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ORGANOCOBALT CLUSTER COMPLEXES

XXX *. CARBON MONOXIDE LIGAND MIGRATION DURING THE SOLVOLYSIS OF HALOMETHYLIDYNETRICOBALT NONACARBONYL COMPLEXES. USEFUL SYNTHESES OF CARBOXYMETHYLIDYNETRICOBALT NONACARBONYL DERIVATIVES

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Summary

The reaction of aliphatic alcohols, ROH, and amines, RR'NH, with bromo- and chloro-methylidynetricobalt nonacarbonyl gives products of types $ROC(O)CCo_3(CO)_9$ and $RR'NC(O)CCo_3(CO)_9$, respectively. These reactions are accelerated by triethylamine. In the presence of triethylamine, the normally unreactive phenols and anilines react to give $ArOC(O)CCo_3(CO)_9$ and $ArNHC(O)CCo_3(CO)_9$, respectively. Methylidynetricobalt nonacarbonyl itself, $HCCo_3(CO)_9$, reacts with alcohols and amines, but product yields are low. Possible mechanisms of these reactions are considered.

Introduction

The first, and for some time, the only, organic reaction of the halomethylidynetricobalt nonacarbonyl complexes, $XCCo_3(CO)_9$ (Fig. 1), to be reported was the intriguing reaction of bromomethylidynetricobalt nonacarbonyl with methanol and ethanol (eq. 1) [3]. Ercoli et al. suggested the following reaction

$$BrCCo_3(CO)_9 \xrightarrow{ROH,\ 55°C} ROC(=O)CCo_3(CO)_9 \qquad (1)$$

($R = CH_3, C_2H_5$)

* For part XXIX see ref. 1, and for a preliminary communication ref. 2.

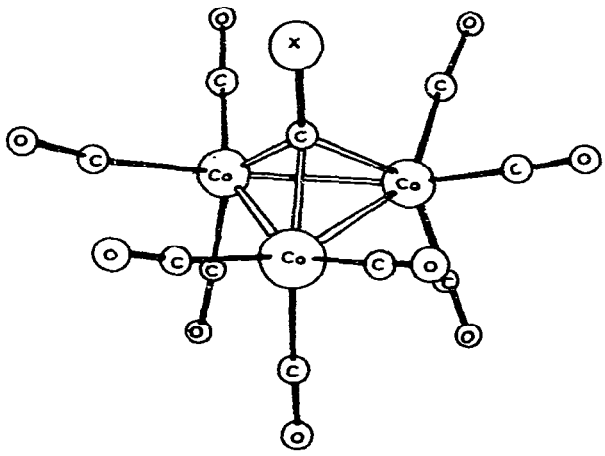


Fig. 1

course for this transformation:

$$BrCCo_3(CO)_9 \xrightarrow{50^\circ C} Co(CO)_4^- + CoBr_2 \quad (2)$$

$$Co(CO)_4^- + BrCCo_3(CO)_9 \rightarrow (OC)_4CoCCo_3(CO)_9 + Br^- \quad (3)$$

$$(OC)_4CoCCo_3(CO)_9 + CO \rightarrow (OC)_4CoC(=O)CCo_3(CO)_9 \quad (4)$$

$$(OC)_4CoC(=O)CCo_3(CO)_9 + ROH \rightarrow ROC(=O)CCo_3(CO)_9 + HCo(CO)_4 \quad (5)$$

Whatever its mechanism, the remarkable feature of the $BrCCo_3(CO)_9$-to-RO_2C-$CCo_3(CO)_9$ conversion is that it occurs readily under a nitrogen atmosphere, i.e., in the absence of external carbon monoxide. Thus the ester carbonyl function must be derived from a CO ligand which originally was bonded to a cobalt atom in $BrCCo_3(CO)_9$.

In earlier research we had discovered the intriguing reaction of $ClCCo_3(CO)_9$ and $BrCCo_3(CO)_9$ with aluminum trihalides which gave the cluster acylium ion salts, $[OCCCo_3(CO)_9]^+[AlX_4]^- \cdot AlX_3$, which in a subsequent step were able to react with a variety of nucleophiles [4]. For instance, on treatment with alcohols they gave esters, $RO_2CCCo_3(CO)_9$; on reaction with secondary amines they gave amides, $R_2NC(O)CCo_3(CO)_9$. Here also, CO ligand migration from a cobalt atom to the apical carbon atom had taken place, since these conversions proceeded readily under a nitrogen atmosphere. As a preparative procedure the cluster acylium route to $YC(O)CCo_3(CO)_9$ complexes was widely applicable and quite satisfactory. However, a procedure which did not require the potentially disruptive aluminum halides could have advantages in certain applications and for this reason we decided to explore the direct reaction of halomethylidynetricobalt nonacarbonyl complexes in more detail.

Results and discussion

Our initial experiments confirmed the observations of the Italian workers: bromo- and chloro-methylidynetricobalt nonacarbonyl were converted to $CH_3O_2CCCo_3(CO)_9$ in yields of 56 and 57%, respectively, when they were heated in refluxing methanol (~ 60°C) for 1 h under a nitrogen atmosphere. The reaction even took place at room temperature in the case of $BrCCo_3(CO)_9$, but multiday reaction times were required to effect comparable yields of the methyl ester. In previous studies (e.g., ref. 5) we had found that in any reaction in which an alkylidynetricobalt nonacarbonyl complex was treated above room temperature the use of carbon monoxide as the protective atmosphere (rather than nitrogen or argon) provided substantial benefits in terms of enhanced cobalt cluster product yields. Presumably the carbon monoxide serves to retard or to block thermal decomposition of $RCCo_3(CO)_9$ molecules. Replacement of nitrogen with a carbon monoxide atmosphere also brought substantial benefits in the present reactions. Thus when the $BrCCo_3(CO)_9$/methanol reaction at reflux was carried out by slowly bubbling carbon monoxide through the reaction solution for 1.5 h, the yield of $CH_3O_2CCCo_3(CO)_9$ (based on $BrCCo_3(CO)_9$) was increased to 86%. Even reactions carried out at room temperature showed considerable improvement when an atmosphere of carbon monoxide was used. Thus, under these conditions, $BrCCo_3(CO)_9$ reacted with methanol during a 24 h period to give $CH_3O_2CCCo_3(CO)_9$ in 46% yield. (This raises the question of whether CO molecules from the protective atmosphere might not be taking part in the $BrCCo_3(CO)_9$ solvolysis processes.)

These reactions all were carried out in neat methanol. However, good results were obtained when the reactions were performed in benzene medium, using only a limited amount of the alcohol.

It was of interest to investigate such reactions of $BrCCo_3(CO)_9$ and $ClCCo_3(CO)_9$ with other types of nucleophiles. Aliphatic amines were found to be very reactive toward these cluster halides, giving $Et_2NC(O)CCo_3(CO)_9$ in yields of 75 and 74%, respectively, in reactions with diethylamine in a reaction time of only 1.5 h at room temperature in benzene solution. Piperidine reacted almost instantaneously at room temperature, giving the expected amide in 68% yield within 5 min. Dimethylamine, monomethylamine and ammonia were brought into reaction simply by passing the gaseous amine over the stirred solution of $BrCCo_3(CO)_9$ in benzene. t-Butylamine reacted more slowly, presumably as a result of steric factors, but a 69% yield of $Me_3CNHC(O)CCo_3(CO)_9$ could be realized after 22 h at room temperature. Aniline and *N*-substituted anilines, as well as anilines with substituents in the benzene nucleus, failed to react with $BrCCo_3(CO)_9$ in benzene at room temperature.

The fact that the basic aliphatic amines and ammonia react so readily with the halomethylidynetricobalt nonacarbonyl complexes, so much more readily than with alcohols or anilines, suggested to us that the $XCCo_3(CO)_9$/alcohol and $XCCo_3(CO)_9$/aniline reactions might be promoted by a base such as a tertiary aliphatic amine. This was found to be the case.

In an experiment in which slightly more than a molar equivalent of triethylamine was present during the reaction of $BrCCo_3(CO)_9$ with methanol, the cluster methyl ester was formed in 73% yield after only 6 h at room tempera-

TABLE 1

REACTIONS OF BROMO- AND CHLORO-METHYLIDYNETRICOBALT NONACARBONYL, $XCCo_3(CO)_9$ (X = Br, Cl) AND OF METHYLIDYNETRICOBALT NONACARBONYL, $HCCo_3(CO)_9$, WITH NUCLEOPHILES; ORIENTATIONAL EXPERIMENTS

Y in $YCCo_3(CO)_9$	Nucleophile	Benzene diluent	Et_3N	Reaction conditions [a] Time (h)/Temp. (°C)	Product $RCCo_3(CO)_9$ R =	Yield [b] (%)
Br	MeOH	—	—	1/63 (under nitrogen)	MeO_2C	56
Br	MeOH	—	—	1.5/60	MeO_2C	86
Cl	MeOH	—	—	1/60 (under nitrogen)	MeO_2C	57
H	MeOH	—	—	1/60 (under nitrogen)	MeO_2C	26
Br	MeOH	—	—	24/rt [c]	MeO_2C	46
Cl	MeOH	—	—	24/rt	MeO_2C	30
H	MeOH	—	—	24/rt	MeO_2C	27
Br	MeOH	+	+	6/rt	MeO_2C	73
Cl	MeOH	+	+	6/rt	MeO_2C	32
H	MeOH	+	+	6/rt	MeO_2C	27
Br	MeOH	+	DABCO	24/rt	MeO_2C	64
Br	MeOH	+	TMEDA	24/rt	MeO_2C	56
Br	Me_2CHOH	—	+	20/rt	Me_2CHO_2C	77
Cl	Me_2CHOH	—	+	20/rt	Me_2CHO_2C	84
H	Me_2CHOH	—	+	20/rt	Me_2CHO_2C	24
Br	Et_2NH	+	—	1.5/rt	$Et_2NC(O)$	75
Cl	Et_2NH	+	—	1.5/rt	$Et_2NC(O)$	74
H	Et_2NH	+	—	1.5/rt	$Et_2NC(O)$	33
Br	PhOH	+	—	24/rt	PhO_2C	0
Br	PhOH	+	+	24/rt	PhO_2C	60
Br	$PhNH_2$	+	—	24/rt	PhNHC(O)	0
Br	$PhNH_2$	+	+	8/rt	PhNHC(O)	77
Br	PhMeNH	+	+	24/rt	PhMeNC(O)	64
Cl	PhMeNH	+	+	24/rt	PhMeNC(O)	14
H	PhMeNH	+	+	24/rt	PhMeNC(O)	5

[a] All reactions were carried out with a slow stream of carbon monoxide bubbling through the reaction solution unless otherwise noted. [b] Yields are based on the $YCCo_3(CO)_9$ complex charged. [c] rt = room temperature, ca. 25 °C.

ture. Longer reaction times (ca. 20—22 h at room temperature) were required in the case of more hindered alcohols such as isopropanol and t-butanol. No comparable improvement was achieved by carrying out room temperature methanolysis of $ClCCo_3(CO)_9$ in the presence of triethylamine. Table 1 summarizes the results of these orientational experiments. Other tertiary amines such as 1,4-diazabicyclo[2.2.2]octane (DABCO) and *N,N,N',N'*-tetramethylethylenediamine were found to promote the $BrCCo_3(CO)_9$/MeOH reaction, but in all further work triethylamine was used.

In the absence of triethylamine, bromomethylidynetricobalt nonacarbonyl did not react with phenols or aniline derivatives at room temperature. In the presence of triethylamine the reactions proceeded well at room temperature in benzene solution and good product yields were obtained.

The preparative reactions which were carried out are listed in Table 2. All of

these reactions were performed at room temperature in the presence of more than one molar equivalent of triethylamine. Benzene was used as the solvent when it was not convenient to use the neat alcohol or amine. Reaction times varied from 1.5 to 30 h, depending on the substrate. The progress of these reactions was monitored by thin layer chromatography (TLC); they were allowed to continue until the starting $BrCCo_3(CO)_9$ had been consumed. In general, it was found that these triethylamine-induced reactions were cleaner than comparable syntheses of cobalt cluster esters and amides by the aluminum halide-induced reactions of chloro- and bromo-methylidynetricobalt nonacarbonyl. In most reactions, products of high purity could be isolated directly following chromatography. As mentioned above, the rates of the reactions of $BrCCo_3(CO)_9$ with amines were considerably faster than those with alcohols. Acylation of ethyl glycinate hydrochloride proceeded readily in the presence of triethylamine, which served to liberate the amino acid. In general, the yields of amines obtained in these reactions were comparable, in some cases higher, than those observed in analogous AlX_3-induced reactions.

Although it was not at all certain that these triethylamine-induced reactions proceeded via the intermediacy of the cluster acylium ion, $[OCCCo_3(CO)_9]^+$, we attempted to apply the $BrCCo_3(CO)_9$/triethylamine system to the acylation of several aromatic systems. In view of the low Friedel—Crafts reactivity which we had observed in the case of the cobalt cluster acylium ion with either hexafluorophosphate [6] or haloaluminate [4] counterion, we restricted our experiments to highly reactive aromatic nucleophiles. *N,N*-Dimethylaniline was not converted to the known *p*-$Me_2NC_6H_4C(O)CCo_3(CO)_9$ [4,6], by $BrCCo_3(CO)_9$/Et_3N, but this reagent system did acylate indole in benzene solution at 60°C to give 3-(acylmethylidynetricobalt nonacarbonyl)indole in 46% yield. Bromomethylidynetricobalt nonacarbonyl also reacted with pyrrole in the presence of triethylamine, but the reactions were more complex. In one experiment the reaction of pyrrole (15 mmol) with $BrCCo_3(CO)_9$ (1.9 mmol) at 60°C in the presence of triethylamine (3.6 mmol) for 24 h gave the expected acylation of the pyrrole nucleus, forming 2-(acylmethylidynetricobalt nonacarbonyl)pyrrole in 20% yield. In contrast, in another experiment in which a larger quantity of triethylamine was used and the reaction mixture heated at 58°C for 8 h, acylation of the NH function occurred instead, giving *N*-(methylidynetricobalt nonacarbonyl)pyrrole in 21% yield. The crucial difference between these reactions most likely is the amount of triethylamine used.

The $BrCCo_3(CO)_9$/Et_3N reagent system also reacts with alkane- and arenethiols [7]. These reactions also are complex, and their discussion is reserved for a subsequent paper of this series [8].

In these reactions of $BrCCo_3(CO)_9$ with alcohols and amines the other product must be hydrogen bromide and hydrogen chloride in the case of $ClCCo_3(CO)_9$. In view of this, it was unexpected and surprising that methylidynetricobalt nonacarbonyl itself, $HCCo_3(CO)_9$, also reacts with alcohols and amines to give cobalt cluster esters and amides. The yields are low, as shown in Table 1 *, but

* These results should be compared with those of comparable reactions with $BrCCo_3(CO)_9$ and $ClCCo_3(CO)_9$ in Table 1.

TABLE 2

REACTIONS OF BROMOMETHYLIDYNETRICOBALT NONACARBONYL WITH NUCLEOPHILES; PREPARATIVE EXPERIMENTS

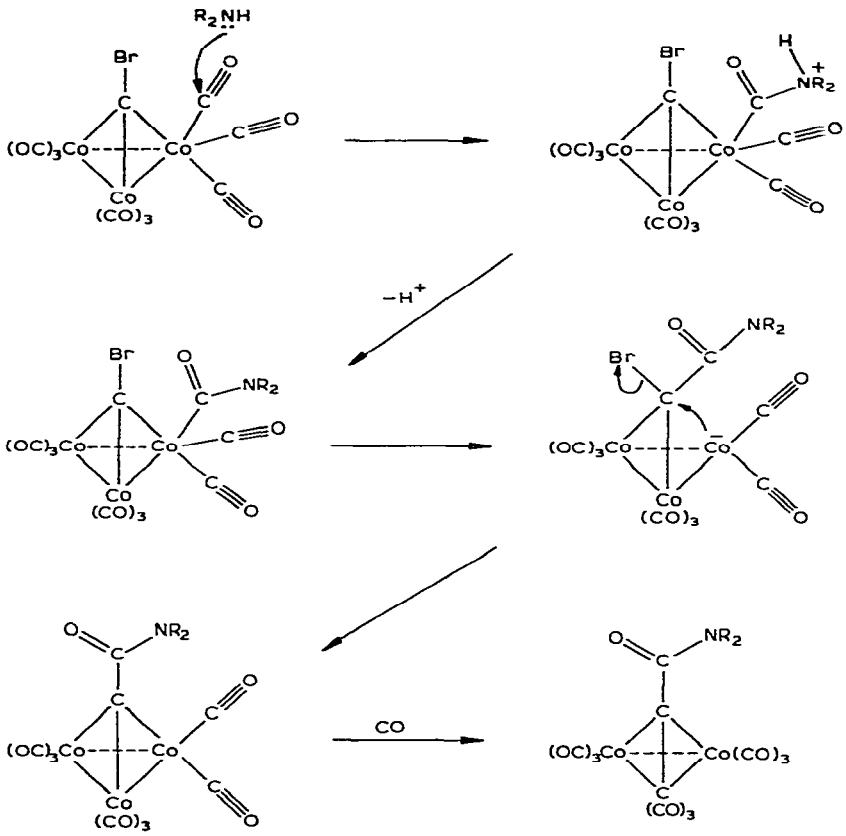
$BrCCo_3(CO)_9$, (mmol)	Nucleophile (mmol)	Benzene diluent	Et_3N (mmol)	Reaction conditions [a] Time (h)/Temp. (°C)	Product $RCCo_3(CO)_9$ R =	Yield (%) [b]
3.8	MeOH (75 ml)	—	—	1.5/60	MeO_2C	86
1.9	MeOH (50 ml)	—	—	24/rt	MeO_2C	46
2.8	MeOH (24.8)	+	3.6	6/rt	MeO_2C	73
1.9	MeOH (40 ml)	—	3.6	5/rt	MeO_2C	80
1.9	EtOH (40 ml)	—	3.6	5/rt	EtO_2C	75
2.2	Me_2CHOH (40 ml)	—	3.6	20/rt	Me_2CHO_2C	77
1.9	Me_3COH (25 ml)	—	3.6	22/rt	Me_3CO_2C	66
1.9	$PhCH_2CH_2OH$ (1 ml)	+	7.2	24/rt	$PhCH_2CH_2O_2C$	66
1.9	$CH_2=CHCH_2OH$ (40 ml)	—	3.6	1.5/rt	$CH_2=CHCH_2O_2C$	73
2.2	PhOH (10)	+	3.6	24/rt	PhO_2C	60
1.9	p-$MeOC_6H_4OH$ (5.0)	+	7.2	24/rt	p-$MeOC_6H_4O_2C$	58
1.9	p-MeC_6H_4OH (10)	+	7.2	6/rt	p-$MeC_6H_4O_2C$	72
1.9	p-ClC_6H_4OH (10)	+	7.2	6/rt	p-$ClC_6H_4O_2C$	58
1.9	o-$O_2NC_6H_4OH$ (10)	+	7.2	6/rt	p-$O_2NC_6H_4O_2C$	51
2.2	NH_3(g) (excess)	+	—	0.33/rt	$H_2NC(O)$	38
1.9	$MeNH_2$(g) (excess)	+	—	1/12/rt	MeNHC(O)	46
2.2	Me_2NH(g) (excess)	+	—	1/12/rt	$Mr_2NC(O)$	35
2.2	Me_2NH(g) (excess)	+	—	1/12/0	$Me_2NC(O)$	50
2.8	Et_2NH (20)	+	—	3.5/rt	$Et_2NC(O)$	79
2.2	Et_2NH (20)	+	—	1.5/rt	$Et_2NC(O)$	75
2.2	Me_3CNH_2 (5.2)	+	—	22/rt	$Me_3CNHC(O)$	69
1.9	$C_5H_{10}NH$ (10)	+	—	1/12/rt	$C_5H_{10}NC(O)$	68
2.8	PhMeNH (5.5)	+	3.6	24/rt	PhMeNC(O)	64
1.9	PhEtNH (8.1)	+	3.6	24/rt	PhEtNC(O)	50
2.2	$PhNH_2$ (11)	+	7.2	8/rt	PhNHC(O)	77
1.9	p-$MeOC_6H_4NH_2$ (10)	+	3.6	24/rt	p-$MeOC_6H_4NHC(O)$	50
1.9	p-$BrC_6H_4NH_2$ (10)	+	3.6	18/rt	p-$BrC_6H_4NHC(O)$	59
1.9	$EtO_2CCH_2NH_3^+Cl^-$ (10)	+	14.4	2/rt	$EtO_2CCH_2NHC(O)$	59

[a] All reactions were carried out with a slow stream of carbon monoxide bubbling through the reaction solution. [b] Yields are based on $BrCCo_3(CO)_9$ charged.

it is noteworthy that alcohols and amines are acylated at all. Longer reaction times did not improve the product yields.

The mechanism of these novel reactions is of interest, but at this time we can only speculate concerning this question. Although Ercoli et al. reported that they identified $CoBr_2$ and $Co(CO)_4^-$ in the reaction mixture from the ethanolysis of $BrCCo_3(CO)_9$, no quantitative data were given, and their proposed mechanism is by no means secure. One can suggest several alternatives. One is an S_N1-type process in which a CO ligand migrates from cobalt to carbon as the bromide ion departs, with subsequent reaction of the acylium cation with the nucleophile and intermolecular transfer to CO to the vacant coordination site on cobalt. Another possibility is that the nucleophile attacks at a coordinated carbon monoxide ligand, with the carboalkoxy or amido substituent thus formed being transferred from cobalt to carbon in a subsequent step as shown in Scheme 1 *. Although these reactions of $BrCCo_3(CO)_9$ and $ClCCo_3(CO)_9$

SCHEME 1



* Schemes 1 and 2 are drawn showing the alkylidynetricobalt nonacarbonyl complexes with a σ-bonded framework for convenience and so that the mechanisms resemble the usual organic type mechanism. The alkylidynetricobalt nonacarbonyls are better regarded as μ_3 carbyne complexes of the $Co_3(CO)_9$ unit, with delocalized bonding. A representation which avoids the σ bond picture is shown in Fig. 2.

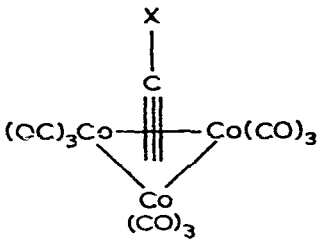
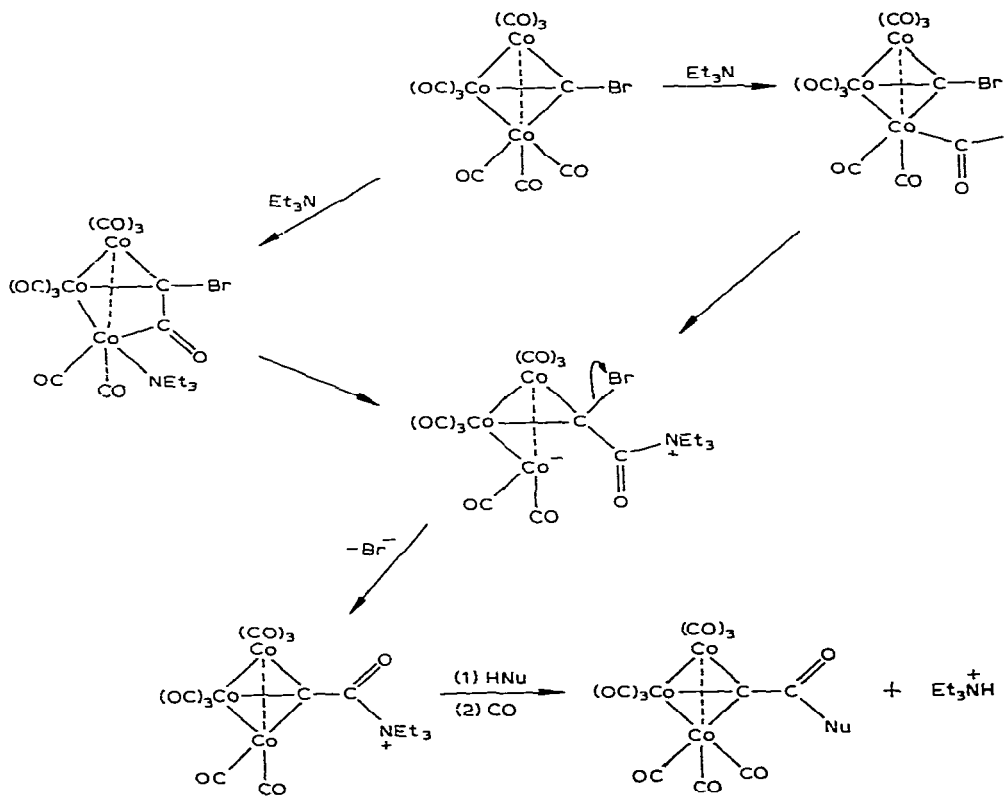


Fig. 2

proceed reasonably well in the absence of external carbon monoxide, the fact that they proceed more rapidly and in substantially higher yield in a carbon monoxide atmosphere even at room temperature could be interpreted in terms of involvement of free CO in these reactions. The promotion of these reactions by triethylamine could simply be a matter of scavenging of hydrogen halide by the amine. On the other hand, the amine could be participating more directly as suggested in Scheme 2. Bromomethylidynetricobalt nonacarbonyl

SCHEME 2



does indeed react slowly at room temperature with triethylamine under carbon monoxide in benzene solution. In experiments in which the terminal C=O

stretching absorptions and two characteristic bands at 835 and 595 cm^{-1} were monitored by infrared spectroscopy it was observed that within 21 h the latter bands of $BrCCo_3(CO)_9$ had begun to diminish in intensity. By the end of 4 days, these bands had disappeared completely and a strong, broad band had grown in at 1880 cm^{-1} with a shoulder at 1925 cm^{-1}. (In metal carbonyls absorptions in the region around 1900 cm^{-1} are indicative of bridging carbonyl ligands.) However, attempts to isolate pure cobalt complexes from such solutions were unsuccessful.

At present, thus, the mechanism of these interesting reactions remains obscure. However, conditions under which they proceed cleanly and in good yield have been defined by the present work, and they are of demonstrated value in the synthesis of novel organofunctional derivatives of the methylidynetricobalt nonacarbonyl cluster system.

Experimental

General comments

The reactions were carried out in a three-necked round-bottomed flask of appropriate size which was equipped with a magnetic stir-bar, a nitrogen inlet tube if carried out under nitrogen or a gas dispersion tube if carbon monoxide was bubbled through the reaction mixture. When the reactions were carried out above room temperature, a reflux condenser and a thermometer were added.

The standard work-up involved pouring the reaction mixture into 100 ml of cold 10% hydrochloric acid, separating and drying the organic layer ($MgSO_4$ or Na_2SO_4), filtering and then concentrating the filtrate at reduced pressure (rotary evaporator). Column chromatography and filtration chromatography were used extensively for the separation of products. Column chromatography was performed using a 4 × 600 mm column fitted with a fritted-glass disk and a Teflon stopcock. Filtration chromatography was carried out using a 60 ml filter funnel fitted with a fritted glass disk. In general, silicic acid (Mallinckrodt, reagent, 100 mesh) was used as the chromatographic support and eluents used included hexane, dichloromethane, benzene and diethyl ether. Thin layer chromatography (TLC) served well for monitoring the progress of reactions (Eastman Chromagram Sheet 6060). The intense colors of the alkylidynetricobalt nonacarbonyl complexes made chemical visualization unnecessary. Solid samples in general were further purified by sublimation (50—60°C at 0.02—0.07 mm Hg) or by crystallization.

Infrared spectra were recorded using a Perkin—Elmer model 457A infrared spectrophotometer. The characteristic stretching frequencies in the 2200—2000 cm^{-1} region of the terminal CO ligands always are much more intense than the rest of the bands in the spectrum. Therefore, the sample was diluted after the initial spectrum was recorded so that an accurate spectrum of these frequencies could be recorded. In general, spectra were taken using 0.1 mm sodium chloride cells. In addition to the normal terminal carbonyl pattern, the following absorptions (cm^{-1}) are indicative of some of the key compounds of this study: $BrCCo_3(CO)_9$: 835m, 595m; $ClCCo_3(CO)_9$, 900s, 595s; $HCCo_3(CO)_9$, 2980w, 865m, 723w; $CH_3OC(O)CCo_3(CO)_9$, 1745.

Proton NMR spectra were recorded using a Varian Associates T60 spectrom-

eter. Chemical shifts are given in δ units, ppm downfield from internal tetramethylsilane. Tetramethylsilane, dichloromethane and chloroform were used as internal standards.

Dicobalt octacarbonyl was purchased from Strem Chemicals, and its reactions with carbon tetrabromide, carbon tetrachloride and bromoform gave $BrCCo_3(CO)_9$, $ClCCo_3(CO)_9$ and $HCCo_3(CO)_9$, respectively [9].

Orientational experiments

The standard apparatus was charged with 2.00 g (3.8 mmol) of $BrCCo_3(CO)_9$ and 75 ml of anhydrous methanol. The solution was stirred under nitrogen at room temperature for 15 min (no reaction by TLC) and subsequently was heated at 60°C for 1 h. It then was cooled to −20°C, filtered to remove 1.06 g (56%) of $CH_3OC(O)CCo_3(CO)_9$ and evaporated to leave 0.08 g (4%) of $BrCCo_3(CO)_9$. A 1 h reaction period of 2.00 g (4.2 mmol) of $ClCCo_3(CO)_9$ with 75 ml of methanol followed by filtration chromatography gave 0.09 g (5%) of $ClCCo_3(CO)_9$ (elution with hexane) and 1.19 g (57%) of $CH_3OC(O)CCo_3(CO)_9$ (elution with dichloromethane). Identical reaction conditions with 1.00 g (2.3 mmol) of $HCCo_3(CO)_9$ in a 1 h reaction time with 40 ml of methanol gave $HCCo_3(CO)_9$, 0.40 g (40% recovery), and 0.28 g (26%) of $CH_3OC(O)CCo_3(CO)_9$.

The methanolysis of $BrCCo_3(CO)_9$ was repeated under an atmosphere of carbon monoxide. A solution of 2.00 g of $BrCCo_3(CO)_9$ in 75 ml of methanol was heated at 60°C for 1.5 h while carbon monoxide was bubbled through it at a slow rate (gas dispersion tube). Work-up as above gave 1.36 g of $CH_3OC(O)CCo_3(CO)_9$ after cooling to −20°C and another 0.27 g after filtration chromatography (CH_2Cl_2 eluent, after hexane had removed 0.10 g of $BrCCo_3(CO)_9$). The total yield of the ester was 86%, based on $BrCCo_3(CO)_9$; its m.p. was 109—110°C (lit. [3] m.p. 108—109°C).

This reaction was repeated at room temperature with 1.00 g of $BrCCo_3(CO)_9$ in 50 ml of methanol with carbon monoxide bubbling through the solution for 24 h. Filtration chromatography gave 0.27 g (27%) of $BrCCo_3(CO)_9$ and 0.44 g (46%) of $CH_3OC(O)CCo_3(CO)_9$. A similar room temperature reaction of $ClCCo_3(CO)_9$ (1.00 g in 40 ml of methanol and 20 ml of benzene) gave a 65% recovery of $CClCCo_3(CO)_9$ and the methyl ester in 30% yield. Methylidynetricobalt nonacarbonyl, $HCCo_3(CO)_9$ reacted with methanol (1.00 g in 40 ml of methanol and 20 ml of benzene) under CO at room temperature during 24 h to give a 27% yield of the ester and a 34% recovery of $HCCo_3(CO)_9$.

Repetition of these room temperature experiments in the presence of an excess of triethylamine used the same procedure except that a reaction time of 6 h was used and the standard work-up procedure (cf. "General Comments") was used. Thus a mixture of 1.50 g (2.80 mmol) of $BrCCo_3(CO)_9$, 1 ml of methanol, 0.50 ml (3.6 mmol) of triethylamine and 45 ml of benzene was stirred at room temperature for 6 h while carbon monoxide was bubbled slowly through it. Standard work-up was followed by filtration chromatography. Elution with hexane gave 0.12 g (8%) of $BrCCo_3(CO)_9$, with dichloromethane, 1.05 g (73%) of $CH_3OC(O)CCo_3(CO)_9$.

These and other orientational experiments are summarized in Table 1.

Preparative experiments

(a) With alcohols. The reaction of $BrCCo_3(CO)_9$ with allyl alcohol is typical. The standard apparatus was charged with 1.00 g (1.9 mmol) of the cobalt complex and 40 ml of allyl alcohol. Triethylamine (0.50 ml, 3.6 mmol) was added by syringe, The resulting solution was stirred at room temperature for 1.5 h while carbon monoxide was bubbled through it. The allyl alcohol then was removed at reduced pressure and the residue was taken up in dichloromethane. Standard work-up followed by filtration chromatography (hexane eluent) yielded a trace of $BrCCo_3(CO)_9$. Elution with dichloromethane gave 0.74 g (73%) of $CH_2{=}CHCH_2OC(O)CCo_3(CO)_9$, m.p. 43—44°C (lit. [4] m.p. 42—44°C), whose IR spectrum was identical with that of an authentic sample. Elution with diethyl ether gave 0.05 g (5%) of $HO_2CCCo_3(CO)_9$ which was identified by its IR spectrum.

(b) With phenols. The reaction of $BrCCo_3(CO)_9$ with *p*-chlorophenol is typical. The standard apparatus was charged with 1.00 g (1.9 mmol) of $BrCCo_3(CO)_9$, 1.29 g (10 mmol) of *p*-chlorophenol and 40 ml of benzene. Triethylamine (1.0 ml, 7.2 mmol) was added by syringe. The mixture was stirred at room temperature for 6 h while carbon monoxide was bubbled slowly through it. Standard work-up followed by filtration chromatography (hexane eluent) yielded 0.25 g (29%) of $HCCo_3(CO)_9$ (identified by its IR spectrum). Elution with dichloromethane gave *p*-$ClC_6H_4OC(O)CCo_3(CO)_9$ which was recrystallized from hexane to give 0.67 g (58%) of pure material, m.p. 56—57°C.

A similar experiment using 1.0 g of $BrCCo_3(CO)_9$, 0.65 g (5.0 mmol) of *p*-chlorophenol, 2.0 ml of triethylamine and 40 ml of benzene, but with a reaction time of 24 h, at room temperature in a slow CO stream, gave $HCCo_3(CO)_9$ as the only cobalt cluster product in 74% yield. The product was identified on the basis of its melting point and IR and NMR spectra. $HCCo_3(CO)_9$ was a by-product in most reactions of $BrCCo_3(CO)_9$ with substituted phenols in the presence of triethylamine. By consideration of the 6 h and 24 h reactions above, it would appear that $HCCo_3(CO)_9$ is derived in some way from the $ArOC(O)CCo_3(CO)_9$ initially formed, perhaps by reaction with triethylamine hydrobromide.

(c) With aliphatic amines and ammonia. The reactions of $BrCCo_3(CO)_9$ with dimethylamine and t-butylamine are described to illustrate procedures used with gaseous and liquid amines.

The standard apparatus was charged with 1.15 g (2.2 mmol) of the cobalt complex and 40 ml of benzene. Gaseous dimethylamine was passed over the solution at room temperature for 5 min, until TLC showed that no $BrCCo_3(CO)_9$ remained. Standard work-up followed by filtration chromatography (dichloromethane eluent) and subsequent recrystallization from hexane gave 0.39 g (35%) of $Me_2NC(O)CCo_3(CO)_9$, m.p. 121—123°C (lit. [6] m.p. 121–123°C dec.)), whose IR spectrum was identical with that recorded previously [10].

In another experiment the $BrCCo_3(CO)_9$ solution was cooled in an ice bath prior to the introduction of the gaseous amine. The yield of $Me_2NC(O)CCo_3(CO)_9$ was increased to 50%; for gaseous amines and ammonia a reaction temperature of 0°C seems to be preferred.

t-Butylamine is a liquid, hindered amine. In its reaction the standard apparatus was charged with 1.15 g (2.2 mmol) of the cobalt complex and 40 ml of

benzene and then 0.25 ml (2.6 mmol) of t-butylamine was added by syringe. The mixture was stirred at room temperature while carbon monoxide was bubbled slowly through the solution. After 4 h TLC showed the presence of an about 1/1 mixture of starting material and product. Another 0.25 ml of the amine was added and the mixture was stirred under CO overnight for a total reaction time of 22 h. Standard work-up followed by filtration chromatography (hexane eluent) gave 0.08 g (7%) of $BrCCo_3(CO)_9$. Elution with dichloromethane followed by recrystallization from hexane yielded 0.82 g (69%) of $Me_3CNHC(O)CCo_3(CO)_9$.

(d) With anilines. The reaction with *p*-bromoaniline is representative. The standard apparatus was charged with 1.00 g (1.9 mmol) of $BrCCo_3(CO)_9$ and 40 ml of benzene. Subsequently 1.72 g (10 mmol) of *p*-bromoaniline and 0.50 ml (3.6 mmol) of triethylamine were added in succession. The mixture was stirred at room temperature for 18 h while carbon monoxide was bubbled slowly through it. Standard work-up was followed by filtration chromatography. Hexane eluted 0.05 g (5%) of $BrCCo_3(CO)_9$, dichloromethane and the product, $p\text{-}BrC_6H_4NHC(O)CCo_3(CO)_9$. Recrystallization from hexane gave 0.72 g (59%).

(e) With indole. The standard apparatus was charged with 1.00 g (1.9 mmol) of the cobalt complex, 0.5 ml (3.6 mmol) of triethylamine and 40 ml of benzene. Solid indole (1.17 g, 10 mmol) then was added and the reaction mixture was heated to 60°C and stirred for 8 h while carbon monoxide was bubbled slowly through it. Standard work-up was followed by filtration chromatography. Hexane eluted 0.18 g (18%) of $BrCCo_3(CO)_9$, dichloromethane, 0.51 g (46%) of 3-(acylmethylidynetricobalt nonacarbonyl)indole, m.p. 164—166°C (dec.) (lit. [6] m.p. 163—165°C (dec.)), whose IR spectrum was identical with that recorded previously [10]. Elution with diethyl ether yielded 0.07 g (8%) of $HO_2CCCo_3(CO)_9$.

(f) With pyrrole. The standard apparatus was charged with 1.00 g (1.9 mmol) of $BrCCo_3(CO)_9$ and 40 ml of benzene; pyrrole (1.00 ml, 14.5 mmol) was added by syringe. After the mixture had been stirred for 20 h at room temperature with carbon monoxide bubbling through it, TLC showed the presence only of $BrCCo_3(CO)_9$. Triethylamine (0.5 ml, 3.6 mmol) was added by syringe and stirring in a stream of carbon monoxide was continued at room temperature. After 24 h no reaction had occurred and therefore the mixture was stirred and heated at 60°C in the CO stream for 24 h. Standard work-up was followed by filtration chromatography. Bromomethylidynetricobalt nonacarbonyl (0.13 g, 13%) was recovered by elution with hexane. Further elution with hexane yielded a yellow-brown and a purple band, both very minor. Elution with benzene gave 0.20 g (20%) of 2-(acylmethylidynetricobalt nonacarbonyl)pyrrole, m.p. 144—145°C (dec.) (lit. [6] m.p. 144—145°C (dec.)), whose infrared spectrum was identical to that reported previously [11]. Diethyl ether eluted 0.21 (23%) of $HO_2CCCo_3(CO)_9$.

In another experiment 1.9 mmol of $BrCCo_3(CO)_9$ was allowed to react with 14.5 mmol of pyrrole in the presence of 9.4 mmol of triethylamine in 40 ml of benzene. The mixture was heated at 58°C for 8 h, while carbon monoxide was bubbled through it. Work-up as above followed by recrystallization of the product from hexane gave 0.20 g (21%) of *N*-(methylidynetricobalt nonacarbonyl)pyrrole.

New compounds

New functionally substituted methylidynetricobalt nonacarbonyl complexes prepared in this study are listed in Table 3 together with their characterizing data. The other products had been prepared previously in earlier studies [4,6]. Either autentic samples or IR and NMR spectra were available for comparison. All methylidynetricobalt nonacarbonyl complexes show a characteristic band pattern in the terminal carbonyl region of their IR spectra (ca. 2100m, 2065vs, 2050s, 2015(sh), 1985w). The cobalt cluster amides are not very stable on storage.

TABLE 3

NEW FUNCTIONALLY SUBSTITUTED METHYLIDYNETRICOBALT NONACARBONYL COMPLEXES

R in $RCCo_3(CO)_9$	M.p. (°C)	Analysis (found (calcd.) (%)		(IR (CCl_4) (cm^{-1}) ν(C=O)	NMR (CCl_4) (ppm)
		C	H		
$C_6H_5CH_2CH_2OC(O)$	65—66	38.82 (38.67)	1.63 (1.54)	1680	3.03 (t, *J* 7 Hz, 2 H, CH_2) 4.53 (t, *J* 7 Hz, 2 H, CH_2) 7.22 (s, 5 H, Ph)
p-$CH_3C_6H_4OC(O)$	62—63	37.50 (37.53)	1.22 (1.23)	1698	2.43 (s, 3 H, CH_3) 6.98—7.28 (AB m, 4 H, Ph)
p-$ClC_6H_4OC(O)$	56—57	34.52 (34.23)	0.79 (0.68)	1700	7.08—7.47 (AB m, 4 H, Ph)
p-$O_2NC_6H_4OC(O)$	85—86	33.66 (33.64)	0.81 (0.67)	1707	7.33—8.38 (AB m, 4 H, Ph)
		% N: 2.27 (2.31)			
$(CH_3)_3CNHC(O)$	72—73	33.15 (33.30)	2.01 (1.87)	1632	1.45 (s, 9 H, CH_3) 5.60 (br, 1 H, NH)
		% N: 2.62 (2.59)			
$C_6H_5(C_2H_5)NC(O)$	91—92	38.88 (38.74)	1.83 (1.71)	1578	1.20 (t, *J* 7 Hz, 3 H, CH_3) 3.77 (q, *J* 7 Hz, 2 H, CH_2) 7.27 (s, 5 H, Ph)
		% N: 2.52 (2.38)			
p-$CH_3OC_6H_4NHC(O)$	86—87(dec.)	36.59 (36.57)	1.62 (1.37)	1638	3.78 (s, 3 H, CH_3) 6.63—7.63 (AB m, 4 H, Ph)
		% N: 2.47 (2.37)			
p-$BrC_6H_4NHC(O)$	99—100	32.15 (31.91)	1.09 (0.79)	1642	7.41 (s)
		% Br: 12.10 (12.49)			
cyclo-C_4H_4N	dec. above 165°	33.42 (33.17)	0.92 (0.80)		6.37 (broad) 7.13 (broad)

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