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CHEMISTRY OF METHYLIDYNETRICOBALT NONACARBONYLS IV*. SYNTHESIS AND SPECTRA OF $Co_8(CO)_{24}C_6$ AND SIMILAR ACETYLENE DERIVATIVES

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SUMMARY

Methods available for the preparation of $Co_8(CO)_{24}C_6$ from methylidynetricobalt nonacarbonyls are described. Spectral data for this compound and the analogous $Co_5(CO)_{15}C_3H$ and $Co_6(CO)_{18}C_4$ are evaluated.

INTRODUCTION

In the course of a general study of methylidynetricobalt nonacarbonyls it was discovered that $ClCCo_3(CO)_9$ or $BrCCo_3(CO)_9$ underwent dehalogenation reactions in arenes to give three polynuclear carbonyls, $Co_5(CO)_{15}C_3H$, $Co_6(CO)_{18}C_4$ and $Co_8(CO)_{24}C_6$[1]. Preparative details for $Co_5(CO)_{15}C_3H$[2] and $Co_6(CO)_{18}C_4$[3] and structures of all three compounds[2-4] have previously been published. Each compound is in effect a $Co_3(CO)_9C$ unit with various acetylene residues linked to the apical carbon atom (Fig. 1). Recently Seyferth and coworkers reported[5] that $Co_8(CO)_{24}C_6$ can also be prepared from the reaction of $Co_2(CO)_8$ with hexachlorocyclopropane, an independent structural determination is also given.

This paper deals with the chemical and physical properties of $Co_8(CO)_{24}C_6$; comparative chemical and spectral data for all acetylene derivatives are also presented.

PREPARATION AND PROPERTIES OF $Co_8(CO)_{24}C_6$

Either $ClCCo_3(CO)_9$ or $BrCCo_3(CO)_9$ undergo dehalogenation in arenes at temperatures above 90° to yield the compound $Co_8(CO)_{24}C_6$ along with $Co_5(CO)_{15}C_3H$ and $Co_6(CO)_{18}C_4$. High temperatures favour the formation of $Co_8(CO)_{24}C_6$ over $Co_5(CO)_{15}C_3H$ but the yield even under optimum conditions is low; $Co_6(CO)_{18}C_4$ is the major product. We have also detected or isolated the Co_8 derivative from a number of other reactions where dehalogenation is involved. For example in preparations of methylidynetricobalt nonacarbonyls from 1,1,1-trihaloalkyls, in particular those carried out in tetrahydrofuran. Another novel route is through the reaction of

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* For Part III see ref. 3.

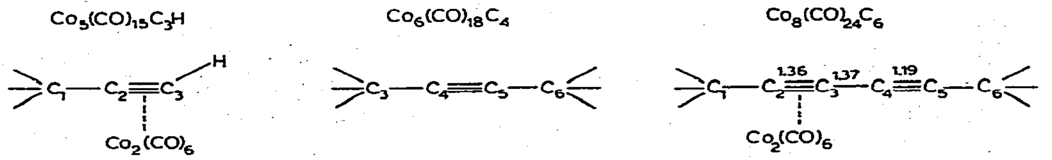

Fig. 1. Structures of acetylene derivatives ($Co_3(CO)_9C$ group is denoted by ⋺C).

metallic sodium with $ClCCo_3(CO)_9$ in tetrahydrofuran[6]. The singular preparation of $Co_8(CO)_{24}C_6$ from hexachlorocyclopropane[5] is unusual in our experience since $Co_5(CO)_{15}C_3H$ and $Co_6(CO)_{18}C_4$ are generally present and in greater yield. It may be possible to prepare a series of $Co_5(CO)_{15}C_3Y$ compounds from the appropriately substituted pentachlorocyclopropanes.

A significant feature of the $Co_8(CO)_{24}C_6$ structure[4,5] is the obvious steric congestion through intramolecular carbonyl interactions. This explains why a

TABLE 1

INFRARED SPECTRA OF ACETYLENE DERIVATIVES OF $Co_3(CO)_9C$ (cm^{-1})[a]

Assignment	$Co_2(CO)_6(C_2H_2)$[b]	$Co_5(CO)_{15}C_3H$	$Co_6(CO)_{18}C_4$	$Co_8(CO)_{24}C_6$
ν(C–H)	3116 w			
ν(C–H)	3086 w	3085 vw		
		2108 m	2107 w	2109 w
ν(CO)	2098 s		2090 s	2098 s
		2084 s		2084 s
ν(C≡C)				2070 vs
		2065 vs	2065 vs	2064 s
	2058 vs	2058 vs		2058 s
		2050 ms		2051 (sh)
		2044 ms	2037 s	2042 s
ν(CO)	2034 vs	2034 s		2035 s
		2030 s		
	2028 vs	2021 w		2020 (br)
	2017 m	2016 w		2014
$\nu(^{13}CO)$?		1982 vw	1983 vw	1982 vw
ν(C≡C)$_{coord.}$				1527 vw
ν(C≡C)$_{coord.}$	1403 m	1466 w		
			1382 m	1384 m
				1322 vw 1299 w
				1160 vw
		1046 w		1098 vw
ρ(C–H)	894 s	864 w		
	768 s	784 w		
		640 m 610 w		657 618 m
ν(Co–C)	605 w 551 m	583 w 554 m	593 579	592 583 s
and δ(MCO)	515 s 492 s	529 517 s	525 502 s	552 w 521 v
	450 m 424 w	496 s 460 w	491 463 m	507 497 s
		447 431 w	438 407 m	471 w 441 m
		414 406 w	389 357 m	410 389 m
		401 w		

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[a] In hexane (2200–1700 cm^{-1}) accuracy, ±1 cm^{-1}, nujol or hexachlorobutadiene where appropriate. There are no bands below 350 cm^{-1}. [b] Figures from Ref. 7.

product of the type $Co_3(CO)_9C{-}C{\equiv}C[Co_2(CO)_6]{-}CCo_3(CO)_9$ has not been isolated; models show quite clearly that carbonyl interactions would be prohibitive. Another manifestation of the steric congestion is the apparent inability of the $-C{\equiv}C-$ bond to behave as a normal acetylene group; for example, this bond could not be hydrogenated and we confirm the finding of Seyferth *et al.*[5] that it does not react with $Co_2(CO)_8$.

INFRARED SPECTRA OF ACETYLENE DERIVATIVES

The complete infrared spectrum of $Co_8(CO)_{24}C_6$ is given in Table 1 together with the spectra and tentative assignments for $Co_5(CO)_{15}C_3H$, $Co_6(CO)_{18}C_4$ and $Co_2(CO)_6C_2H_2$[7]. There is a surprising similarity between the spectra of compounds with isostructural units; that is, between $Co_6(CO)_{18}C_4$, $Co_5(CO)_{15}C_3H$ and $Co_8(CO)_{24}C_6$ and $Co_5(CO)_{15}C_3H$, $Co_8(CO)_{24}C_6$ and $Co_2(CO)_6C_2H_2$.

The vibrations associated with the acetylene chain can be assigned, assuming the remainder of the molecule can be ignored, by reference to the comprehensive analysis of $Co_2(CO)_6C_2H_2$ by Iwashita[7]. In this latter compound $\nu(C{\equiv}C)_{coord}$ occurs at 1402 cm^{-1}; the comparable band for $Co_5(CO)_{15}C_3H$ is obviously that at 1466 cm^{-1}. A similar assignment for $Co_8(CO)_{24}C_6$ is less certain because of the similar bond lengths, $C_2{-}C_3$ and $C_3{-}C_4$ (1.37 and 1.38 Å respectively), but it is reasonable to assign the band at 1527 cm^{-1} to a carbon chain mode involving principally a stretching of the coordinated acetylene.

The uncoordinated acetylene stretching mode, IR inactive under the D_{3d} symmetry of $Co_6(CO)_{18}C_4$, should appear in the spectrum of $Co_8(CO)_{24}C_6$ in the region, 2200–2000 cm^{-1}. It is significant that the spectrum of $Co_8(CO)_{24}C_6$ can be reproduced if the spectra of $Co_5(CO)_{15}C_3H$ and $Co_6(CO)_{18}C_4$ are superimposed, with one exception. The band at 2070 cm^{-1} has no counterpart in either spectrum and this may be $\nu(C{\equiv}C)$.

A number of other bands in the region 1400–900 cm^{-1} can be assigned to $\nu(C{-}C)$. Those between 1200–900 cm^{-1} in $Co_5(CO)_{15}C_3H$ and $Co_8(CO)_{24}C_6$ are probably associated with C(apical)–C(acetylene) bonds. The bands at 1382 (Co_6) and 1384 cm^{-1} (Co_8) are comparable with $\nu(C{=}C)$ found in similar delocalized systems where the C–C bond is about 1.37 Å. They can therefore be assigned to coupled stretching vibrations involving the C–C bonds adjacent to the triple bond.

Detailed assignments for $\nu(CO)$ cannot be made without Raman spectra. The high frequency of the symmetrical in-phase stretching mode (2109 cm^{-1}), as discussed earlier[2,3], reflects the electron-withdrawing property of the acetylene residue.

VISIBLE-ULTRAVIOLET SPECTRA

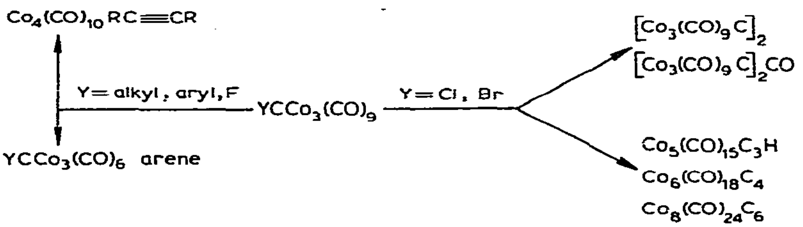
Two intense bands in the visible were found in the spectra of all derivatives, at 18,200 (ε 2250) and 23,300 (10,300), 17,550 (4500) and 22,950 (30,150), and 17,500 (6000) and 23,250 cm^{-1} (36,000) for $Co_5(CO)_{15}C_3H$, $Co_6(CO)_{18}C_4$ and $C_8(CO)_{24}C_6$ respectively. These bands, characteristic of the Co_3C unit, are probably due to transitions within molecular orbitals delocalised over the whole cluster.

Strong cluster absorption in the ultraviolet made an assignment of the triple bond chromophore in $Co_6(CO)_{18}C_4$ and $Co_8(CO)_{24}C_6$ difficult. Nevertheless, both compounds had an intense absorption band centred around 34,500 cm^{-1} which was absent in $Co_5(CO)_{15}C_3H$ and $Co_2(CO)_6(HC{\equiv}CH)$. This is considerably higher in energy than an isolated acetylene chromophore although it is not unreasonable if the carbon chain is regarded as a fully conjugated system[8].

DISCUSSION

Scheme 1 summarizes the known reactions of methylidyne tricobalt nonacarbonyls with arenes. Conditions for optimum yields of the acetylene derivatives have been given in an earlier paper[3].

SCHEME 1



The origin of the extra carbon atoms in the acetylene derivatives is of some interest both from a mechanistic viewpoint and for future synthetic routes. Whatever mechanism is proposed, the crucial step is probably the homolytic cleavage of the carbon–halogen bond to give a solvent-stabilised radical species.

$$Y\text{–}CCo_3(CO)_9 \rightarrow {\cdot}Y + {\cdot}CCo_3(CO)_9$$

Cleavage processes of this type are presumably involved in the formation of CH_3O_2-$CCo_3(CO)_9$[9], $[CCo_3(CO)_9]_2$[10,11], $OC[CCo_3(CO)_9]_2$[11] and $C_6H_5CCo_3(CO)_9$ from $ClCCo_3(CO)_9$ by Friedel–Crafts[12] and organomercurial reactions[13]. It is also consistent with the observation that only the chloro- and bromo-clusters yield acetylene derivatives. There are three sources of carbon in these systems, the arene solvent, the carbonyl group and the apical carbon atom but there is no difinitive experimental support available as yet. It has been shown that the dimer $[CCo_3(CO)_9]_2$ is not an intermediate and, that an arene solvent is necessary [although C_6F_6 gave no Co_5-$(CO)_{15}C_3F$] and that yields are not improved by adding $Co_2(CO)_6C_2H_2$. Further studies using isotopically-substituted reagents are currently underway.

One feature of these derivatives deserving special mention is the shortC–C bonds especially the C_{apical}–$C_{linkages}$ (see Fig. 1). Clearly the short bond distances are a result of strong σ bonding and extensive electron delocalization throughout the cluster and carbon chains. Indeed it seems that, in the cluster $CCo_3(CO)_9$, there is an overall polarization in the apical direction and this is reflected, for example in unusually high ν(C–Y)[14], a short C–C bond in $[Co_3(CO)_9C]_2$ (1.37 Å)[15] and the short C–C bonds mentioned above. There is a considerable body of experimental evidence which shows that the $CCo_3(CO)_9$ unit is effectively an electron-reservoir and electron-withdrawing apical groups like an acetylene residue readily polarize the cluster in the apical direction. This does weaken the Co–Co bonding and as a result these acetylene derivatives are less stable thermally and to nucleophilic attack when compared with, for example, $CH_3CCo_3(CO)_9$. Axial Co–CO bonds are significantly longer than equivalent equatorial Co–CO bonds in the acetyelene derivatives [and in other $CCo_3(CO)_9$ derivatives] a phenomenon perhaps related to this apical polarization. In fact a *trans* effect is operating, a feature already noted by Cetini *et al.*[16] in their studies of ^{14}CO exchange in the parent clusters.

In conclusion it is worthwhile emphasising the overall stability of the $CCo_3(CO)_9$ derivatives, and in many respects they behave like $Ru_3(CO)_{12}$ and $Os_3(CO)_{12}$. The latter trimeric clusters react with a number of solvents with retention of the cluster unit[17] and it is anticipated that methyltricobalt clusters will behave in a similar manner.

EXPERIMENTAL

All reactions were carried out under a dry nitrogen atmosphere. Elemental analyses were performed in the microanalytical laboratory of this department.

Preparation of $Co_8(CO)_{24}C_6$

Bromomethylidynetricobalt nonacarbonyl (1.6 g) was dissolved in dry *m*-xylene (12 cm^3) and the solution added dropwise over a period of 20 min to further *m*-xylene (6 ml) held at 125°. The reaction was continued for five min after the $BrCCo_3(CO)_9$ solution had been added. The solvent was then removed under reduced pressure at 50–60° and the residue extracted with 4 × 10 ml portions of pentane. This extract was applied to three 20 × 20 cm × 1.25 mm silica plates which when developed in pentane gave four bands due to (in order) $BrCCo_3(CO)_9$ and $HCCo_3(CO)_9$ (traces), $HC_3Co_5(CO)_{15}$, $C_4Co_6(CO)_{18}$ and $C_6Co_8(CO)_{24}$.

The latter dark brown band was eluted with benzene, the benzene removed *in vacuo* and the residue recrystallised from hexane to give long dark needles of μ_2, μ_3, μ_3-hexa-2,4-diyne-1,6-diylidyne(dicobalthexacarbonyl)bis(tricobalt nonacarbonyl), $C_6Co_8(CO)_{24}$. (Found: C, 29.71; H, 0.20; Co, 40.1; mol. wt., 1100 (in $CHCl_3$). $C_{30}Co_8O_{24}$, calcd.: C, 29.64; H, 0.00; Co, 38.78%; mol. wt., 1216.)

The compound is soluble without decomposition in common organic solvents and stable in air. Thermal decomposition occurs above 60° *in vacuo* and for this reason it was not possible to obtain a mass spectrum. Overall the Co_8 derivative is less stable to oxidation and to nucleophilic attack than the Co_5 and Co_6 compounds.

There are other products from the above reaction in addition to those mentioned. Acetone soluble carbonyl-containing compounds have been isolated in yields comparable with those of $C_6Co_8(CO)_{24}$. However, because of the experimental difficulties involved in separation these products were not extensively investigated. The major by-product was cobalt metal.

A similar procedure may be used to isolate $C_6Co_8(CO)_{24}$ from other arene reactions with $ClCCo_3(CO)_9$ or $BrCCo_3(CO)_9$. Likewise this derivative has been detected or isolated using preparative scale silica plates in the preparation of $YCCo_3(CO)_9$ (Y = Cl, Br, CH_3, H and F) from the appropriate $CYCl_3$ compound in alcohol or ether solvents and in reactions involving $ClCCo_3(CO)_9$ and organolithium compounds.

Attempted reaction of $Co_5(CO)_{15}C_3H$ and $Co_6(CO)_{24}C_6$

Pure samples of $Co_5(CO)_{15}C_3H$ and $Co_6(CO)_{18}C_4$ (1/1 mole ratio) were treated in hexane and *p*-xylene for varying reaction times ($\frac{1}{2}$–24 h). In every case the only products were the reactants and cobalt metal (as shown by TLC and IR).

Reaction of $Co_3(CO)_9C_2$ with arenes

A solution of $[Co_3(CO)_9C]_2$ (0.74g) in *p*-xylene was heated to 130° for 6 h. The solution was filtered to remove an insoluble black solid (cobalt metal) and the xylene removed *in vacuo*.

The residue dissolved in warm benzene and TLC analysis showed that only one compound was present, $[Co_3(CO)_9C]_2$.

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