

Formation of a cluster-substituted cyclopentadienone from $\text{PhC}_2\text{CCo}_3(\text{CO})_9$. Crystal structure of $\text{Ph}_2\text{C}_4\text{C}(\text{O})[\text{CCo}_3(\text{CO})_9]_2$

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Abstract

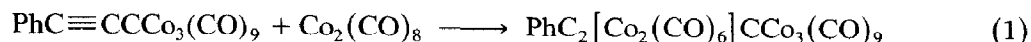
The cluster-substituted alkyne $\text{PhC}\equiv\text{CCC}_3(\text{CO})_9$ (**1**), obtained by a coupling reaction between $\text{BrCCo}_3(\text{CO})_9$ and $\text{PhC}\equiv\text{CH}$, rearranges to give the cyclopentadienone $\text{Ph}_2\text{C}_4\text{C}(\text{O})[\text{CCo}_3(\text{CO})_9]_2$ (**2**). Alkyne **1** with $\text{Co}_2(\text{CO})_8$ gives $\text{PhC}_2[\text{Co}_2(\text{CO})_6]\text{CCo}_3(\text{CO})_9$ (**3**). Compound **2** was characterised by X-ray crystallography at 123 K. The structure is that of a symmetrically substituted cyclopentadienone with tricobaltcarbon cluster moieties substituted α to the carbonyl group and phenyl substituents in the β positions. Various findings suggest that the formation of **2** does not proceed via a metallacycle. Electrochemical data shows that the clusters and the cyclopentadienone ring act as independent redox centres, indicating that there is no contiguous π -interaction.

Cyclization of transition metal-acetylene complexes to give η^4 -cyclopentadienone complexes is a common reaction when the transition metal fragment is a metal carbonyl or when the cyclization is carried out under carbon monoxide [1,2]. These reactions generally occur via the intermediacy of a metallacycle, and the importance of this reaction relative to the alternative trimerization pathway to give aromatic products is a function of the electronic nature of the substituents on the alkyne [2]. Thermal decomposition of alkyne-metal carbonyl complexes or attempted cyclization of alkyne-metal complexes at elevated temperatures [1–4] can give, amongst other products, uncomplexed cyclopentadienones. However, in the absence of a metal catalyst or template, the cyclization of alkynes does not give cyclopentadienones; rather cyclopentenones are produced if the ketone functionality is inherent in one of the reagents [5] or, in what is described as an anomalous carbonylation, by carrying out the cyclization of PhC_2Ph under synthesis gas [6].

In this paper we describe a cluster-substituted cyclopentadienone which is formed at ambient temperatures from an alkyne derivative seemingly without the intermediacy of a metallacycle.

Results and discussion

The cluster-substituted alkyne $\text{PhC}\equiv\text{CCCo}_3(\text{CO})_9$ (**1**) was prepared by a Cadiot–Chodkiewicz coupling reaction between $\text{BrCCo}_3(\text{CO})_9$ and the terminal alkyne $\text{HC}\equiv\text{CPh}$ [7,8]. It was identified by mass spectrometry and from the typical $\nu(\text{CO})$ profile of tricobalt carbon clusters [9]. Further characterization came from the high yield synthesis of the alkyne complex $\text{PhC}_2[\text{Co}_2(\text{CO})_6]\text{CCo}_3(\text{CO})_9$ (**3**) by the reaction of **1** with $\text{Co}_2(\text{CO})_8$.



An analysis of the $\nu(\text{CO})$ spectrum of **3** is given elsewhere [8] but the spectrum is a superposition of the spectra of tricobalt carbon clusters and $\text{RC}_2[\text{Co}_2(\text{CO})_6]\text{R}'$ derivatives [2]; the band at 2081 cm^{-1} is assigned to the $A_1(\text{sym})$ mode of the $\text{Co}_2(\text{CO})_6$ moiety and that at 2105 cm^{-1} to the same mode for the $\text{CCo}_3(\text{CO})_9$ unit. An analytically-pure sample of solid **1** was not obtained because on standing in a concentrated solution, or as a solid in vacuo, it was transformed into a stable green-black compound **2**. Elemental analysis and mass spectra suggested a formulation $\text{Ph}_2\text{C}_4\text{C}(\text{O})[\text{CCo}_3(\text{CO})_9]_2$, but while infrared and NMR spectra were consistent with the presence of phenyl and $\text{CCo}_3(\text{CO})_9$ groups no unambiguous ketone vibration or ^{13}C NMR resonance was found. Confirmation that **2** was a tetrasubstituted cyclopentadienone was provided by the X-ray structural analysis.

The compound crystallises with two unique molecules in the asymmetric unit of the triclinic unit cell. The closest intermolecular contact (not involving H atoms) is $2.878(8)\text{Å}$, between O(151) and O(251). Bond distances and angles are given for

(continued on p. 343)

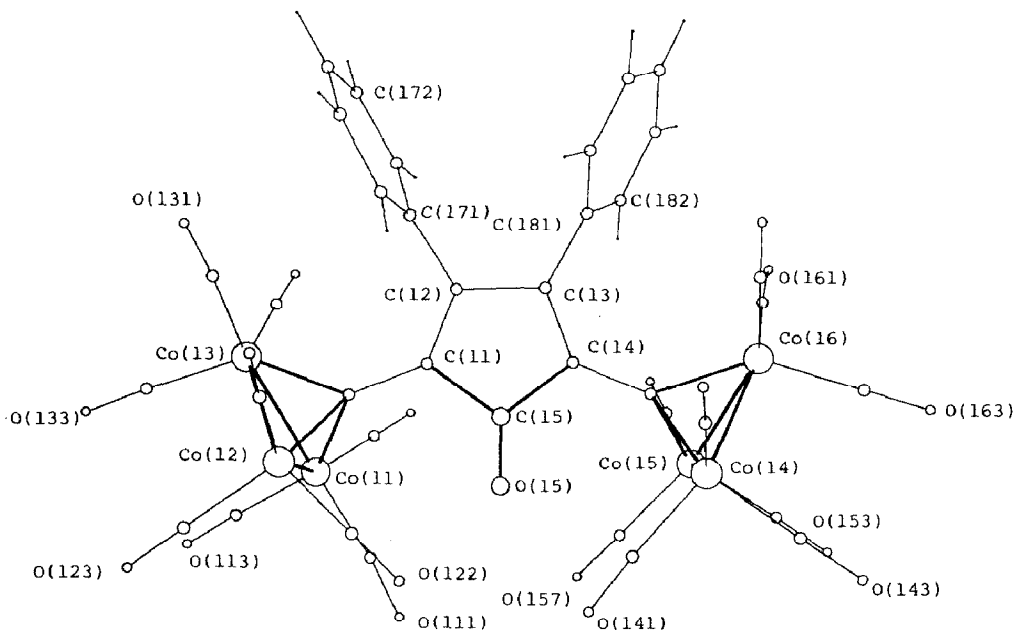


Fig. 1. Structure of molecule 1 of compound **2** showing the atom numbering scheme. For clarity only the first two C atoms of the consecutively numbered phenyl rings and the O atoms of the carbonyl ligands have been labelled.

Table 1

Selected bond lengths (Å) and angles (°) for compound 2

| Molecule 1 | | Molecule 2 | |
|---------------------|----------|----------------|----------|
| <i>Bond lengths</i> | | | |
| Co(11)–Co(12) | 2.462(1) | Co(21)–Co(22) | 2.453(2) |
| Co(11)–Co(13) | 2.442(2) | Co(21)–Co(23) | 2.466(2) |
| Co(11)–Cap(11) | 1.931(9) | Co(21)–Cap(21) | 1.898(9) |
| Co(11)–C(111) | 1.788(9) | Co(21)–C(211) | 1.78(1) |
| Co(11)–C(112) | 1.789(7) | Co(21)–C(212) | 1.810(7) |
| Co(11)–C(113) | 1.81(1) | Co(21)–C(213) | 1.84(1) |
| Co(12)–Co(13) | 2.477(1) | Co(22)–Co(23) | 2.467(2) |
| Co(12)–Cap(11) | 1.920(6) | Co(22)–Cap(21) | 1.931(6) |
| Co(12)–C(121) | 1.80(1) | Co(22)–C(221) | 1.791(9) |
| Co(12)–C(122) | 1.79(1) | Co(22)–C(222) | 1.79(1) |
| Co(12)–C(123) | 1.84(1) | Co(22)–C(223) | 1.80(1) |
| Co(13)–Cap(11) | 1.924(9) | Co(23)–Cap(21) | 1.93(1) |
| Co(13)–C(131) | 1.79(1) | Co(23)–C(231) | 1.82(1) |
| Co(13)–C(132) | 1.768(7) | Co(23)–C(232) | 1.778(8) |
| Co(13)–C(133) | 1.84(1) | Co(23)–C(233) | 1.84(1) |
| Cap(11)–C(11) | 1.41(1) | Cap(21)–C(21) | 1.42(1) |
| C(111)–O(111) | 1.13(1) | C(211)–O(211) | 1.13(1) |
| C(112)–O(112) | 1.132(9) | C(212)–O(212) | 1.133(9) |
| C(113)–O(113) | 1.16(1) | C(213)–O(213) | 1.11(2) |
| C(121)–O(121) | 1.14(1) | C(221)–O(221) | 1.14(1) |
| C(122)–O(122) | 1.15(1) | C(222)–O(222) | 1.13(2) |
| C(123)–O(123) | 1.12(1) | C(223)–O(223) | 1.17(1) |
| C(131)–O(131) | 1.14(1) | C(231)–O(231) | 1.13(1) |
| C(132)–O(132) | 1.154(9) | C(232)–O(232) | 1.150(9) |
| C(133)–O(133) | 1.15(1) | C(233)–O(233) | 1.13(1) |
| Co(14)–Co(15) | 2.470(1) | Co(24)–Co(25) | 2.452(1) |
| Co(14)–Co(16) | 2.451(1) | Co(24)–Co(26) | 2.474(1) |
| Co(14)–Cap(12) | 1.953(7) | Co(24)–Cap(22) | 1.921(8) |
| Co(14)–C(141) | 1.82(1) | Co(24)–C(241) | 1.806(9) |
| Co(14)–C(142) | 1.792(9) | Co(24)–C(242) | 1.79(1) |
| Co(14)–C(143) | 1.82(1) | Co(24)–C(243) | 1.82(1) |
| Co(15)–Co(16) | 2.456(2) | Co(25)–Co(26) | 2.466(2) |
| Co(15)–Cap(12) | 1.927(8) | Co(25)–Cap(22) | 1.912(8) |
| Co(15)–C(151) | 1.81(1) | Co(25)–C(251) | 1.803(8) |
| Co(15)–C(152) | 1.794(8) | Co(25)–C(252) | 1.79(1) |
| Co(15)–C(153) | 1.84(1) | Co(25)–C(253) | 1.83(1) |
| Co(16)–Cap(12) | 1.916(9) | Co(26)–Cap(22) | 1.923(9) |
| Co(16)–C(161) | 1.774(7) | Co(26)–C(261) | 1.797(9) |
| Co(16)–C(162) | 1.80(1) | Co(26)–C(262) | 1.79(1) |
| Co(16)–C(163) | 1.84(1) | Co(26)–C(263) | 1.84(1) |
| Cap(12)–C(14) | 1.43(1) | Cap(22)–C(24) | 1.44(1) |
| C(141)–O(141) | 1.13(1) | C(241)–O(241) | 1.13(1) |
| C(142)–O(142) | 1.13(1) | C(242)–O(242) | 1.12(1) |
| C(143)–O(143) | 1.16(1) | C(243)–O(243) | 1.14(1) |
| C(151)–O(151) | 1.13(2) | C(251)–O(251) | 1.129(9) |
| C(152)–O(152) | 1.13(1) | C(252)–O(252) | 1.15(1) |
| C(153)–O(153) | 1.12(2) | C(253)–O(253) | 1.13(1) |
| C(161)–O(161) | 1.153(8) | C(261)–O(261) | 1.12(1) |
| C(162)–O(162) | 1.13(1) | C(262)–O(262) | 1.15(1) |
| C(163)–O(163) | 1.12(1) | C(263)–O(263) | 1.10(2) |
| C(11)–C(12) | 1.36(1) | C(21)–C(22) | 1.37(1) |
| C(11)–C(15) | 1.53(1) | C(21)–C(25) | 1.53(1) |
| C(12)–C(13) | 1.50(1) | C(22)–C(23) | 1.49(1) |

(continued)

Table 1 (continued)

| Molecule 1 | | Molecule 2 | |
|-----------------------|----------|-----------------------|----------|
| C(12)–C(171) | 1.49(1) | C(22)–C(271) | 1.49(1) |
| C(13)–C(14) | 1.36(1) | C(23)–C(24) | 1.35(1) |
| C(13)–C(181) | 1.46(1) | C(23)–C(281) | 1.49(1) |
| C(14)–C(15) | 1.51(1) | C(24)–C(25) | 1.51(1) |
| C(15)–O(15) | 1.18(1) | C(25)–O(25) | 1.205(9) |
| C(171)–C(172) | 1.401(9) | C(271)–C(272) | 1.39(1) |
| C(171)–C(176) | 1.40(1) | C(271)–C(276) | 1.37(1) |
| C(172)–C(173) | 1.38(1) | C(272)–C(273) | 1.37(1) |
| C(173)–C(174) | 1.37(1) | C(273)–C(274) | 1.39(1) |
| C(174)–C(175) | 1.38(1) | C(274)–C(275) | 1.35(1) |
| C(175)–C(176) | 1.38(1) | C(275)–C(276) | 1.39(1) |
| C(181)–C(182) | 1.40(1) | C(281)–C(282) | 1.40(1) |
| C(181)–C(186) | 1.41(1) | C(281)–C(286) | 1.39(1) |
| C(182)–C(183) | 1.39(1) | C(282)–C(283) | 1.39(1) |
| C(183)–C(184) | 1.38(2) | C(283)–C(284) | 1.36(1) |
| C(184)–C(185) | 1.38(1) | C(284)–C(285) | 1.37(1) |
| C(185)–C(186) | 1.38(1) | C(285)–C(286) | 1.40(1) |
| <i>Bond angles</i> | | | |
| Co(12)–Co(11)–Co(13) | 60.70(1) | Co(22)–Co(21)–Co(23) | 60.20(1) |
| Co(12)–Co(11)–Cap(11) | 50.1(2) | Co(22)–Co(21)–Cap(21) | 50.8(2) |
| Co(12)–Co(11)–C(111) | 92.2(3) | Co(22)–Co(21)–C(211) | 92.3(3) |
| Co(12)–Co(11)–C(112) | 144.7(4) | Co(22)–Co(21)–C(212) | 154.6(3) |
| Co(12)–Co(11)–C(113) | 107.7(3) | Co(22)–Co(21)–C(213) | 101.2(3) |
| Co(13)–Co(11)–Cap(11) | 50.6(3) | Co(23)–Co(21)–Cap(21) | 50.4(3) |
| Co(13)–Co(11)–C(111) | 152.2(3) | Co(23)–Co(21)–C(211) | 149.8(3) |
| Co(13)–Co(11)–C(112) | 103.0(3) | Co(23)–Co(21)–C(212) | 101.6(3) |
| Co(13)–Co(11)–C(113) | 97.3(3) | Co(23)–Co(21)–C(213) | 97.7(4) |
| Cap(11)–Co(11)–C(111) | 108.3(4) | Cap(21)–Co(21)–C(211) | 103.4(5) |
| Cap(11)–Co(11)–C(112) | 94.9(4) | Cap(21)–Co(21)–C(212) | 104.4(4) |
| Cap(11)–Co(11)–C(113) | 145.7(4) | Cap(21)–Co(21)–C(213) | 143.6(4) |
| C(111)–Co(11)–C(112) | 96.1(4) | C(211)–Co(21)–C(212) | 99.7(4) |
| C(111)–Co(11)–C(113) | 97.0(4) | C(211)–Co(21)–C(213) | 100.0(5) |
| C(112)–Co(11)–C(113) | 105.2(4) | C(212)–Co(21)–C(213) | 98.7(5) |
| Co(11)–Co(12)–Co(13) | 59.30(1) | Co(21)–Co(22)–Co(23) | 60.20(1) |
| Co(11)–Co(12)–Cap(11) | 50.5(3) | Co(21)–Co(22)–Cap(21) | 49.6(3) |
| Co(11)–Co(12)–C(121) | 150.0(2) | Co(21)–Co(22)–C(221) | 152.3(3) |
| Co(11)–Co(12)–C(122) | 102.7(3) | Co(21)–Co(22)–C(222) | 102.4(3) |
| Co(11)–Co(12)–C(123) | 93.8(3) | Co(21)–Co(22)–C(223) | 96.3(4) |
| Co(13)–Co(12)–Cap(11) | 49.9(3) | Co(23)–Co(22)–Cap(21) | 50.2(3) |
| Co(13)–Co(12)–C(121) | 94.5(3) | Co(23)–Co(22)–C(221) | 92.9(3) |
| Co(13)–Co(12)–C(122) | 153.1(2) | Co(23)–Co(22)–C(222) | 144.5(3) |
| Co(13)–Co(12)–C(123) | 99.4(3) | Co(23)–Co(22)–C(223) | 106.8(4) |
| Cap(11)–Co(12)–C(121) | 102.3(3) | Cap(21)–Co(22)–C(221) | 109.2(3) |
| Cap(11)–Co(12)–C(122) | 103.5(4) | Cap(21)–Co(22)–C(222) | 94.5(4) |
| Cap(11)–Co(12)–C(123) | 139.9(4) | Cap(21)–Co(22)–C(223) | 144.0(5) |
| C(121)–Co(12)–C(122) | 95.6(4) | C(221)–Co(22)–C(222) | 96.4(5) |
| C(121)–Co(12)–C(123) | 105.7(4) | C(221)–Co(22)–C(223) | 98.1(4) |
| C(122)–Co(12)–C(123) | 101.7(4) | C(222)–Co(22)–C(223) | 105.6(5) |
| Co(11)–Co(13)–Co(12) | 60.00(1) | Co(21)–Co(23)–Co(22) | 59.60(1) |
| Co(11)–Co(13)–Cap(11) | 50.8(3) | Co(21)–Co(23)–Cap(21) | 49.3(3) |
| Co(11)–Co(13)–C(131) | 157.6(4) | Co(21)–Co(23)–C(231) | 154.3(4) |
| Co(11)–Co(13)–C(132) | 95.4(4) | Co(21)–Co(23)–C(232) | 94.6(3) |
| Co(11)–Co(13)–C(133) | 97.1(3) | Co(21)–Co(23)–C(233) | 100.5(3) |
| Co(12)–Co(13)–Cap(11) | 49.8(2) | Co(22)–Co(23)–Cap(21) | 50.3(2) |
| Co(12)–Co(13)–C(131) | 100.1(3) | Co(22)–Co(23)–C(231) | 102.6(3) |

(continued)

Table 1 (continued)

| Molecule 1 | | Molecule 2 | |
|-----------------------|----------|-----------------------|----------|
| Co(12)–Co(13)–C(132) | 148.6(4) | Co(22)–Co(23)–C(232) | 150.4(4) |
| Co(12)–Co(13)–C(133) | 99.9(2) | Co(22)–Co(23)–C(233) | 94.5(3) |
| Cap(11)–Co(13)–C(131) | 109.2(5) | Cap(21)–Co(23)–C(231) | 105.4(4) |
| Cap(11)–Co(13)–C(132) | 100.1(4) | Cap(21)–Co(23)–C(232) | 102.6(4) |
| Cap(11)–Co(13)–C(133) | 142.3(3) | Cap(21)–Co(23)–C(233) | 140.4(4) |
| C(131)–Co(13)–C(132) | 98.8(4) | C(231)–Co(23)–C(232) | 96.0(4) |
| C(131)–Co(13)–C(133) | 96.6(5) | C(231)–Co(23)–C(233) | 99.2(5) |
| C(132)–Co(13)–C(133) | 102.7(5) | C(232)–Co(23)–C(233) | 105.2(5) |
| Co(11)–Cap(11)–Co(12) | 79.5(3) | Co(21)–Cap(21)–Co(22) | 79.7(3) |
| Co(11)–Cap(11)–Co(13) | 78.6(4) | Co(21)–Cap(21)–Co(23) | 80.2(4) |
| Co(11)–Cap(11)–C(11) | 128.3(6) | Co(21)–Cap(21)–C(21) | 138.9(6) |
| Co(12)–Cap(11)–Co(13) | 80.2(3) | Co(22)–Cap(21)–Co(23) | 79.5(3) |
| Co(12)–Cap(11)–C(11) | 131.3(6) | Co(22)–Cap(21)–C(21) | 128.6(6) |
| Co(13)–Cap(11)–C(11) | 137.3(5) | Co(23)–Cap(21)–C(21) | 128.7(6) |
| Co(11)–C(111)–O(111) | 173(1) | Co(21)–C(211)–O(211) | 178.9(9) |
| Co(11)–C(112)–O(112) | 175(1) | Co(21)–C(212)–O(212) | 177(1) |
| Co(11)–C(113)–O(113) | 177.6(7) | Co(21)–C(213)–O(213) | 177.8(9) |
| Co(12)–C(121)–O(121) | 177(1) | Co(22)–C(221)–O(221) | 174.8(7) |
| Co(12)–C(122)–O(122) | 177.2(8) | Co(22)–C(222)–O(222) | 177.9(8) |
| Co(12)–C(123)–O(123) | 175.2(7) | Co(22)–C(223)–O(223) | 175(1) |
| Co(13)–C(131)–O(131) | 174(1) | Co(23)–C(231)–O(231) | 176(1) |
| Co(13)–C(132)–O(132) | 178(1) | Co(23)–C(232)–O(232) | 177(1) |
| Co(13)–C(133)–O(133) | 177.1(6) | Co(23)–C(233)–O(233) | 178(1) |
| Co(15)–Co(14)–Co(16) | 59.90(1) | Co(25)–Co(24)–Co(26) | 60.10(1) |
| Co(15)–Co(14)–Cap(12) | 50.0(2) | Co(25)–Co(24)–Cap(22) | 50.1(2) |
| Co(15)–Co(14)–C(141) | 99.6(3) | Co(25)–Co(24)–C(241) | 154.6(3) |
| Co(15)–Co(14)–C(142) | 149.3(2) | Co(25)–Co(24)–C(242) | 96.2(2) |
| Co(15)–Co(14)–C(143) | 100.9(3) | Co(25)–Co(24)–C(243) | 95.6(2) |
| Co(16)–Co(14)–Cap(12) | 50.0(2) | Co(26)–Co(24)–Cap(22) | 50.0(3) |
| Co(16)–Co(14)–C(141) | 155.4(3) | Co(26)–Co(24)–C(241) | 95.6(3) |
| Co(16)–Co(14)–C(142) | 95.6(2) | Co(26)–Co(24)–C(242) | 145.1(3) |
| Co(16)–Co(14)–C(143) | 100.8(3) | Co(26)–Co(24)–C(243) | 103.6(3) |
| Cap(12)–Co(14)–C(141) | 107.1(4) | Cap(22)–Co(24)–C(241) | 109.7(4) |
| Cap(12)–Co(14)–C(142) | 100.8(4) | Cap(22)–Co(24)–C(242) | 95.4(4) |
| Cap(12)–Co(14)–C(143) | 144.7(3) | Cap(22)–Co(24)–C(243) | 142.6(3) |
| C(141)–Co(14)–C(142) | 98.2(4) | C(241)–Co(24)–C(242) | 101.6(4) |
| C(141)–Co(14)–C(143) | 96.1(4) | C(241)–Co(24)–C(243) | 97.5(4) |
| C(142)–Co(14)–C(143) | 101.8(4) | C(242)–Co(24)–C(243) | 104.0(4) |
| Co(14)–Co(15)–Co(16) | 59.70(1) | Co(24)–Co(25)–Co(26) | 60.40(1) |
| Co(14)–Co(15)–Cap(12) | 50.9(2) | Co(24)–Co(25)–Cap(22) | 50.4(2) |
| Co(14)–Co(15)–C(151) | 100.3(3) | Co(24)–Co(25)–C(251) | 150.2(3) |
| Co(14)–Co(15)–C(152) | 150.4(3) | Co(24)–Co(25)–C(252) | 99.8(2) |
| Co(14)–Co(15)–C(153) | 97.9(3) | Co(24)–Co(25)–C(253) | 99.2(2) |
| Co(16)–Co(15)–Cap(12) | 50.1(3) | Co(26)–Co(25)–Cap(22) | 50.2(3) |
| Co(16)–Co(15)–C(151) | 155.5(3) | Co(26)–Co(25)–C(251) | 93.5(3) |
| Co(16)–Co(15)–C(152) | 98.7(4) | Co(26)–Co(25)–C(252) | 149.5(3) |
| Co(16)–Co(15)–C(153) | 97.2(4) | Co(26)–Co(25)–C(253) | 104.5(4) |
| Cap(12)–Co(15)–C(151) | 107.0(4) | Cap(22)–Co(25)–C(251) | 102.7(4) |
| Cap(12)–Co(15)–C(152) | 100.1(4) | Cap(22)–Co(25)–C(252) | 99.5(4) |
| Cap(12)–Co(15)–C(153) | 141.5(4) | Cap(22)–Co(25)–C(253) | 145.8(4) |
| C(151)–Co(15)–C(152) | 93.7(4) | C(251)–Co(25)–C(252) | 97.1(4) |
| C(151)–Co(15)–C(153) | 99.8(5) | C(251)–Co(25)–C(253) | 101.2(4) |
| C(152)–Co(15)–C(153) | 105.2(4) | C(252)–Co(25)–C(253) | 101.4(5) |
| Co(14)–Co(16)–Co(15) | 60.50(1) | Co(24)–Co(26)–Co(25) | 59.50(1) |
| Co(14)–Co(16)–Cap(12) | 51.4(2) | Co(24)–Co(26)–Cap(22) | 49.9(2) |
| Co(14)–Co(16)–C(161) | 154.0(4) | Co(24)–Co(26)–C(261) | 151.1(4) |
| Co(14)–Co(16)–C(162) | 101.8(2) | Co(24)–Co(26)–C(262) | 98.7(2) |

(continued)

Table 1 (continued)

| Molecule 1 | | Molecule 2 | |
|-----------------------|----------|-----------------------|----------|
| Co(14)–Co(16)–C(163) | 95.8(2) | Co(24)–Co(26)–C(263) | 98.2(3) |
| Co(15)–Co(16)–Cap(12) | 50.5(2) | Co(25)–Co(26)–Cap(22) | 49.8(2) |
| Co(15)–Co(16)–C(161) | 94.5(3) | Co(25)–Co(26)–C(261) | 99.5(4) |
| Co(15)–Co(16)–C(162) | 150.7(3) | Co(25)–Co(26)–C(262) | 154.0(3) |
| Co(15)–Co(16)–C(163) | 103.5(3) | Co(25)–Co(26)–C(263) | 96.9(4) |
| Cap(12)–Co(16)–C(161) | 108.4(4) | Cap(22)–Co(26)–C(261) | 101.7(5) |
| Cap(12)–Co(16)–C(162) | 100.3(4) | Cap(22)–Co(26)–C(262) | 106.1(4) |
| Cap(12)–Co(16)–C(163) | 143.9(3) | Cap(22)–Co(26)–C(263) | 140.7(4) |
| C(161)–Co(16)–C(162) | 97.9(4) | C(261)–Co(26)–C(262) | 94.7(4) |
| C(161)–Co(16)–C(163) | 96.9(4) | C(261)–Co(26)–C(263) | 104.4(5) |
| C(162)–Co(16)–C(163) | 101.3(5) | C(262)–Co(26)–C(263) | 100.5(5) |
| Co(14)–Cap(12)–Co(15) | 79.1(3) | Co(24)–Cap(22)–Co(25) | 79.5(3) |
| Co(14)–Cap(12)–Co(16) | 78.6(3) | Co(24)–Cap(22)–Co(26) | 80.1(4) |
| Co(14)–Cap(12)–C(14) | 127.2(4) | Co(24)–Cap(22)–C(24) | 134.2(4) |
| Co(15)–Cap(12)–Co(16) | 79.4(3) | Co(25)–Cap(22)–Co(26) | 80.0(3) |
| Co(15)–Cap(12)–C(14) | 131.2(7) | Co(25)–Cap(22)–C(24) | 131.6(6) |
| Co(16)–Cap(12)–C(14) | 139.2(6) | Co(26)–Cap(22)–C(24) | 130.6(6) |
| Co(14)–C(141)–O(141) | 176.5(9) | Co(24)–C(241)–O(241) | 176(1) |
| Co(14)–C(142)–O(142) | 179.5(6) | Co(24)–C(242)–O(242) | 178.0(8) |
| Co(14)–C(143)–O(143) | 178.7(6) | Co(24)–C(243)–O(243) | 178.7(9) |
| Co(15)–C(151)–O(151) | 174.7(7) | Co(25)–C(251)–O(251) | 179.4(8) |
| Co(15)–C(152)–O(152) | 176.8(9) | Co(25)–C(252)–O(252) | 177.8(8) |
| Co(15)–C(153)–O(153) | 177.1(8) | Co(25)–C(253)–O(253) | 178(1) |
| Co(16)–C(161)–O(161) | 176(1) | Co(26)–C(261)–O(261) | 177(1) |
| Co(16)–C(162)–O(162) | 178.7(6) | Co(26)–C(262)–O(262) | 175.3(7) |
| Co(16)–C(163)–O(163) | 179.1(7) | Co(26)–C(263)–O(263) | 179.5(8) |
| Cap(11)–C(11)–C(12) | 133.9(8) | Cap(21)–C(21)–C(22) | 133.9(8) |
| Cap(11)–C(11)–C(15) | 121.5(7) | Cap(21)–C(21)–C(25) | 122.2(6) |
| C(12)–C(11)–C(15) | 104.5(7) | C(22)–C(21)–C(25) | 103.8(8) |
| C(11)–C(12)–C(13) | 112.3(7) | C(21)–C(22)–C(23) | 110.7(7) |
| C(11)–C(12)–C(171) | 126.5(8) | C(21)–C(22)–C(271) | 129.4(8) |
| C(13)–C(12)–C(171) | 121.1(7) | C(23)–C(22)–C(271) | 119.8(6) |
| C(12)–C(13)–C(14) | 108.7(7) | C(22)–C(23)–C(24) | 111.5(7) |
| C(12)–C(13)–C(181) | 120.2(7) | C(22)–C(23)–C(281) | 118.9(7) |
| C(14)–C(13)–C(181) | 131.0(8) | C(24)–C(23)–C(281) | 129.5(8) |
| Cap(12)–C(14)–C(13) | 132.0(8) | Cap(22)–C(24)–C(23) | 132.7(8) |
| Cap(12)–C(14)–C(15) | 120.5(7) | Cap(22)–C(24)–C(25) | 122.3(6) |
| C(13)–C(14)–C(15) | 107.4(8) | C(23)–C(24)–C(25) | 105.0(8) |
| C(11)–C(15)–C(14) | 106.9(6) | C(21)–C(25)–C(24) | 108.8(6) |
| C(11)–C(15)–O(15) | 125.7(8) | C(21)–C(25)–O(25) | 124.4(8) |
| C(14)–C(15)–O(15) | 127.4(9) | C(24)–C(25)–O(25) | 126.7(8) |
| C(12)–C(171)–C(172) | 122.7(7) | C(22)–C(271)–C(272) | 120.3(7) |
| C(12)–C(171)–C(176) | 119.0(6) | C(22)–C(271)–C(276) | 120.1(6) |
| C(172)–C(171)–C(176) | 118.2(8) | C(272)–C(271)–C(276) | 119.5(7) |
| C(171)–C(172)–C(173) | 120.7(8) | C(271)–C(272)–C(273) | 120.2(8) |
| C(172)–C(173)–C(174) | 120.1(7) | C(272)–C(273)–C(274) | 119.7(7) |
| C(173)–C(174)–C(175) | 120.3(9) | C(273)–C(274)–C(275) | 120.0(8) |
| C(174)–C(175)–C(176) | 120.6(8) | C(274)–C(275)–C(276) | 120.3(9) |
| C(171)–C(176)–C(175) | 119.9(6) | C(271)–C(276)–C(275) | 120.3(7) |
| C(13)–C(181)–C(182) | 120.2(8) | C(23)–C(281)–C(282) | 119.7(8) |
| C(13)–C(181)–C(186) | 122.0(6) | C(23)–C(281)–C(286) | 120.5(6) |
| C(182)–C(181)–C(186) | 117.8(7) | C(282)–C(281)–C(286) | 119.6(7) |
| C(181)–C(182)–C(183) | 121.5(9) | C(281)–C(282)–C(283) | 119.0(8) |
| C(182)–C(183)–C(184) | 119.5(7) | C(282)–C(283)–C(284) | 121.3(7) |
| C(183)–C(184)–C(185) | 119.9(8) | C(283)–C(284)–C(285) | 120.2(7) |
| C(184)–C(185)–C(186) | 120(1) | C(284)–C(285)–C(286) | 120.0(9) |
| C(181)–C(186)–C(185) | 120.5(7) | C(281)–C(286)–C(285) | 119.8(7) |

both molecules in Table 1 with the overall molecular geometry and numbering scheme for molecule I displayed in Fig. 1. Unless otherwise stated, molecular parameters for molecule I will be used in the subsequent discussion. Small differences in bond lengths and angles between the independent molecules can best be assigned to crystal packing effects.

The structure is that of a tetrasubstituted cyclopentadienone with two $\text{CCo}_3(\text{CO})_9$ cluster moieties closest to the carbonyl group in the α positions and the phenyl rings in the β positions. The resulting structure may be related to that of the precursor $\text{PhC}\equiv\text{CCCo}_3(\text{CO})_9$ by considering the symmetrical aggregation of carbon monoxide with two of the cluster substituted acetylenes. The cyclopentadienone ring has discrete double bonds between C(11)–C(12) and C(13)–C(14) with the remaining C–C bonds close to the single bond length. This precludes any significant π -delocalisation through the ring system. A similar effect was observed in the structure of 2,5-di-*t*-butyl-3(4-chlorophenyl)cyclopentadienone [10].

The tricobalt carbon cluster units exhibit the anticipated pyramidal core with terminal carbonyl ligands on both cluster polyhedra. Deviations from the idealised C_{3v} geometry found in less sterically cluttered systems [11,12] show up in small but significant differences in the Co–Co bond lengths of both basal Co_3 triangles. Similar variations are found in the Co–Cap bond distances to the capping carbon atoms. These distortions can best be ascribed to a response by the molecule to the steric crowding imposed on the cluster systems by the linking cyclopentadienone moiety. Steric congestion around the cluster unit is exacerbated by the shortness of the C–C bonds (Cap(11)–C(11) 1.41(1), Cap(12)–C(14) 1.43(1) Å) linking the clusters to the cyclopentadienone ring. These distances contrast with values in the range 1.47–1.50 Å for bonds between capping C atoms and the substituent C atoms of phenyl rings [13]. A closer comparison is obtained with the C–C bond length of 1.45 Å observed in the ferrocene capped tricobalt carbon cluster $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}[\eta^5\text{-C}_5\text{H}_4\text{-CCo}_3(\text{CO})_9]$ [14], where the shortening was interpreted in terms of a significant cooperative interaction between the cluster and ferrocene moieties. In compound **2**, the discrete nature of the alkene groups in the cyclopentadienone rules out the possibility of interaction between the two cluster units through the cyclopentadienone ring, although there may be some delocalisation between the apical C atoms and the individual alkene moieties.

The conformation of the four substituents of the cyclopentadienone ring is determined by an overall balance of non-bonded contacts. The planes of the phenyl rings make angles of 102.0(3) (C(171)–C(176)) and 64.7(3)° (C(181)–C(186)) with the plane of the 5-membered ring in order to minimise contact with the adjacent cluster substituents. Furthermore, the significant widening of the angles Co(13)–Cap(11)–C(11) (137.3(5)) and Co(16)–Cap(12)–C(14) (139.2(6)°), in comparison with the other angles subtended at the apical carbon atoms, serves to skew the cluster away from contact with the phenyl rings. The inclination of the Cap(11)–C(11) and Cap(12)–C(14) bonds away from the Co(13) and Co(16) atoms respectively can be explained similarly. The orientation of the cobalt triangles with respect to the 5-membered ring brings Co(13) and Co(16) close to the dienone ring plane so as to minimise contact between the carbonyl substituents on the remaining Co atoms with the O atom of the cyclopentadienone.

Given the structure of **2** it is surprising that no ketone $\nu(\text{CO})$ stretch or ^{13}C NMR resonance could be seen. The weak band at 2103 cm^{-1} is indicative of a CCO_3

cluster with an unsymmetrical substituent bound to the carbyne apical groups [8,15], but the overall $\nu(\text{CO})$ profile is not typical of $\text{CCo}_3(\text{CO})_9$ molecules. However, the weak/strong $A_1(\text{sym})$ $\nu(\text{CO})$ pattern of 2103(mw)/2093(m) cm^{-1} is similar to that for cluster molecules in which the two tricobalt carbon moieties are linked via a delocalised centre [15]. Other data do not support a direct interaction between the two clusters (*vide infra*), so the complex profile must be due to coupling of the carbonyl, ketone and ring vibrations.

Transformation mechanism

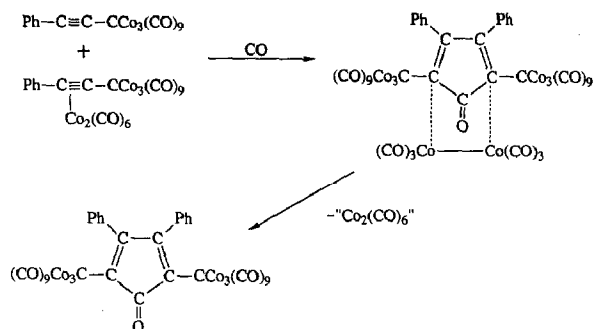
Two intriguing features of the coupling reaction to give **2** are the regioselectivity and the ease with which the transformation takes place.

Metallacycles are the essential species in the mechanism for the formation of cyclopentadienone–metal complexes or cyclopentadienones from the thermal decomposition of alkyne complexes [1,2]. Coupling of the alkynes and CO-insertion is not normally regioselective, and systematic studies on the isomer distribution [3,16] showed that the electronic character of the substituents primarily determined whether the substituent was α or β to the ketone function. Electronegative substituents tend to occupy the α site since the carbon atoms adjacent to the CO are the sites of greatest electron density [17], and it is only with very bulky substituents (e.g. *t*-butyl) that an unsymmetrical substitution is adopted. In this study there was no evidence from the chromatographic or spectrometric analysis for regioisomers of **2** other than that shown in Fig. 1. A stereochemistry in which the clusters are not staggered is surprising given the bulk of the $\text{CCo}_3(\text{CO})_9$ substituents [12]. However, the cluster moiety is a strong electron-withdrawing group so it seems that the electronic character is dominant; this is certainly consistent with the short C–Cap bonds noted in the structure (Table 1) indicative of an interaction between the cluster and the alkene function of the cyclopentadienone ring.

Metallacycles with a variety of structures are known intermediates in oligomerisation reactions of alkynes involving metal substrates or catalysts. Cyclopentadienone and cyclobutadiene complexes and substituted arenes are known to result from coupling reactions with both mononuclear and polynuclear primary metallacycles; the type of product isolated can be dependent on the reaction conditions but cyclopentadienone complexes are favoured if the reactions are carried out under a pressure of CO. Alkynes with bulky substituents do not normally prohibit these reactions; indeed, the control of alkyne reactivity is often better with alkynes such as $\text{Me}_3\text{SiC}_2\text{SiMe}_3$ and this facet of their chemistry has been extensively explored by Vollhardt [18]. Consequently, there are a number of mechanistic possibilities for the **1** \rightarrow **2** transformation. During the transformation trace amounts of several carbonyl-containing compounds were detected and fragmentation of the tricobalt carbon cluster substituent could provide $\text{Co}_2(\text{CO})_6$ fragments for the formation of **3** (this was isolated in this reaction). Thermal decomposition of **3** or the reaction between **1** and **3** could give **2** via a dicobalt-dienone intermediate (Scheme 1).

A cobaltacyclopentadiene intermediate is unlikely as the thermal decomposition of **3** takes place above 50°C and neither thermal decomposition nor oxidative decomposition yields **2**. Several other observations argue against metallacycles as intermediates:

- 1. 2** is not detected at any stage during the preparation of $\text{PhC}_2\text{CCo}_3(\text{CO})_9$ even if the reaction is carried out under CO.



Scheme 1

2. The slow transformation $1 \rightarrow 2$ occurred when solvent was being removed from a chromatographically purified sample of **1** in vacuo or on recrystallisation of **1** from concentrated hexane solutions at ambient temperatures (the transformation was first noted during an attempt to produce X-ray quality crystals of **1**). The transformation process is not affected by the presence of nucleophiles such as Et_3N .
3. Solid crystalline **1** is itself unstable although it can be sublimed in vacuo with decomposition. In solution, **1** does not decompose to give **2**.
4. When dilute hexane solutions of **1** are placed under an atmosphere of CO or irradiated with UV no transformation to **2** occurs.
5. Analogues of **1** bearing bulkier substituents than phenyl, e.g. $\text{Me}_3\text{SiC}\equiv\text{CCC}(\text{CO})_9$, do not undergo a similar alkyne \rightarrow cyclopentadienone transformation [8].
6. There is no evidence for the formation of $\text{Co}(\text{CO})_3$ derivatives of **2**.

The factors which encourage the transformation are not clear, but it seems that an intramolecular coupling reaction takes place in very concentrated solutions or solid samples which still contain a trace of solvent. (We were unable to establish with certainty that it was a genuine solid-state reaction.) Intramolecular CO-insertion into the apical C–R bond of the tricobalt carbon cluster is a facile process and many acyl compounds have been prepared by this route [19]. An example of insertion into a C–C bond is $\text{Co}[\text{CCo}_3(\text{CO})_9]_2$ formally derived from the dimer $[\text{CCo}_3(\text{CO})_9]_2$ [20]. The steric congestion within the carbonyl sphere and close approach of the equatorial carbonyl groups to the apical carbon atom encourages facile insertion processes.

We are not suggesting a $2\pi + 2\pi$ metal-mediated coupling but rather a step-wise coupling which may not necessarily involve just **1**.

Redox properties

The electrochemistry of **2** is complex because of the twin redox processes due to the cyclopentadienone moiety and the tricobalt carbon cluster. The simplest picture is provided by the cyclic voltammograms at 202 K (Fig. 2). At this temperature there are two major reduction processes **A** and **B** at $E_p \sim -0.55$ V and -0.70 V vs. Ag/AgCl respectively. Precise analysis of the i/v curves was difficult because the electron transfer was not diffusion controlled but chemical reversibility was indicated for both **A** and **B** by i_{pc}/i_{pa} of ~ 1 for both steps. Chemical reversibility is not dependent on the scan rate, on the nature of the electrode (Pt, C or Au) or

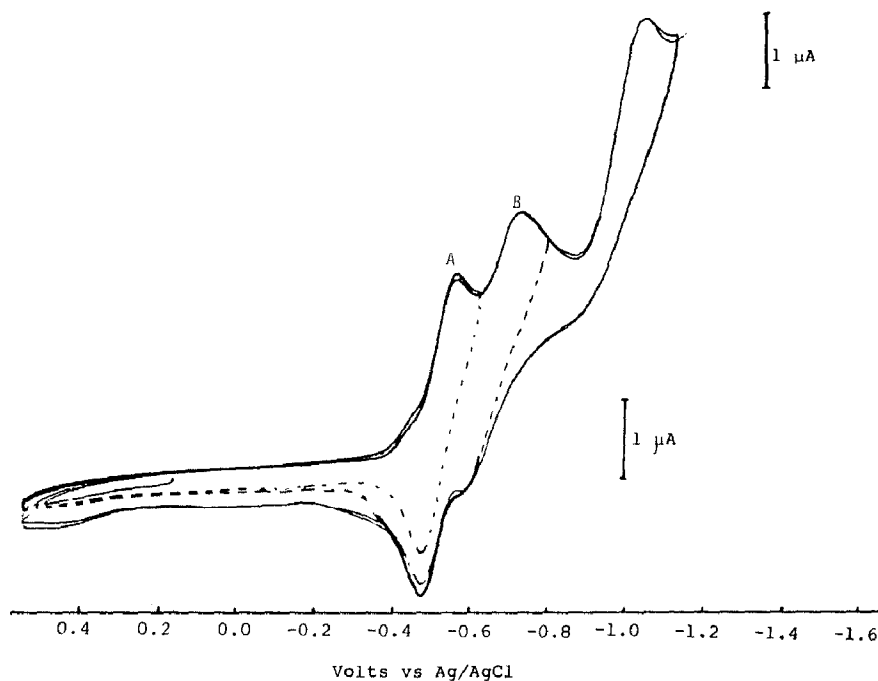
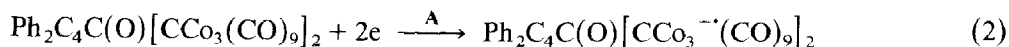


Fig. 2. Cyclic voltammograms at 202 K of **2** at Pt in $\text{CH}_2\text{Cl}_2/\text{TBAP}$ under argon, 50 mV s^{-1} . Repeat scans illustrating reversibility of first and second reduction processes.

whether dissolved CO is present; **A** has a diffusion current corresponding to the transfer of two electrons (using ferrocene as an in situ reference and assuming that the diffusion coefficient of **2** is approximately the same as $\text{PhCCo}_3(\text{CO})_9$) [21] and **B** corresponds to a one-electron reduction step. **A** and **B** are followed by an irreversible multi-electron wave **D**. On the reverse scan, apart from the companion oxidation waves to **A** and **B**, there is a small wave corresponding to the oxidation of $\text{Co}(\text{CO})_4^-$ when the reduction scan is taken past **D**. $\text{Co}(\text{CO})_4^-$ is a common feature in the electrochemistry of tricobalt carbon clusters because the unstable dianions fragment by cleavage of the cobalt–cobalt bonds [22].

Assignments for **A**, **B** and **D** can be made on the basis of the clusters and the cyclopentadienone ring acting as mutually independent redox centres. The reduction potential for **A** is similar to those for other molecules containing the $\text{CCo}_3(\text{CO})_9$ unit [21] and since the profile corresponds to a 2-electron transfer occurring at a single potential, we can assign **A** to the reduction of two independent cluster centres (eq. 2). The separation between **D** and **A** of 0.8 V is typical of that between the cluster radical anion and dianion reduction potentials [22,23] and wave **D** is partially due to the reduction of the cluster radical anions (vide infra).



The redox behaviour of a number of cyclopentadienones has been investigated [24,25]. The primary reduction processes give rise to quasi-reversible reduction waves in the cyclic voltammograms in the range -0.80 to -1.5 V (vs. SCE). Preparative reduction of substituted cyclopentadienones leads to the corresponding

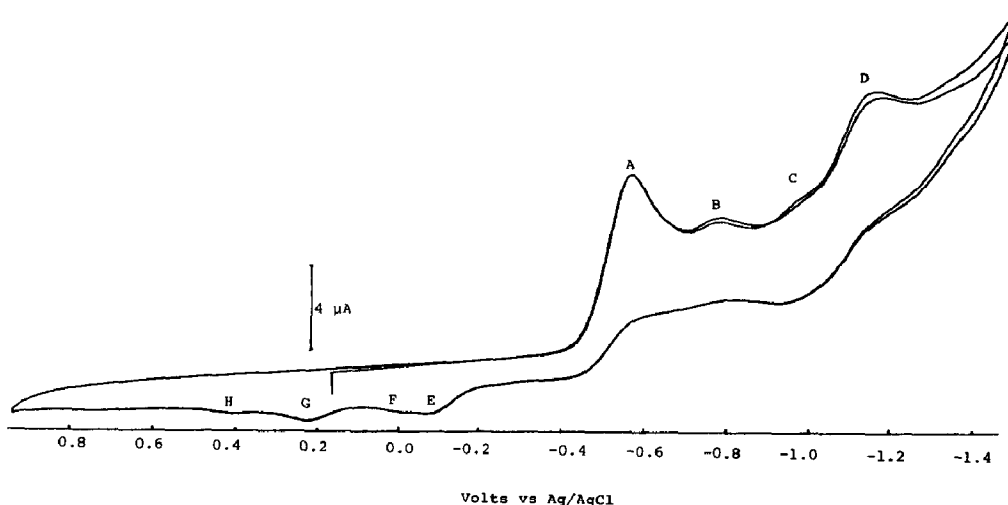
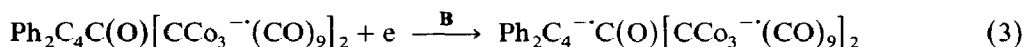


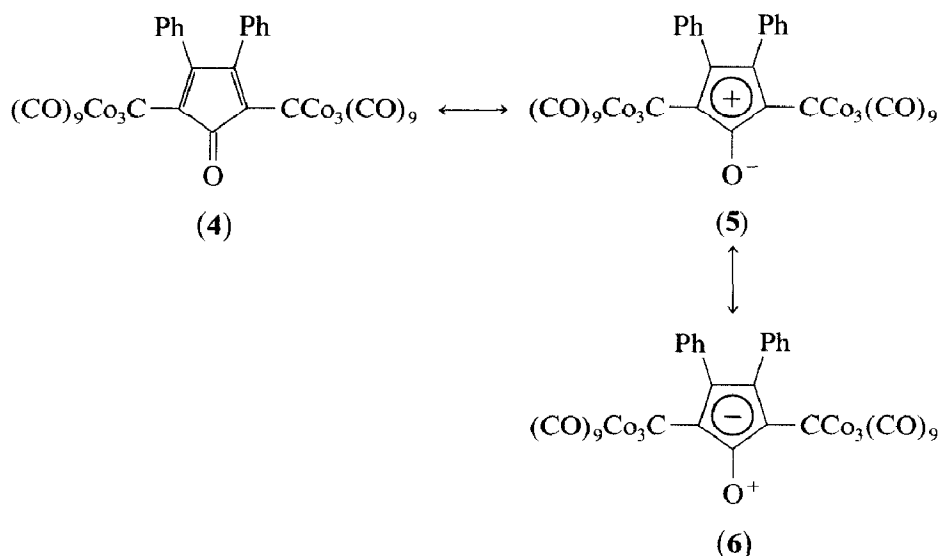
Fig. 3. Cyclic voltammograms at 293 of **2** at Pt in $\text{CH}_2\text{Cl}_2/\text{TBAP}$ under argon, 50 mV s^{-1} .

enones in good yield. We therefore assign **B** to the one-electron reduction of the cyclopentadienone ring (eq. 3).



The contiguous interaction of the cyclic π -system in cyclopentadienones could extend to include the cluster entities and this would provide a mechanism for electrochemical coupling of the cluster and ring redox centres. Photoelectron data suggest that the π -system in the clusters, which includes the electron-rich carbyne carbon, is sufficiently flexible for Co_3C to act as donor or acceptor [26]. This flexibility is manifested in a number of chemical and spectroscopic properties of the tricobalt carbon compounds including electrochemical data where the characteristic electron-withdrawing response of the clusters is modified if the apical substituent has appropriate orbitals to interact with the π -system [8]. It is conceivable that electrochemical coupling of the cyclopentadienone and cluster redox centres gives rise to **A** and **B** but, on this basis, it is difficult to explain the current ratio of 2/1. The two-electron wave **A** is compatible with either two totally interacting centres or two individual centres [26] but the 202 K data do not distinguish between the two options on strictly electrochemical criteria.

The cluster reduction potential of $E_{1/2} = -0.54 \text{ V}$ shows that the cyclopentadienone is acting like a phenyl substituent ($E_{1/2}$ $\text{PhCCO}_3(\text{CO})_9$ is -0.56 V in the same electrode/solvent system [22]) despite the strong inductive effect of a CO adjacent to the cluster. Similarly, the ring reduction potential is similar to that of tetraphenylcyclopentadienone [25]. Trends in reduction potentials and photoelectron data suggest that the polar canonical forms **5** and **6** make an important contribution to the electronic character of cyclopentadienones. In general, the first one-electron reduction potentials of cyclopentadienones in the range $-0.80 \rightarrow -1.5 \text{ V}$ (vs. SCE) are more negative than anticipated from a localisation induced by structure **4**. Fox and co-workers [24] have detailed how potentials for a localised ring can be estimated based on cyclohexenone. Using their procedure for **2** it

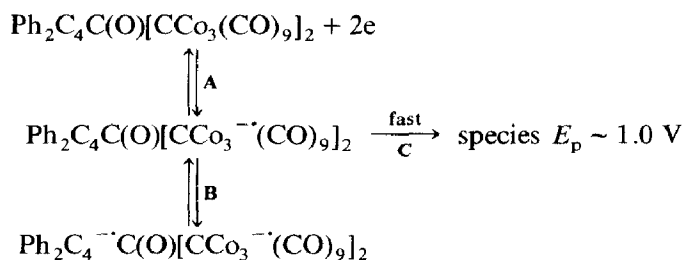


Scheme 2

appears the charge is not dispersed onto the clusters and/or that the positive electron-withdrawing effect of the cluster is counter-balanced by the negative effect of steric interactions between substituents.

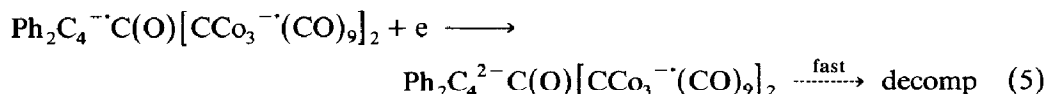
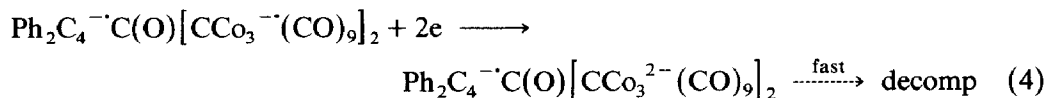
The electrochemical behaviour of **2** at higher temperatures is informative (Fig. 3). As the temperature increases **A** becomes progressively less reversible and at room temperature the reduction step is chemically irreversible; **B** is relatively unchanged. In tandem with the increasing irreversibility of **A** a new quasi-reversible reduction wave **C** appears and new oxidation waves are seen on the reverse scan. This i/v response is independent of scan rate or presence of CO except that the B/C current ratio is larger at fast scan rates. In polarograms of **2** at 293 K the waves corresponding to **A** and **C** have significantly larger currents than those for **B** and **D** and the $E_{1/4} - E_{3/4}$ value of ~ 40 mV for **A** is consistent with a two-electron reduction process. Irreversible formation of Co_3CR radical anions is unusual but is found where rapid reactions occur involving the apical C–R group [22,23].

Clearly the radical anion species from the reduction of clusters, **A**, is involved in a chemical reaction which gives rise to a species which in turn undergoes the reduction process **C** (an $\vec{\text{ECE}}$ process). This reaction causes a rearrangement of **2** such that the cyclopentadienone ring is no longer electrochemically active and the current for **B** decreases. One can also infer that the reduction of the cyclopentadienone **B** is independent of the cluster reduction process giving rise to **C**.



It has not been possible to identify the product of process C as the controlled electroreduction of **2** at -0.6 V only gave unstable species with short lifetimes which precluded characterisation.

Two possible assignments for **D** are shown below.



The potential difference between the first reduction and second reduction step for both the Co_3C clusters and cyclopentadienones is usually $0.7\text{--}0.9$ V and it is likely that **D** is a combination of both reduction steps (4) and (5).

In addition to the reduction processes an oxidation step **E** is found at $E_a = 1.1$ V (at 200 mV s^{-1}) for which the chemical reversibility is dependent on temperature

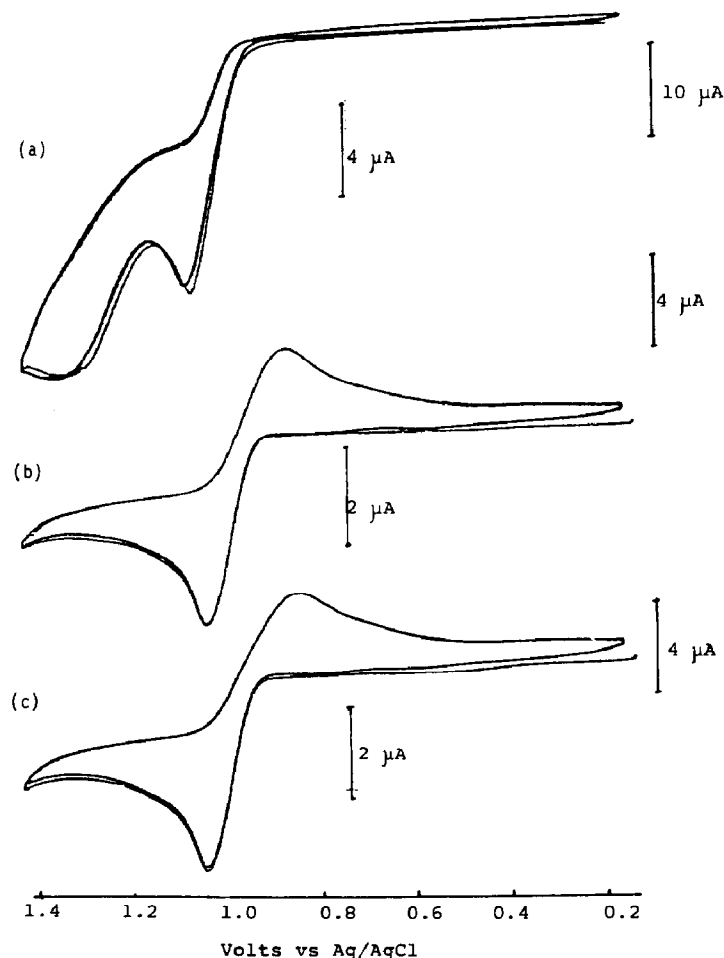


Fig. 4. Cyclic voltammograms of **2** at Pt in $\text{CH}_2\text{Cl}_2/\text{TBAP}$ at 50 mV s^{-1} ; oxidation process. (a) at 293 K, under argon (b) at 201 K, under CO (c) at 210 K, under argon.

and scan rate (Fig. 4). A similar oxidation step is found in the electrochemistry of cyclopentadienones [24,25].

Experimental

All reactions were carried out under dry argon or nitrogen. The clusters $\text{BrCCo}_3(\text{CO})_9$ and $\text{HCCo}_3(\text{CO})_9$ were prepared by published methods [12,19]. All i/v measurements were made with a PAR Model 174A Polarographic analyser and a PAR 175 Universal Programmer. Controlled potential electrolysis was performed using a homebuilt potentiostat or the PAR equipment. For transient electrochemical measurements a three-electrode cell was used with Pt electrodes referenced against a vycor-tipped AgCl-coated Ag wire immersed in a saturated LiCl/acetone solution. In order to provide a valid comparison with literature data the system was also referenced against ferrocene ($E_{1/2} = 0.72$ V) and fluorenone ($E_{1/2} = -1.16$ V in CH_2Cl_2 against ferrocene). The Pt electrodes were carefully cleaned prior to use, and thrice recrystallised $^n\text{Bu}_4\text{NPF}_6$ was used as the supporting electrolyte in CH_2Cl_2 . Electrochemical parameters for the $[\text{ferrocene}]^{+/0}$ sample under the same conditions were taken as those for electrochemical reversibility to account for uncompensated resistance efforts.

Reaction of $\text{PhC}\equiv\text{CH}$ with $\text{BrCCo}_3(\text{CO})_9$

Copper(I) chloride (50 mg) was added to a stirred solution of ethylamine (0.20 g) in dioxane (12 ml) followed by phenylacetylene (~ 0.2 ml). The temperature was held at 25°C by external cooling. A solution of the cluster $\text{BrCCo}_3(\text{CO})_9$ (1 g) in dioxane (10 ml) was then added dropwise during 20–30 minutes. The resultant brown solution was stirred for several minutes, then filtered, and the solvent was removed in vacuo. The thick syrup containing some unreacted phenylacetylene was dissolved in CH_2Cl_2 and separated on silica gel plates (eluent hexane). The following bands were eluted from the silica with CH_2Cl_2 : (1) red-brown oil (< 0.10 g) $\text{PhC}_2[\text{Co}_2(\text{CO})_6]\text{H}$; $\nu(\text{CO})$: 2095 (ms), 2056 (vs), 2031 (vs), 2016 (sh), 1984 (w) cm^{-1} [2]; (2) purple (< 0.005 g) $\text{HCCo}_3(\text{CO})_9$; (3) purple (0.311 g) $\text{BrCCo}_3(\text{CO})_9$; (4) brown (0.230 g); (5) green (< 0.005 g) $\text{PhC}_2[\text{Co}_2(\text{CO})_6]\text{CCo}_3(\text{CO})_9$, identified by comparison with authentic sample; (6) dark brown $\text{EtN(H)CCo}_3(\text{CO})_9$, identified by mass spectrum.

The solvent was rapidly removed from the solution of band four to leave a dark-brown moist solid. A mass spectrum of the freshly prepared solid gave m/e : 542 $[\text{PhC}_2\text{CCo}_3(\text{CO})_9]^+$, 514 $[M^+ - \text{CO}]$, 486 $[M^+ - 2\text{CO}]$, 458 $[M^+ - 3\text{CO}]$, 430 $[M^+ - 4\text{CO}]$, 402 $[M^+ - 5\text{CO}]$, 374 $[M^+ - 6\text{CO}]$, 346 $[M^+ - 7\text{CO}]$, 318 $[M^+ - 8\text{CO}]$, 290 $[\text{PhC}_2\text{CCo}_3]^+$. $\nu(\text{CO})(\text{hexane})$: 2103 (ms), 2058 (vs), 2041 (vs), 2025 (m), 2014 (sh), 1981 (w) cm^{-1} .

It is not possible to recrystallise this compound or obtain an analytically pure sample as it rapidly undergoes a transformation to give a number of other products, as described below.

Preparation of $\text{Ph}_2\text{C}_4\text{C(O)}[\text{CCo}_3(\text{CO})_9]_2$

(i) $\text{PhC}_2\text{CCo}_3(\text{CO})_9$ isolated by column chromatography as described above can be converted into the cyclopentadienone derivative by leaving a sample in vacuo for one day. Alternatively, the crude reaction mixture from the preparation of alkyne is

not separated by chromatography but is dried in vacuo (0.3 mmHg) for at least 12 h. Either of the vacuum-dried solids is then separated by preparative plate chromatography (silica gel) with CH_2Cl_2 as eluant. Several were bands eluted: (1) red-brown $\text{PhC}_2[\text{Co}_2(\text{CO})_6]\text{H}$; (2) brown $\text{PhC}_2\text{CCo}_3(\text{CO})_9$; (3) green-brown $\text{PhC}_2[\text{Co}_2(\text{CO})_6]\text{-CCo}_3(\text{CO})_9$ (3); (4) dark green; (5) grey (trace amount). $\nu(\text{CO})$: 2106 (mw), 2097 (mw), 2081 (vw), 2058 (s), 2039 (ms), 2010 (w), 1997 (w) cm^{-1} . The solid from band 4 was recrystallised from hexane and identified as **2**. Found: C, 38.36; H, 1.31. $\text{C}_{37}\text{H}_{10}\text{Co}_6\text{O}_{19}$ calcd.: C, 39.89; H, 0.96%. Mass spectrum m/e (FAB): 1112 (M^+). ^1H NMR (CDCl_3): δ 7.00 (m). UV-visible, λ_{max} (CDCl_3): 700, 530, 405 nm. $\nu(\text{CO})(\text{hexane})$: 2103 (mw), 2093 (m), 2064 (s), 2056 (vs), 2037(s), 2027 (sh), 2012 (w), 1975 (vw) cm^{-1} .

(ii) Freshly prepared $\text{PhC}_2\text{CCo}_3(\text{CO})_9$ (~ 8 mg) was dissolved in hexane (15 ml) at 20°C under an atmosphere of CO. No reaction was observed during 2 h. The temperature was then raised to 50°C . No change had occurred after a further 2 h. However, the presence of **2** was detected after ~ 0.5 h by evaporation of the hexane to leave a damp solid.

(iii) A freshly prepared dry sample of $\text{PhC}_2\text{CCo}_3(\text{CO})_9$ was placed under an atmosphere of EtNH_2 in a sealed flask. An immediate exothermic reaction occurred. The flask was left at -20°C for three weeks. When it was opened an unknown gas was released. Separation by PTLC revealed trace quantities of a number of compounds, none of which corresponded to **2**.

Reaction of $\text{PhC}_2\text{CCo}_3(\text{CO})_9$ with $\text{Co}_2(\text{CO})_8$

To a solution of freshly prepared $\text{PhC}_2\text{CCo}_3(\text{CO})_9$ (~ 0.05 g) in hexane (10 ml) at room temperature was added an excess of $\text{Co}_2(\text{CO})_8$. Monitoring of the reaction

(continued on p. 354)

Table 2

Crystal data, data collection and refinement of compound **2**

| Crystal data | Data collection and refinement |
|---|--|
| Formula: $\text{C}_{37}\text{H}_{10}\text{O}_{19}\text{Co}_6$ | Diffraction: Nicolet P3 |
| Formula weight: 1112.08 g mol $^{-1}$ | Temperature: 123 ± 5 K |
| Crystal system: triclinic | Radiation: Mo- K_α (λ 0.71069 Å) |
| Space group: $P\bar{1}$ (No. 2) [28] | Scan type (ω - 2θ) |
| a 14.303(3) Å | Scan speed: variable |
| b 15.292(3) Å | Data limits: $4 < 2\theta < 50^\circ$ |
| c 21.341(7) Å | Reflections measured: $h, \pm k, \pm l$ |
| α 98.17(2) $^\circ$ | Crystal decay: $< 10\%$ ^a |
| β 107.39(2) $^\circ$ | Total observed data: 14763 ^b |
| γ 110.69(2) $^\circ$ | Absorption correction: analytical [30] |
| V 3996(2) Å 3 | Transmission: 0.797 (max) |
| D_M 1.58 g cm $^{-3}$ | 0.579 (min) |
| D_C 1.57 g cm $^{-3}$ | Unique data: 9275 ($I > 2\sigma I$) |
| $Z = 4$ | Number of variables: 199/361 ^c |
| Crystal size 0.45 \times 0.22 \times 0.22 mm | $R(\sum F_o - F_c / \sum F_o) = 0.058$ |
| $\mu(\text{Mo-}K_\alpha)$ 24.74 cm $^{-1}$ | $R_w[\sum w(\Delta F)^2 / \sum w F_o^2]^{1/2} = 0.057$ |
| $F(000) = 2184$ | $w = [1.7349 / (\sigma^2 F + 0.00096 F^2)]$ |

^a Standard reflections (5 0 0) (0 8 0) (0 0 7) measured after every 100 reflections. ^b Lorentz and polarisation corrections were applied by use of the SHELXTL system [31]. ^c In alternating blocked matrix cycles, Ref. 30.

Table 3

Final positional and equivalent thermal parameters for compound **2**

| Atom | x | y | z | U_{eq} |
|-------------------|-----------|-----------|-----------|----------|
| <i>Molecule 1</i> | | | | |
| Co(11) | 0.4386(1) | 0.3558(1) | 0.3193(1) | 0.020 |
| Co(12) | 0.3590(1) | 0.1778(1) | 0.2975(1) | 0.020 |
| Co(13) | 0.4409(1) | 0.2860(1) | 0.4155(1) | 0.022 |
| Cap(11) | 0.5049(6) | 0.2712(5) | 0.3494(3) | 0.019 |
| C(111) | 0.4210(7) | 0.3467(6) | 0.2317(4) | 0.027 |
| O(111) | 0.4027(5) | 0.3439(4) | 0.1760(3) | 0.039 |
| C(112) | 0.5618(7) | 0.4639(6) | 0.3543(4) | 0.033 |
| O(112) | 0.6433(6) | 0.5284(5) | 0.3763(4) | 0.068 |
| C(113) | 0.3345(7) | 0.3966(6) | 0.3191(4) | 0.030 |
| O(113) | 0.2658(5) | 0.4212(5) | 0.3166(3) | 0.047 |
| C(121) | 0.3576(6) | 0.0711(6) | 0.3238(4) | 0.033 |
| O(121) | 0.3590(5) | 0.0033(4) | 0.3393(3) | 0.046 |
| C(122) | 0.3609(7) | 0.1363(6) | 0.2153(4) | 0.031 |
| O(122) | 0.3602(5) | 0.1058(4) | 0.1625(3) | 0.040 |
| C(123) | 0.2202(7) | 0.1676(6) | 0.2747(4) | 0.029 |
| O(123) | 0.1386(4) | 0.1682(4) | 0.2617(3) | 0.037 |
| C(131) | 0.4446(7) | 0.1991(7) | 0.4630(4) | 0.036 |
| O(131) | 0.4409(6) | 0.1448(5) | 0.4948(4) | 0.057 |
| C(132) | 0.5476(8) | 0.3910(7) | 0.4778(5) | 0.039 |
| O(132) | 0.6173(6) | 0.4608(5) | 0.5172(4) | 0.066 |
| C(133) | 0.3208(7) | 0.2958(6) | 0.4242(4) | 0.026 |
| O(133) | 0.2433(6) | 0.2995(5) | 0.4268(3) | 0.049 |
| Co(14) | 0.7614(1) | 0.2279(1) | 0.1724(1) | 0.020 |
| Co(15) | 0.8382(1) | 0.4070(1) | 0.2154(1) | 0.022 |
| Co(16) | 0.9437(1) | 0.3175(1) | 0.2600(1) | 0.020 |
| Cap(12) | 0.8096(5) | 0.3106(5) | 0.2646(3) | 0.012 |
| C(141) | 0.6202(7) | 0.2028(6) | 0.1292(4) | 0.029 |
| O(141) | 0.5330(5) | 0.1847(5) | 0.0997(3) | 0.041 |
| C(142) | 0.7423(6) | 0.1124(6) | 0.1889(4) | 0.027 |
| O(142) | 0.7299(5) | 0.0396(4) | 0.1997(3) | 0.046 |
| C(143) | 0.7914(7) | 0.2145(6) | 0.0955(4) | 0.032 |
| O(143) | 0.8122(5) | 0.2077(5) | 0.0470(3) | 0.041 |
| C(151) | 0.7169(8) | 0.4272(6) | 0.1845(4) | 0.036 |
| O(151) | 0.6461(6) | 0.4472(5) | 0.1675(4) | 0.055 |
| C(152) | 0.9072(7) | 0.5159(7) | 0.2852(4) | 0.034 |
| O(152) | 0.9491(6) | 0.5819(5) | 0.3310(3) | 0.057 |
| C(153) | 0.8933(8) | 0.4371(6) | 0.1498(5) | 0.044 |
| O(153) | 0.9228(7) | 0.4535(5) | 0.1076(4) | 0.067 |
| C(161) | 1.0501(7) | 0.4209(6) | 0.3248(5) | 0.030 |
| O(161) | 1.1222(5) | 0.4883(4) | 0.3648(3) | 0.042 |
| C(162) | 0.9599(7) | 0.2264(6) | 0.3012(4) | 0.029 |
| O(162) | 0.9714(6) | 0.1703(5) | 0.3284(3) | 0.046 |
| C(163) | 1.0148(7) | 0.3117(6) | 0.2017(4) | 0.026 |
| O(163) | 1.0590(5) | 0.3096(5) | 0.1665(3) | 0.046 |
| C(11) | 0.6045(6) | 0.2726(5) | 0.3497(4) | 0.016 |
| C(12) | 0.6890(6) | 0.2665(5) | 0.3964(3) | 0.016 |
| C(13) | 0.7831(6) | 0.2862(5) | 0.3748(3) | 0.016 |
| C(14) | 0.7544(6) | 0.2976(5) | 0.3109(4) | 0.018 |
| C(15) | 0.6402(6) | 0.2901(5) | 0.2899(4) | 0.019 |
| O(15) | 0.5870(5) | 0.2950(4) | 0.2373(3) | 0.033 |
| C(171) | 0.6909(6) | 0.2374(5) | 0.4603(4) | 0.020 |
| C(172) | 0.7480(7) | 0.3039(6) | 0.5254(4) | 0.029 |

(continued)

Table 3 (continued)

| Atom | x | y | z | U_{eq} |
|---------|------------|------------|-----------|----------|
| C(173) | 0.7516(7) | 0.2729(6) | 0.5835(4) | 0.036 |
| C(174) | 0.7012(7) | 0.1763(6) | 0.5780(4) | 0.033 |
| C(175) | 0.6467(7) | 0.1092(6) | 0.5149(4) | 0.031 |
| C(176) | 0.6385(7) | 0.1388(6) | 0.4559(4) | 0.029 |
| C(181) | 0.8860(6) | 0.2958(6) | 0.4220(4) | 0.022 |
| C(182) | 0.9759(7) | 0.3853(6) | 0.4468(4) | 0.027 |
| C(183) | 1.0739(7) | 0.3976(7) | 0.4937(4) | 0.036 |
| C(184) | 1.0831(7) | 0.3200(7) | 0.5170(5) | 0.037 |
| C(185) | 0.9953(7) | 0.2305(7) | 0.4927(4) | 0.034 |
| C(186) | 0.8976(6) | 0.2181(6) | 0.4465(4) | 0.026 |
| Co(21) | 0.5858(1) | 0.2407(1) | 0.7586(1) | 0.024 |
| Co(22) | 0.6353(1) | 0.3205(1) | 0.8792(1) | 0.027 |
| Co(23) | 0.5822(1) | 0.1438(1) | 0.8417(1) | 0.023 |
| Cap(21) | 0.5014(6) | 0.2186(5) | 0.8134(4) | 0.022 |
| C(211) | 0.5758(7) | 0.3439(7) | 0.7330(4) | 0.034 |
| O(211) | 0.5694(6) | 0.4087(5) | 0.7157(4) | 0.060 |
| C(212) | 0.5014(7) | 0.1474(6) | 0.6785(4) | 0.031 |
| O(212) | 0.4515(5) | 0.0900(4) | 0.6276(3) | 0.042 |
| C(213) | 0.7183(8) | 0.2568(8) | 0.7567(4) | 0.042 |
| O(213) | 0.7991(6) | 0.2660(7) | 0.7575(4) | 0.074 |
| C(221) | 0.6400(6) | 0.3180(6) | 0.9637(4) | 0.030 |
| O(221) | 0.6513(5) | 0.3197(4) | 1.0191(3) | 0.039 |
| C(222) | 0.5882(9) | 0.4143(7) | 0.8737(5) | 0.049 |
| O(222) | 0.5558(9) | 0.4713(6) | 0.8688(4) | 0.099 |
| C(223) | 0.7783(9) | 0.3795(8) | 0.8994(5) | 0.055 |
| O(223) | 0.8720(6) | 0.4127(7) | 0.9144(5) | 0.100 |
| C(231) | 0.5452(7) | 0.1021(6) | 0.9099(4) | 0.030 |
| O(231) | 0.5238(6) | 0.0724(5) | 0.9519(3) | 0.047 |
| C(232) | 0.5045(8) | 0.0299(7) | 0.7783(4) | 0.035 |
| O(232) | 0.4515(6) | -0.0432(4) | 0.7370(3) | 0.046 |
| C(233) | 0.7213(8) | 0.1550(7) | 0.8704(4) | 0.040 |
| O(233) | 0.8078(6) | 0.1646(6) | 0.885(3) | 0.062 |
| Co(24) | 0.0530(1) | 0.1061(1) | 0.8952(1) | 0.020 |
| Co(25) | 0.2315(1) | 0.1867(1) | 0.9878(0) | 0.021 |
| Co(26) | 0.1521(1) | 0.2852(1) | 0.9279(1) | 0.024 |
| Cap(22) | 0.1902(6) | 0.1849(5) | 0.8935(4) | 0.018 |
| C(241) | -0.0543(7) | 0.0985(6) | 0.8206(4) | 0.026 |
| O(241) | -0.1242(5) | 0.0938(4) | 0.7761(3) | 0.035 |
| C(242) | 0.0602(6) | -0.0078(6) | 0.8705(4) | 0.025 |
| O(242) | 0.0675(5) | -0.0775(4) | 0.8549(3) | 0.038 |
| C(243) | -0.0227(6) | 0.0858(6) | 0.9509(4) | 0.027 |
| O(243) | -0.0700(5) | 0.0714(5) | 0.9855(3) | 0.042 |
| C(251) | 0.3649(7) | 0.2845(6) | 1.0260(4) | 0.027 |
| O(251) | 0.4483(5) | 0.3459(4) | 1.0494(3) | 0.041 |
| C(252) | 0.2723(7) | 0.0888(6) | 0.9846(4) | 0.029 |
| O(252) | 0.3013(5) | 0.0276(4) | 0.9820(3) | 0.040 |
| C(253) | 0.1903(7) | 0.1841(6) | 1.0611(4) | 0.034 |
| O(253) | 0.1656(5) | 0.1805(5) | 1.1068(3) | 0.046 |
| C(261) | 0.2728(8) | 0.3939(7) | 0.9477(4) | 0.038 |
| O(261) | 0.3463(6) | 0.4612(5) | 0.9588(4) | 0.067 |
| C(262) | 0.0750(7) | 0.3084(6) | 0.8545(5) | 0.031 |
| O(262) | 0.0314(5) | 0.3292(4) | 0.8083(3) | 0.043 |
| C(263) | 0.0939(9) | 0.3158(7) | 0.9892(5) | 0.046 |
| O(263) | 0.0586(8) | 0.3334(6) | 1.0258(4) | 0.082 |
| C(21) | 0.3942(6) | 0.2006(5) | 0.8077(4) | 0.020 |

(continued)

Table 3 (continued)

| Atom | <i>x</i> | <i>y</i> | <i>z</i> | <i>U</i> _{eq} |
|--------|------------|-----------|-----------|------------------------|
| C(22) | 0.2997(6) | 0.1761(5) | 0.7537(4) | 0.018 |
| C(23) | 0.2093(6) | 0.1636(5) | 0.7778(4) | 0.017 |
| C(24) | 0.2430(6) | 0.1796(5) | 0.8561(4) | 0.019 |
| C(25) | 0.3611(6) | 0.2000(5) | 0.8693(4) | 0.017 |
| O(25) | 0.4205(4) | 0.2118(4) | 0.9265(3) | 0.035 |
| C(271) | 0.2791(6) | 0.1619(5) | 0.6794(4) | 0.019 |
| C(272) | 0.2181(7) | 0.0696(6) | 0.6336(4) | 0.033 |
| C(273) | 0.1932(8) | 0.0577(7) | 0.5650(4) | 0.044 |
| C(274) | 0.2315(8) | 0.1382(6) | 0.5412(4) | 0.036 |
| C(275) | 0.2900(7) | 0.2280(6) | 0.5856(4) | 0.031 |
| C(276) | 0.3155(6) | 0.2402(6) | 0.6553(4) | 0.024 |
| C(281) | 0.0987(6) | 0.1332(6) | 0.7264(3) | 0.021 |
| C(282) | 0.0251(6) | 0.0355(6) | 0.7045(3) | 0.025 |
| C(283) | −0.0739(7) | 0.0068(6) | 0.6521(4) | 0.031 |
| C(284) | −0.1025(7) | 0.0726(6) | 0.6238(4) | 0.029 |
| C(285) | −0.0317(7) | 0.1691(6) | 0.6457(4) | 0.032 |
| C(286) | 0.0705(7) | 0.1999(6) | 0.6966(4) | 0.030 |

with TLC indicated complete reaction of the cluster after 15 min; the solvent was removed in vacuo and the products separated on silica plates which were developed in hexane. The following bands were removed: (1) brown $\text{Co}_4(\text{CO})_{12}$; $\nu(\text{CO})$: 2063 (s), 2038 (w), 2028 (w), 1867 (m) cm^{-1} . Mass spectrum m/e : 572 (M^+); (2) green; (3) green-grey $\nu(\text{CO})$: 2016 (w), 2097 (w), 2093 (sh), 2058 (vs), 2038 (vs), 2010 (w), 1987 (w), 1887 (w) cm^{-1} .

The solid from band 2 was recrystallised as black crystals from hexane and identified as $\text{PhC}_2[\text{Co}_2(\text{CO})_6]\text{CCo}_3(\text{CO})_9$ (**3**), m/e : 828 (M^+) (two separate fragmentation patterns could be identified; $[M^+ - n\text{CO}]$ and $[\text{PhC}_3\text{Co}_4(\text{CO})_{10}^+ - n\text{CO}]$. $\nu(\text{CO})$ (hexane): 2105 (w), 2081 (s), 2060 (vs), 2041 (w), 2029 (m), 2012 (w), 1981 (w) cm^{-1} . UV-visible (CHCl_3): 610, 540, 395, 295 nm.

The grey compound from band 3 was not identified, but it was the same as that from band 5 in the preparation of **2**.

X-ray data collection and reduction for $\text{Ph}_2\text{C}_4(\text{CO})[\text{CCo}_3(\text{CO})_9]_2$

A sample of **2** prepared as outlined above was recrystallised from hexane to yield purple/black rhombs. Precession photography (Cu-K_α radiation) indicated a triclinic unit cell and the space group was confirmed as $P\bar{1}$ (No. 2) [28] by the success of the structure refinement. Details of the crystals, data collection and structure solution are summarised in Table 2. The structure was solved by direct methods by use of the EEES option of SHELX76 [30]. The resulting E -map revealed the 12 Co atoms, corresponding to the Co_3 triangles from the two unique molecules in the unit cell. The remaining non-hydrogen atoms were found in subsequent difference Fourier, least-squares refinement cycles [30]. Hydrogen atoms on the phenyl rings were included in calculated positions ($d(\text{C-H})$ 0.98 Å) with fixed isotropic thermal parameters. Weighted refinement continued with all non-hydrogen atoms assigned anisotropic temperature factors and portions of the two independent molecules refined in alternating blocked-matrix cycles. The function minimised was $w(F_o - F_c)^2$ by use of a version of SHELX76 adapted for large structures [30]. Refinement

converged with $R = 0.058$ and $R_w = 0.057$. The final difference map showed no peaks higher than $0.83 \text{ e } \text{\AA}^{-3}$.

Final positional and equivalent thermal parameters are listed in Table 3. Tables of thermal parameters, H-atom parameters, observed and calculated structure factors and mean-plane data can be obtained from the authors (J.S.)

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