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Reaction of mesitylenetetracobaltnonacarbonyl with $[Mo(CO)_3C_5H_5]_2$. Syntheses and structures of the clusters $C_5H_5(CO)_2MoCo_3(CO)_6(\mu\text{-}CO)_3$ and $(C_5H_5)_2(CO)_3Mo_2Co_2(CO)_4(\mu\text{-}CO)_3$

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Abstract

Interaction of (mesitylene)$Co_4(CO)_9$ (I) with $[Mo(CO)_3Cp]_2$ (II) has been shown to result in a mixture of clusters $Cp(CO)_2MoCo_3(CO)_6(\mu\text{-}CO)_3$ (III) and $Cp_2(CO)_3Mo_2Co_2(CO)_4(\mu\text{-}CO)_3$ (IV). Complexes III and IV have also been obtained by an independent synthesis from $Co_2(CO)_8$ and II, the latter route is the most convenient and the simplest for the synthesis of III. X-ray diffraction studies on III and IV reveal that the successive replacement of Co atoms in Co_4 tetrahedron by the $Mo(CO)_2Cp$ groups results in a considerable distortion of the metal core of the cluster.

Introduction

Many examples of the replacement of one metal-containing group (ML_n) by another ($M'L'_m$) in various clusters are known. A special review outlining such substitutions in carbyne cobalt clusters of the $RCCo_3(CO)_9$ (V) type has appeared [1]. However, such substitutions in the related arenecarbonyl cobalt clusters (arene) $Co_4(CO)_9$ [2] have not yet been studied. The mesitylene complex $Me_3C_6H_3Co_4(CO)_9$ (I) is the most accessible of these complexes. We have compared its behaviour in the substitution reactions with that of the complexes of the type V. $Mn_2(CO)_{10}$, $Fe_2(CO)_9$, $[Fe(CO)_2Cp]_2$, Cp_2Ni and $[Mo(CO)_3Cp]_2$ were used as the metal-containing reactants. It has been shown that cluster I differs considerably in its properties from those of cluster V.

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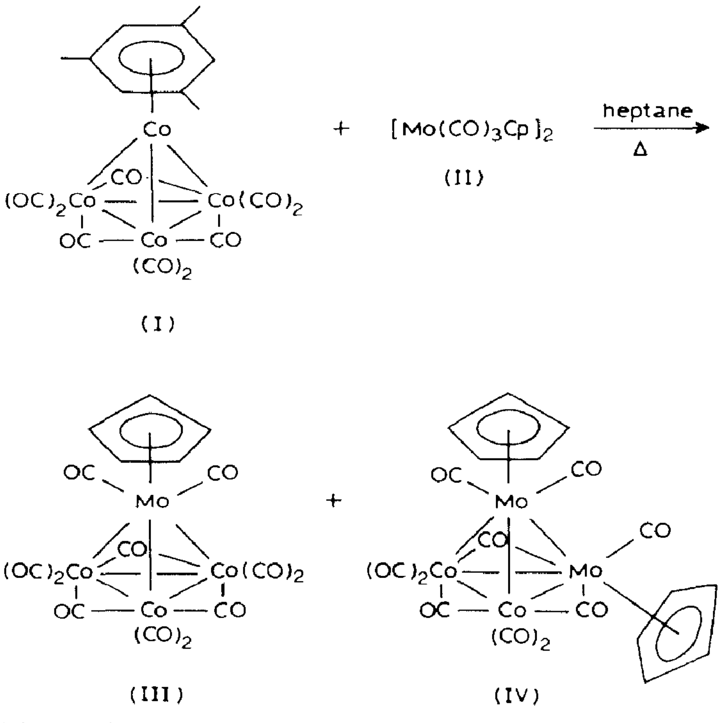
Results and discussion

All attempts to replace the metal in I by other metals by reaction with $Mn_2(CO)_{10}$, $Fe_2(CO)_9$ or $[Fe(CO)_2Cp]_2$ under various experimental conditions were unsuccessful (see Experimental); either the initial compounds or (under more rigid conditions) their decomposition products were recovered. Reaction with nickelocene leads to cluster breakdown (two products, $CpCo(CO)_2$ and $[Ni(CO)Cp]_2$ were identified from the IR spectra):

$$2Me_3C_6H_3Co_4(CO)_9 + 6Cp_2Ni \rightarrow 6CpCo(CO)_2 + 3[Ni(CO)Cp]_2 + 2Me_3C_6H_3 + 2CO$$

Only the reaction of I with the dimeric molybdenum derivative $[Mo(CO)_3C_5H_5]_2$ (II) in heptane under reflux gave the tetrahedral clusters III (16%) and (IV) (11%), which are probably the products of the replacement of one or two Co atoms in the tetrahedron by Mo; both complexes obtained contain no arene ligand:



The products can be separated from the initial compounds by chromatography on a silica gel column. It is noteworthy that complex III, and a very small admixture of IV, have also been obtained in 25% yield from a mixture of the dimer II and $Co_2(CO)_8$ in heptane under reflux. The synthesis of complex III from the far less accessible initial compounds has been reported earlier [3,4], but our method is probably the most convenient.

It is noteworthy that a mixture of III with mesitylene in heptane under reflux results in a reaction which to some extent is reversed and is accompanied by "disproportionation":

$$\mathrm{III} + Me_3C_6H_3 \xrightarrow{\Delta} \mathrm{I} + \mathrm{II}$$

The direction of this reaction depends on which reactant is in excess (dimer II or mesitylene). In general the data obtained indicate that interaction of I and II leads to decomposition of I into fragments, which in the presence of II give the clusters III and IV, rather than a simple substitution at the vertices in I.

The structures of compounds III and IV have been determined by X-ray diffraction: they are in good agreement with the IR spectral data in the metal–carbonyl range, and in the case of III with the of ^1H and ^{13}C NMR spectral data (see Experimental).

X-Ray diffraction study of III and IV

The unit cell parameters and the intensities of the 3759 (for III) and 3823 (for IV) independent reflections were measured on an automated Hilger & Watts Y/290 diffractometer at room temperature (λ Mo-K_α, graphite monochromator, $\theta/2\theta$ scan, $2\theta \leq 56°$). 3031 (for III) and 2661 (for IV) observed reflections with $I > 2\sigma(I)$ were used for calculations.

Crystals of III and IV are monoclinic; III: a 15.5356(8), b 8.7359(7), c 15.727(2) Å, β 109.144(5)°, space group $P2_1/n$, $Z = 4$; IV: a 13.218(1), b 9.982(1), c 16.507(3) Å, β 92.77(1)°, space group $P2_1/c$, $Z = 4$.

The structures of III and of IV were solved by direct methods (MULTAN) and refined isotropically by block-diagonal least squares technique to $R = 0.094$ and 0.098 respectively. The absorption correction (μ(Mo-K_α) = 27.15 cm^{-1}) for IV was carried out with DIFABS; as it gave no substantial improvement of results it was not used for III (μ(Mo-K_α) = 23.17 cm^{-1}). In the last stage of refinement of all non-hydrogen atoms was anisotropic, all the H atoms located in the difference Fourier synthesis and were included in the isotropic approximation. The final discrepancy factors are: for III $R = 0.037$, $R_w = 0.042$ (for 2812 reflections with $I > 4\sigma(I)$ and for IV $I = 0.039$, $R_w = 0.040$ (for 2372 reflections with $I > 3\sigma(I)$. All calculations were carried out using the INEXTL [5] program package on an Eclipse S/200 computer. Atomic coordinates have been deposited at the Cambridge crystal structure Database *.

Molecular and crystal structures of III and IV

The structures of molecules III and IV are given in Figs. 1 and 2. The bond lengths for IV are listed in Table 1, the most essential mean bond lengths for III and IV are compared with the analogous characteristics of related compounds in Table 2. The major interligand bond angles in III and IV are tabulated in the Table 3.

The crystal structure of III has been previously studied and described by Schmid [3]. The bond lengths we observed in III are consistent with the data from ref. 3

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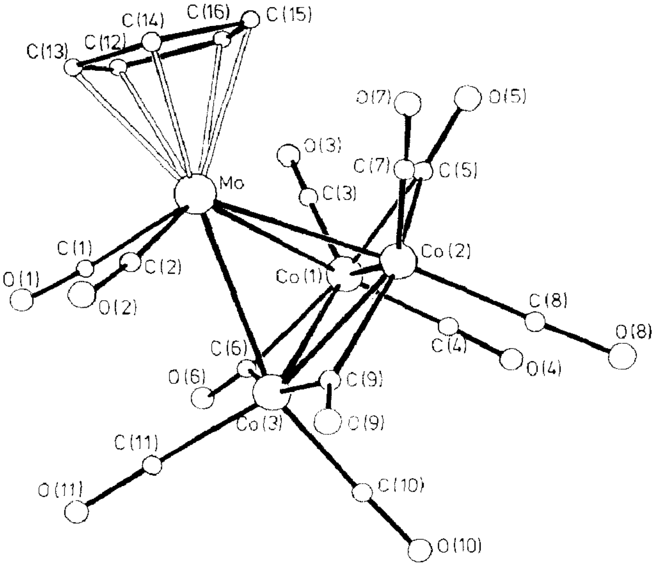


Fig. 1. Molecule III (H atoms are omitted).

within experimental error. Clusters III and IV form common molecular crystals with intermolecular contacts corresponding to the sums of the van der Waals radii.

The bond lengths in IV coincide with those reported for other multinuclear carbonyl derivatives of Mo and Co. According to the number of the valence electrons in the metal core (60) the tetrahedral clusters III and IV meet the requirements of the EAN rule, the metal–metal bonds in them are thus regarded as single bonds. The Mo(I)–Mo(2) distance in IV 3.024(1) Å is close to the value of

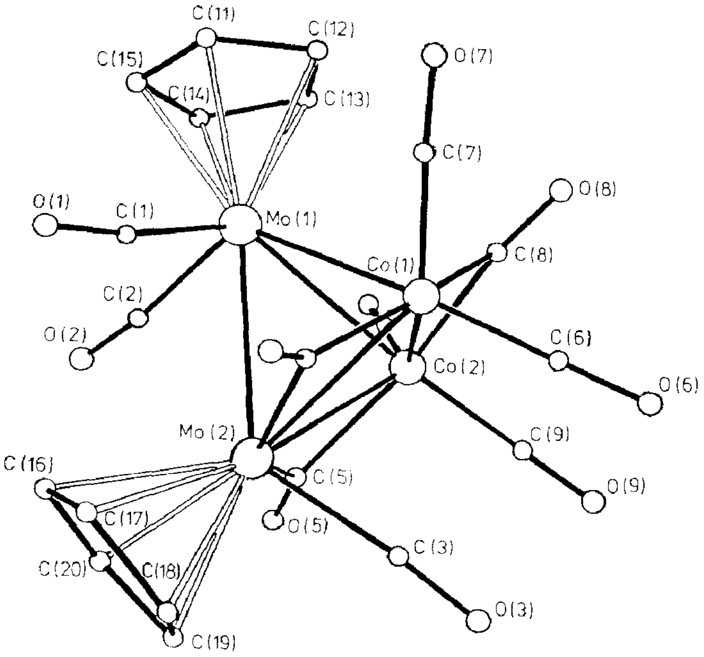


Fig. 2. Molecule IV (H atoms are omitted).

Table 1

Bond lengths (Å) in $\mathrm{Mo_2Co_2Cp_2(\mu\text{-}CO)_3(CO)_7}$ (IV)

Mo(1)–Mo(2)	3.024(1)	Co(2)–C(5)	1.975(9)
Mo(1)–Co(1)	2.760(1)	Co(2)–C(8)	1.892(9)
Mo(1)–Co(2)	2.752(1)	Co(2)–C(9)	1.797(9)
Mo(1)–C(1)	1.968(9)	Co(2)–C(10)	1.749(9)
Mo(1)–C(2)	1.995(9)	O(1)–C(1)	1.15(1)
Mo(1)–C(11)	2.30(1)	O(2)–C(2)	1.14(1)
Mo(1)–C(12)	2.364(9)	O(3)–C(3)	1.15(1)
Mo(1)–C(13)	2.372(9)	O(4)–C(4)	1.14(1)
Mo(1)–C(14)	2.33(1)	O(5)–C(5)	1.16(1)
Mo(1)–C(15)	2.275(9)	O(6)–C(6)	1.14(1)
Mo(2)–Co(1)	2.769(1)	O(7)–C(7)	1.14(1)
Mo(2)–Co(2)	2.758(1)	O(8)–C(8)	1.16(1)
Mo(2)–C(3)	1.990(9)	O(9)–C(9)	1.14(1)
Mo(2)–C(4)	2.266(9)	O(10)–C(10)	1.15(1)
Mo(2)–C(5)	2.131(9)	C(11)–C(12)	1.41(1)
Mo(2)–C(16)	2.374(9)	C(11)–C(15)	1.38(2)
Mo(2)–C(17)	2.31(1)	C(12)–C(13)	1.39(2)
Mo(2)–C(18)	2.276(9)	C(13)–C(14)	1.41(2)
Mo(2)–C(19)	2.269(9)	C(14)–C(15)	1.41(2)
Mo(2)–C(20)	2.312(9)	C(16)–C(17)	1.40(2)
Co(1)–Co(2)	2.481(2)	C(16)–C(20)	1.39(1)
Co(1)–C(4)	1.908(9)	C(17)–C(18)	1.39(1)
Co(1)–C(6)	1.782(9)	C(18)–C(19)	1.43(2)
Co(1)–C(7)	1.77(1)	C(19)–C(20)	1.40(1)
Co(1)–C(8)	1.988(9)		

3.085 Å for the single metal–metal bond in the 48-electron triangular cluster $\mathrm{[Cp_3Mo_3(\mu_3\text{-}S)(\mu\text{-}CO)_3(CO)_3]^+}$ [6] and the Mo–W distance in the chiral tetrahedral cluster $\mathrm{Cp_2MoWCoFe(\mu_3\text{-}S)(\mu\text{-}AsMe_2)(CO)_8}$ (3.036 Å) [7]. However in the dimeric molecule $\mathrm{[CpMo(CO)_3]_2}$ the single (on the basis of the EAN-rule) Mo–Mo bond is elongated to 3.235 Å [8], which is probably because of the mutual non-valent repulsion of its half-sandwich fragments, linked only by the metal–metal bond. The mean Mo–C (CO, Cp) and Co–C (CO) bond lengths in III and IV have the usual values (Table 2). The slight variation in the Mo–C distances up to η^5-Cp ligands in III (2.283–2.394 Å) and IV (2.269–2.374 Å) is also typical of the η^5-Cp derivatives of molybdenum that are consistent with the EAN rule. The analogous interval of the Mo–C distances (2.27–2.38 Å) has in particular been observed in the structure of the tetrahedral cluster $\mathrm{CpMoIr_3(\mu\text{-}CO)(CO)_8}$ [4].

Heteronuclear clusters III and IV are regarded as derivatives of $\mathrm{Co_4(\mu\text{-}CO)_3(CO)_9}$ [9] formed as a result of the subsequent replacement of the "apical" fragment $\mathrm{Co(CO)_3}$ (i.e. the fragment without the bridging μ-CO ligands) by an isoelectronic fragment $\mathrm{CpMo(CO)_2}$ (III) and the replacement of the $\mathrm{Co(CO)_2}$ fragment in the base of the trigonal pyramid $\mathrm{MoCo_3}$ by the isoelectronic fragment CpMo(CO) (IV). Interestingly, the substitutions at the vertices of the M_4 tetrahedral do not change the general configuration of its ligand environment: (as has been found in structures of chiral tetrahedral clusters [7]). However the successive introduction of one or two bulky Cp ligands into the coordination sites of the terminal CO ligands in the ligand sphere of the cluster results in a considerable distortion of the bond angles (Table 3).

Table 2

Comparison of the bond lengths in III, IV and related clusters

Cluster	Mo–Mo	Mo–Co	Co–Co	Mo–Cp_{ct} [a]	Mo–CO_t [b]	Mo–CO_b [c]	Co–CO_t [b]	Co–CO_b [c]	No of valence electrons	ref.
$(C_5H_5)MoCo_3(CO)_{11}$ (III) [d]	–	2.74	2.48	2.34	2.00	–	1.79	1.95	60	This work
		(2.74)	(2.48)	(2.36)	(2.02)		(1.80)	(1.95)		
$(C_5H_5)_2Mo_2Co_2(CO)_{10}$ (IV)	3.02	2.76	2.48	2.34	1.98	2.20	1.77	1.94	60	This work
$(C_5H_5)_2(C_5Me_5)_2Mo_2Co_2(CO)_4$	2.57 [e]	2.71	2.40 [e]	[g]	–	2.05	–	1.87	60	17
$(C_5H_5)MoCO_2MS(AsMe_2)(CO)_8$ [e]	–	2.69 [f]	2.50 [f]	[g]	[g]	[g]	[g]	[g]	60	7
		(2.69)	(2.50)							
$(C_5H_5)_2Mo_2(CO)_6$	3.24	–	–	2.34	1.98	–	–	–	34	8
$[(C_5H_5)_3Mo_3(CO)_6]^+$	3.09	–	–	[g]	–	[g]	–	–	48	6
$Co_2(CO)_8$	–	–	2.52	–	–	–	1.79	1.92	34	18
$Co_4(CO)_{10}(PMe_2Ph)_2$	–	–	2.49	–	–	–	1.78	1.94	60	13

[a] Cp_{ct} = centroid of Cp ring. [b] CO_t = C atom of terminal CO. [c] CO_b = C atom of bridging CO. [d] The taken from ref. 3 are in parentheses. [e] Multiple metal–metal bond. [f] Without parentheses, M = Fe; in parentheses, M = Ru. [g] No data available.

Table 3

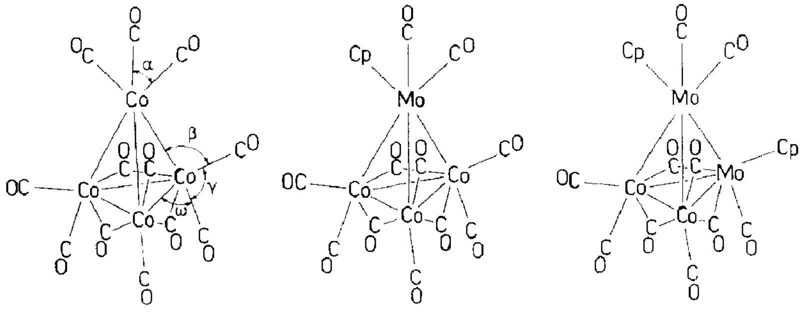
Comparison of the main interligand angles in the molecules III, IV and $Co_4(\mu\text{-}CO)_3(CO)_9$ [9] (designation of angles see Fig. 3)

III			IV		
α	CpMoC(1)	107.8	α	Cp(1)Mo(1)C(1)	108.7
	CpMoC(2)	109.4		Cp(1)Mo(1)C(2)	109.7
	C(1)MoC(2)	84.6(3)		C(1)MoC(2)	86.5(4)
β	MoCo(1)C(3)	93.6(2)	β	Mo(1)Co(1)C(7)	87.2(3)
	MoCo(2)C(7)	89.6(2)		Mo(1)Co(2)C(10)	85.5(3)
	MoCo(3)C(11)	102.2(2)		Mo(1)Mo(2)Cp(2)	125.6
γ	C(3)Co(1)C(4)	99.2(3)	γ	C(6)Co(1)C(7)	101.4(4)
	C(7)Co(2)C(8)	101.1(3)		C(9)Co(2)C(10)	99.9(4)
	C(10)Co(3)C(11)	100.4(3)		Cp(2)Mo(2)C(3)	105.9
ω	Co(2)Co(1)C(4)	104.0(2)	ω	Mo(2)Co(1)C(6)	110.7(3)
	Co(3)Co(1)C(4)	108.2(2)		Co(2)Co(1)C(6)	105.3(3)
	Co(1)Co(2)C(8)	106.2(2)		Mo(2)Co(2)C(9)	113.0(3)
	Co(3)Co(2)C(8)	109.4(2)		Co(1)Co(2)C(9)	109.5(3)
	Co(1)Co(3)C(10)	96.8(2)		Co(1)Mo(2)C(3)	77.5(3)
	Co(2)Co(3)C(10)	99.4(2)		Co(2)Mo(2)C(3)	78.4(3)
Δ_C: C(5) 0.24, C(6) 0.08, C(9) −0.08			Δ_C: C(4) 0.03, C(5) −0.04, C(8) 0.18		
$Co_4(\mu\text{-}CO)_3(CO)_9$					
$\alpha = 93°$					
$\beta = 102°$					
$\gamma = 105°$					
$\omega = 105°$					
$\Delta_C = 0.14$ Å [a]					

[a] Δ_C = deviation of the C atoms of μ-CO ligands from the M_3 plane

Of the derivatives of the tetrahedral cluster $(Co_4(\mu\text{-}CO)_3(CO)_8L$, only the anion $[Co_4(CO)_{11}I]^-$ has the ligand L in the apical position, however an admixture of the isomer having the axial orientation (Fig. 3) of the Co–I bond at the base of the metal polyhedron in the distorted structure of a cluster, $[Co_4(\mu\text{-}CO)_3(CO)_8I]^-[Et_4N]^+$ has been reported [10]. In the phosphine clusters $Co_4(CO)_{11}(PMe_3)$ [11] and $Co_4(CO)_{11}(PPh_3)$ [12] the PR_3 ligand is located in the axial position. It is noteworthy that in the Ir analogue of cluster III, formulated as $CpMoIr_3(\mu\text{-}CO)_3(CO)_8$, the molybdenum atom is located in the base of the cluster and is coordinated by the two bridging and the one terminal (equatorial) CO ligands, while the Cp ligand is in the axial position [4]. The apical coordination of the Cp ligand in cluster III evidently causes the least steric overcrowding about its compact metal core.

The apical-equatorial location of the Cp-ligands in IV has not been observed previously among the disubstituted clusters $Co_4(\mu\text{-}CO)_3(CO)_7L_2$. Up to now the following clusters of this type have been studied by means of X-ray diffraction: $Co_4(CO)_{10}[P(OMe)_3]_2$ (the axial–axial location of the phosphine ligands) [12], $Co_4(CO)_{10}(Me_2PCH_2CH{=}CH_2)_2$ [13] and $FeCo_3(H)(CO)_{10}(PMe_2Ph)_2$ [11] (both with the apical–axial location of the phosphine ligands), and the iridium analogue $Ir_4(CO)_{10}(PPh_3)_2$ (axial–equatorial) [14]. The variations in the orientations of the ligands of I indicates that the clusters, $M_4(CO)_{12-n}L_n$ having an isomeric ligand sphere are close in energy. Thus location of the bulky ligand L at the cluster core may vary with slight changes in the steric characteristics of L.



$Co_4(\mu_2\text{-}CO)_3(CO)_9$ $CpMoCo_3(\mu_2\text{-}CO)_3(CO)_8$ $Cp_2Mo_2Co_2(\mu_2\text{-}CO)_3(CO)_7$

(III) (IV)

Fig. 3. Structures of $Co_4(CO)_9(\mu\text{-}CO)_3$, III and IV. The major interligand angles and orientation of the terminal CO ligands are shown a = apical, e = equatorial, ax = axial.

A comparison of the bond angles in the ligand surroundings of the clusters III and IV (Table 3) reveals that replacement of the terminal CO ligands in the initial $M_4(CO)_{12}$ structure by the far bulkier Cp-ligands results in similar distortions. Decreases in "scissor" type γ angles (Fig. 3) by 4–6° indicate that there is an increase in the "steric pressure" in the ligand sphere of III; this peculiarity is preserved in the case of the remaining two $Co(CO)_2$ vertices of IV. The introduction of one Cp ligand decreases the symmetry of the ligand environment from C_{3v} to C_s and results in non-equivalency of the β angles (as well as the ω angles) at the atoms comprising the base of the cluster in III and IV, where the second Cp ligand is located in the idealized symmetry plane of the molecule *. Thus the geometrical distortions of the ligand sphere in III and IV are likely to be determined by introduction of the first Cp ligand in III and can only be reinforced by the second Cp ligand in IV.

The most remarkable feature of the clusters III and IV is the existence of a region of "diminished steric pressure", which in III is in the equatorial position at the Co(3) atom where the distortions of the interligand angles are minimal. In IV it is this equatorial position in the idealized symmetry plane which is occupied by the bulky Cp ligand. Thus the peculiarities of structures III and IV suggest internal "steric induction", i.e. the appearance, as a result of the redistribution within the coordination sphere, of regions with diminished steric overcrowding, in which the CO ligands can be readily replaced by bulkier ligands (such as the Cp ligands in the structures studied here). Such a phenomenon has been observed in the 10-nuclear clusters $Pd_{10}(CO)_{14}L_4$ and $Pd_{10}(CO)_{12}L_6$ ($L = PBu^n_3$); the existence of such regions of "diminished steric pressure" around the two terminal CO ligands in the first cluster facilitates their replacement by the phosphine ligands L [15].

The subsequent increased overcrowding in the ligand sphere of the cluster can lead to distortion of the metal core and could make the common geometry

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* Slight deviations of III and IV from C_s symmetry manifest themselves in unique differences by 3–5° of the β and ω angles at the equivalent fragments $Co(CO)_2$ (Table 3), and in some asymmetry of the μ-CO bridges (Table 1).

energetically unfavourable. For example two η^5-C_5Me_5 ligands in the tetrahedral cluster $(C_5Me_5)_2Co_4(CO)_7$ result in the greater variation of the Co–Co bond lengths in a rather broad range of 2.386–2.554 Å [16] (this interval is much smaller in the symmetrical $Co_4(CO)_{12}$, viz., 2.457–2.527 Å [9]). Two more η^5-C_5H_5 ligands in the coordination sphere such as in the 60-electron cluster $Cp_2Mo_2Co_2(C_5Me_5)_2(CO)_4$ [17] results in a rather strange "spiky" metal polyhedron with the two Mo=Mo and two Co=Co bonds (although the double-bondedness of the latter bond is not mentioned in ref. 17, its length 2.404 Å, the geometry of the cluster, as well as the requirements of the EAN rule, suggest it). It is seen from the Tables 1 and 2 that the metal–metal bond lengths in the clusters III and IV do not show any pronounced anomalies, however the structure of the next, as yet hypothetical, member $Cp_3Mo_3Co(CO)_9$, in the series of the heteronuclear clusters may be distorted considerably.

Experimental

All operations for the synthesis and isolation of the compounds studied were carried out under argon in absolute solvents. A "PRK-4" lamp was used for UV irradiation. IR spectra were measured in heptane on a Specord 75IR instrument, ^1H NMR spectrum of the complex II was recorded on a Bruker WP-200SY (200 MHz) spectrometer in C_6D_6 using HMDC as an internal standard; ^{13}C NMR spectra were measured on the same spectrometer in CD_3COCD_3.

Reaction of I with $[Mo(CO)_3C_5H_5]_2$ (II)

A mixture of 0.1 g (0.165 mmol) of I and 0.1 g (0.2 mmoL) of II was refluxed in 70 ml of heptane for 8 h, chromatographed on a silica gel column (1.5 × 20 cm). A 1 : 10 mixture of benzene: petroleum ether (1 : 10) elutes first a pink layer containing a small amount of II and then a green layer containing 0.02 g (20%) of initial I, and then ca. 1 : 5 mixture of benzene: petroleum ether elutes a brown layer containing 18 mg (16%) of III, and a green layer—14 mg (11%) of IV.

The complex III was recrystallized from hexane. The darkbrown (but not black [3]) crystals decompose without melting at 178–183°C a decomposition temperature of 192°C is given in ref. 3. IR ($\nu(C\equiv O)$, cm^{-1}): 2077s, 2039s, 2031s, 2020s, 1998m, 1992s, 1978m, 1951m, 1915w, 1882w, 1861m, 1832m. ^1H NMR: 4.05(s); ^{13}C NMR 91.85(Cp) 212.71(CO at Co), 215.18(CO at Mo). Found: C 29.78; H 0.81. $C_{16}H_5Co_3MoO_{11}$ calc.: C 29.63, H 0.77%. Complex IV was reprecipitated by heptane from CH_2Cl_2 (with the partial evaporation). IV decomposes without melting at 150–160°C. IR ($\nu(C\equiv O)$, cm^{-1}): 2053s, 2024s, 1990m, 1981m, 1960w, 1934m, 1889m, 1816w, 1803w. Found: C 32.52; H 1.60 $C_{20}H_{10}Co_2Mo_2O_{10}$ calc: C 33.36; H 1.40%.

Reaction of I with Cp_2Ni

(a) A mixture of 0.1 g (0.165 mmol) of I and 0.1 g (0.53 mmol) of nickelocene in 70 ml of THF was stirred with a magnetic stirrer for 18 hours. After chromatography on an SiO_2 column, only 0.09 g (90%) of the initial I and traces of $Co(CO)_2Cp$ were isolated. (In this experiment and in the other cases the products were identified by IR spectroscopy in heptane and from their R_f's on silufol).

(b) A mixture of 0.1 g of I and 0.1 g of Cp_2Ni was refluxed in 60 ml of hexane for 8 hours to yield 12 mg of $Co(CO)_2Cp$ and 23 mg (23%) of I, respectively after chromatography.

(c) A mixture of 0.1 g of I and 0.1 g of Cp_2Ni was refluxed in 60 ml of heptane for 1.5 hours. The IR spectrum reveals that $Co(CO)_2Cp$ is the main carbonyl-containing ligand, and only traces of $[Ni(CO)Cp]_2$ were found.

Reaction of I with $Mn_2(CO)_{10}$

(a) A mixture of 0.1 g of I and 0.1 g (0.26 mmol) of $Mn_2(CO)_{10}$ in 70 ml of benzene was stirred at room temperature for 16 hours. After chromatography on an SiO_2 column, 95% of the initial I was recovered.

(b) A mixture of 0.1 g of I and 0.1 g of $Mn_2(CO)_{10}$ in 70 ml of benzene was stirred at 50 °C for 7 hours. After chromatography, 82% of I was isolated.

Reaction of I with $Fe_2(CO)_9$

A mixture of 0.1 g of I and 0.2 g (0.55 mmol) of $Fe_2(CO)_9$ in 70 ml of benzene was stirred at 40 °C for 5 hours. After chromatography, 59 mg of $Fe_3(CO)_{12}$ and 28 mg (28%) of the initial I were isolated.

Reaction of I with $[Fe(CO)_2Cp]_2$ *(VI)*

(a) A mixture of 0.1 g of I and 0.1 g (0.28 mmol) of VI in 70 ml of heptane was refluxed for 7 hours. After chromatography, in addition to a small amount of VI, 90% of the initial I was recovered.

(b) A mixture of 0.1 g of I and 0.1 g of VI in 60 ml of THF was refluxed for 6 hours. After chromatography, 38% of I was isolated.

(c) A mixture of 0.1 g of I and 0.1 g of VI in 100 ml of benzene was irradiated with UV light at room temperature for 8 hours. After chromatography, 85% of I was isolated.

(d) A mixture of 0.1 g of I and 0.1 g of VI in 100 ml of THF was irradiated with UV light at room temperature for 8 hours. After chromatography, 81% of I was isolated.

Reaction of $Co_2(CO)_8$ *with II*

A mixture of 0.49 g (1 mmol) of II and 0.5 g (1.5 mmol) of $Co_2(CO)_8$ in 100 ml of heptane was refluxed for 8 hours. After chromatography on the silica gel column, in addition to a small amounts of the initial compounds, 0.18 g (25%) of III and 0.01 g of IV were isolated.

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