Linked arene clusters: the interaction of tetracobalt nonacarbonyl with [2.2.2]paracyclophane

Paul Schooler,[a] Brian F. G. Johnson,*[a]† Caroline M. Martin,[a] Paul J. Dyson[b] and Simon Parsons[c]

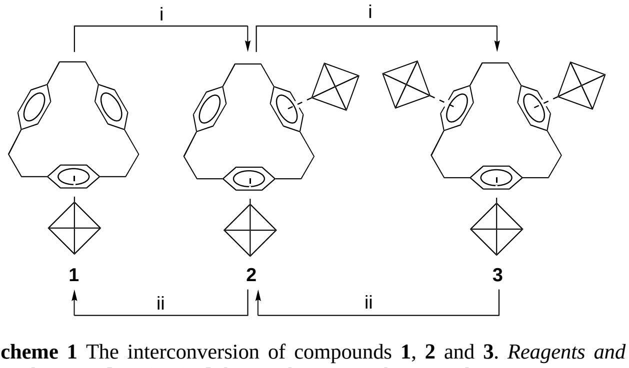
[a] *University Chemical Laboratory, Lensfield Road, Cambridge, UK CB2 1EW*
[b] *Department of Chemistry, Imperial College of Science, Technology and Medicine, South Kensington, London, UK SW7 2AY*
[c] *Department of Chemistry, University of Edinburgh, West Mains Road, Edinburgh, UK EH9 3JJ*

The thermolysis of [2.2.2]paracyclophane in the presence of an excess of $[Co_4(CO)_{12}]$ yields three new arene clusters $[\{Co_4(CO)_9\}_n(C_{24}H_{24})]$ (n = 1, 2 and 3): the molecular structures of the mono- and bis-cluster complexes have been established by single crystal X-ray diffraction while the tris-complex has been characterised by spectroscopy.

The interaction of the $[2_n]$cyclophanes with transition and main group metals has received much attention since their conception by Cram several decades ago.[1] These complexes were initially used to probe the unusual electronic properties of the $[2_n]$cyclophane ligands, which stem from the interpenetration of arene π molecular orbitals, giving rise to unusual and unique effects.[2] More recently, interest has been stimulated by the potential for the $[2_n]$cyclophane ligands to serve as bridging units between metal centres in organometallic polymers and networks which should have interesting electrical and non-linear optical properties.[3]

Metal atoms and ions may bond to [2.2.2]paracyclophane by either endo- or exo-coordination. In the former the metal atom resides in or near the ligand cavity such as in the π cryptates formed with gallium(I) and silver(I) salts[4] while in the latter the metal atom interacts with the external face of the aromatic rings as in the piano-stool complexes formed with $[M(CO)_3]$ (M = Cr, Mo or W) fragments.[5] There are few reports concerning the coordination of more than one metal atom to [2.2.2]paracyclophane; only recently has diffraction data become available for the mono- and bis-$[Cr(CO)_3]$ complexes,[6] and structural data for the tris-chromium tricarbonyl has not yet been obtained. Here, we report the molecular structure of the complexes $[Co_4(CO)_9(\eta\text{-}C_{24}H_{24})]$ **1** and $[\{Co_4(CO)_9\}_2(\eta:\eta\text{-}C_{24}H_{24})]$ **2** in which one and two of the C_6-rings of [2.2.2]paracyclophane are coordinated to $[Co_4(CO)_9]$ cluster units respectively. Spectroscopic characterisation of the tris-$[Co_4(CO)_9]$ complex, $[\{Co_4(CO)_9\}_3(\eta:\eta:\eta\text{-}C_{24}H_{24})]$ **3**, is also reported. These latter two compounds represent the first examples of clusters linked *via* a cyclophane ligand.

The thermolysis of [2.2.2]paracyclophane with 10 molar equiv. of $[Co_4(CO)_{12}]$ in hexane under reflux over 5 h affords three new complexes $[Co_4(CO)_9(\eta\text{-}C_{24}H_{24})]$ **1** (20%), $[\{Co_4(CO)_9\}_2(\eta:\eta\text{-}C_{24}H_{24})]$ **2** (2%) and $[\{Co_4(CO)_9\}_3(\eta:\eta:\eta\text{-}C_{24}H_{24})]$ **3** (*ca.* 0.1%) which were separated by thin layer chromatography on silica using dichloromethane–hexane (1:3 v/v) as the eluent. These complexes can be conveniently interconverted (Scheme 1) by either adding cluster units to compounds **1** and **2** by thermolysis with $[Co_4(CO)_{12}]$ in hexane or by the thermolysis of compounds **2** and **3** in toluene whereby cluster units are removed from the cyclophane ligand *via* arene exchange. The molecular structures of compounds **1** and **2** are shown in Figs. 1 and 2, respectively. In both molecules the coordinated rings of the cyclophane ligands lie parallel to, and staggered with respect to, the metal triangle defined by Co(2)Co(3)Co(4). The cobalt–ring carbon distances indicate that the coordinated rings are not planar as the average distances involving the bridgehead carbon atoms are slightly longer than the remaining four carbon atoms [*cf.* 2.174(6) and 2.107(8) Å in **1** and 2.174(5) and 2.120(12) Å in **2**]. Although the coordinated rings of the cyclophane in both compounds are expanded owing



Scheme 1 The interconversion of compounds **1**, **2** and **3**. *Reagents and Conditions* i, $[Co_4(CO)_{12}]$, heat in hexane; ii, heat in toluene.

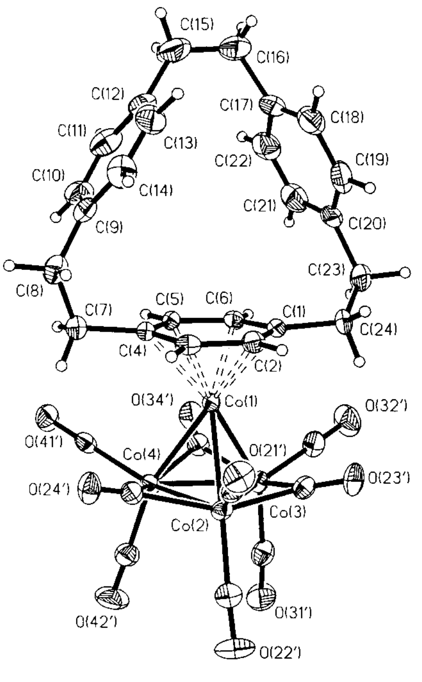


Fig. 1 The molecular structure of $[Co_4(CO)_9(\eta\text{-}C_{24}H_{24})]$ **1**. Important bond lengths (/Å): Co(1)–Co(2) 2.4614(13), Co(1)–Co(3) 2.4823(11), Co(1)–Co(4) 2.4626(10), Co(2)–Co(3) 2.4823(11), Co(2)–Co(4) 2.4740(12), Co(3)–Co(4) 2.4552(11), Co(1)–C(1) 2.175(4), Co(1)–C(2) 2.131(4), Co(1)–C(3) 2.103(4), Co(1)–C(4) 2.172(4), Co(1)–C(5) 2.115(4), Co(1)–C(6) 2.095(4), C(1)–C(2) 1.402(6), C(1)–C(6) 1.408(5), C(2)–C(3) 1.397(6), C(3)–C(4) 1.397(5), C(4)–C(5) 1.400(5), C(5)–C(6) 1.405(5), C(9)–C(10) 1.363(7), C(9)–C(14) 1.362(6), C(10)–C(11) 1.376(7), C(11)–C(12) 1.367(7), C(12)–C(13) 1.371(7), C(13)–C(14) 1.367(7), C(17)–C(18) 1.369(7), C(17)–C(22) 1.366(7), C(18)–C(19) 1.394(7), C(19)–C(20) 1.390(7), C(20)–C(21) 1.359(7), C(21)–C(22) 1.341(7), average C–O (terminal) 1.133(12) and average C–O (bridging) 1.164(8).

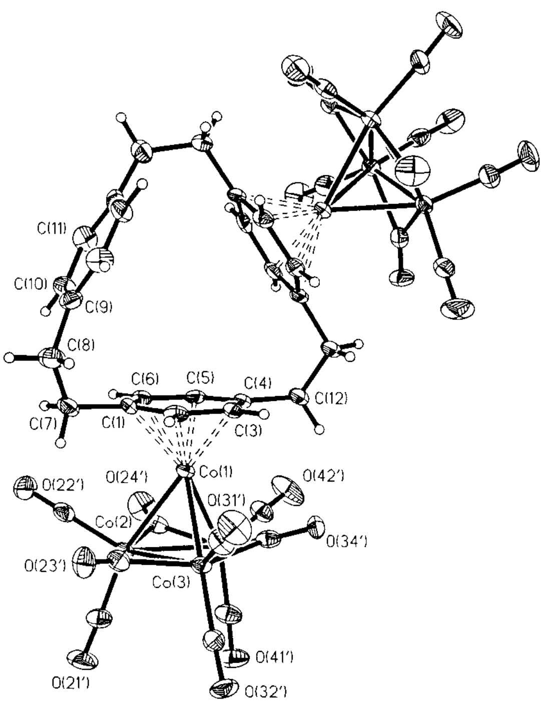


Fig. 2 The molecular structure of $[\{Co_4(CO)_9\}_2(\eta\text{-}C_{24}H_{24})]$ **2**. Important bond lengths (/Å): Co(1)–Co(2) 2.5078(12), Co(1)–Co(3) 2.4646(12), Co(1)–Co(4) 2.4758(12), Co(2)–Co(3) 2.4628(13), Co(2)–Co(4) 2.4413(14), Co(3)–Co(4) 2.4513(13), Co(1)–C(1) 2.166(7), Co(1)–C(2) 2.104(6), Co(1)–C(3) 2.141(6), Co(1)–C(4) 2.179(6), Co(1)–C(5) 2.111(6), Co(1)–C(6) 2.122(6), C(1)–C(2) 1.396(10), C(1)–C(6) 1.398(10), C(2)–C(3) 1.409(10), C(3)–C(4) 1.408(11), C(4)–C(5) 1.429(11), C(5)–C(6) 1.387(10), C(9)–C(10) 1.346(11), C(10)–C(11) 1.389(11), average C–O (terminal) 1.13(2) and average C–O (bridging) 1.173(16).

to the electron-withdrawing nature of the cluster [*cf.* average C–C distances of 1.401(13) and 1.37(2) Å in **1** and 1.40(2) and 1.36(3) Å in **2**], little significance can be placed upon this observation owing to the magnitude of the electron shift densities. It should be noted that the cyclophane ligand in compound **1** is much less symmetrically coordinated than in **2**; this is reflected in the dihedral angles made between the bow and stern of the C_6 rings of 5.9° (coordinated), 2.8 and 0.9° while the ethano bridge C(15)–C(16) lies some 2.17 Å out of the plane defined by Co(1)C(1)C(4)C(7)C(24).

The average Co–Co bond distances in the base of the clusters are short compared to the sides owing to the contracting action of the bridging CO groups [2.459(2), 2.469(2) Å in **1** and 2.452(2), 2.483(2) Å in **2**, respectively]. Both bridging and equatorial terminal carbonyl ligands point upwards toward the cyclophane.

Compounds **2** and **3** are of particular interest as precursors to organometallic one and two-dimensional networks and polymers since the [2.2.2]paracyclophane ligands in these complexes bridge cluster units. However, it should be noted that we have been unable to introduce a second cyclophane ligand to a Co_4 cluster in order to sustain chain growth: the weakness of the metal–arene interaction (as demonstrated by arene exchange reactions with toluene) permits multiple complexation of clusters by a single ligand but is too weak to allow the substitution of further carbonyl ligands with poorer π-acceptors upon the arene cluster. We have also found that, for example in compound **1**, the cobalt cluster is unwilling to share the cyclophane ligand with more electronically demanding subunits such as $[Ru_6C(CO)_{14}]$, Ga^I or Ag^I. Although the linkage of cobalt clusters through arene systems in itself is not novel (this has been previously achieved using diphenylmethane),[7] the combination of the unique electronic properties of clusters and cyclophanes may allow novel types of electronic communication. Our preliminary electrochemical analyses, although complex, indicate this and our investigation is ongoing.

We wish to thank the EPSRC, Cambridge University, and the Newton Trust (P. S.) for financial support. P. J. D. would like to thank the Royal Society for a University fellowship.

Notes and References

† E-mail: bfgj1@cus.cam.ac.uk

‡ *Spectroscopic data*: **1**, IR (CH_2Cl_2) ν_{CO}/cm^{-1} 2072s, 2046w, 2028vs, 2009s, 1995w (sh) and 1814m (br). FABMS: *m/z* 800 (calc. 800) with the loss of all nine CO ligands observed. ^1H NMR ($CDCl_3$): δ 6.53 (d, 4 H, *J* 7.2 Hz, free aromatic), 6.45 (d, 4 H, *J* 7.2 Hz, free aromatic), 5.66 (s, 4 H, bound aromatic), 3.28 (m, 4 H), 2.90 (m, 4 H) and 2.81 (s, 4 H).

2, IR (CH_2Cl_2) ν_{CO}/cm^{-1} 2069s, 2026vs, 2007s, 1992w (sh) and 1815m (br). FABMS: *m/z* 1290 (calc. 1288) with the loss of all eighteen CO ligands and four cobalt atoms observed. ^1H NMR ($CDCl_3$): δ 6.28 (s, 4 H, free aromatic), 5.48 (d, 4 H, *J* 7.0 Hz, bound aromatic), 5.38 (d, 4 H, *J* 7.0 Hz, bound aromatic), 3.20 (s, 4 H), 3.12 (m, 4 H) and 2.75 (s, 4 H).

3, IR (CH_2Cl_2) ν_{CO}/cm^{-1} 2072s, 2028vs, 2008s, 1996w (sh) and 1837m (br). FABMS: *m/z* 1778 (calc. 1777) with the loss of eight CO ligands observed.

§ *Crystal data*: Structures solved by direct methods (SIR92) and refined by full-matrix least squares on F^2 (SHELXTL version 5).

1, $C_{33}H_{24}Co_4O_9$, M = 800.24, triclinic, space group $P\bar{1}$, a = 10.594(4), b = 12.060(5), c = 14.506(6) Å, α = 110.37(2), β = 111.20(2), γ = 93.78(2), U = 1580.4(11) Å^3, Z = 2, D_c = 1.682 Mg m^{-3}, T = 250(2) K, $F(000)$ = 804, R_1 = 0.0371 [3977 reflections with $F_0 > 4\sigma(F_o)$], wR_2 = 0.0800 for 5576 independent reflections corrected for adsorption [μ(Mo-Kα) = 2.177 mm^{-1}] and 416 parameters 0.39 × 0.38 × 0.29 mm black block obtained from dichloromethane at −20 °C. The crystal lattice contained no solvent. The final difference map extrema were +0.67 and −0.40 e Å^{-3}.

2, $C_{42}H_{24}Co_8O_{18}\cdot 0.43CH_2Cl_2$, M = 1324.57, trigonal, space group $P3_121$, a = 15.4261(12), c = 18.282(3), U = 3767.7(8) Å^3, Z = 3 (the molecule lies on a two-fold axis), D_c = 1.751 Mg m^{-3}, T = 220(2) K, $F(000)$ = 1962, R_1 = 0.0460 [3598 reflections with $F_o > 4\sigma(F_o)$], wR_2 = 0.1069 for 4358 independent reflections corrected for adsorption [μ(Mo-Kα) = 2.687 mm^{-1}] and 308 parameters. The Flack absolute structure parameter was 0.01(3). 0.39 × 0.38 × 0.29 mm dark green block obtained from dichloromethane at −20 °C. The crystal lattice contained disordered solvent molecules which were treated in the manner described by van der Sluis and Spek.[8] This amounted to 36 e per cell or 0.43 CH_2Cl_2 per formula unit. The final difference map extrema were +0.05 and −0.62 e Å^{-3}. CCDC 182/783.

1 D. J. Cram, in *Cyclophanes I*, ed. P. M. Keehn and S. M. Rosenfeld, Academic Press, New York, 1983.
2 D. J. Cram and D. I. Wilkinson, *J. Am. Chem. Soc.*, 1960, **82**, 5721.
3 E. D. Laganis, R. H. Voegeli, R. T. Swann, R. G. Finke, H. Hopf and V. Boekelheide, *Organometallics*, 1982, **1**, 1415.
4 H. Schidbaur, R. Hager, B. Huber and G. Muller, *Angew. Chem., Int. Ed. Engl.*, 1987, **26**, 338; J.-L. Pierre, P. Baret, P. Chautemps and M. Armand, *J. Am. Chem. Soc.*, 1981, **103**, 2986.
5 C. Elschenbroich, J. Schneider, M. Wünsch, J.-L. Pierre, P. Baret and P. Chautemps, *Chem. Ber.*, 1988, **121**, 177.
6 P. J. Dyson, D. G. Humphrey, J. E. McGrady, P. Suman and D. Tocher, *J. Chem. Soc., Dalton Trans.*, 1997, 1601.
7 A. I. Yanovsky, F. M. Dolgushin, Y. T. Struchov, V. S. Kaganovich and M. I. Rybinskaya, *Russ. Chem. Bull.*, 1995, **44**, 1072; E. Kolehmainen, K. Laihia, J. Kaganovich, M. I. Rybinskaya and Z. A. Kezerina, *J. Organomet. Chem.*, 1995, **485**, 109.
8 P. van der Sluis and A. L. Spek, *Acta Crystallogr., Sect. A*, 1990, **46**, 194.

Received in Cambridge, UK, 26th January 1998; 8/00715B