. Chem., 38 (1972) C11.
5 D. Seyferth and A.T. Wehman, J. Amer. Chem. Soc., 92 (1970) 5520.
6 D. Seyferth, G.H. Williams and J.E. Hallgren, J. Amer. Chem. Soc., 95 (1973) 266.
7 G. Pályi, F. Piacenti, M. Bianchi and E. Benedetti, Acta Chim. Sci. Hung., 66 (1970) 127.
8 D.N. Kursanov and Z.N. Parnes, Russ. Chem. Rev., 38 (1969) 812.
9 F.A. Carey and H.S. Tremper, J. Org. Chem., 36 (1971) 758, and earlier papers of that series.
10 (a) M.P. Doyle, D.J. DeBruyn and D.A. Kooistra, J. Amer. Chem. Soc., 94 (1972) 3659;
(b) C.T. West, S.J. Donnelly, D.A. Kooistra and M.P. Doyle, J. Org. Chem., 38 (1973) 2675.
11 (a) D.A. Kursanov, Z.N. Parnes and N.M. Loim, Izv. Akad. Nauk SSSR, Ser. Khim., (1966) 1289;
(b) D.N. Kursanov, Z.N. Parnes, G.I. Bassova, N.M. Loim and V.I. Zdanovich, Tetrahedron, 23 (1967) 2235.
12 D.N. Kursanov, Z.N. Parnes, N.M. Loim and G.V. Bakalova, Dokl. Akad. Nauk SSSR, 179 (1968) 1106.
13 H. Gilman and D. Wittenberg, J. Org. Chem., 23 (1958) 501.
14 R. Calas and N. Duffaut, C.R. Acad. Sci. Paris, 245 (1957) 906.
15 (a) R. Calas, E. Frainnet and J. Bonastre, C.R. Acad. Sci. Paris, 251 (1960) 2987;
(b) R. Calas, Pure Appl. Chem., 13 (1966) 61.
16 (a) S.I. Sadykh-Zade and A.D. Petrov, Zh. Obshch. Khim., 29 (1959) 3194;
(b) M.A. Miropol'skaya, S.Ya. Mel'nik, T.S. Fradkina, G.I. Samokhvalov and A.D. Petrov, Dokl. Akad. Nauk SSSR, 144 (1962) 1312.
17 (a) I. Ojima, M. Nihonyanagi and Y. Nagai, J. Chem. Soc. Chem. Commun., (1972) 938;
(b) I. Ojima, T. Kogure, M. Nihonyanagi and Y. Nagai, Bull. Chem. Soc. Jap., 45 (1972) 3506.
18 G. Stork, P.A. Grieco and M. Gregson, Tetrahedron Lett., (1969) 1393.