Chemistry of the Tricobalt Carbon Cluster. Part XI.[1] Bicyclo[2.2.1]-hepta-2,5-diene, Cyclohexa-1,3-diene, and Cyclopentadienyl Derivatives

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The reactivity of dienes towards methylidynetricobalt enneacarbonyls is discussed; in particular the preparation and physicochemical properties of $[YCCo_3(CO)_7(diene)]$ {diene = bicyclo[2.2.1]hepta-2,5-diene (bhd) and cyclohexa-1,3-diene (chd)} and the η-cyclopentadienyl derivatives $[YCCo_3(CO)_4(cp)_2]$ (Y = alkyl, aryl, or F) are described. The ^1H n.m.r. spectra show that the bhd derivatives are non-rigid in solution. Stereospecific dimerization of bhd is not observed during formation or thermal decomposition of its complexes. Electrophiles attack the unique bridging carbonyl group, but not the dienyl ring, of the cp derivatives.

THE co-ordination chemistry of the basal cobalt triangle in tricobalt carbon clusters, $[YCCo_3]$, is influenced by the type of substituent on the apical carbon atom and the steric requirements of the ligands.[2] Severe steric constraints imposed by the tetrahedral clusters force a complex to adopt a structure that minimizes both ligand–carbonyl and intramolecular carbonyl–carbonyl interactions. For example, six-electron π-donors either

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[1] Part X, T. W. Matheson and B. H. Robinson, *J. Organometallic Chem.*, 1975, **88**, 367.

[2] B. Penfold and B. H. Robinson, *Accounts Chem. Res.*, 1973, **6**, 73.

co-ordinate to one cobalt [3,4] or symmetrically to three cobalt atoms.[5,6] Extension of these studies to dienes has indicated a wider range of reactivity, the diene either co-ordinating to one cobalt atom (when Y = aryl, alkyl, or F) [7,8] or inserting in the apical Y–C linkage [8,9] in reactions related to the CO-insertion reactions widespread in halogenotricobalt carbon chemistry.[10-12] However, a unique reaction occurs with cyclopentadiene to give cyclopentadienyl complexes.

In this paper the physicochemical properties and structures of $[YCCo_3(CO)_7(bhd)]$, $[YCCo_3(CO)_7(chd)]$, and $[YCCo_3(CO)_4(cp)_2]$ derivatives are described.* Pauson and his co-workers reported the preparation of $[PhCCo_3(CO)_7(bhd)]$,[13] while Kamijo *et al.*[8] isolated analogous bhd derivatives and discussed the catalytic dimerization of bhd to Binor S by $[ClCCo_3(CO)_9]$. However, the spectroscopic properties of the bhd complexes described here show significant differences to those reported by the Japanese workers.

RESULTS AND DISCUSSION

Preparation and Reactivity of the Diene Derivatives.—Direct reaction between the tricobalt carbon cluster and the diene (bhd or chd) in a refluxing hydrocarbon, arene, or halogenocarbon solvent (b.p. < 358 K) afforded the dark green complexes $[YCCo_3(CO)_7(diene)]$ (Table 1).

$$[YCCo_3(CO)_9] + \text{diene} \longrightarrow [YCCo_3(CO)_7(\text{diene})] + 2\,CO \quad (Y = \text{alkyl, aryl, or F}) \qquad (1)$$

The crystalline bhd complexes are stable in air and soluble in common organic solvents, but solutions of the complexes decompose rapidly, even under anaerobic conditions and revert to the parent cluster if there is a trace of CO in solution. Maximum stability in solution is found with the aryltricobalt carbon complexes as with the arene [3] and cyclo-octatetraene [5] complexes. The chd derivatives are even more labile and were characterized by mass-spectral analysis as it was not possible to obtain analytically pure crystals.

No comparable derivatives were formed in reactions with cyclo-octadienes, cycloheptadiene, or butadiene nor was it possible to replace the co-ordinated bhd by any of these dienes. In these systems the organic moiety is polymerized and/or carbonylated and the only cobalt-containing products were brown insoluble powders of indefinite composition. In contrast, all the cyclic dienes underwent a facile insertion reaction with $[YCCo_3(CO)_9]$ (Y = H, Cl, or Br); these will be the subject of a later paper.

Addition of phosphines or phosphites to $[PhCCo_3(CO)_7(bhd)]$ resulted in evolution of CO and formation of the complex $[PhCCo_3(CO)_6(PR_3)(bhd)]$ in small yield. The diene is extremely labile and the major products are usually the phosphine or phosphite derivatives, $[PhCCo_3(CO)_8PR_3]$ or (to a lesser extent) $[PhCCo_3(CO)_7(PPh_3)_2]$ [14] and in this respect these reactions are similar to those of $[M(CO)_4(bhd)]$ (M = Cr or Mo).[15] An attempt to prepare $[YCCo_3(CO)_6(PR_3)(bhd)]$ complexes using $[Pt(PR_3)_4]$ failed as did all reactions with fluoro- or methyl-tricobalt carbon derivatives. The lability of the bhd complexes also hindered all attempts to investigate the reactivity of the co-ordinated bhd (see Experimental section).

Structure and Spectroscopic Properties of the Diene Complexes.—An *X*-ray analysis [16] of $[EtCCo_3(CO)_7(bhd)]$ has shown that the chelating bhd co-ordinates to one cobalt atom in the basal triangle with the ring in a *cis–cis* (*cis* with respect to the apical substituent) or equatorial–equatorial orientation, not *cis–trans* as originally proposed (Figure 1).[7] The other diene derivatives presumably have a similar structure. A consistent pattern of ν(CO) bands was observed in the solid and solution, shifts to higher frequency with electron-withdrawing apical substituents being expected from previous work [2,14] (Table 1). In some cases a band at *ca.* 1 970 cm^{-1} was not found in the solution spectrum and a change in the orientation of the diene ring may occur on going from the crystal lattice to solution. This may explain why our i.r. and some ^{1}H n.m.r. data are incompatible with those of Kamijo *et al.*[8] {our i.r. and n.m.r. spectrum of $[PhCCo_3(CO)_7(bhd)]$ is identical to

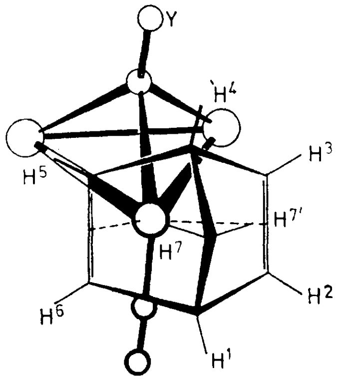

FIGURE 1 Structure of $[YCCo_3(CO)_7(bhd)]$. Six CO groups have been omitted for clarity

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* bhd = Bicyclo[2.2.1]hepta-2,5-diene, chd = cyclohexa-1,3-diene, and cp = η-cyclopentadienyl.

[3] B. H. Robinson and J. Spencer, *J. Chem. Soc.* (*A*), 1971, 2045.

[4] R. J. Dellaca and B. R. Penfold, *Inorg. Chem.*, 1972, **11**, 1855.

[5] B. H. Robinson and J. Spencer, *J. Organometallic Chem.*, 1971, **33**, 97.

[6] M. D. Brice, R. J. Dellaca, B. R. Penfold, and J. L. Spencer, *J.C.S. Chem. Comm.*, 1972, 72.

[7] P. A. Elder and B. H. Robinson, *J. Organometallic Chem.*, 1972, **36**, C45.

[8] T. Kamijo, T. Kitamura, N. Sakamoto, and T. Joh, *J. Organometallic Chem.*, 1973, **54**, 265.

[9] P. Elder, unpublished work.

[10] R. Dolby and B. H. Robinson, *J.C.S. Dalton*, 1972, 2046.

[11] R. Dolby and B. H. Robinson, *J.C.S. Dalton*, 1973, 1794.

[12] R. Dolby, T. W. Matheson, B. K. Nicholson, B. H. Robinson, and J. Simpson, *J. Organometallic Chem.*, 1972, **43**, C13.

[13] I. U. Khand, G. R. Knox, P. L. Pauson, and W. E. Watts, *Chem. Comm.*, 1971, 36.

[14] T. W. Matheson, B. H. Robinson, and W. S. Tham, *J. Chem. Soc.* (*A*), 1971, 1457.

[15] L. K. Atkinson and D. C. Smith, *J. Organometallic Chem.*, 1971, **33**, 189.

[16] B. R. Penfold and N. Y. Sun, personal communication.

Pauson's [13]}, although the ^1H n.m.r. data imply a *cis–cis* orientation in solution for most derivatives (see below).

The ^1H n.m.r. spectra of the bhd complexes varied with both solvent and temperature. Complexes where bhd is acting as a chelate usually exhibit a 4(=CH) : 2($\rangle$CH) : 2($\rangle CH_2$) spectrum and at ambient temperatures the majority of the bhd derivatives did indeed display this profile, irrespective of the solvent used (Table 2). Nonetheless while the alkyltricobalt carbon complexes had a 4 : 2 : 2 profile in C_6D_6 and acetone, a 6 : 2 spectrum was found in $CDCl_3$, CCl_4, and CS_2 over a wide range of solute concentration. A 4 : 2 : 2 profile was regained in these latter solvents at 243 K, or when a 9 : 1 $CDCl_3$–C_6D_6 solvent mixture was used. Other examples of 6 : 2 spectra are known, the accidental degeneracy of the olefinic and bridgehead protons being brought about by a large upfield shift of the olefinic resonance on complex formation.[17] With the tricobalt carbon derivatives, however, the resonance at τ 6.22 is the mean of the olefinic (τ 6.10) and bridgehead (τ 6.33) resonances and it is necessary to postulate an equal but opposite solvent shift for the two types of structurally non-equivalent sets of protons. The unique influence of alkyl substituents does suggest some electronic control but it is difficult to see why or how.

TABLE 1

Carbonyl-stretching bands (cm^{-1}) of bhd, chd, and cp derivatives *

(*a*) [$YCCo_3(CO)_7(bhd)$]						
Y						
Ph	2 076vs	2 030vs	2 026vs	1 993m	1 983mw	
	2 074s	2 029s	2 024ms	1 992mw	1 983w	1 968w
Me	2 074	2 028	2 020	1 994	1 983	
	2 071	2 023	2 018	1 991	1 981	1 969
Et	2 073	2 027	2 020	1 994	1 983	
	2 071	2 024	2 016	1 992	1 981	1 968
F	2 082	2 036	2 029	2 005	1 992	
	2 079	2 032	2 026	2 002	1 991	1 970
$MeCO_2$	2 082	2 040	2 031	2 006	1 996	1 985
	2 090	2 054	2 030	1 997	1 993	1 981
		[2 040 (sh)]				
$EtCO_2$	2 082	2 040	2 031	2 006	1 996	1 985
	2 086	2 032vbr		1 997	1 993	1 981
o-MeC_6H_4	2 073	2 028	2 023	1 992	1 980	
	2 074	2 024vbr		1 991	1 980	1 969
p-MeC_6H_4	2 076	2 029	2 025	1 993	1 983	
	2 076	2 024		1 999	1 989	1 980
m-MeC_6H_4	2 075	2 030	2 025	1 993	1 982	
	2 074	2 026	2 007	1 994	1 991	1 980
p-$MeOC_6H_4$	2 075	2 029	2 024	1 992	1 981	
	2 076	2 028	2 010	1 998	1 990	1 980
(*b*) [$PhCCo_3(CO)_6(PPh_3)(bhd)$]						
	2 054m	2 030w	1 993ms			
(*c*) [$YCCo_3(CO)_7(chd)$]						
Y						
Ph	2 060vs	2 032s, br	1 996m	1 991mw		
Me	2 060	2 022	1 999	1 995		
Et	2 058		2 006	2 000		
(*d*) [$YCCo_3(CO)_4(cp)$]						
Y						
Ph	2 046vs	2 002vs	1 988vs	1 799s		
Me	2 044	1 999	1 981	1 796		
Et	2 042	1 998	1 980	1 794		
F	2 045	1 999	1 981	1 794		
H	2 052	1 999	1 989	1 795		
o-ClC_6H_4	2 056	2 002	1 992	1 803		
o-BrC_6H_4	2 058	2 002	1 992	1 808		
$C_{10}H_7$	2 054	1 999	1 992	1 805		
PhC_6H_4	2 053	1 998	1 991	1 805		
(*e*) [$YCCo_3(CO)_3(cp)_2PR_3$]						
Y	R					
Ph	Ph	1 994vs	1 951vs	1 757s		
	C_6H_{11}	1 987	1 942	1 746		
	Ph_2Me	1 989	1 946	1 750		
Me	Ph	1 991	1 947	1 750		
Et	Ph	1 986	1 940	1 735		

* In hexane, ±1 cm^{-1}. Relative intensities are given for the first member of each series unless otherwise stated.

The temperature dependence of the spectra show clearly that the bhd ligand is non-rigid. With a *cis–cis* orientation of the diene the bridgehead protons become magnetically non-equivalent, H^1 being in close proximity to an axial carbonyl group whereas H^4 is directed toward

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[17] M. L. H. Green, L. Pratt, and G. Wilkinson, *J. Chem. Soc.*, 1960, 989.

the apical substituent (Figure 1). In all limiting spectra observed the bridgehead resonance was indeed split but further complications arise because of accidental coincidence of olefinic and bridgehead resonances (Table 2). Thus at 223 K the spectra of [$YCCo_3(CO)_7(bhd)$] (Y = Ph or Me) exhibited a 2 : 3 : 1 : 2 pattern implying that resonances due to two equivalent olefinic protons (either $H^{2,6}$ or $H^{3,5}$) and one bridgehead proton (either H^1 or H^4) are accidentally degenerate. This simplifies the expected 2 : 2 : 1 : 1 : 2 profile. An identical pattern was found for the anion [$RuX_3(CO)(bhd)$]$^-$ in which there is a similar bhd configuration.[18] The limiting spectrum varied with the apical substituent, the respective profiles being 4 : 1 : 1 : 2 and 5 : 1 : 2 when Y = CO_2R and F.

Collapse and coalescence of the individual olefinic and bridgehead resonances at higher temperatures led eventually to the 4 : 2 : 2 pattern. It is suggested that equivalence of the bridgehead protons is achieved by flipping or rotation of the bhd moiety about the Co–bhd axis or by rotation *via* a *cis–trans* configuration (Figure 2). Local rotation of carbonyl groups about one cobalt atom has been established for the phosphine complexes [$YCCo_3(CO)_8PR_3$].[1] The ^1H n.m.r. spectrum of [$PhCCo_3(CO)_7(chd)$] supports the proposed structure with broad unresolved peaks centred at τ 4.5, 6.5, and 7.88.[19]

TABLE 2

^1H N.m.r. data (τ) for bhd and cp complexes [a]

(*a*) [$YCCo_3(CO)_7(bhd)$] [b]

	T/K						
Y	293	273	263	253	243	233	223
Ph	6.22(4)	6.24(4)	6.76(4)	*c*	6.03(2)	6.03(2)	6.01(2)
	6.90(2)	6.90(2)		*c*	6.46(3)	6.46(3)	6.46(3)
	9.13(2)	9.13(2)	9.13(2)	9.13(2)	7.25(1)	7.25(1)	7.25(1)
					9.12(2)	9.12(2)	9.12(2)
Me	6.22(6)	6.22(6)		*c*	6.14(4)	6.10	6.05(2)
	8.95(2)	8.95(2)		*c*	6.29(2)	6.33	6.27(3)
				8.95	8.95(2)	8.95	6.65(1)
							8.95(2)
Et	6.24(6)	6.23(6)	6.23(8)	6.21(6)	6.16(4)	6.14(4)	6.12(5)
	8.96(2)	8.95(2)	8.95(2)	8.95(2)	6.28(2)	6.32(2)	6.32(1)
					8.95(2)	8.95(2)	8.95(2)
F	5.95(4)	6.93(4)	6.93(6)	*c*	5.94(5)	5.94(5)	5.95(5)
	6.30(2)	6.30(2)	6.25(2)	*c*	6.47(1)	6.46(1)	6.46(1)
	8.95(2)	8.95(2)	8.95(2)	8.95(2)	8.93(2)	8.93(2)	8.94(2)
$MeCO_2$	5.89(4)	5.90(4)	5.89(4)	5.89(4)	5.89(4)	5.89(4)	5.89(4)
	6.33(2)	*c*	6.25(1)	6.24(1)	6.24(1)	6.27(1)	6.25(1)
	8.92(2)	*c*	6.39(1)	6.40(1)	6.39(1)	6.39(1)	6.39(1)
		8.92(2)	8.91(2)	8.90(2)	8.89(2)	8.89(2)	8.89(2)
$EtCO_2$	5.88(4)	5.89(4)	*c*	5.89(4)	5.89(4)	5.89(4)	5.89(4)
	6.33(2)	6.32(2)	*c*	6.19(1)	6.20(1)	6.20(1)	6.20(1)
	8.92(2)	8.92(2)	8.92(2)	6.41(1)	6.40(1)	6.40(1)	6.39(1)
				8.90(2)	8.90(2)	8.90(2)	8.89(2)

(*b*) [$YCCo_3(CO)_7(bhd)$] at 293 K

Y	*o*-MeC_6H_4	*m*-MeC_6H_4	*p*-MeC_6H_4	*p*-$MeOC_6H_4$
	$\left.\begin{matrix}2.65\\2.78\end{matrix}\right\}4$	$\left.\begin{matrix}2.22\\2.63\end{matrix}\right\}4$	$\left.\begin{matrix}2.08\\2.15\\2.76\end{matrix}\right\}4$	2.06(2) 2.86(3) 6.06(3)
	6.19(4)	6.23(4)	6.25(4)	6.24(4)
	6.86(2)	6.87(2)	6.86(2)	6.86(2)
	7,18(3)	7.53(3)	7.59(3)	9.14(2)
	9.11(2)	9.13(2)	9.15(2)	
Y	Me [d]	Me [e]	Me [f]	Et [d]
	5.61(3)	5.17(3)	5.47(3)	5.27(2)
	6.69(4)	5.97(4)	6.50(4)	6.62(4)
	7.04(2)	6.87(2)	6.60(2)	7.00(2)
	9.19(2)	9.10(2)	9.20(2)	8.17(3)
				9.03(2)

(*c*) [$YCCo_3(CO)_4(cp)_2$] at 293 K [g]

Y	Ph	Me	PhC_6H_4	$C_{10}H_7$
	$\left.\begin{matrix}2.30\\2.66\end{matrix}\right\}5$	5.32(3)	$\left.\begin{matrix}2.34\\2.53\end{matrix}\right\}9$	$\left.\begin{matrix}2.10\\2.47\\2.75\end{matrix}\right\}7$
	5.32(10)	5.23(10)	5.30(10)	5.43(10)

[a] Relative to $SiMe_4$ in $CDCl_3$ unless otherwise stated. Intensities are given in parentheses. [b] Apical Y resonances have been omitted for clarity in this section. [c] Collapse of the resonances at higher temperatures occurred. [d] In C_6D_6. [e] In $(CD_3)_2CO$. [f] In $CDCl_3$–C_6D_6 (4 : 1). [g] Temperature invariant.

Organic Products formed in bhd Reactions with Tricobalt Carbon Clusters.—Thermolysis of [$YCCo_3(CO)_7(bhd)$] derivatives or reaction of alkyl or aryltricobalt carbon clusters with bhd in high-boiling solvents, *e.g.* n-octane, resulted in insoluble cobalt residues and form-

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[18] T. A. Stephenson, E. S. Swilkes, and L. R. Ramirez, *J.C.S. Dalton*, 1973, 2113.

[19] E. O. Fischer and H. Werner, 'Metal π-Complexes,' Elsevier, Amsterdam, 1966.

ation of a number of organic products, (I)—(VI). Dimer (I), the *exo–trans–exo* isomer, is one of the most abundant isomers produced in dimerization reactions catalysed by transition-metal complexes,[20] and is the major organic product in all [$YCCo_3(CO)_7(bhd)$] decomposition processes. The *exo–trans–endo* isomer, (II), is also found to be a major product, together with dimeric ketone (VI), identical to that isolated by Cookson and his co-workers.[21]

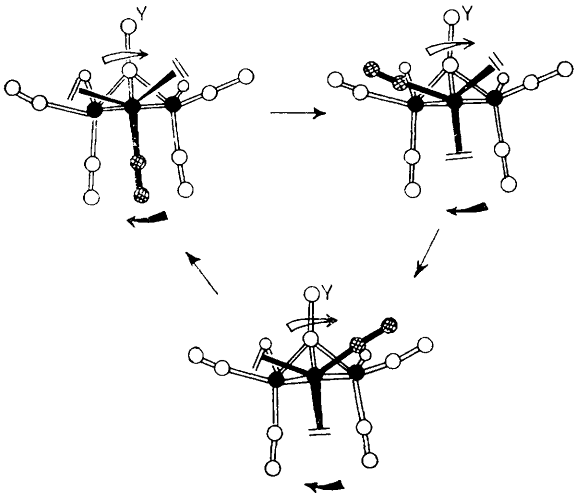


FIGURE 2 Possible mechanism leading to equivalence of bridgehead protons

Oligomerization of bhd in these reactions is therefore not stereospecific and this is in complete contrast to the specific catalytic dimerization to the *endo–cis–endo* isomer [Binor S, (VII)] under the influence of [$YCCo_3(CO)_9$] (Y = Br or Cl) which has been independently investigated by Kamijo *et al.*[8] The observation that Binor S is never found in bhd reactions with alkyl- or aryl-tricobalt carbon clusters gives credence to the mechanism for its selective formation proposed by Schrauzer,[22] the so-called ' π-multicentre reaction ' concept. Contrary to Kamijo *et al.*[8] we believe that this concept is applicable to catalysis by [$ClCCo_3(CO)_9$]. The crucial step is insertion of the diene at the apical position for which there is ample evidence for bhd and other dienes. Co-ordination of the second mole of diene to one cobalt atom then places the two molecules in a comparable configuration to that postulated by Schrauzer.[22] Further support for this mechanism comes from the observation [23] that the rate of Binor S formation is accelerated by the addition of Lewis acids like $AlCl_3$ which are known to attack the apical C–Cl bond.[11] The rate law is also consistent with the proposed mechanism.[23]

The lack of Binor S non-stereospecific oligomerization of bhd in reactions with alkyl- or aryl-tricobalt carbon clusters is then readily understood as insertion of the diene at the apical position is not possible. Moreover, in this case the rate of formation, or type of dimeric or trimeric products, is not altered by the presence of Lewis acids.

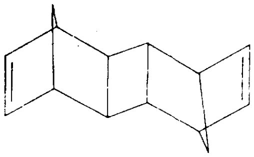
Cyclopentadienyl Derivatives.—The dark green air-stable cp derivatives [$YCCo_3(CO)_4(cp)_2$] (Y = alkyl, aryl, or F) were prepared by two routes in *ca.* 25% yield (Table 1). These are the only known examples where

$$[YCCo_3(CO)_9] + C_5H_6 \xrightarrow{\text{thf}} [YCCo_3(CO)_4(cp)_2] \quad (2)$$

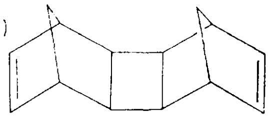
$$[YCCo_3(CO)_9] + Na(cp) \xrightarrow{\text{thf}} [YCCo_3(CO)_4(cp)_2] \quad (3)$$

two organic moieties are co-ordinated to the tricobalt-carbon cluster.

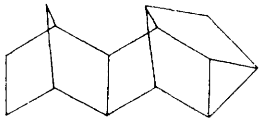
The spectroscopic data in solution (Table 1) are consistent with the solid-state configuration (Figure 3).[24] A unique structural feature is the bridging carbonyl group which is at 90° to the basal cobalt plane, a hitherto unknown conformation in triangular or tetrahedral carbonyl clusters. This gives rise to a very low ν(CO) at *ca.* 1 795 cm^{-1} compared to other bridged tricobalt carbon clusters, and electrophiles such as $AlBr_3$ rapidly



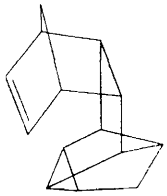
exo-trans-exo diene, (I)



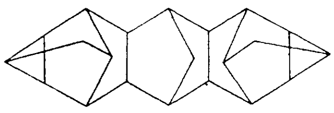
exo-trans-endo diene,(II)



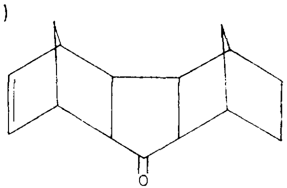
Dimer (III)



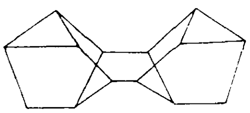
Dimer (IV)



Trimer (V)



exo-trans-exo ketone, (VI)



Binor S, (VII)

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[20] G. N. Schrazuer, *Adv. Catalysis*, 1968, **18**, 373.

[21] C. W. Bird, R. C. Cookson, and J. Hudec, *Chem. and Ind.*, 1960, 20.

[22] G. N. Schrauzer, B. N. Bastion, and G. N. Fosselius, *J. Amer. Chem. Soc.*, 1966, **88**, 4890.

[23] J. Howells and M. Mays, personal communication.

[24] B. R. Penfold and R. S. McCallium, personal communication.

attack the nucleophilic carbonyl oxygen[25] to give unstable complexes of the type $[YCCo_3(CO)_3(cp)_2(\mu\text{-}CO)(AlBr_3)]$. It is worth noting that a carbonyl-bridged configuration is necessary in order to satisfy the electronic requirements of the cobalt atoms but a configuration in which the bridged carbonyl group is in the basal cobalt plane would result in prohibitive intramolecular ring–CO interaction.

Labile phosphine derivatives $[YCCo_3(CO)_3(cp)_2PR_3]$ were isolated and by analogy with the $[YCCo_3(CO)_8PR_3]$ structures[26] it is suggested that the phosphine is co-ordinated in an equatorial configuration. There was a marked shift of the bridging-carbonyl absorption in the phosphine derivatives to lower frequencies, as expected. Steric congestion in the $[YCCo_3(CO)_3(cp)_2PR_3]$ clusters presumably accounts for the lability of the phosphine ligand and why it is not possible to prepare complexes of the type $[YCCo_3(CO)_2(cp)_2(diene)]$.

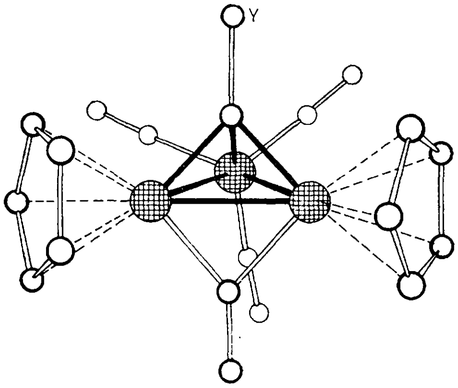

FIGURE 3 Structure of $[YCCo_3(CO)_4(cp)_2]$

It was of interest to examine the reactivity of the cp ring in such a congested environment but all attempts to acetylate, formylate, *etc.* the ring failed, although it was possible to acetylate the apical aryl group of $[PhCCo_8(CO)_4(cp)_2]$ to give $[p\text{-}ROCC_6H_4CCo_3(CO)_4(cp)_2]$. The failure to substitute on the ring is probably due to steric congestion (particularly from the axial CO and apical substituent) preventing electrophilic attack at the metal atom, which may well be the initial step in electrophilic reactions of this type, or direct attack on the ring.[27]

Conclusion.—In general diene and triene complexes of tricobalt carbon clusters are extremely labile and difficult to characterize at ambient temperatures. This is undoubtedly a consequence of the steric congestion in the clusters and it seems that the bhd geometry gives the ' best fit '. Larger cyclic dienes such as cyclo-octadiene cannot adopt the alternative less-congested configuration open to large cyclic trienes,[6] namely to co-ordinate symmetrically to two cobalt atoms beneath the basal cobalt triangle, and do not give cluster products. The polymerization and/or carbonylation of dienes that takes place in these reactions with large ring systems is probably caused by cobalt residues resulting from decomposition of the cluster.[8] Formation of cp derivatives from cyclopentadiene may also reflect the instability of diene complexes and it is suggested that a $[YCCo_3(CO)_9]$ cluster acts as the base to remove the proton.

The $YCCo_3$ unit is a delocalized system[2] and clearly electron-withdrawing apical groups such as Ph should stabilize a diene complex as is observed. Insertion of the diene into the apical C–Y bond only occurs when Y is chlorine, bromine, or an acidic hydrogen atom and the reason for this will be discussed in a subsequent paper.

EXPERIMENTAL

All reactions and manipulations were carried under nitrogen using dry solvents. The methylidynetricobalt enneacarbonyls were prepared by published procedures[13] and purified by vacuum sublimation or recrystallization; the phosphines and dienes were commercial reagents.

I.r., mass, and ^1H n.m.r. spectra were recorded on Perkin-Elmer 225, Varian CH-7, and Varian HA 100 spectrometers respectively. Analyses and yields are given in Table 3.

TABLE 3

bhd and cp derivatives

	Analysis(%)				
	Found		Calc.		
Compound *	C	H	C	H	Yield (%)
$[YCCo_3(CO)_7(bhd)]$					
Ph	45.5	2.40	45.5	2.35	60
Me	39.25	2.30	39.0	2.25	60
Et	40.55	2.95	40.3	2.55	85
F	36.0	1.85	36.3	1.60	25
$MeCO_2$	38.75	2.35	38.05	2.05	20
$EtCO_2$	39.5	2.45	39.25	2.35	20
$o\text{-}MeC_6H_4$	46.45	3.00	46.5	2.65	20
$m\text{-}MeC_6H_4$	46.95	2.85	46.5	2.65	10
$p\text{-}MeC_6H_4$	46.5	2.80	46.5	2.65	15
$p\text{-}MeOC_6H_4$	46.45	3.10	45.2	2.55	20
$[YCCo_3(CO)_4(cp)_2]$					
Ph	50.3	3.25	49.6	2.95	
Me	43.25	3.15	43.05	2.90	
$C_{10}H_7$	60.4	4.95	53.75	3.05	
$C_{12}H_{10}$	59.1	4.40	55.5	3.25	

* All compositions were confirmed by mass-spectral analysis.

Preparation of Bicyclo[2.2.1]*hepta-2,5-diene Derivatives.*—The following is a typical preparation. The cluster $[PhCCo_3(CO)_9]$ (0.1 g, 0.19 mol) was dissolved in benzene (15 cm^3) and the solution brought to the boil. Excess of bhd (3 cm^3) was then added and the solution heated under reflux for 4 h. The solution was filtered and the solvent and unchanged bhd removed under reduced pressure. Adsorption of the residue, dissolved in hexane (5 cm^3), on preparative silica-gel plates and development in hexane gave two major bands, one due to unchanged $[PhCCo_3(CO)_9]$ and the other dark green band to the product, $[PhCCo_3(CO)_9(bhd)]$. The second band was removed, eluted with diethyl ether, the ether removed *in vacuo*, and the residue recrystallized from hexane at 263 K. The product was obtained as dark green glistening needles, yield 0.065 g (60%). It had similar physicochemical properties to the compound described by Kamijo *et al.*[8] except for the spectroscopic data.

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[25] *Cf.* J. S. Kristoff and D. F. Schriver, *Inorg. Chem.*, 1974, **13**, 499.

[26] M. D. Brice, B. R. Penfold, W. T. Robinson, and S. R. Taylor, *Inorg. Chem.*, 1970, **9**, 362.

[27] H. L. Lentzner and W. E. Watts, *Tetrahedron*, 1972, **28**, 121.

Other bhd compounds were prepared by this procedure. A change from hexane to benzene or dichloromethane did not affect the yield although the maximum yield of $[FCCo_3(CO)_7(bhd)]$ was obtained in diethyl ether.

Reaction of Phosphines and Electrophiles with $[YCCo_3(CO)_7(bhd)]$ *Complexes.*—Triphenylphosphine (0.047 g, 0.18 mmol) was added to a solution of $[PhCCo_3(CO)_7(bhd)]$ (0.10 g, 0.18 mmol) in hexane (10 cm^3) and the solution stirred for 2 h, after which time a black crystalline solid had precipitated. This hexane-insoluble product was collected and dissolved in chloroform and absorbed on preparative silica-gel plates. Development in diethyl ether–hexane (1 : 9) gave two bands, the first due to $[PhCCo_3(CO)_8PPh_3]$ (identified by i.r. spectroscopy[13]) and the second to $[PhCCo_3(CO)_6(PPh_3)(bhd)]$. The latter was crystallized in the usual way but chemical and mass-spectral analysis and t.l.c. spot checks showed that traces of $[PhCCo_3(CO)_8PR_3]$ were also present. The best analysis was on the product which precipitated from solution [Found: C, 57.9; H, 3.65%; *M* (in $CHCl_3$) 829. $C_{38}H_{28}Co_3O_6P$ requires C, 57.8; H, 3.55%; *M* 788].

Reactions with more basic phosphine or alkyl phosphites invariably gave high yields of the complexes $[YCCo_3(CO)_8L]$, and with $EtPh_2P$ $[PhCCo_3(CO)_7(PEtPh_2)]$, which were identified by their i.r. spectra.[13] However, the i.r. spectra of the reaction solutions showed that the complexes $[PhCCo_3(CO)_6L(bhd)]$ were formed in small amounts but pure crystalline products could not be isolated. Other bhd complexes with alkyl apical substituents gave the complexes $[YCCo_3(CO)_8L]$. The reverse reaction, $[PhCCo_3(CO)_8PPh_3]$ with bhd, gave small amounts of $[PhCCo_3(CO)_7(bhd)]$ but no mixed bhd–phosphine complexes.

The bhd complexes dissolve in trifluoroacetic acid with gas evolution and an immediate colour change from dark green to brown due to formation of $[YCCo_3(CO)_9H]^+$.[11] Addition of concentrated aqueous solutions of $[NH_4][PF_6]$ precipitated the neutral cluster $[YCCo_3(CO)_9]$. In an attempt to formylate the ring,[28] $[PhCCo_3(CO)_7(bhd)]$ (0.1018 mmol) in dichloromethane (10 cm^3) was cooled to 273 K and $TiCl_4$ (0.03 mmol) added dropwise over 1 min. Dichloromethyl methyl ether (0.015 mmol) was then added dropwise over 15 min and the solution brought to 298 K and stirred for 45 min before being poured into crushed ice (5 cm^3). The colour immediately changed from black to brown with formation of $[PhCCo_3(CO)_9]$.

Organic Products formed during the Preparation and Decomposition of bhd Complexes.—The cluster $[PhCCo_3(CO)_9]$ (0.11 g, 0.19 mmol) and bhd (3 cm^3) were dissolved in n-octane and the solution heated under reflux for 1 h. T.l.c. and i.r. analysis showed that there was no cobalt-containing material in solution so the solvent was stripped under reduced pressure. Purification on silica-gel FP_{254} plates–hexane followed by fractional sublimation gave: (I) [Found: C, 90.6; H, 8.60%; *M* 184 (molecular ion). Calc. for $C_{14}H_{16}$: C, 91.3; H, 8.70%], m.p. 338 K (uncorrected), ^1H n.m.r. τ 8.80 (*anti*-CH_2), 8.66 (ring), 8.32 (*syn*-CH_2), 7.39 (–CH), and 3.99 (=CH); (II), oil identified by mass-spectral analysis, molecular ion 184, ν(C=C) at 1 510 cm^{-1}; (V), m.p. 447 K (uncorrected), molecular ion 276, strong band at 810 cm^{-1} in i.r. spectrum (nortricyclene absorption), no band between 1 700 and 1 500 cm^{-1}; (VI), m.p. 354 K (uncorrected), molecular ion 212, ν(C=O) at 1 730, ν(C=C) at 1 570 cm^{-1}; and (VII), molecular ion 228, ν(C=O) at 1 730, ν(C=C) at 1 570 cm^{-1}, ^1H n.m.r. τ 3.99 (intensity 2), 4.08(2), 7.39(4), 7.87(2), 8.10(1), 8.76(4), and 8.75(r). Exactly the same products were found with other clusters $[YCCo_3(CO)_9]$ (Y = F, alkyl, or aryl) when various amounts of $AlCl_3$ were added to the reaction solutions and when the complexes $[YCCo_3(CO)_7(bhd)]$ were heated above 353 K *in vacuo*. The cobalt residues appeared to be mainly cobalt metal and cobalt oxides. When $[ClCCo_3(CO)_9]$ or $[BrCCo_3(CO)_9]$ was substituted for the alkyl or aryl clusters Binor S was the only organic product; this is fully described by Kamijo *et al.*[8]

Preparation and Reactions of cp Derivatives.—The cluster (0.4 mmol) was dissolved in thf (26 cm^3) and the solution brought to the boil. Freshly distilled cyclopentadiene (2 cm^3) was then added and the solution heated under reflux for 4 h. The solvent was removed *in vacuo* and the resulting dark brown oil purified by chromatography on silica-gel plates developed in hexane. The second band was removed, eluted, and the product crystallized from hexane to give fine green needles of the complex $[YCCo_3(CO)_4(cp)_2]$.

The crystalline complexes are stable in air for long periods and dissolve in all common organic solvents Decomposition to $[YCCo_3(CO)_9]$ and insoluble material rapidly occurs in solution except at low temperatures. The complexes were also prepared from Na(cp) at 293 K in thf; work-up was identical to that described above. The other product was $[(YCCY)Co_4(CO)_{10}]$ and yields were lower than obtained by using C_5H_6.

Reactions. (a) Phosphines were treated with $[PhCCo_3(CO)_4(cp)_2]$ using the same procedure outlined for the bhd complexes except that the silica-gel plates were developed in benzene–hexane (1 : 1). In one or two cases black crystals were obtained but usually the phosphine derivatives came out of solutions as oils, which is reflected in the poor analytical figures {$[YCCo_3(CO)_3(cp)_2PR_3]$ (Y = Ph, R = Ph). Found: C, 61.45; H, 4.05. Calc.: C, 61.75; H, 4.25. Y = Ph, R_3 = $MePh_2$. Found: C, 61.45; H, 6.25. Calc.: C, 58.25; H, 6.30. Y = Ph, R = C_6H_{11}. Found: C, 57.1; H, 6.50. Calc.: C, 40.0; H, 6.30. Y = Et, R = Ph. Found: C, 65.35; H, 6.10. Calc.: C, 58.8; H, 4.32%}.

(b) A slurry of $AlCl_3$ (0.15 mmol) in dichloromethane (50 cm^3) was cooled to 273 K and acetyl chloride (0.5 mmol) added. The slurry was stirred for 10 min after which time $[PhCCo_4(CO)_4(cp)_2]$ (0.15 mmol) in dichloromethane (50 cm^3) was slowly added. The solution was stirred at 273 K for 15 min and at 293 K for 2 h and then poured into water. The dichloromethane layer was separated and the aqueous layer extracted with dichloromethane. Solvent was stripped from the combined dichloromethane solutions and the residue crystallized from hexane to give dark green crystals of $[MeCO{\cdot}C_6H_4CCo_3(CO)_4(cp)_2]$ (Found: C, 50.4; H, 3.35%; *M* 550. $C_{23}H_{17}Co_3O_5$ requires C, 50.2; H, 3.10%; *M* 550), ν(CO) at 2 052, 1 999, 1 991, and 1 805 cm^{-1}.

Another procedure for acetylation of cp rings using acetic anhydride and H_3PO_4 was followed but no carbonyl compound could be isolated.

(c) The procedure and apparatus for reaction with $AlBr_3$ was essentially that described by Kristoff.[25] A black precipitate was observed as soon as toluene solutions of $AlBr_3$ and $[PhCCo_3(CO)_9]$ came in contact but within 2 min this had completely changed to a green colour and the solid contained no ν(CO) bands. All attempts to isolate a pure sample of the black precipitate were unsuccessful. However, the ν(CO) bands of this precipitate were only shifted by

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[28] T. E. Graf and C. P. Lillya, *J.C.S. Chem. Comm.*, 1973, 271.

ca. 5 cm^{-1} to lower frequency compared to those of $[PhCCo_3(CO)_4(cp)_2]$ showing that the tricobalt carbon unit is retained. Very small shifts in ν(CO) bands have been noted for some other clusters where there are no bridging CO groups when $AlBr_3$ is co-ordinated [25] and there is the possibility, albeit unlikely, that $AlBr_3$ is actually attacking a terminal CO.

Reaction of Other Dienes with $[PhCCo_3(CO)_9]$.—Cycloocta-1,5-diene, butadiene, cycloheptadiene, and cyclohexa-1,3- and -1,4-diene were treated with $[PhCCo_3(CO)_9]$ under the same conditions described above for bhd. Only with the cyclohexadienes was there i.r. evidence for formation of a hexane-soluble product, but decomposition of the cyclohexadiene complexes was rapid on silica-gel plates and it was not possible to obtain crystalline products free from $[PhCCo_3(CO)_9]$. Mass-spectral analysis established the complex as $[PhCCo_3(CO)_7(chd)]$, molecular ion 554, followed by successive loss of seven CO groups to the ion $[PhCCo_3(C_6H_8)]^+$. Two secondary fragmentation patterns were observed, one involving loss of cobalt as for $[YCCo_3(CO)_9]$ the other ring fission, identical to that found in the mass spectrum of $[Fe(CO)_3(chd)]$.

No cobalt-containing products were found in reactions with the other dienes which were soluble in organic solvents. The organic products will be described elsewhere.

We thank the New Zealand Grants Committee for support, the University of Otago for the award of a Senior Demonstratorship (to P. E.), and Professor P. L. Pauson (University of Strathclyde) and Dr. M. Mays for communicating unpublished work and for helpful discussions.

[4/2563 *Received, 9th December,* 1974]