Tetracobalt Complexes with Co_3 Face-Capping Cycloheptatrienyl and Cyclooctatetraene Ligands

Hubert Wadepohl,* Stefan Gebert, Hans Pritzkow, Fabrizia Grepioni, and Dario Braga*

Dedicated to Professor H. P. Latscha on the occasion of his 60th birthday

Abstract: The novel tetracobalt cluster complexes $[Co_4(CO)_6(\eta^5\text{-}C_7H_9)(\mu_3\text{-}C_7H_7)]$ (**8**) and $[Co_4(CO)_6(\eta^4\text{-}C_8H_8)(\mu_3\text{-}C_8H_8)]$ (**9**), which contain facial C_nH_n ligands, were obtained in high yield from $[Co_4(CO)_{12}]$ (**5**) and cycloheptatriene or cyclooctatetraene, respectively, in boiling *n*-heptane. Treatment of **9** with $[Fe(CO)_5]$, cyclohexadiene or 6,6-diphenylfulvene gave the derivatives $[Co_4(CO)_6(L)(\mu_3\text{-}C_8H_8)]$, **10** $[L = (CO)_2]$, **11** $(L = \eta^4\text{-}C_6H_8)$, and **12** $(L = \eta^4\text{-}C_5H_4CPh_2)$. The crystal structures of **8**–**11** were determined. The facial (face-capping) C_7H_7 ligand in **8** adopts a $\mu_3\text{-}\eta^2{:}\eta^3{:}\eta^3$ coordination mode to a Co_3 face of the tetracobalt cluster. The coordination geometry of the facial C_8H_8 ligands in **9**–**11** can be viewed as within a continuum limited by $\mu_3\text{-}\eta^2{:}\eta^3{:}\eta^3$ and $\mu_3\text{-}\eta^3{:}\eta^3{:}\eta^3$. In solution, **8**–**12** are highly fluxional (rapid reorientation of the $\mu_3\text{-}C_nH_n$ ligands, rapid haptotropic shifts involving the apical C_nH_n ligand in **9**). The crystal packing of **8**–**11** has been examined in detail; the hydrogen atoms of the cycloheptatrienyl and cyclooctatetraene ligands take part in intra- and intermolecular hydrogen bonding interactions of the $C{-}H\cdots O$ type.

Keywords: carbocycles • clusters • cobalt • facial ligands • hydrogen bonds

Introduction

The cyclic π-perimeters C_nH_n have been popular ligands in transition metal complexes right from the start of modern-day organometallic chemistry. Complexes with such ligands, for example $[(C_5H_5)_2Fe]$, $[(C_6H_6)_2Cr]$, and $[(C_8H_8)_2U]$, are among the milestones of organo transition metal chemistry. The intermediate-sized C_nH_n rings ($n = 5-8$) are not only capable of bonding to a single metal, but are also able to bridge metal–metal-bonded M_2 or M_3 entities. Complexes where a M_3 triangle is capped by the C_nH_n ligand are important test cases for the postulated analogy between (metal) surfaces and molecular (metal) clusters,[1] since this type of facial coordination is thought to resemble the adsorption states of such ligands on metal surfaces.[3] It is somewhat surprising that up to now significant molecular chemistry of such species (i.e. $\mu_3\text{-}C_nH_n$ cluster complexes) exists only for μ_3-arenes ($n = 6$), and that it has emerged only in the last ten years or so.[4] In contrast to a considerable number of dinuclear μ_2-arene complexes with quite diverse structures and chemistry, there are still only two major types of cluster complexes with μ_3-arene ligands.[4] These are complexes based on M_3, M_5, and M_6 (M = Ru, Os) metal carbonyl clusters[5] on the one hand and systems with a $[(\eta\text{-}C_5H_5)M]_3$ (M = Co, Rh) skeleton on the other.[4] This mismatch is even more pronounced with cyclopentadienyl ($n = 5$), cycloheptatrienyl ($n = 7$) and cyclooctatetraene (cot, $n = 8$). Many mononuclear and a considerable number of dinuclear complexes are known with these ligands,[6] but reports of triply bridged oligonuclear species have been very sparse.[9–11] For $n = 5$, 7, and 8, only one example of each has been characterized structurally: $[\{(\eta\text{-}C_5H_5)Rh\}_3(\mu_3\text{-}H)(\mu_3\text{-}C_5H_5)]$ (**1**),[9] $[\{(CO)_2Ru\}_3(\mu_3\text{-}S\mathit{t}Bu)(\mu_3\text{-}C_7H_7)]$ (**2**),[10] and $[\{(CO)Ni\}_3\{\mu_3\text{-}(CF_3)_2C_2\}(\mu_3\text{-}C_8H_8)]$ (**3**).[11] The C_8H_8 ligand in $[\{(CO)_2Co\}_3(\mu_3\text{-}CPh)(\mu_3\text{-}C_8H_8)]$ (**4**) is also face-capping; however, only six carbon atoms of the C_8 ring are bonded to the metal cluster.[12]

As an extension to our studies on μ_3-arene clusters,[13] we have been searching for synthetic routes to cluster complexes with facial (μ_3-coordinated) conjugated unsaturated hydrocarbon ligands other than arenes. Recent reports in the literature on the complex surface chemistry of cyclopolyenes, especially cot,[14,15] sparked our interest in the possible

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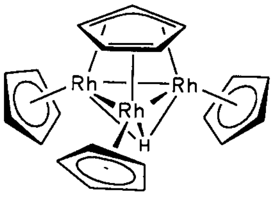
[*] Priv.-Doz. Dr. H. Wadepohl, Dr. S. Gebert, Dr. H. Pritzkow
Anorganisch-Chemisches Institut der Ruprecht-Karls-Universität
Im Neuenheimer Feld 270, D-69120 Heidelberg (Germany)
Fax: Int. code + (49) 6221 544197
e-mail: bu9@ix.urz.uni-heidelberg.de

Prof. Dr. D. Braga, Dr. F. Grepioni
Dipartimento di Chimica G. Ciamician, Università degli Studi di Bologna
Via Selmi, 2, I-40126 Bologna (Italy)
Fax: Int. code + (39) 51 259456
e-mail: dbraga@ciam.unibo.it



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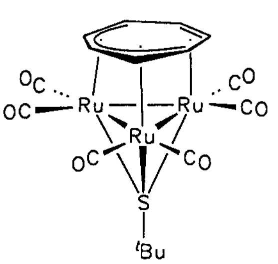

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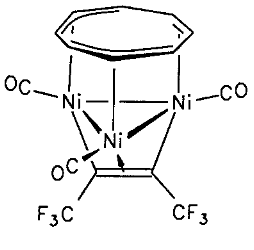

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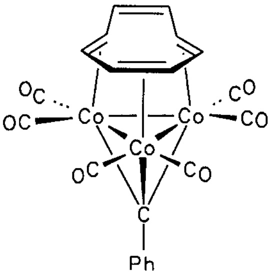

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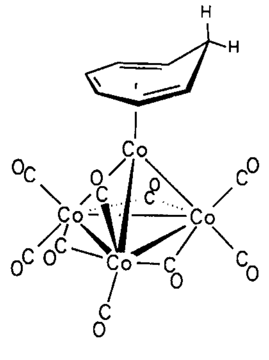
coordination modes of the ligands C_nH_n, in which $n > 6$, to molecular metal clusters. Here we report on a very simple synthetic route to tetracobalt carbonyl clusters with facial C_7H_7 and C_8H_8 ligands.

Another impetus stems from the possible participation of the face-capping carbacycles in intramolecular and intermolecular interactions. Now that the issue of crystal engineering is attracting so much attention under the general appeal of supramolecular and materials chemistry, it is recognized that organometallic crystals may possess important new properties arising from the external interactions of the ligands.[16] For example, the CO ligand has been shown to act as a Lewis base with respect to C–H donors in crystalline organo transition metal carbonyl complexes.[17] Carbon monoxide provides hydrogen-bonding acceptor sites of tunable basicity because its coordination mode with metal centers in polymetallic systems can be varied. The order of basicity is μ_3-CO > μ_2-CO > terminal CO and is reflected, in the solid state, in an increase in the same direction of the (C)H ··· O distances.[18] The importance of such interactions of varying strength in crystals of small organometallic clusters has recently been demonstrated.[19] The class of compounds discussed in this article combines the presence of CO ligands in their different bonding modes with the presence of many potential C–H donors. The roles played by C–H ··· O bonds and ring–ring interactions will be examined.

Results and Discussion

Preparation: The reaction of $[Co_4(CO)_{12}]$ (**5**) with a number olefins was previously studied by Kitamura and Joh.[20] With cycloheptatriene in boiling *n*-hexane, these authors obtained two products formulated as $[Co_4(CO)_9(C_7H_8)]$ (**6**) and $[Co_4(CO)_6(C_7H_8)_2]$. On the basis of ^1H NMR data, an apically η^6-coordinated cycloheptatriene ligand was suggested for **6**. No detailed structure was suggested for the latter complex, because of its alleged instability in solution, which was claimed to preclude even NMR spectroscopy. In the same investigation, a dinuclear complex, $[Co_2(CO)_4(C_8H_8)]$ (**7**), was obtained in 2% yield as the only isolable product of the reaction of **5** with cot in refluxing benzene.



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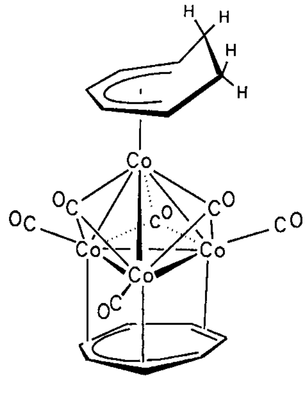

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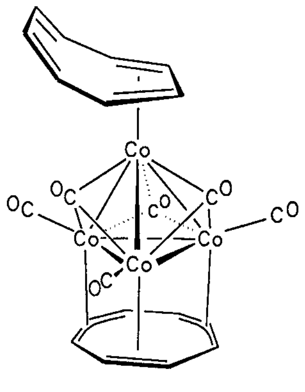

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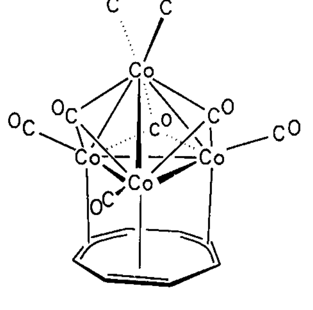

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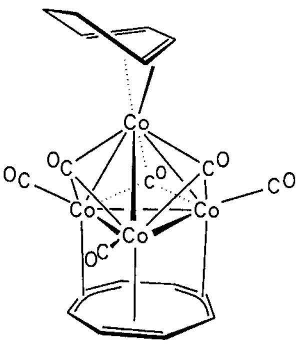

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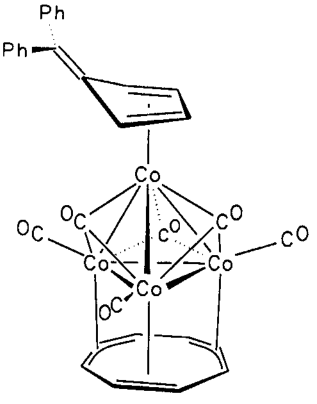

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In the course of our reinvestigation of this work, we found that **5** readily reacted with cycloheptatriene and cot in boiling *n*-heptane to give the tetranuclear μ_3-C_nH_n derivatives **8** and **9**, respectively. The dark green (**8**) and dark brown complexes (**9**) precipitated from the reaction mixtures and were isolated in 65% and 95% yield. During the formation of **8**, the IR bands of **6** are observed in the reaction mixture. The latter complex is presumably formed in the first step of the reaction. As judged from the relative intensities of the IR bands, its stationary concentration is quite low under our reaction conditions. A second, short-lived intermediate could be a cluster complex with two cycloheptatriene ligands, which would then undergo intramolecular hydrogen transfer to give **8**. We were unable to detect such an intermediate in the reaction mixture. It is also obvious that Kitamura and Joh's alleged $[Co_4(CO)_6(C_7H_8)_2]$ is no such intermediate. A comparison of the published IR data[20] with those of **8** clearly shows that their product was in fact contaminated **8**.

Complex **9** slowly decomposed in solution to give, in addition to other products not yet identified, another cluster complex with a face-capping cot ligand, $[Co_4(CO)_8(\mu_3\text{-}C_8H_8)]$ (**10**). Complex **10** was isolated in about 15% yield after heating a solution of **9** in toluene at 80 °C. Much better yields (about 80%) of **10** were obtained when **9** was heated with $[Fe(CO)_5]$ in toluene at 80 °C. Here the iron carbonyl simultaneously serves as a source of carbon monoxide and as an acceptor for the cot ligand (the complex $[(CO)_3Fe(cot)]$ was identified as one of the products). In an atmosphere of CO, **9** was readily degraded to $[Co_2(CO)_8]$. During this reaction, **10** was detected as an intermediate. With an excess of cyclooctatetraene, **10** was converted back into the bis(cyclooctatetraene) derivative **9**. This reaction crucially depends on the solvent. In *n*-heptane, where the solubility of both **9** and **10** is low, clean conversion is effected at 100 °C.

From the above observations it appears reasonable to assume that cycloheptatriene first enters the tetracobalt carbonyl cluster in an apical position to give **6**. A second molecule of cycloheptatriene encounters a sterically unfavorable situation as it becomes attached to a second apex of the Co_4 cluster (necessarily adjacent to the $Co(\eta^6\text{-}C_7H_8)$ moiety). Therefore, migration of the cyclopolyene into the Co_3 face-capping position may occur, accompanied or followed by transfer of a hydrogen atom[21] to the apical cycloheptatriene ligand. It is even possible that a species in which both C_7H_8 molecules are apically coordinated to the cluster in the η^6-mode may actually never be involved at all.

For the cyclooctatetraene tetracobalt cluster complexes the situation is less clear-cut. For obvious reasons, some tetracobalt mono-cot derivative must be formed in the first step of the reaction. Indeed, complex **10** with only one (face-capping) cot ligand was detected along with **9** in the precipitate if the reaction was quenched after a short time. We cannot, however, rule out the formation of **10** by the reaction of **9** with CO, which is, of course, present in the reaction mixture. Therefore, it is not quite clear if the first cot ligand enters the Co_4 cluster directly at the facial coordination site (to give **10**), or if an as yet undetected intermediate with an apical C_8H_8 ligand is involved. Such a primary species could either lose CO and take up a second cot ligand, which would then go into the facial position, or else rearrange to give **10**.

In the tricobalt alkylidyne cluster complex $[Co_3(CO)_9(\mu_3\text{-}CPh)]$, substitution of CO by cot results in a facially coordinated μ_3-η^2:η^2:η^2-C_8H_8 ligand (complex **4**), whereas with arenes, only products with an apical η^6-coordinated benzene derivative are formed.[12] Furthermore, the latter species were found to react with cot to give the μ_3-C_8H_8 derivative **4**, that is, the apical η^6-arene is replaced by the facial μ_3-η^2:η^2:η^2-C_8H_8. Hence, it appears that cyclooctatetraene exhibits a preference for the facial coordination site in cobalt carbonyl cluster complexes.

When treated with 1,3-cyclohexadiene or 6,6-diphenylfulvene, the apical η^4-cot ligand in **9** was selectively substituted. Red **11** and red-purple **12** were isolated in 62% and 27% yield. The more reactive 6,6-dimethylfulvene caused degradation of the Co_4 cluster, and did not result in a simple substitution product. In line with the above arguments, the selective substitution reactions also point to an inherently greater stability of the facial (μ_3) compared to the apical η^4-coordination mode of cyclooctatetraene on the Co_4 cluster.

Table 1. Selected bond lengths [Å] for the complexes $[Co_4(CO)_6(\eta^5\text{-}C_7H_9)(\mu_3\text{-}\eta^2{:}\eta^3{:}\eta^3\text{-}C_7H_7)]$ (**8**) and $[Co_4(CO)_6(\eta^4\text{-}C_8H_8)(\mu_3\text{-}\eta^2{:}\eta^3{:}\eta^3\text{-}C_8H_8)]$ (**9**).

	8	**9**
Co(1) – Co(2)	2.4440(11)	2.466(2)
Co(1) – Co(3)	2.6268(12)	2.462(2)
Co(1) – Co(4)	2.4841(11)	2.526(2)
Co(2) – Co(3)	2.4622(14)	2.540(2)
Co(2) – Co(4)	2.4942(12)	2.507(2)
Co(3) – Co(4)	2.4796(13)	2.522(3)
Co(1) – C(14)	2.200(4)	
Co(1) – C(15)	2.070(4)	2.246(5)
Co(1) – C(16)	2.094(4)	2.027(5)
Co(1) – C(17)	2.081(4)	2.021(5)
Co(1) – C(18)	2.142(4)	2.188(5)
Co(2) – C(1)	2.089(4)	2.086(5)
Co(2) – C(2)	2.083(4)	2.105(5)
Co(3) – C(3)	2.257(4)	2.364(5)
Co(3) – C(4)	2.066(4)	2.054(5)
Co(3) – C(5)	2.467(4)	2.181(5)
Co(4) – C(5)	2.430(4)	
Co(4) – C(6)	2.032(4)	2.239(5)
Co(4) – C(7)	2.223(4)	2.057(5)
Co(4) – C(8)		2.386(5)
C(1) – C(2)	1.425(6)	1.411(8)
C(1) – C(7)	1.422(6)	
C(1) – C(8)		1.414(8)
C(2) – C(3)	1.428(6)	1.417(7)
C(3) – C(4)	1.405(7)	1.415(7)
C(4) – C(5)	1.427(7)	1.416(7)
C(5) – C(6)	1.404(7)	1.417(8)
C(6) – C(7)	1.409(6)	1.402(7)
C(7) – C(8)		1.408(7)
C(14) – C(15)	1.390(6)	
C(14) – C(20)	1.505(6)	
C(15) – C(16)	1.412(6)	1.432(7)
C(15) – C(22)		1.433(7)
C(16) – C(17)	1.424(6)	1.395(7)
C(17) – C(18)	1.412(5)	1.424(7)
C(18) – C(19)	1.488(6)	1.428(7)
C(19) – C(20)	1.508(7)	1.357(7)
C(20) – C(21)		1.423(8)
C(21) – C(22)		1.346(7)

Crystal structure analyses: X-ray structure analyses were carried out with single crystals of **8**–**11**. Crystal details are given in the experimental section. There are two independent molecules in the asymmetric units of **10** and **11**. Those of **10** are quite similar, while there are differences in the orientation of the μ_3-cot ligands with respect to the rest of the molecules in **11**.[22] Important bond lengths are summarized in Tables 1 and 2.

Table 2. Selected bond lengths [Å] for the complexes $[Co_4(CO)_8(\mu_3\text{-}\eta^2{:}\eta^3{:}\eta^3\text{-}C_8H_8)]$ (**10**) and $[Co_4(CO)_6(\eta^4\text{-}C_6H_8)(\mu_3\text{-}\eta^2{:}\eta^3{:}\eta^3\text{-}C_8H_8)]$ (**11**).[a]

	10		**11**	
Co(1/5) – Co(2/6)	2.405(2)	2.407(2)	2.4373(13)	2.5354(14)
Co(1/5) – Co(3/7)	2.496(2)	2.528(2)	2.4408(12)	2.4389(13)
Co(1/5) – Co(4/8)	2.604(2)	2.575(2)	2.5408(14)	2.4479(12)
Co(2/6) – Co(3/7)	2.537(2)	2.530(2)	2.5376(13)	2.5241(14)
Co(2/6) – Co(4/8)	2.538(2)	2.534(2)	2.5258(13)	2.5289(13)
Co(3/7) – Co(4/8)	2.518(2)	2.518(2)	2.5225(13)	2.5238(12)
Co(1/5) – C(15/35)			2.097(4)	2.102(4)
Co(1/5) – C(16/36)			2.020(4)	2.024(3)
Co(1/5) – C(17/37)			2.024(3)	2.031(3)
Co(1/5) – C(18/38)			2.106(4)	2.121(3)
Co(2/6) – C(1/21)	2.069(7)	2.068(6)	2.137(4)	2.077(4)
Co(2/6) – C(2/22)	2.083(6)	2.116(6)	2.064(4)	2.152(4)
Co(3/7) – C(3/23)	2.399(6)	2.318(6)	2.460(4)	2.292(4)
Co(3/7) – C(4/24)	2.059(6)	2.068(6)	2.061(4)	2.052(4)
Co(3/7) – C(5/25)	2.186(6)	2.243(6)	2.155(4)	2.263(4)
Co(4/8) – C(6/26)	2.200(6)	2.162(6)	2.274(4)	2.166(4)
Co(4/8) – C(7/27)	2.071(7)	2.090(6)	2.060(4)	2.060(4)
Co(4/8) – C(8/28)	2.429(7)	2.491(6)	2.300(4)	2.479(4)
C(1/21) – C(2/22)	1.406(9)	1.400(9)	1.409(5)	1.418(6)
C(1/21) – C(8/28)	1.427(10)	1.420(8)	1.419(5)	1.402(6)
C(2/22) – C(3/23)	1.413(9)	1.431(9)	1.420(5)	1.426(6)
C(3/23) – C(4/24)	1.415(8)	1.410(9)	1.416(5)	1.418(6)
C(4/24) – C(5/25)	1.412(8)	1.407(9)	1.416(5)	1.403(6)
C(5/25) – C(6/26)	1.431(8)	1.422(8)	1.430(5)	1.406(5)
C(6/26) – C(7/27)	1.399(9)	1.414(8)	1.402(5)	1.407(5)
C(7/27) – C(8/28)	1.417(10)	1.407(8)	1.417(5)	1.418(5)
C(15/35) – C(16/36)			1.410(5)	1.414(5)
C(15/35) – C(20/40)			1.510(6)	1.505(5)
C(16/36) – C(17/37)			1.417(5)	1.414(5)
C(17/37) – C(18/38)			1.396(5)	1.405(5)
C(18/38) – C(19/39)			1.512(5)	1.504(5)
C(19/39) – C(20/40)			1.532(6)	1.533(5)

[a] For each complex, the two values given in each line correspond to equivalent distances in the two independent molecules.

The approximately tetrahedral Co_4 cluster cores have one Co_3 face[23] capped by a μ_3-C_7H_7 (**8**) or μ_3-C_8H_8 (**9**–**11**) ligand (Figures 1–4). An apical η^5-cycloheptadienyl (**8**) or η^4-cot (**9**) or η^4-cyclohexadiene (**11**) ligand or two terminal carbonyls (**10**), respectively, are coordinated to the fourth cobalt atom of each cluster. The face-capping C_nH_n ligands are slightly puckered towards a chair conformation (fold angles are 6–14°). However, the best planes through all ring carbons are still parallel to the basal Co_3 plane. Carbon–carbon bond lengths and endocyclic bond angles are largely equalized (1.40–1.43 Å, 125–130° in **8**; 1.40–1.42 Å, 132–137° in **9**, 1.40–1.43 Å, 132–137° in **10**, 1.40–1.43 Å, 132–137° in **11**).

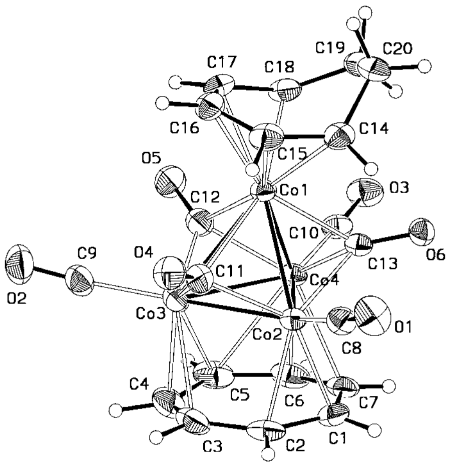

Figure 1. Molecular structure of **8**.

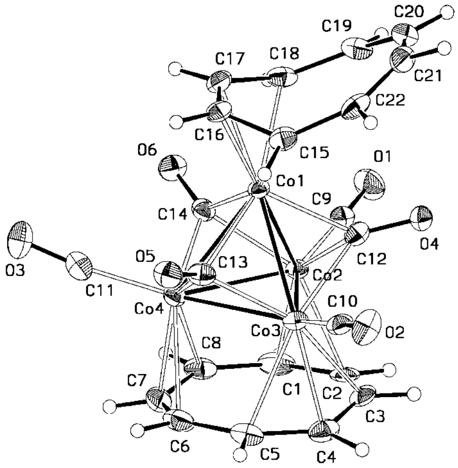

Figure 2. Molecular structure of **9**.

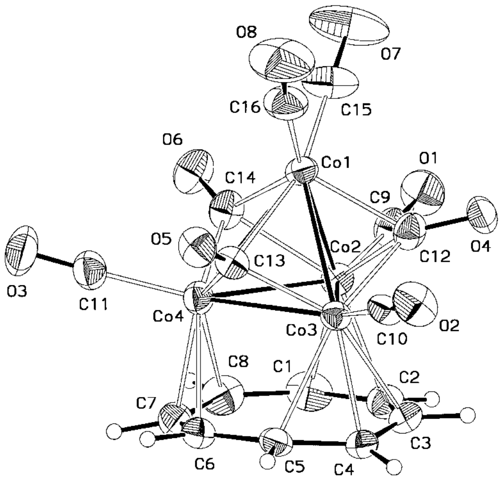

Figure 3. Molecular structure of **10**. Only one of the two crystallographically independent molecules is shown.

The facial C_7H_7 ligand in **8** is bonded to the Co_4 cluster in the μ_3-$\eta^2{:}\eta^3{:}\eta^3$ fashion through all its carbon atoms. The two η^3-enyl systems in the μ_3-C_7 ring share one carbon atom [C(5)], which is also bonded to two cobalt atoms [Co(3) and Co(4)]. Although these bonds are very long [2.430(4) Å and 2.467(4) Å], such a situation is not without precedent. In the literature there are a few complexes where cobalt–carbon distances longer than 2.4 Å have been described as bonding.

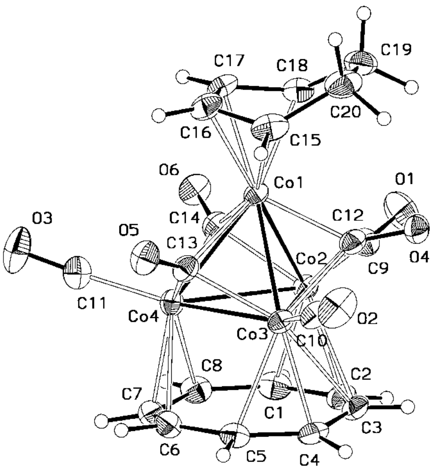

Figure 4. Molecular structure of **11**. Only one of the two crystallographically independent molecules is shown.

A clear example of this is found in $[\{P(OMe)_3\}_3Co(\eta^3$-benzyl)][24] where the distance $Co-C_{ortho}$ is 2.408(3) Å and must be assumed to be bonding because of the diamagnetism of the molecule. The bonding interaction between C(5) and Co(3), Co(4) in **8** is also reflected in a shift of C(5) from the mean plane of the C_7-ring towards these two cobalt atoms. There is a similar 1-3-η^3:3-5-η^3 coordination of a 1,3-dienyl system (within a six-membered ring) to two atoms of a Co_3 cluster in the cations $[\{(\eta\text{-}C_5H_5)Co\}_3(\mu\text{-benzyl})]^+$.[25] The coordination geometry of the facial C_7H_7 ring to the Ru_3 cluster in **2** is also similar.[10]

The coordination geometry of the facial C_8H_8 ring, with respect to the metal cluster in **9**–**11**, may be described as within a continuum between the μ_3-η^2:η^3:η^3 and μ_3-η^3:η^3:η^3 bonding modes. Only a slight reorientation (essentially a rotation by 7.5°) is in fact necessary to convert these two extremes into one another. Quite significantly, in crystalline **11** two independent molecules with somewhat different arrangements of the μ_3-C_8H_8 rings with respect to the basal Co_3 plane are found. This is a clear indication of the presence of several energy minima of comparable depth. From the NMR spectra in solution (vide infra) it is obvious that the energy barriers associated with the rotation of the facial C_nH_n rings must be very small. Interestingly, the ellipsoids which represent the anisotropic displacement parameters of the μ_3-C_nH_n ring carbons are only slightly elongated in the direction tangential to the ring (Figures 1–4). In addition, we did not observe evidence for a rotational disorder of the face-capping C_nH_n rings, which appear to occupy fairly well defined positions in the solid.

In the complexes **9**–**11,** every μ_3-ring carbon is essentially connected to one cobalt atom only; this results in a separation of the two η^3-enyl systems within that ring by a carbon–carbon bond. However, the relative arrangement of the Co_3 and C_8 rings is less symmetric in some cases, approaching the μ_3-η^3:η^3:η^3 bonding mode. This is most pronounced in one of the two independent molecules of **11** (Figure 5), in which C(3) is only slightly further away from Co(2) [2.505(4) Å] than from Co(3) [2.460(4) Å]. A similar but somewhat more symmetrical μ_3-η^3:η^3:η^3 coordination of a facial cot ligand was found in the trinickel cluster complex **3**.[11]

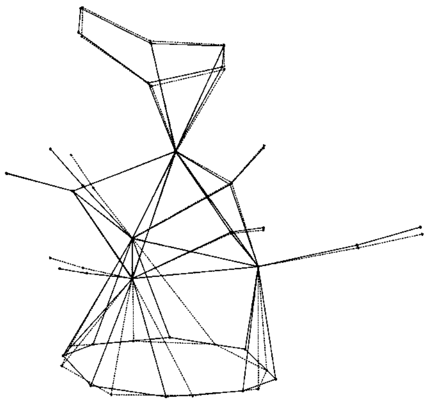

Figure 5. Superposition of the two crystallographically independent molecules of **11**.

Three terminal and three face-capping carbonyl ligands complete the coordination sphere of the Co_4 clusters. The nearly linear terminal CO ligands are bent away from the basal Co_3 plane of the cluster, towards the unique cobalt atom [(Co(1) and Co(5), respectively]. Such a distortion is not usually found in metal carbonyl cluster complexes with facially coordinated μ_3-benzene ligands.[4] It is, however, also present in **2** and **3**, and is probably caused by the larger size of the C_7 and C_8 rings.

Crystal packing and hydrogen bonding: In the solid state, neutral transition metal cluster molecules aggregate in typical van der Waals fashion.[16] It was previously shown that organometallic complexes and clusters also afford hydrogen-bond acceptors and hydrogen-bond donors.[17,18] For instance, sp^2-hybridized carbons in cyclopentadienyl or arene ligands behave as good H donors if acceptors such as carbon monoxide are present.[18,26] The cluster complexes discussed here carry carbocyclic rings and CO ligands in different bonding modes. Furthermore, these complexes are highly fluxional in solution with respect to reorientation of the carbocycles in their respective coordination sites. Therefore, the crystalline environment could have considerable influence on the structural features that are observed by crystallographic or spectroscopic techniques.

It is worth recalling that in terms of molecular interlocking and crystal packing cohesion, these derivatives do not differ from other carbonyl arene clusters discussed previously,[4c] that is in the simultaneous presence of flat and cylindrical ligands, and the π-ring ligands and the carbonyl groups with their specific spatial requirements pose a specific problem of recognition and interlocking optimization.

Indeed, all four structurally characterized complexes show networks of hydrogen-bonding interactions (Table 3). The μ_3-coordinated ligands are the most involved, both the rings and the carbonyls. The facial C_7H_7 or C_8H_8 ligands participate with three to six hydrogens in intermolecular bonding interactions. But the apical ligands also join in these intermolecular H ··· O networks (1–3H). As expected, μ_3-carbonyls are preferred. Besides, the apical rings also form intramolecular H bonds to the μ_3-carbonyl groups. In this way, the apical ring ligands are fixed in a symmetrical position relative to the carbonyls; this allows effective H ··· O interactions.

Table 3. Geometric characteristics of the C–H··O hydrogen bonds in the crystals of $[Co_4(CO)_6(\eta^5\text{-}C_7H_9)(\mu_3\text{-}\eta^2{:}\eta^3{:}\eta^3\text{-}C_7H_7)]$ (**8**) and $[Co_4(CO)_6(L)(\mu_3\text{-}\eta^2{:}\eta^3{:}\eta^3\text{-}C_8H_8)]$ **9** ($L = \eta^4\text{-}C_8H_8$), **10** ($L = (CO)_2$) and **11** ($L = \eta^4\text{-}C_6H_8$).

Type	Atoms involved	C···O [Å]	H···O [Å]	C-H-O [°]	H-O-C [°]
Complex **8**					
intra	C(15)–H(15)···O(4)	3.05	2.43	115.2	88.0
intra	C(17)–H(17)···O(5)	3.04	2.55	106.3	90.1
intra	C(18)–H(18)···O(5)	3.10	2.55	110.3	85.1
C_7H_7	C(3)–H(3)···O(1)	3.33	2.57	126.6	153.6
C_7H_7	C(4)–H(4)···O(4)	3.43	2.53	140.1	160.8
C_7H_7	C(5)–H(5)···O(3)	3.18	2.45	123.3	131.0
C_7H_7	C(7)–H(7)···O(6)	3.33	2.49	134.0	117.3
C_7H_9	C(16)–H(16)···O(1)	3.32	2.50	132.3	138.6
C_7H_9	C(17)–C(17)···O(1)	3.35	2.58	128.1	100.3
Complex **9**					
intra	C(15)–H(15)···O(5)	3.16	2.40	125.7	74.1
intra	C(18)–H(18)···O(6)	3.05	2.24	130.3	76.7
$\mu_3\text{-}C_8H_8$	C(1)–H(1)···O(5)	3.65	2.60	164.3	136.9
$\mu_3\text{-}C_8H_8$	C(2)–H(2)···O(3)	3.52	2.47	162.6	121.2
$\mu_3\text{-}{}_8H_8$	C(7)–H(7)···O(4)	3.32	2.57	125.9	161.4
$\mu_3\text{-}C_8H_8$	C(8)–H(8)···O(4)	3.35	2.54	131.1	114.3
$\eta^4\text{-}C_8H_8$	C(20)–H(20)···O(1)	3.40	2.60	130.6	97.7
Complex **10**					
C_8H_8 (M1)	C(1)–H(1)···O(16)	3.26	2.37	138.9	132.2
C_8H_8 (M1)	C(3)–H(3)···O(15)	3.25	2.49	126.1	116.3
C_8H_8 (M1)	C(4)–H(4)···O(15)	3.18	2.38	129.0	157.6
C_8H_8 (M1)	C(5)–H(5)···O(14)	3.29	2.45	134.3	149.6
C_8H_8 (M1)	C(7)–H(7)···O(11)	3.51	2.60	141.7	122.6
C_8H_8 (M2)	C(22)–H(22)···O(5)	3.29	2.46	132.6	114.0
C_8H_8 (M2)	C(23)–H(23)···O(5)	3.32	2.50	131.8	140.5
C_8H_8 (M2)	C(25)–H(25)···O(4)	3.26	2.26	153.4	125.0
C_8H_8 (M2)	C(26)–H(26)···O(2)	3.48	2.51	150.0	123.2
C_8H_8 (M2)	C(27)–H(27)···O(6)	3.20	2.44	126.7	140.5
C_8H_8 (M2)	C(28)–H(28)···O(6)	3.27	2.61	119.3	109.2
Complex **11**					
intra	C(16)–H(16)···O(5)	3.07	2.58	106.7	85.4
intra	C(19)–H(19a)···O(4)	3.09	2.52	111.7	97.2
intra	C(20)–H(20a)···O(4)	3.13	2.59	110.4	94.6
intra	C(36)–H(36)···O(16)	3.05	2.58	105.4	85.3
intra	C(39)–H(39a)···O(15)	3.15	2.59	110.9	95.7
C_8H_8 (M1)	C(3)–H(3)···O(4)	3.38	2.58	130.4	126.7
C_8H_8 (M1)	C(4)–H(4)···O(4)	3.28	2.52	126.4	166.5
C_8H_8 (M1)	C(5)–H(5)···O(3)	3.37	2.57	129.8	139.1
C_8H_8 (M1)	C(5)–H(5)···O(14)	3.35	2.55	129.9	130.7
C_8H_8 (M1)	C(6)–H(6)···O(3)	3.40	2.61	129.9	88.7
C_8H_8 (M1)	C(6)–H(6)···O(5)	3.46	2.60	136.3	116.5
C_8H_8 (M2)	C(25)–H(25)···O(15)	3.52	2.60	142.2	122.2
C_8H_8 (M2)	C(27)–H(27)···O(16)	3.29	2.42	136.0	171.9
C_8H_8 (M2)	C(28)–H(28)···O(13)	3.48	2.59	139.9	100.8
C_6H_8 (M1)	C(17)–H(17)···O(11)	3.24	2.51	123.5	117.5
C_6H_8 (M1)	C(18)–H(18)···O(12)	3.15	2.40	125.6	154.7
C_6H_8 (M2)	C(37)–H(37)···O(3)	3.15	2.37	127.7	149.1

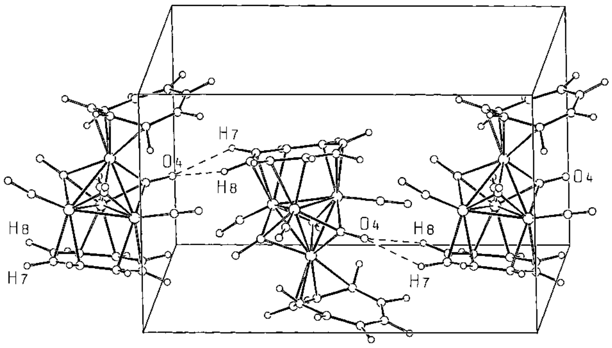

Figure 6. The bifurcated C–H···O interactions in crystalline **9**.

In the crystal of $[Co_4(CO)_6(C_8H_8)_2]$ (**9**), layers are formed by four different H bonds involving the face-bridging cot ligand. Each molecule is connected to four neighbors within these layers, which can also be described by a crossed-chain motif: one chain formed by H(1)···O(5) and H(2)···O(3) interactions in the [101] direction, the other formed by O(4)···H(7)/H(8) links along the *b* axis of the crystal. The layers are connected in the crystal by two types of interaction. On the one hand, there are additional H···O links [H(20)···O(1)] including the apical cot ligand in the H network. In this way two molecules in a centrosymmetric orientation are connected to dimers by two H bonds. Figure 6 shows one view of the crystal packing of **9** with the bifurcated O···H(7)/H(8) interaction linking molecules in chains along the *b* axis of the crystal. It is worth noting how the interaction between the cyclopolyene fragments and the presence of C–H···O bonds are reconciled. Figure 7 shows the graphitic-type interactions involving the cot ligands: each μ_3-cot faces an apical cot, thus forming molecular rods along the *a* axis. This face-to-face arrangement of cyclic π-ligands has been observed in a number of crystalline bisarene cluster complexes.[4c] The most representative example is given by the isomeric pair of bisbenzene clusters $[Ru_6C(CO)_{11}(\mu_3\text{-}\eta^2{:}\eta^2{:}\eta^2\text{-}C_6H_6)(\eta^6\text{-}C_6H_6)]$ and $[Ru_6C(CO)_{11}(\eta^6\text{-}C_6H_6)_2]$.[27] In both crystals the benzene ligands face each other forming molecular snakes and rods, respectively.

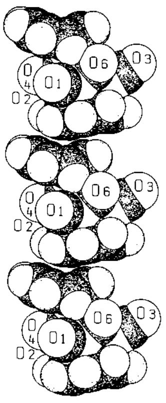

Figure 7. The interactions between facial and apical cot ligands in crystalline **9**.

A complicated network of intermolecular H···O bonds is present in crystalline $[Co_4(CO)_6(\mu_3\text{-}C_7H_7)(\eta^5\text{-}C_7H_9)]$ (**8**). Four hydrogens of the face-bridging and two of the apical C_7 ligand participate in intermolecular interactions with four different carbonyl groups. Altogether, one molecule is connected to eight neighbors. The carbonyl oxygen O(1) is involved in a trifurcated interaction as shown in Figure 8. Dimers held together by two O(1)···H(3) interactions are additionally linked (O(1)···H(16)/H(17)) to two other molecules related by a center of symmetry.

In crystalline $[Co_4(CO)_8(cot)]$ (**10**), on the other hand, the two independent molecules (M1, M2) present in the asymmetric unit are tightly linked by a total of eleven C–H···O interactions (< 2.6 Å), as shown in Figure 9. Each molecule M1 is connected with three molecules M2 (with the cot ligand exposed in opposite direction) and vice versa.

As in the case of **9**, the molecules also establish ring–ring interactions (see Figure 10). The mono-cot clusters form dimers of molecules generated by a center of inversion (M1–M1′, M2–M2′). The separation between the best planes through the carbon rings is comparable to that in graphite (< 3.5 Å).

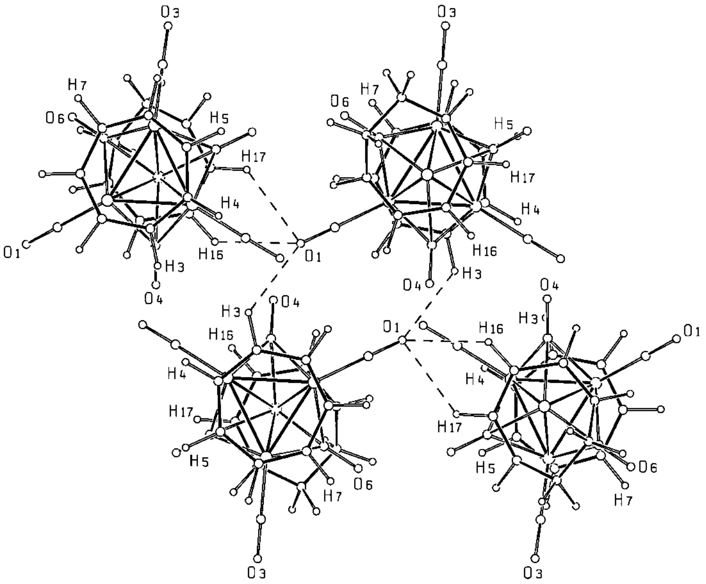

Figure 8. A network motif of C–H···O interactions in **8**.

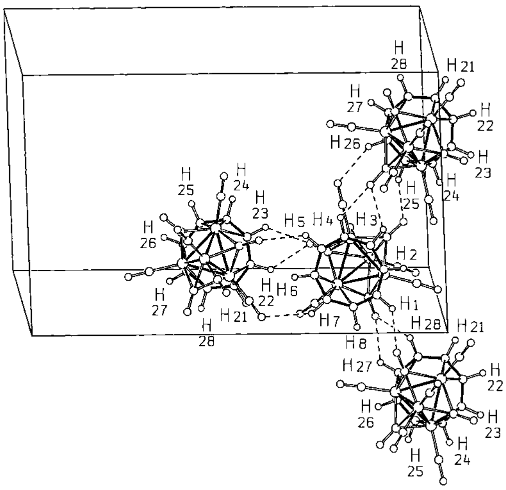

Figure 9. The network of C–H···O interactions in **10**.

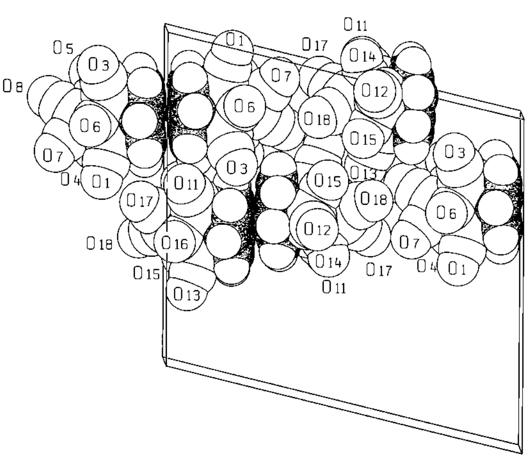

Figure 10. The ring–ring interactions in crystalline **10**.

The two independent molecules (M1, M2) of crystalline $[Co_4(CO)_6(\mu_3\text{-}C_8H_8)(C_6H_8)]$ (**11**) form twelve C–H···O interactions involving seven cot hydrogens and three cyclohexadiene hydrogens. Each molecule M1 or M2 is connected to five neighboring molecules. Figure 11 shows how the molecules are arranged in pairs obtained by cot–cot juxtaposition. Indeed, this example lends further support to the general idea that the crystal packing of transition metal clusters possessing both flat cyclopolyene and tubular CO ligands is best coped with by packing together the fragments with similar shape.

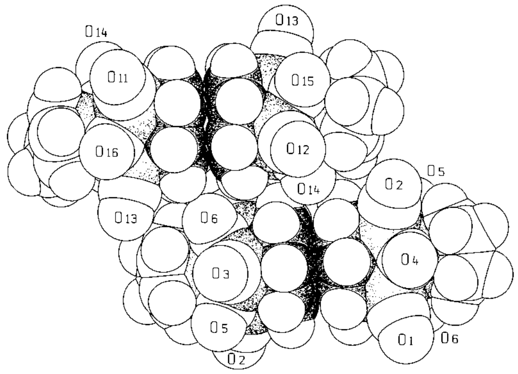

Figure 11. The ring–ring interactions in crystalline **11**.

Spectroscopic investigations: There is only one ^1H and ^{13}C resonance each at comparatively high field for the $\mu_3\text{-}C_7H_7$ and $\mu_3\text{-}C_8H_8$ ligands in **8**–**12**. Low-temperature ^1H and ^{13}C NMR data were acquired for **8** and **9**. The spectra were independent of the temperature down to 200 K. This indicates highly dynamic structures in solution. The barriers to rotation for the μ_3-coordinated rings in **8**, **9**, and probably also the other derivatives **10**–**12** must be considerably lower than those observed[4a,4c,13c] for face-capping benzene. Surprisingly, the (averaged) chemical shifts [$\delta(^1H, C_7H_7, C_6D_6) = 3.09$, $\delta(^{13}C, C_7H_7) = 61.5$; $\delta(^1H, \text{cot}, C_6D_6) = 3.5\text{–}3.7$, $\delta(^{13}C, \text{cot}) = 70\text{–}71$] fall in the same region as those of some μ_2-bridging C_7H_7 and C_8H_8 ligands, respectively.[28,29] This is a major difference from **2**, $[\{(CO)_2Ru\}_2(C_7H_9)Ru(\mu_3\text{-}S)(\mu_3\text{-}C_7H_7)]$, and $[\{(CO)_2Ru\}_3(\mu_3\text{-}S)(\mu_3\text{-}C_8H_8)]$, which show much larger ^{13}C coordination shifts of the μ_3-ligands [$\delta(C_7H_7) \approx 39$, $\delta(C_8H_8) = 48$].[10]

The ^1H and ^{13}C NMR resonances of the terminally bound 1-5-η-cycloheptadienyl, 1-4-η-cyclohexadiene, and 1-4-η-diphenylfulvene ligands correspond to the twofold symmetry usually observed for these ligands. In contrast, all eight protons and ^{13}C nuclei of the apical C_8H_8 ligand in **9** are isochronous, even at 220 K. This is indicative of an equilibration of all eight CH groups, caused by rapid haptotropic shifts of the 1-4-η^4 coordinated polyolefin.

Due to limited solubility of the complexes, the ^{13}C resonances of the carbonyl ligands could be detected only for **8**, **11**, and **12** at ambient temperature. In these cases, two resonances were found, consistent with sets of isochronous terminal ($\delta \approx 200$) and face-capping CO ligands ($\delta \approx 260$). Hence, no scrambling of terminal and bridging carbonyls takes place on the NMR timescale.

Conclusion

The results presented in this paper clearly illustrate that facial coordination of a C_nH_n π-perimeter to a molecular metal cluster is by no means restricted to the arenes ($n = 6$). On the contrary, it appears that cycloheptatriene and cyclooctatetraene can be forced into a facial coordination site more easily than benzene, probably owing to their polyolefinic character. However, the apical or edge-bridging coordination modes of these ligands still appear to be preferred, if such coordination sites are accessible. This is illustrated by the formation of $[Ru_3(CO)_6(\mu_2\text{-}C_7H_7)(\eta^5\text{-}C_7H_9)]$[30] and $[Ru_3(CO)_4(\mu_2\text{-}C_8H_8)_2]$[31] from $[Ru_3(CO)_{12}]$ with cycloheptatriene and cyclooctatetraene, respectively. In trinuclear systems like these, an apical and a facial C_nH_n ligand cannot both be accommodated for obvious steric reasons. A general strategy for facial coordination of C_nH_n hydrocarbons may be devised, which involves blocking of apical coordination sites by large ligands (which may be the C_nH_n substrate itself), thus forcing a second C_nH_n ligand into the facial position. We are currently investigating this scheme, which is not restricted to tetranuclear systems. We predict that a rich chemistry of μ_3-cyclopolyenes will develop in the near future.

Experimental Section

General procedures: All operations were carried out under an atmosphere of purified nitrogen (BASF R3-11 catalyst) by Schlenk techniques. Solvents were dried by conventional methods. NMR spectra were obtained on a Bruker AC200 instrument (200.1 MHz for ^1H, 50.3 MHz for ^{13}C). ^1H and ^{13}C chemical shifts are reported against $SiMe_4$ and were determined by reference to internal $SiMe_4$ or residual solvent peaks. The multiplicities of the ^{13}C resonances were determined by the DEPT technique. Mass spectra were measured in the field desorption (FD) ionization mode on a Finnegan MAT8230 spectrometer. Infrared spectra were recorded in the ν_{CO} region in CaF_2 cells with a Bruker IFS-28 Fourier transform spectrometer (optical resolution: 0.5 cm^{-1}). Elemental analyses were performed locally by the microanalytical laboratory of the Organisch-chemisches Institut der Universität Heidelberg and by Mikroanalytisches Labor Beller, Göttingen.

$[Co_4(CO)_6(\eta^5\text{-}C_7H_9)(\mu_3\text{-}C_7H_7)]$ (8): A sample of $[Co_4(CO)_{12}]$ (**5**, 3.89 g, 6.8 mmol) and cycloheptatriene (5 mL) were refluxed in *n*-heptane (200 mL). When the IR bands of **5** were no longer detectable, the mixture was cooled to room temperature. The black precipitate was collected and washed with *n*-pentane to give pure polycrystalline **8** (2.52 g, 63 %). ^1H NMR (in C_6D_6): $\delta = 0.61$ (m, 2H, $CH_2\text{-}H_{exo}$), 2.35 (m, 2H, $CH_2\text{-}H_{endo}$), 3.09 (s, 7H, C_7H_7), 5.09 (m, 4H, H-1/5, H-2/4), 6.80 (m, 1H, H-3); (in CD_2Cl_2): $\delta = 1.33$ (m, 2H, $CH_2\text{-}H_{exo}$), 2.73 (m, 2H, $CH_2\text{-}H_{endo}$), 3.89 (s, 7H, C_7H_7), 5.30 (m, 2H, H-1/5 or H-2/ 4), 5.46 (m, 2H, H-2/4 or H-1/5), 7.47 (m, 1H, H-3); $^{13}C\{^1H\}$ NMR (in C_6D_6): $\delta = 33.9$ (CH_2), 61.6 (C_7H_7), 95.3 (CH), 98.4 (CH), 107.5 (CH), 200.0 (CO), 256.6 (CO); IR (CH_2Cl_2): $\nu_{CO} =$: 2008 (sh), 1981 (vs, br), 1762 (sh), 1729 (s, br) cm^{-1}; anal. calcd for $C_{20}H_{14}Co_4O_6$: C 40.85, H 2.74; found C 40.98, H 2.73.

$[Co_4(CO)_6(\eta^4\text{-}C_8H_8)(\mu_3\text{-}C_8H_8)]$ (9): Following the above procedure, **9** (6.08 g, 96 %) was obtained as black microcrystals from **5** (5.94 g, 10.4 mmol) and cyclooctatetraene (6 mL). After recrystallization (CH_2Cl_2/*n*-hexane, 5:1 or CH_2Cl_2/toluene, 5:1) the yield of **9** was below 50 %, due to partial decomposition and formation of **10**. ^1H NMR (in C_6D_6): $\delta = 3.65$ (s), 5.63 (s); (in CD_2Cl_2): $\delta = 4.43$ (s), 5.76 (s); $^{13}C\{^1H\}$ NMR (in C_6D_6): $\delta = 70.2$ ($\mu_3\text{-}C_8H_8$), 108.3 ($\eta^4\text{-}C_8H_8$), carbonyl carbons not detected; IR (CH_2Cl_2): $\nu_{CO} = 2017$ (sh), 1995 (vs), 1724 (s, br) cm^{-1}; anal. calcd for $C_{22}H_{16}Co_4O_6$: C 43.17, H 2.63; found C 43.25, H 2.71.

$[Co_4(CO)_8(\mu_3\text{-}C_8H_8)]$ (**10**): A mixture of **9** (900 mg, 1.5 mmol) and $[Fe(CO)_5]$ (0.5 mL, 3.7 mmol) in toluene (150 mL) was heated at 80 °C for 5 h. After cooling to room temperature, a small amount of precipitate was removed by fitration. All volatiles were removed from the filtrate in vacuo, and the residue was washed with *n*-hexane until nearly colorless. Yield: 640 mg (77 %) dark red microcrystalline **10**. In the hexane solution, $[(CO)_3Fe(cot)]$[32] was detected by IR spectroscopy. ^1H NMR (in C_6D_6): $\delta = 3.47$ (s, C_8H_8); $^{13}C\{^1H\}$ NMR (in C_6D_6): $\delta = 71.2$ (carbonyl carbons not detected); IR (toluene): $\nu_{CO} = 2065$ (s), 2021 (vs), 1998 (sh), 1762 (s, br) cm^{-1}; anal. calcd for $C_{16}H_8Co_4O_8$: C 34.08, H 1.43; found C 33.84, H 1.68.

$[Co_4(CO)_6(\eta^4\text{-}C_6H_8)(\mu_3\text{-}C_8H_8)]$ (**11**): Following the above procedure, deep red **11** (280 mg, 62 %) was obtained from **8** (440 mg, 0.77 mmol) and 1,3-cyclohexadiene (0.5 mL). Reaction conditions: 80 °C, 2 h. Recrystallization from toluene. ^1H NMR (in C_6D_6): $\delta = 0.66$ (m, 2H, $CH_2\text{-}H_{exo}$ or $CH_2\text{-}H_{endo}$), 1.83 (m, 2H, $CH_2\text{-}H_{endo}$ or $CH_2\text{-}H_{exo}$), 3.74 (s, 8H, C_8H_8), 4.09 (m, 2H, H-1/ 4), 5.77 (m, 2H, H-2/3); (in CD_2Cl_2): $\delta = 1.18$ (m, 2H, $CH_2\text{-}H_{exo}$ or $CH_2\text{-}H_{endo}$), 1.86 (m, 2H, $CH_2\text{-}H_{endo}$ or $CH_2\text{-}H_{exo}$), 4.14 (m, 2H, H-1/4), 4.46 (s, 8H, C_8H_8), 5.98 (m, 2H, H-2/3); $^{13}C\{^1H\}$ NMR (in C_6D_6): $\delta = 24.0$ (CH_2), 70.0 (C_8H_8), 80.3 (CH), 100.8 (CH), 201.1 (CO), 262.7 (CO); IR (toluene): $\nu_{CO} = 2010$ (sh), 1987 (vs), 1752 (sh), 1734 (s), 1725 (s) cm^{-1}; FD-MS: 588 (100 %, $[M^+]$); anal. calcd for $C_{20}H_{16}Co_4O_6$: C 40.85, H 2.74; found C 40.90, H 2.82.

$[Co_4(CO)_6(\eta^4\text{-}6,6\text{-}Ph_2C_6H_4)(\mu_3\text{-}C_8H_8)]$ (**12**): Following the above procedure, crystalline purple-red **12** (200 mg, 27 %) was obtained from **9** (600 mg, 1.0 mmol) and 6,6-diphenylfulvene (230 mg, 1.0 mmol). Reaction conditions: 80 °C, 3 h. Recrystallization from toluene. ^1H NMR (in C_6D_6): $\delta =$ 3.68 (s, 8H, C_8H_8), 5.18 (m, 2H, H-1/4), 5.97 (m, 2H, H-2/3), 6.97 (m, 1H, Ph), 7.25 (m, 2H, Ph), 7.41 (m, 2H, Ph); $^{13}C\{^1H\}$ NMR (in C_6D_6): $\delta = 71.2$ (C_8H_8), 86.3 (CH), 97.9 (CH), 127.6 (Ph-CH), 129.4 (C-6), 131.7 (Ph-CH), 141.1 (Ph-C-*ipso*), 196.1 (CO), 257.2 (CO); IR (toluene): $\nu_{CO} = 2013$ (sh),

Table 4. Details of the crystal structure determinations of the complexes $[Co_4(CO)_6(\eta^5\text{-}C_7H_9)(\mu_3\text{-}\eta^2{:}\eta^3{:}\eta^3\text{-}C_7H_7)]$ (**8**) and $[Co_4(CO)_6(\eta^4\text{-}C_8H_8)(\mu_3\text{-}\eta^2{:}\eta^3{:}\eta^3\text{-}C_8H_8)]$ (**9**).

	8	9
formula	$C_{20}H_{16}Co_4O_6$	$C_{22}H_{16}Co_4O_6$
crystal size [mm]	0.70 × 0.35 × 0.04	0.35 × 0.30 · 0.06
crystal system	monoclinic	monoclinic
space group	$P2_1/c$	$P2_1/n$
a [Å]	12.748(6)	9.165(8)
b [Å]	9.782(5)	15.11(2)
c [Å]	15.186(8)	14.343(13)
β [°]	93.55(3)	90.63(7)
V [Å^3]	1890(2)	1986(3)
Z	4	4
M_r	588.05	612.07
ρ_{calcd} [g cm^{-3}]	2.067	2.047
F_{000}	1168	1216
μ ($Mo_{K\alpha}$) [mm^{-1}]	3.49	3.32
λ [Å]	$Mo_{K\alpha}$, graphite monochromated, 0.71069	
T [K]	203	203
$2\theta_{max}$ [°]	52	50
hkl range	− 15/15, 0/12, 0/18	− 10/10, 0/17, 0/17
measured reflns	3716	3486
unique reflns	3716	3486
observed reflns [$I \geq 2\sigma(I)$]	3335	2699
absorption correction	empirical	empirical
parameters refined	336	353
GoF	1.104	1.026
R (obs. reflns only)	0.036	0.034
w$R2$ (all reflns)	0.101	0.086
($w = 1/[\sigma^2(F_o^2) + (A \cdot P)^2 + B \cdot P]$)		
A, B	0.062, 1.55	0.0419, 1.63
P	$[\max(F_o^2, 0) + 2F_c^2]/3$	

Table 5. Details of the crystal structure determinations of the complexes $[Co_4(CO)_8(\mu_3\text{-}\eta^2{:}\eta^3{:}\eta^3\text{-}C_8H_8)]$ (**10**) and $[Co_4(CO)_6(\eta^4\text{-}C_6H_8)(\mu_3\text{-}\eta^2{:}\eta^3{:}\eta^3\text{-}C_8H_8)]$ (**11**).

	10	**11**
formula	$C_{16}H_8Co_4O_8$	$C_{20}H_{16}Co_4O_6$
crystal size [mm]	0.50 × 0.45 · 0.20	0.65 · 0.50 · 0.15
crystal system	monoclinic	triclinic
space group	$C2/c$	$P\bar{1}$
a [Å]	24.33(2)	9.824(5)
b [Å]	13.448(10)	10.990(6)
c [Å]	21.92(2)	17.852(9)
a [°]	90	82.64(3)
b [°]	103.21(6)	86.74(3)
g [°]	90	82.24(3)
V [Å^3]	6983(9)	1893(2)
Z	16	4
M_r	563.94	588.05
ρ_{calcd} [g cm^{-3}]	2.146	2.064
F_{000}	4416	1168
μ (Mo$_{K\alpha}$) [mm^{-1}]	3.78	3.48
λ [Å]	Mo$_{K\alpha}$, graphite monochromated, 0.71069	
T, [K]	203	203
$2\theta_{max}$ [°]	50	50
hkl range	− 28/28, 0/15, 0/26	− 11/11, − 12/13, 0/21
measured reflns	6134	6669
unique reflns	6134	6668
observed reflns [$I \geq 2\sigma(I)$]	4796	5678
absorption correction	empirical	empirical
parameters refined	569	670
GoF	1.081	1.054
R (obs. reflns only)	0.043	0.029
w$R2$ (all reflns)	0.116	0.074
(w = 1/[$\sigma^2(F_o^2)$ + (A · P)^2 + B · P])		
A, B	0.0626, 9.48	0.0466, 0.41
P	[max(F_o^2, 0) + 2F_c^2]/3	

1994 (vs), 1757 (sh), 1726 (s) cm^{-1}; anal. calcd for $C_{32}H_{22}Co_4O_6$: C 52.06, H 3.00; found C 52.05, H 3.26.

Crystal structure determinations: Single crystals were grown by slowly cooling hot (80 °C) toluene solutions. Intensity data were collected on a Siemens-Stoe AED 2 four-circle diffractometer at low temperature and corrected for Lorentz, polarization, and absorption effects (Tables 4, 5). The structures were solved by direct methods, and refined by full-matrix least-squares on F^2 with all measured unique reflections. All non-hydrogen atoms were given anisotropic displacement parameters. All hydrogen atoms were localized in difference Fourier syntheses and refined isotropically.[33] The calculations were performed with the programs SHELXS-86 and SHELXL-93.[34] Graphical representations were drawn with ORTEP-II[35] and SCHAKAL-92.[36] Ellipsoids are drawn on the 40% probability level. For the analysis of the geometric features of the intra- and intermolecular hydrogen-bonding networks the refined coordinates of the hydrogen atoms were normalized by extending the CH distances along the C–H vectors to the typical neutron-derived value of 1.08 Å.[37] Selection criteria have been based on C(H) ⋯ O interatomic separations < 2.6 Å. The computer program PLATON[38] was used to analyze the metrical features of the hydrogen-bonding pattern.

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