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Preliminary communication

A new route to *C*-carbonyl derivatives of the methylidynetricobalt nonacarbonyl cluster

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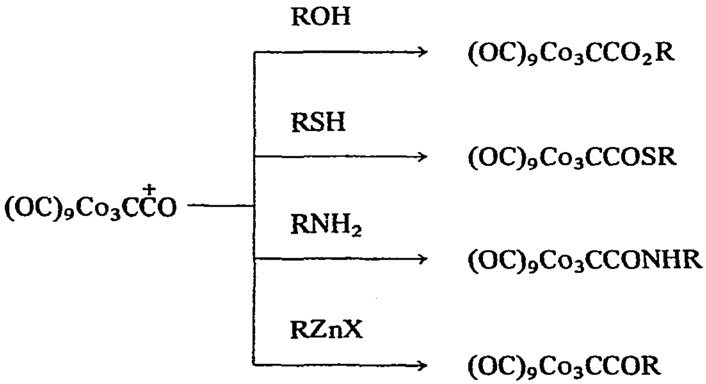
We have reported recently concerning the synthesis of the carbatricobalt decacarbonyl cation, a novel acylating agent (eqn. 1)[1]. Its reactions with alcohols, thiols, primary and secondary amines, ammonia, an amino acid ester, a tripeptide and

$$(OC)_9Co_3CCO_2R \xrightarrow[(EtCO)_2O]{HPF_6} [(OC)_9Co_3C\overset{+}{C}O]\ PF_6^- \qquad (1)$$

(R = H or alkyl)

organometallic reagents were described, *e.g.*:



$$(OC)_9Co_3C\overset{+}{C}O \xrightarrow{ROH} (OC)_9Co_3CCO_2R$$
$$(OC)_9Co_3C\overset{+}{C}O \xrightarrow{RSH} (OC)_9Co_3CCOSR$$
$$(OC)_9Co_3C\overset{+}{C}O \xrightarrow{RNH_2} (OC)_9Co_3CCONHR$$
$$(OC)_9Co_3C\overset{+}{C}O \xrightarrow{RZnX} (OC)_9Co_3CCOR$$

We report here an alternative route to such products which is based on observations made during attempts to extend the Friedel–Crafts synthesis of $ArCCo_3(CO)_9$ complexes[2] (eqn. 2) to a general preparation of alkylidynetricobalt

$$(OC)_9Co_3CCl + ArH \xrightarrow{AlCl_3} (OC)_9Co_3CAr + HCl \qquad (2)$$

nonacarbonyls. The reaction chosen for investigation was the $AlCl_3$-catalyzed interaction of tetraalkyltin compounds with chloromethylidynetricobalt nonacarbonyl. In analogy with a known ketone synthesis (eqn. 3)[3], this reaction might be expected to give $RCCo_3(CO)_9$ as product. Such, however, was not the case. When a reaction mixture containing

$$R_4Sn + R'COCl \xrightarrow{AlCl_3} R'COR + R_3SnCl \qquad (3)$$

4.45 mmoles of $AlCl_3$ and 3.5 mmoles of $ClCCo_3(CO)_9$ in 35 ml of dichloromethane was stirred for 45 min under nitrogen and then treated with 3.9 mmoles of Me_4Sn, the product obtained after hydrolysis and work-up by column chromatography and crystallization was $CH_3COCCo_3(CO)_9$ (26%) rather than the expected $CH_3CCo_3(CO)_9$; $ClCCo_3(CO)_9$ was recovered in 45% yield.

A possible explanation for this observation was that the assumed initial species formed in the $ClCCo_3(CO)_9$ + $AlCl_3$ reaction, $(OC)_9Co_3C^+\text{--}\bar{C}l\text{—}AlCl_3$, was carbonylated via an inter- or intramolecular CO transfer, and that the resulting $(OC)_9Co_3CCO^+\text{--}Cl\text{—}AlCl_3$ species then reacted with tetramethyltin. (Note the formation of $CH_3COCCo_3(CO)_9$ by reaction of $(OC)_9Co_3CCO^+$ PF_6^- with Me_4Sn[1].)

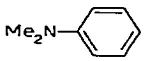
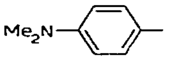
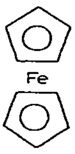
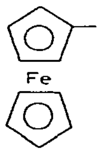
The acylating agent formed from the readily accessible $ClCCo_3(CO)_9$[4,5] and $AlCl_3$ is a very useful reagent and shows for the most part a chemistry comparable with that of $(OC)_9Co_3CCO^+PF_6^-$. It is prepared in high yield in the following manner: A solution of 6.1 mmoles of $AlCl_3$ and 2.2 mmoles of $ClCCo_3(CO)_9$ in 50 ml of dichloromethane is prepared under nitrogen (a minor amount of solid, probably impurities from the $AlCl_3$, remains undissolved). This purple solution is stirred for 30 min, during which time the color changes to an intense yellow-brown. At this point, thin layer chromatography shows the $ClCCo_3(CO)_9$ to have been totally consumed and the reagent formed is completely dissolved or almost so. Such reagent solutions are stable at room temperature at least for 2 days and probably longer. Treatment of such reagent solutions with suitable nucleophilic substrates at room temperature results in formation of the expected acylated product, usually in high yield, in what appear to be nearly instantaneous reactions as indicated by the observed color changes. Among the reactions carried out (summarized in Table 1) thus far have been acylations of alcohols, thiols, amines, ammonia; reactions with tetraalkyltins to give ketones; Friedel—Crafts acylation of reactive aromatic compounds; hydride abstraction from triethyl- and triphenylsilane. It is this excellent utility in synthesis which prompts this communication.

We must note, since the reactions of our reagent solutions with alcohols produce esters, $(OC)_9Co_3CCO_2R$, that $(OC)_9Co_3CBr$ reacts directly with methanol at 55° to give $(OC)_9Co_3CCO_2CH_3$ in 59% yield[5]. However, $ClCCo_3(CO)_9$ is less reactive, giving $(OC)_9Co_3CCO_2Et$ in only 6% yield upon treatment with an excess of ethanol for 15 days at room temperature. Clearly, our reactions involve a species other than $ClCCo_3(CO)_9$.

The conversion of $ClCCo_3(CO)_9$ to the acylating agent is a remarkable process. The transfer of CO to the apical carbon atom is extremely efficient. If one recalculates the yield of $(OC)_9Co_3CCO_2CH_3$ in the reaction of the reagent solution with methanol

TABLE 1

SYNTHETIC APPLICATIONS OF THE $(OC)_9Co_3CCO^{+}\text{---}\bar{Cl}\text{–}AlCl_3$ REAGENT

Reactant	*Product* $R\underset{O}{\underset{\|}{C}}CCo_3(CO)_9$	*Yield*[a] *(%)*	*m.p. (°C)*
CH_3OH	R = CH_3O	83	109–111
C_2H_5OH	C_2H_5O	78	45–47
Me_2CHOH	Me_2CHO	78	62–64
Me_3COH	Me_3CO	77	49–51
PhOH	PhO	66	63–65
PhSH	PhS	58	91–92
NH_3	H_2N	64	dec. without melting
Me_2NH	Me_2N	55	121–123
Et_2NH	Et_2N	75	59–60
$PhNH_2$	PhHN	76	98–99
$(CH_3)_4Sn$	CH_3	61	dec. without melting
$(C_2H_5)_4Sn$	C_2H_5	66	111–113 (dec.)
		69	145–146
		41	104
Et_3SiH	H	63	dec. above 120

[a] Yields are based on the quantity of $ClCCo_3(CO)_9$ charged. All new compounds have been characterized by satisfactory elemental analyses and their IR and NMR spectra.

(Table 1) based on the available $(OC)_9Co_3CCO^+$ from the $ClCCo_3(CO)_9$ charged (assuming the destruction of an amount of $ClCCo_3(CO)_9$ equivalent to the theoretically required amount of CO for the transfer to carbon), it is 92%. No improvement in yield was achieved in a reagent preparation carried out under an atmosphere of carbon monoxide rather than nitrogen. Some other observations may be pertinent with respect to the questions concerning the species present in these reagent solutions and their mode of formation: (1) At least 2 moles of $AlCl_3$ (and preferably 3) per mole of $ClCCo_3(CO)_9$ are required for high yield conversion to the acylating agent. (2) The acylating agent is not formed instantaneously. When a mixture of 2 molar equivalents of $AlCl_3$ and one of $ClCCo_3(CO)_9$ in CH_2Cl_2 was quenched with methanol immediately after mixing, no ester was formed and a high recovery of $ClCCo_3(CO)_9$ was obtained. However, the $ClCCo_3(CO)_9$ is "activated" before CO transfer takes place: when such a $ClCCo_3(CO)_9$–$AlCl_3$ solution in CH_2Cl_2 was quenched with bromobenzene immediately after mixing, p-$BrC_6H_4CCo_3(CO)_9$ was obtained in 54% yield. (However, bromobenzene is not acylated by our acylating agent solutions at room temperature.)

It is clear that the course of events leading to the final acylating agent is complex, and, indeed, the exact constitution of this reagent remains unknown at the present time. We suggest that initially a $(OC)_9Co_3CCl \cdot AlCl_3$ complex is formed, which is capable of Friedel–Crafts substitution on aromatic systems, and that subsequent complexation of a second molecule of $AlCl_3$ at a carbon monoxide ligand (a known reaction in carbonyl chemistry[6,7]) provides the activation for CO migration from cobalt to the apical carbon atom. In view of the fact that bridging carbonyl ligands in metal carbonyl systems are better Lewis basic sites than terminal carbonyl ligands[6,7], and in the light of the report by Shriver *et al.*[8] that aluminium alkyls promote a terminal to bridge carbonyl shift in a ruthenium carbonyl complex, it is tempting to speculate that such structural changes play a part in the chemistry of the formation of our acylating agent. Efforts at expanding the synthetic applications of this new reagent and at obtaining a better understanding of its constitution and mode of formation are in progress.

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