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Preliminary communication

ORGANOCOBALT CLUSTER COMPLEXES

XIX*. A NEW ROUTE TO FUNCTIONALLY-SUBSTITUTED ALKYLIDYNETRICOBALT NONACARBONYL COMPLEXES VIA BASE-INDUCED REACTIONS OF BROMOMETHYLIDYNETRICOBALT NONACARBONYL

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Summary

Ammonia and primary and secondary aliphatic amines react readily with bromomethylidynetricobalt nonacarbonyl to give the corresponding amides, $(OC)_9Co_3CC(O)NRR'$ (R,R' = H or alkyl). Triethylamine was found to facilitate the known reaction of $(OC)_9Co_3CBr$ with methanol and showed the same function in the reactions of $(OC)_9Co_3CBr$ with other alcohols, phenol, anilines and indole.

The halomethylidynetricobalt nonacarbonyl complexes have some very strange and interesting chemistry [2]. Of particular interest are the cobalt-to-carbon CO transfer reactions which they undergo. Thus, 14 years ago, Italian workers [3] reported the following reaction which proceeds readily in the absence of external carbon monoxide (eq. 1)**. With chloromethylidynetricobalt nonacarbonyl the rate of this process is negligible at room temperature,

$$(OC)_9Co_3CBr \xrightarrow[\text{50 min}]{CH_3OH,\ 55^\circ C} (OC)_9Co_3CCO_2CH_3 \quad (59\%) \qquad (1)$$

but in earlier research we found that the addition of at least two molar equivalents of aluminum chloride induces the rapid conversion of this compound to the acylium ion I (eq. 2) [4]. The addition of nucleophiles other than methanol allowed the synthesis of many other organofunctional alkyl-

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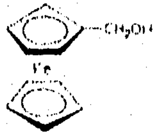
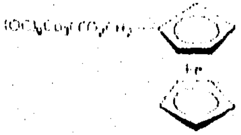
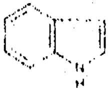
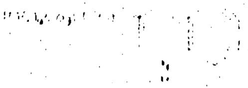
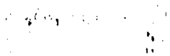
[*] Part XVIII: ref. 1

[**] We have found that this reaction can be effected in 86% yield when it is carried out while bubbling carbon monoxide slowly through the reaction mixture at 60°C for 1.5 h.

TABLE 1. REACTIONS OF BROMOMETHYLIDYNETRICOBALT NONACARBONYL WITH NUCLEOPHILES AT ROOM TEMPERATURE [a]

Nucleophile	Benzene diluent	Triethyl-amine	Reaction time (h)	Product	Yield (%)
MeOH			1.5 (at 60°C)	$(OC)_9Co_3CCO_2Me$	86
MeOH	+		3.5 (at 62°C)	$(OC)_9Co_3CCO_2Me$	57
MeOH			24	$(OC)_9Co_3CCO_2Me$	46
MeOH		+	5	$(OC)_9Co_3CCO_2Me$	80
MeOH	+	+	6	$(OC)_9Co_3CCO_2Me$	73
EtOH		+	5	$(OC)_9Co_3CCO_2Et$	75
Me_2CHOH		+	20	$(OC)_9Co_3CCO_2CHMe_2$	77
Me_3COH		+	22	$(OC)_9Co_3CCO_2CMe_3$	66
$CH_2{=}CHCH_2OH$		+	1.5	$(OC)_9Co_3CCO_2CH_2CH{=}CH_2$	73
PhOH	+	+	24	$(OC)_9Co_3CCO_2Ph$	60
	+	+	18		61 [b]
NH_3 (g)	+		20 min	$(OC)_9Co_3CC(O)NH_2$	38
Me_2NH(g)	+		15 min (at −5°C)	$(OC)_9Co_3CC(O)NMe_2$	50
$MeNH_2$ (g)	+		5 min	$(OC)_9Co_3CC(O)NHMe$	46
Et_2NH	+		3.5	$(OC)_9Co_3CC(O)NEt_2$	79
Me_3CNH_2	+		22	$(OC)_9Co_3CC(O)NHCMe_3$	69 [b]
$PhNH_2$	+	+	8	$(OC)_9Co_3CC(O)NHPh$	77
PhNHMe	+	+	24	$(OC)_9Co_3CC(O)N(Me)Ph$	64
p-$MeC_6H_4NH_2$	+	+	5	$(OC)_9Co_3CC(O)NHC_6H_4Me$-$p$	41 [b]
p-$BrC_6H_4NH_2$	+	+	18	$(OC)_9Co_3CC(O)NHC_6H_4Br$-$p$	59 [b]
	+	+	8 (at 60°C)		46
	+	+	24 (at 60°C)		20

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[a] Typical reaction procedure: bromomethylidynetricobalt nonacarbonyl (~ 2 mmol), benzene (40–50 ml, when used), triethylamine (~ 3.6 mmol minimum when used) and the nucleophile (large excess) were charged into a 100 ml flame-dried three-necked flask equipped with gas inlet and outlet tubes and a magnetic stirring unit. The reaction mixture was stirred for the stated time at room temperature (unless otherwise stated) while CO was bubbled slowly through the solution, until TLC showed that most of the starting bromide had been consumed. The reaction mixture was poured into 100 ml of 10% HCl. The organic layer was washed with water dried and evaporated at reduced pressure. Subsequently, crystallization or column chromatography served to isolate the product. [b] New compound; satisfactory characterization.

$$(OC)_9Co_3CCl \xrightarrow[CH_2Cl_2,\ 25^\circ C]{2\text{--}3\ AlCl_3} \underset{(I)}{(OC)_9Co_3CCO^+\ AlCl_4^-} \xrightarrow{MeOH} (OC)_9Co_3CCO_2Me \qquad (2)$$

idynetricobalt nonacarbonyl complexes. We have now found that this process also can be induced very effectively by a Lewis base such as a tertiary amine.

During the course of investigations of the chemistry of bromomethylidynetricobalt nonacarbonyl we examined its reaction with diethylamine and found the latter to be unexpectedly reactive (eq. 3). The reaction time required to obtain this good yield was only 3.5 h, in comparison to the 46% yield obtained in a reaction of $(OC)_9Co_3CBr$ with neat methanol at room temperature during a 24 h reaction time. (A reaction with less methanol in benzene diluent was even slower.)

$$(OC)_9Co_3CBr + Et_2NH \xrightarrow{C_6H_6,\ 25^\circ C} (OC)_9Co_3CC(O)NEt_2 \quad (79\%) \qquad (3)$$

The fact that diethylamine, a fairly strong organic base, reacted more rapidly than methanol suggested to us that such reactions of bromomethylidynetricobalt nonacarbonyl with alcohols might be promoted by a base such as a tertiary amine. This, we found, is the case.

The slow room temperature reaction of methanol with $(OC)_9Co_3CBr$ is accelerated considerably when it is carried out in the presence of about 2 molar equivalents of triethylamine under an atmosphere of carbon monoxide*. A 5 h reaction time sufficed to give $(OC)_9Co_3CCO_2CH_3$ in 80% yield. The reaction proceeded equally satisfactorily (73% yield in 6 h at room temperature) in the presence of triethylamine when the reaction mixture was diluted with benzene and a lesser amount of methanol was used. Other alcohols, as well as phenol, reacted equally well (Table 1). Longer reaction times were required for more hindered alcohols. The case of ferrocenylmethanol is of special interest since $(OC)_9Co_3CCO_2CH_2C_5H_4FeC_5H_5$ could not be prepared by routes involving the preformed acylium ion I. Apparently, ferrocenylmethanol is too easily converted to the ferrocenylmethyl carbonium ion by the aluminum chloride-containing system and hence is not available for reaction with the acylium ion.

Ammonia and aliphatic primary and secondary amines reacted readily with bromomethylidynetricobalt nonacarbonyl (Table 1). The reaction with t-butylamine required a longer reaction time, very likely because of the steric factors involved. Aniline and its derivatives did not react at room temperature in benzene solution with $(OC)_9Co_3CBr$, but addition of triethylamine caused the reactions to take place and good product yields were obtained (Table 1).

Acylation of indole and pyrrole could be effected with the $(OC)_9Co_3CBr/Et_3N$ reagent at 60°C, but the product yields were not good. Furthermore, this reaction is not applicable to many other aromatic substrates.

At the present time we have no useful information concerning the mechanism of this new, preparatively useful reaction. We view the reaction

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*All preparative reactions described in this paper were carried out with carbon monoxide bubbling slowly through the reaction mixture.

which occurs between $(OC)_9Co_3CBr$ and methanol in the absence of triethylamine as proceeding via C—Br ionization followed by or in concert with CO migration from cobalt to the electron-deficient apical carbon atom to give the acylium ion which reacts rapidly with methanol. Intermolecular CO transfer fills the vacant coordination site on cobalt. The function of the triethylamine in this reaction may simply be that of an HBr acceptor. However, other possibilities are conceivable. If such an S_N1-type mechanism were operative, it might be the function of the amine to facilitate C—Br heterolysis and to stabilize the intermediate apical carbonium ion through coordination at carbon so that further reactions (CO migration followed by acylation of the nucleophile) can occur. Alternatively, it is conceivable that the amine serves to assist the cobalt-to-carbon CO migration and to stabilize, via weak coordination at cobalt, the CO-deficient intermediate remaining until intermolecular CO transfer can occur. In any case, the presence of the amine does modify the reactivity of the $(OC)_9Co_3CCO^+$ intermediate, very likely via coordination at the acylium function. The $(OC)_9Co_3CBr/Et_3N$ system seems to be much less reactive toward weaker nucleophiles such as aromatic compounds than the reagent derived from the $(OC)_9Co_3CCl/AlCl_3$ interaction. Future research hopefully will shed some light on this question of mechanism.

The $(OC)_9Co_3CBr/Et_3N$ reagent seems to be very useful for the further development of organofunctional organocobalt cluster chemistry. It has unique applicability, because of its non-acidic reaction conditions, in those cases in which the nucleophile substrate is easily converted to the corresponding carbonium ion in acidic medium. Full details of this work and of our continuing studies will be reported in due course.

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