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Preliminary communication

Reactions of methinyltricobalt enneacarbonyls with electrophiles and nucleophiles: New silicon derivatives

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The tricobalt carbon cluster, Co_3C, may be pictured as an electronegative electron reservoir. This property leads to diverse coordination behaviour[1,2] and also to some unusual chemistry of the apical carbon atom and its substituents. The apical substituent is susceptible to electrophilic attack[3–6], and it has been suggested that the apical carbon will be readily attacked by nucleophiles[3]. Here we summarise some of the more important reactions with typical electrophiles and nucleophiles (Tables 1 and 2).

Reactions with nucleophiles under CO invariably give products formed through intramolecular CO insertion into the apical bond (the exact mechanism is under investiga-

TABLE 1

REACTIONS OF METHINYLTRICOBALT ENNEACARBONYLS WITH NUCLEOPHILES

Cluster	*Reagent(s)*	*Products yield (%)*	*Comment*
1 $BrCCo_3(CO)_9$	$RMgX, N_2$	$RCCo_3(CO)_9$ (80)	$RMgX$/cluster > 9/1,
2	$RMgX, CO$	$HO_2CCCo_3(CO)_9$ (10)	R = aryl only.
3	RLi/H_2O	$HO_2CCCo_3(CO)_9$ (20) $[Co_3(CO)_9C]_2C_2$ (5)	Under CO only, decomp. under N_2.
4	H_2O	$HO_2CCCo_3(CO)_9$ (15) $HCCo_3(CO)_9$ (20)	
5	OH^-(aq)	$HO_2CCCo_3(CO)_9$ (5)	
6	OEt^-	$EtO_2CCCo_3(CO)_9$ (10)	
7	Li or Na or Mg/H_2O	$HO_2CCCo_3(CO)_9$ (10)	under CO.
8 $RCCo_3(CO)_9$	OH^- (>6*M*)/H^+	$Co_4(CO)_{12}$, $HCo(CO)_4$	
9	OH^- or BH_4^-/H^+	$Co_2(CO)_8$, $HCo(CO)_4$	
	OH^-, R^1OH/H^+	$RCCRCo_4(CO)_{10}$ (15), $Co_2(CO)_8$, Co^{II}	
	OD^-, R^1OD/D^+	$RCCRCo_4(CO)_{10}$ (15), $Co_2(CO)_8$, Co^{II}	

tion). A possible reason for facile CO insertion is the favourable conformation of six equatorial CO groups pointing towards, and adjacent to, the apical group. The versatility and stereospecificity of the Grignard reactions is particularly noteworthy. Although phenol derivatives cannot be synthesized by this route they have been prepared via reaction (10).

$$MeOC_6H_4CCo_3(CO)_9 \xrightarrow[CH_2Cl_2]{BBr_3} HOC_6H_4CCo_3(CO)_9 \qquad (10)$$

TABLE 2

REACTIONS OF METHINYLTRICOBALT ENNEACARBONYLS WITH ELECTROPHILES

	Cluster	*Reagent(s)*	*Products yield (%)*
11	$YCCo_3(CO)_9$	strong acids	$[YCCo_3(CO)_9H]^+$
12	$R_2NC_6H_4CCo_3(CO)_9$	H^+ (2*M*)	$[R_2NHC_6H_4CCo_3(CO)_9]^+$
13	$BrCCo_3(CO)_9$	$AlCl_3$, CO	$[OCCCo_3(CO)_9]^+$
	$ClCCo_3(CO)_9$	$AlCl_3$, CO/H_2O	$HO_2CCCo_3(CO)_9$ (50)
		$AlCl_3$, CO/EtOH	$EtO_2CCCo_3(CO)_9$ (70)
		$AlCl_3$, CO/PhOH	$PhO_2CCCo_3(CO)_9$ (60)
14	$BrCCo_3(CO)_9$	BF_3, CO	same products as $AlCl_3$ reactions
	$EtO_2CCCo_3(CO)_9$	BF_3, N_2	$HO_2CCCo_3(CO)_9$ (75)
15	$HO_2CCCo_3(CO)_9$	$R_3O^+BF_4^-$	$RO_2CCCo_3(CO)_9$ (80)

Seyferth and co-workers have shown[7] that the ester, $EtO_2CCCo_3(CO)_9$, dissolves in H_2SO_4 to form the acylium cation, $^+OCCCo_3(CO)_9$, a precursor of some importance. Electrophilic attack on the apical halogen substituent, followed by CO insertion to give this cation [ν(CO), 2107, 2097, 2076, 2058 cm^{-1} ★], is a general reaction and in the past we have found the *in situ* synthesis (reactions 13 and 14) very convenient.

Reports in the literature of silicon analogues of Co_3C have been disproved[8]. A possible reason for the non-existence of such compounds is indicated by the above work; the silicon would be readily attacked by even weak nucleophiles and this would lead to complete decomposition. Indeed all our attempts to prepare silicon-containing clusters from halosilanes have failed but we do find that in ether solvents, carbon clusters are formed in small yields (5%) *e.g.* $H_5C_2CCo_3(CO)_9$.

However, purple volatile air-stable silicon derivatives of the Co_3C cluster can be isolated in high yield using the appropriate trihalomethane.

$$R_3SiCBr_3 + Co_2(CO)_8 \xrightarrow[25^\circ]{benzene} R_3SiCCo_3(CO)_9 \qquad (16)$$

★ This spectrum differs from that given in ref. 7; the latter spectrum is very similar to that of $HO_2CCCo_3(CO)_9$. Reaction (13) probably represents the most convenient route to the acid $HO_2CCCo_3(CO)_9$ from $Co_2(CO)_8$.

An interesting feature of the mass spectrum of these compounds is the observation of Co_nSi fragments, formed presumably by silicon transfer from carbon to cobalt. Work is in progress to extend reaction (16) to the preparation of cluster derivatives with elements from Groups III, IV and V on the apical carbon atom.

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