Metal atoms in the synthesis of metal clusters

VI *. Reactivity of cobalt and nickel atoms towards the mononuclear complexes $(\eta^5\text{-Cp}^R)\text{Co(CO)}_2$ (R = H, Me$_4$Et, Me$_5$, ^{t}Bu$_2$, ^{i}Pr$_2$) and $(\eta^5\text{-Cp}^{Me})\text{Mn(CO)}_3$. Crystal structure and redox behaviour of $[(\eta^6\text{-mesitylene})\text{Co}]_2\text{Co}(\eta^5\text{-Cp}^R)(\mu_3\text{-CO})_2$ (R = Me$_5$,^{t}Bu$_2$) **

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Abstract

The reaction of alkyl-substituted $(\eta^5\text{-Cp}^R)(\text{CO})_2$ complexes with cobalt or nickel atoms in the presence of Cp*H or an arene has been shown to give homo- and heteronuclear M$_2$- and M$_3$-bridged metal carbonyl clusters. The crystal structures of the two homonuclear species obtained in the metal atom reactions, namely $[(\eta^6\text{-mesitylene})\text{Co}]_2\text{Co}(\eta^5\text{-Cp}^R)(\mu_3\text{-CO})_2$ with R = Me$_5$ or ^{t}Bu$_2$, have been determined. The electrochemical behaviour of the clusters $[(\eta^6\text{-mesitylene})\text{Co}]_2\text{Co}(\eta^5\text{-Cp}^R)(\mu_3\text{-CO})_2$ (R = Me$_5$, ^{t}Bu$_2$,^{i}Pr$_2$) was studied by cyclic voltammetry and the results are discussed in detail. The reaction of $(\eta^5\text{-Cp}^{Me})\text{Mn(CO)}_3$ with nickel atoms and Cp*H does not give heteronuclear Mn–Ni cluster compounds, but instead the compound $[(\eta^5\text{-Cp*})\text{Ni}]_2\text{Ni}(\eta^5\text{-Cp})(\mu_3\text{-CO})_2$.

Key words: Cobalt; Nickel; Cyclopentadienyl; Metal atom chemistry; Cluster; Metal vapour synthesis

1. Introduction

Naked metal atoms generated from bulk metal show a high potential for the synthesis of small discrete metal clusters. In the early days of metal vapour chemistry, matrix-isolated bare metal dimers, trimers and higher aggregates were the first examples produced and examined [2]. In spite of such observation of the formation of ligand-free metal clusters, reports of the

synthesis and subsequent characterization of ligand-stabilized metal cluster compounds are still rare [3].

Very recently we showed that metal atoms can react with pure organic ligands or mononuclear organometallic complexes, or a combination of both, to give metal ligand cluster compounds which are stable and isolable at room temperature [4]. In these studies we observed that the naked metal atoms used in the synthesis of the cluster compounds can either (a) become an integral part of the newly formed organometallic cluster or (b) can mediate the formation of a cluster without being incorporated into the new cluster formed [5]. In a continuation of these investigations we now present some new results concerning the reaction of cobalt and nickel atoms with various mononuclear organometallic compounds.

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* For Part V, see ref. 1.
** Dedicated to Professor K.J. Klabunde, on the occasion of his 50th birthday.
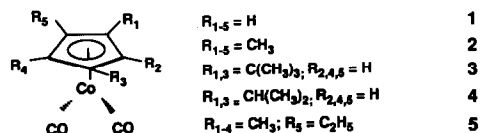[1] X-Ray structure investigations.

Fig. 1. Structure of the starting organometallic complexes 2–5.

2. Results and discussion

As the organometallic starting complexes we chose a series of complexes of the general formula $(\eta^5\text{-}Cp^R)Co(CO)_2$, as shown in Fig. 1. Of these complexes only 2 is a crystalline solid at room temperature. All the others are liquids or highly viscous oils. Because of the alkyl substituents in 2–5 all the compounds are highly soluble in organic solvents even at very low temperature, and this property is important for reaction with metal atoms since most of these reactions usually have to be performed in solution at temperatures of ca. $-100°C$. In addition, there are also electronic and steric reasons for using these compounds in the reaction with metal atoms. Electronically the formal electron releasing effect of the alkyl substituents in 2–5 stabilizes the $Co\text{-}Cp^R$ bond, and the steric effects stabilize the metal cluster core kinetically.

Compound 1 was brought into reaction with metal atoms in a co-condensation reaction in which the vapours of 1 and the appropriate metal were condensed together onto the walls of a static reactor at $N_2(l)$ temperature, together with an additional organic ligand, e.g. mesitylene. The late transition metal atoms (e.g. Fe, Co, Ni) are well known to form metal atom solvates with most of the arenes under these conditions [6]. In these metal atom solvates the metal atoms are complexed in a sandwich fashion [6a,7], but the ligands are lost very readily well below $-30°C$. For this reason these solvates are excellent sources of naked metal atoms or even metal ligand fragments over a temperature range of ca. $-100°C$ to $-40°C$ [7]. By this technique of using three different components in a metal vapour reaction we hoped to obtain cluster compounds incorporating the initial organometallic complexes 2–5 as well as metal ligand fragments formed by the reaction of an additional organic ligand with the metal atoms.

Reaction of 1, Co atoms and mesitylene at $-196°C$, followed by warming of the reaction mixture to room temperature during several hours, afforded a brown to black solution from which black crystals of the compound $[(\eta^5\text{-}Cp)Co]_3(\mu\text{-}CO)_3$ (6) were isolated (see eqn. (1)).

We attribute the formation of 6 to the generation of
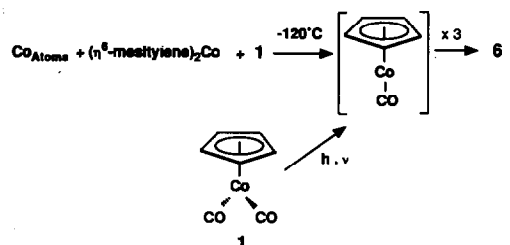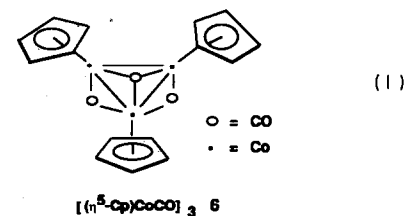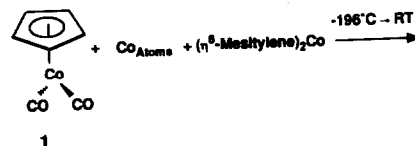
Scheme 1. Formation of cluster 6 via the metal vapour route and by photolytic displacement of CO from 1.

the reactive $[(\eta^5\text{-}Cp)Co]$ species, formed from compound 1 by reaction with metal atoms according to Scheme 1. The photolytic synthesis of 6 has been studied by Vollhardt et al. [8] and King [9].

The structure of 6 was established previously by Cotton and coworkers [10*]. ^1H-NMR studies of 6 in solution indicate fluxional behaviour of the bridging CO ligands; at temperatures down to $-80°C$ only one signal for the Cp rings is observed. A facile site exchange between μ_2- and μ_3-bridging positions might explain this behaviour.

The mixture of the substituted Co complexes 2, 3, or 4 and an excess of mesitylene were brought into reaction with cobalt atoms and mesitylene in methylcyclohexane solution in a three-component system (eqn. (2)). Workup and chromatographic separation of the individual reaction mixtures gave various metal cluster compounds together with small amounts of recovered starting material.

In addition to the well-known dinuclear complexes of type 7 [11], the trinuclear cobalt clusters 8a–c were formed. In these new clusters the three metal atoms

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* Reference number with asterisk indicates a note in the list of references.
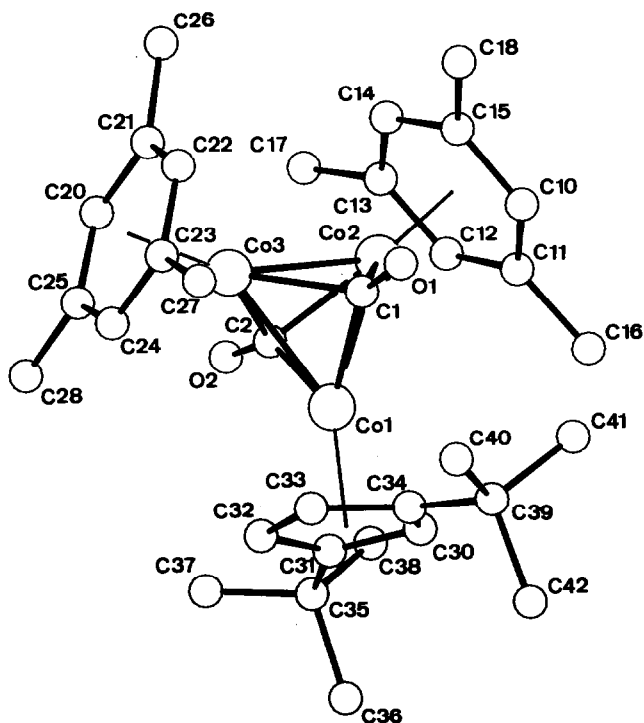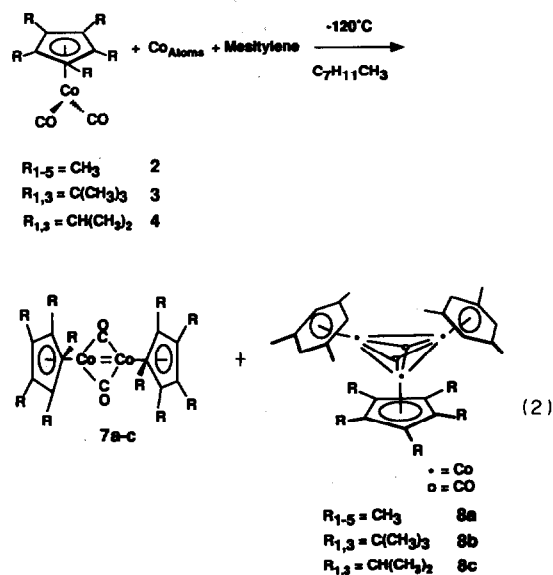
Fig. 3. Molecular structure of 8b as found in the crystal.
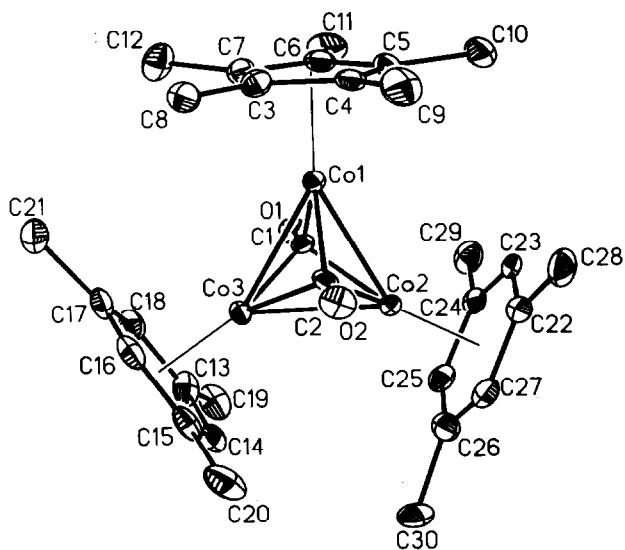
Fig. 2. Molecular structure of 8a as found in the crystal.

form an equilateral triangle which is capped by two triply-bridging CO groups to form a trigonal bipyramid as the resulting coordination polyhedron of the clusters. The results of crystal structure investigations of the clusters 8a and 8b are shown in Figs. 2 and 3 and Tables 1–4.

The Co–Co bond lengths in 8a and 8b (see Table 2) are in good agreement with corresponding distances in related compounds, such as [(η⁵-Cp*)Co]₃(μ₃-CO)₂ (Co–Co 2.370(1) Å) [12], [(η⁵-Cp)Ni]₂Co(η⁵-Cp*)(μ₃-CO)₂ (Co–Ni 2.371 Å) [13] and [(η⁵-Cp)Co]₃(μ₃-CO)₂ (Co–Co 2.390(1) Å) [14].

The formation of the homonuclear clusters 8a–c can best be understood in terms of the formal reaction of one of the mononuclear complexes 2–4 with [(η⁶-mesitylene)Co] fragments formed during the metal vapour reaction. Agglomeration of two of these fragments with complexes 2–4 results in the build-up of the clusters 8a–c. Obviously there is a distinct difference between the reaction of 2 and those of the substituted complexes 3–5.

The formation of 7 can be explained by the combination of two [(η⁵-Cp*)Co] fragments generated by the interaction of metal atoms with the mononuclear compounds 2–4.

Reaction of Ni atoms, Cp*H and the organometallic complex 5 in methylcyclohexane solution at −120°C affords three products as shown in eqn. (3).

The main products are the η⁵-η³-coordinated nickel sandwich complex 9 (as a mixture of cis and trans isomers) and the dinuclear Ni cluster 10. Formation of 9, together with 10, was observed in earlier studies of the reaction of Ni atoms with mixtures of Fe(CO)₅ and Cp*H [4a].

The important product shown in eqn. (3) is the heteronuclear cluster 11, to which we assign a structure analogous to that of 8a–c on the basis of spectral data. In this case, two [(η⁵-Cp*)Ni] fragments combine with compound 5 to form the desired cluster compound 11.

TABLE 1. Crystallographic data and refinement details for [(η⁶-Mes)Co]₂Co(η⁵-Cp*)(μ₃-CO)₂ (8a) and [(η⁶-Mes)Co]₂Co(η⁵-ᵗBu₂Cp)(μ₃-CO)₂ (8b)

	8a [b]	8b [a]
Formula	$C_{30}H_{39}Co_3O_2$	$C_{33}H_{47}Co_3O_2$
Mol. wt.	608.4	652.5
Crystal size (mm)	0.34×0.26×0.21	0.18×0.49×0.32
a (Å)	23.456(6)	14.244(4)
b (Å)	10.702(3)	12.503(2)
c (Å)	10.378(2)	17.720(2)
β (°)	90.00	100.95(1)
V (Å³)	2605.1	3098.5
D_{calcd} (g cm⁻³)	1.551	1.40
μ (cm⁻¹)	19.1	16.12
$F(000)$ (e)	1264	1368
Z	4	4
Space group [No.]	$Pna2_1$ [33]	$P2_1/n$ [14]
Diffractometer	Nicolet R3mV	Enraf-Nonius-CAD4
Temperature (K)	120	293
Mo Kα radiation, λ (Å)	0.71069	0.71069
Absorption correction	Empirical	None
(Min. to max.)	0.63–0.67	–
No. of measured reflections	4587	7626
$[(\sin\theta)/\lambda]_{max}$ (Å⁻¹)	0.8	0.65
R_{av}	0.01	0.01
No. of independent reflections	4587	7058
No. of observed reflections	4390 ($F_o \geq 4\sigma(F)$)	4571 ($I > 2\sigma(I)$)
No. of refined parameters	312	343
R	0.046	0.055
R_w ($w = 1/\sigma^2(F_o)$)	0.046	0.053
Maximum residual electron density (e Å⁻³)	1.073	0.71

[a] Structures were solved using heavy-atom methods; H-atom positions were calculated and kept fixed in the final refinement stages.
[b] The atoms in the Cp* group are treated as rigid bodies and have standard deviations only for the pivot atom C(3).
Further details of the crystal structure investigation, e.g. full listings of atomic coordinates and bond lengths and angles, are available on request from the Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, D-76344 Eggenstein-Leopoldshafen, on quoting the depository numbers CSD 57351 and 400197, the names of the authors and the journal citation.

This is entirely comparable with the formation of the homonuclear Co₃ cluster compounds 8a–c in eqn. (2).

Although all the complexes listed in Table 5 (see also Fig. 4) are 48 VE clusters and are isostructural, the stretching frequencies of their μ₃-CO groups differ by up to 110 cm⁻¹ (8a–c vs. 13 and 14). This indicates a quite large variation in the binding energies of these bridging CO groups to the individual M₃ cluster cores in these complexes.

With the intention of synthesizing a heteronuclear Ni–Mn cluster compound the reaction involving the three starting materials shown in eqn. (4) was examined.
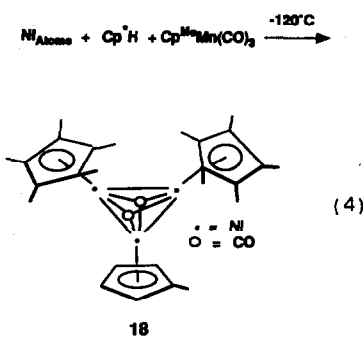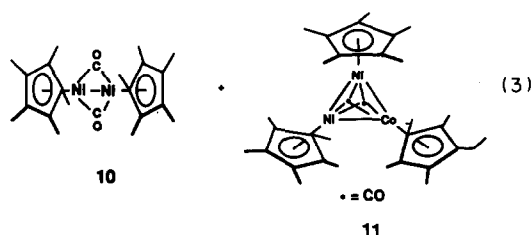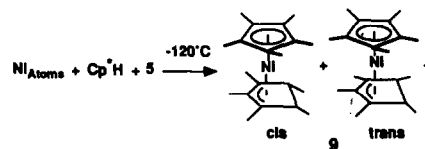
TABLE 2. Selected bond lengths and bond angles in [(η⁶-mesitylene)Co]₂Co(η⁵-Cp*)(μ₃-CO)₂ (8a) and [(η⁶-mesitylene)Co]₂Co(η⁵-ᵗBu₂Cp)(μ₃-CO)₂ (8b)

Selected bond lengths (Å)

8a		8b	
Co(1)–Co(2)	2.403(1)	Co(1)–Co(2)	2.429(1)
Co(1)–Co(3)	2.451(1)	Co(1)–Co(3)	2.385(1)
Co(2)–Co(3)	2.406(1)	Co(2)–Co(3)	2.433(1)
Co(1)–C(1)	1.876(6)	Co(1)–C(1)	1.895(5)
Co(1)–C(2)	1.866(5)	Co(1)–C(2)	1.900(5)
Co(2)–C(1)	1.984(3)	Co(2)–C(1)	1.962(5)
Co(2)–C(2)	1.984(3)	Co(2)–C(2)	1.951(5)
Co(3)–C(1)	1.956(5)	Co(3)–C(1)	1.977(5)
Co(3)–C(2)	1.970(5)	Co(3)–C(2)	1.982(5)
C(1)–O(1)	1.210(7)	C(1)–O(1)	1.197(6)
C(2)–O(2)	1.208(6)	C(2)–O(2)	1.210(6)

Selected bond angles (°)

8a		8b	
Co(2)–Co(1)–Co(3)	59.9(1)	Co(3)–Co(1)–Co(2)	60.7(1)
Co(1)–Co(2)–Co(3)	60.3(1)	Co(2)–Co(3)–Co(1)	60.6(1)
Co(1)–Co(3)–Co(2)	59.8(1)	Co(3)–Co(2)–Co(1)	58.8(1)

The Ni atoms were vapourized into a cooled solution of (η⁵-Cp^{Me})Mn(CO)₃ and Cp*H in methylcyclohexane. The only new cluster product which we were able

$$Ni_{Atoms} + Cp^*H + 5 \xrightarrow{-120°C} \quad cis \quad 9 \quad trans +$$

(3)

10   11

• = CO

$$Ni_{Atoms} + Cp^*H + Cp^{Me}Mn(CO)_3 \xrightarrow{-120°C}$$

(4)

• = Ni
O = CO

18

to isolate (as brown crystals) was the homonuclear paramagnetic M_3 cluster **18**. Only trace amounts of **9** and **10** were isolated in a forerun when the product mixture was chromatographed. Compound **18** was characterized by mass spectrometry and elemental analysis, as well as by a partial X-ray structure determination. Crystals of **18** were highly disordered, and no further discussion is presented here [15]. We encountered similar disorder problems in crystal structure determinations of CO-bridged M_3 cluster compounds, and such problems have been reported for other related systems [16].

The above results show that metal atoms or metal ligand fragments can be incorporated into both homo- and heteronuclear metal cluster compounds using the metal vapour technique. However, the yields of the

TABLE 3. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement coefficients ($\text{Å}^2 \times 10^3$) for **8a**

Atom	x	y	z	U_{eq} [a]
Co(1)	911(1)	7858(1)	10000	13(1)
Co(2)	1264(1)	7473(1)	7863(1)	13(1)
Co(3)	1670(1)	6367(1)	9661(1)	14(1)
C(1)	874(2)	6343(5)	9096(5)	15(2)
O(1)	539(2)	5494(3)	8951(4)	20(1)
C(2)	1646(2)	8189(5)	9400(5)	15(2)
O(2)	2003(2)	8997(3)	9504(4)	22(1)
C(3)	852(1)	8702(3)	11793(3)	20(2)
C(4)	707	9589	10829	19(2) [b]
C(5)	223	9132	10153	20(1) [b]
C(6)	70	7963	10699	21(2) [b]
C(7)	458	7698	11713	19(2) [b]
C(8)	1340(2)	8844(5)	12734(6)	23(2)
C(9)	1014(3)	10810(6)	10650(7)	32(2)
C(10)	−102(3)	9791(7)	9112(6)	33(2)
C(11)	−413(2)	7147(7)	10326(6)	32(2)
C(12)	409(3)	6603(6)	12614(6)	29(2)
C(13)	1899(3)	4495(5)	9226(6)	24(2)
C(14)	2328(3)	5317(6)	8837(6)	24(2)
C(15)	2570(2)	6190(5)	9705(6)	23(2)
C(16)	2358(2)	6216(6)	10955(6)	23(2)
C(17)	1937(3)	5391(6)	11392(6)	26(2)
C(18)	1708(3)	4527(5)	10499(6)	23(2)
C(19)	1624(3)	3618(6)	8281(6)	30(2)
C(20)	3012(3)	7102(6)	9238(7)	33(2)
C(21)	1766(3)	5343(6)	12779(6)	34(2)
C(22)	1238(2)	9090(6)	6695(5)	20(2)
C(23)	712(2)	8426(5)	6614(5)	19(2)
C(24)	689(2)	7148(6)	6269(5)	20(2)
C(25)	1216(2)	6533(5)	6032(5)	21(2)
C(26)	1743(3)	7166(6)	6090(5)	22(2)
C(27)	1745(2)	8448(6)	6418(5)	21(2)
C(28)	1250(3)	10427(6)	7094(6)	29(2)
C(29)	138(3)	6489(6)	6225(6)	29(2)
C(30)	2293(3)	6539(6)	5748(6)	30(2)

[a] Equivalent isotropic U defined as one-third of the trace of the orthogonalized U_{ij} tensor. [b] Atoms in rigid groups have standard deviations only for the pivot atom.

TABLE 4. Atomic fractional coordinates and equivalent isotropic thermal parameters (Å^2) for **8b**

Atom	x	y	z	U_{eq} [a]
Co(1)	0.3122(1)	0.1906(1)	0.0144(1)	0.029(1)
Co(2)	0.2290(1)	0.3176(1)	0.0820(1)	0.032(1)
Co(3)	0.3951(1)	0.2701(1)	0.1304(1)	0.033(1)
O(1)	0.3648(3)	0.4135(3)	−0.0007(2)	0.047(2)
O(2)	0.2571(2)	0.1089(3)	0.1547(2)	0.042(2)
C(1)	0.3388(3)	0.3380(4)	0.0314(3)	0.035(3)
C(2)	0.2808(3)	0.1766(4)	0.1134(3)	0.030(3)
C(10)	0.1400(4)	0.4412(5)	0.0236(3)	0.054(4)
C(11)	0.0866(4)	0.3470(5)	0.0208(3)	0.051(4)
C(12)	0.0833(4)	0.2958(4)	0.0908(4)	0.052(4)
C(13)	0.1333(4)	0.3341(4)	0.1607(3)	0.046(4)
C(14)	0.1870(4)	0.4264(5)	0.1605(3)	0.053(4)
C(15)	0.1916(4)	0.4822(4)	0.0918(4)	0.054(4)
C(16)	0.0316(4)	0.3061(6)	−0.0544(4)	0.077(5)
C(17)	0.1309(5)	0.2741(6)	0.2334(4)	0.077(5)
C(18)	0.2535(5)	0.5803(5)	0.0945(4)	0.082(5)
C(20)	0.4510(4)	0.2399(6)	0.2482(3)	0.057(4)
C(21)	0.4559(4)	0.3511(5)	0.2350(3)	0.059(4)
C(22)	0.5020(4)	0.3847(5)	0.1767(4)	0.058(4)
C(23)	0.5412(4)	0.3125(5)	0.1310(3)	0.049(3)
C(24)	0.5331(3)	0.2025(4)	0.1455(3)	0.043(3)
C(25)	0.4898(4)	0.1648(4)	0.2046(3)	0.047(3)
C(26)	0.4189(5)	0.4298(6)	0.2867(4)	0.092(6)
C(27)	0.5870(4)	0.3503(5)	0.0662(4)	0.072(5)
C(28)	0.4814(4)	0.0473(5)	0.2184(4)	0.068(5)
C(30)	0.2427(3)	0.1183(4)	−0.0881(3)	0.036(3)
C(31)	0.2740(3)	0.0363(4)	−0.0339(3)	0.033(3)
C(32)	0.3748(3)	0.0488(4)	−0.0124(3)	0.038(3)
C(33)	0.4029(3)	0.1347(4)	−0.0558(3)	0.039(3)
C(34)	0.3227(3)	0.1759(4)	−0.1045(3)	0.037(3)
C(35)	0.2139(4)	−0.0540(4)	0.0120(3)	0.044(3)
C(36)	0.1936(4)	−0.1303(5)	−0.0809(4)	0.068(4)
C(37)	0.2661(4)	−0.1143(4)	0.0584(3)	0.058(4)
C(38)	0.1187(4)	−0.0125(5)	0.0038(3)	0.055(4)
C(39)	0.3187(4)	0.2543(5)	−0.1705(3)	0.051(4)
C(40)	0.4130(5)	0.3144(5)	−0.1634(3)	0.071(5)
C(41)	0.2374(5)	0.3346(5)	−0.1749(3)	0.069(5)
C(42)	0.3041(5)	0.1870(6)	−0.2452(3)	0.081(5)

[a] $U_{eq} = \frac{1}{3} \sum_i \sum_j U_{ij} a_i^* a_j^* (\vec{a}_i \vec{a}_j)$.

desired cluster compounds are fairly low. The formation of homonuclear clusters is achieved by the reaction of Co and Ni atoms with organometallic Co complexes. With the related Mn organometallic complex $(\eta^5\text{-Cp}^{Me})Mn(CO)_3$ the Ni atoms did not give a heteronuclear Mn–Ni cluster, but instead a homonuclear Ni_3 cluster compound.

2.1. Electrochemical investigations on the M_3 clusters 8a–c

The cluster compounds **8a–c** were studied by cyclic voltammetry. Table 6 lists the electrochemical data and Fig. 5 shows the cyclic voltammograms for **8a–c**.

All three clusters show two reversible one-electron redox couples ($[Co_3]^0/[Co_3]^+$ and $[Co_3]^0/[Co_3]^-$), which indicate the existence of the monocations and
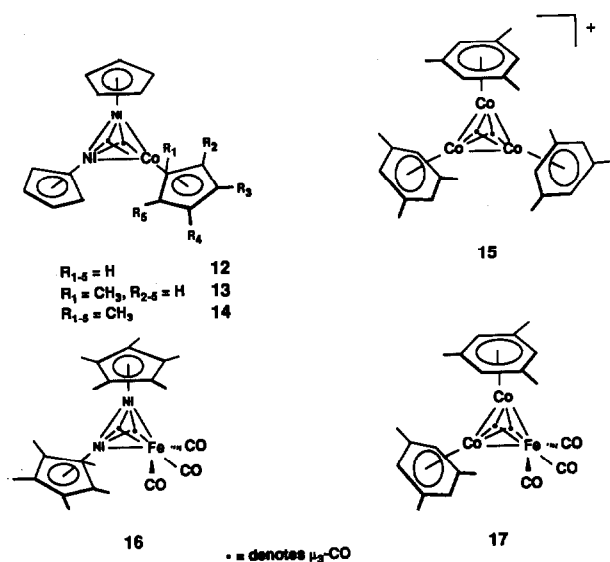
Fig. 4. Structures of the clusters 12–17 [4a,12,13].

TABLE 6. Cyclovoltammetric data of clusters 8a–8c and isoelectronic clusters 12–14

Cyclovoltammetric details	8a [a]	8b	8c	12 [13]	13 [13]	14 [13]
$E_{1/2}^{0/+}$ [b]	−0.40	−0.28	−0.30			
$E_{p/a}$ [c]	−0.31	−0.20	−0.16			
$E_{p/k}$ [d]	−0.49	−0.36	−0.44			
ΔE_p [d,e]	0.18	0.16	0.28			
r [e,f]	0.94	0.97	0.98			
$E_{1/2}^{0/-}$	−1.98	−1.91	−1.92	−1.525	−1.558	−1.693
$E_{p/a}$	−1.87	−1.83	−1.78			
$E_{p/k}$	−2.10	−2.00	−2.07			
ΔE_p	0.23	0.17	0.29	0.070	0.085	0.085
r	0.65	0.95	1.02	1.00	1.00	1.00

[a] In the region 0.6–0.8 V, one additional irreversible oxidation is observed for each cluster 8a–c. [b] In V, $E_{1/2} = 0.5(E_{p/a} + E_{p/k})$. [c] Anodic peak potential in V. [d] Cathodic peak potential in V. [e] Peak separation in V, $\Delta E_p = E_{p/a} - E_{p/k}$. [f] $r = I_{p/a}I_{p/k}^{-1}$.

monoanions of 8a–c under the conditions of the cyclovoltammetric experiment. The resulting anions are isoelectronic with a series of heteronuclear [CoNi$_2$] clusters, e.g. [(η^5-Cp)Ni]$_2$Co(η^5-C$_5$H$_{5-n}$Me$_n$)(μ_3-CO)$_2^-$ (n = 0,1,5) 12$^-$–14$^-$, synthesized and investigated by Dahl and coworkers [12a,13], as well as the neutral paramagnetic [(η^5-Cp)Ni]$_3$(μ_3-CO)$_2$ cluster 19 [17]. The striking difference between the new clusters 8a–c and those studied by Dahl is that the latter exhibit only one reversible redox couple compared with the two observed for 8a–c.

The observed cathodic shift of the redox couples 8a–c^0/8a–c$^-$ can be understood in terms of the different electronic situations in these compounds. The cluster systems 8a–c differ in the number n of methyl groups on the Cp^R rings (8a, n: Σ = 11 CH$_3$; 8b, n: Σ = 12 CH$_3$; 8c, n: Σ = 10 CH$_3$). Comparison of the $E_{1/2}$ values for 8a$^-$–8c$^-$ with the corresponding $E_{1/2}$

value for the isoelectronic system 12$^-$ (n = 0), which bears no methyl substituents on the Co-coordinated Cp ring, reveals differences of 450 mV (8a$^{0/-}$), 380 mV (8b$^{0/-}$) and 390 mV (8c$^{0/-}$) between these couples and the couple 12$^{0/-}$ [12a] (Table 6), and hence a correlation between the $E_{1/2}$ values and the value of n. Values of 40.9 mV, 31.6 mV and 39 mV for 8a$^-$, 8b$^-$ and 8c$^-$ respectively, for the change in the cathodic shift of $E_{1/2}$ for every additional methyl group relative to that for 12$^-$, are observed.

These observations can be understood in terms of the electron releasing effect of the methyl groups in the series of clusters 8a–8c, which raises the reduction potential on going from cluster 8a to cluster 8c. Similar variations as a result of ligand substitution are not without precedent [18,19]; thus Rieke and coworkers [19] have observed comparable effects on introduction of electron donating groups into Cr(CO)$_3$ complexes of biphenyls. Here the reduction potential of (η^6:η^6-bi-

TABLE 5. IR stretching frequencies for 8a–8c and related clusters

| Compound	ν(CO) (cm^{-1}) [a]	Reference
[(η^6-Mes)Co]$_2$Co(η^5-Cp*)(μ_3-CO)$_2$ (8a)	1620	This work
[(η^6-Mes)Co]$_2$Co(η^5-^{t}Bu$_2$Cp)(μ_3-CO)$_2$ (8b)	1619	This work
[(η^6-Mes)Co]$_2$Co(η^5-^{i}Pr$_2$Cp)(μ_3(CO)$_2$ (8c)	1624	This work
[(η^5-Cp*)Ni]$_2$Co(η^5-EtMe$_4$Cp)(μ_3-CO)$_2$ (11)	1680 (CH$_2$Cl$_2$)	This work
[(η^5-Cp)Ni]$_2$Co(η^5-Cp)(μ_2-CO)$_2$ (12)	1720	[13]
[(η^5-Cp)Ni]$_2$Co(η^5-Cp^{Me})(μ_3-CO)$_2$ (13)	1671	[13]
[(η^5-Cp)Ni]$_2$Co(η^5-Cp*)(μ_3-CO)$_2$ (14)	1737	[13]
[(η^6-Benzene)Co]$_3$(μ_3-CO)$_2^+$ (15)	1736	[12]
[(η^5-Cp*)Ni]$_2$Fe(CO)$_3$(μ_3-CO)$_2$ (16)	2005, 1970, 1940, 1712	[4a]
[(η^6-Mes)Co]$_2$Fe(CO)$_3$(μ_3-CO)$_2$ (17)	1985, 1920, 1905, 1645	[4a]

[a] All measurements in KBr unless otherwise stated.
Mes = mesitylene.
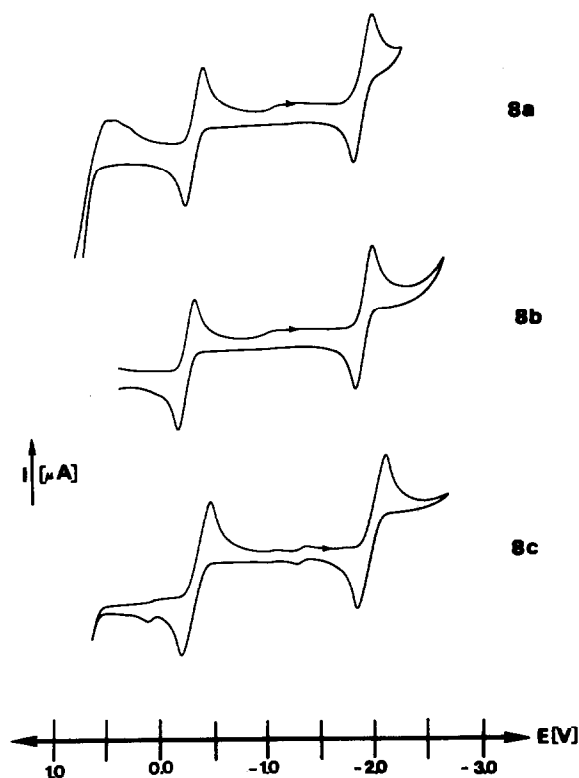
Fig. 5. Cyclic voltammograms (CVs) of the clusters 8a–c measured in 1,2-dimethoxyethane (DME)/0.1 M $^nBu^+ClO_4^-$ at −40°C vs. saturated calomel electrode (SCE). 100 mV scan rate. → indicates the scan direction of the CVs.

mesityl)bis(tricarbonyl)chromium 20 is lower than that for the parent compound (η^6-biphenyl)(tricarbonyl)chromium 21. The most obvious reason for this is the effect of the electron release by the six methyl groups on going from 20 to 21. Similar effects are known for substitution of H by $P(CH_3)_2$ in (η^6-benzene)V^0/(η^6-benzene)V^- and (η^6-benzene)Cr^0/(η^6-benzene)Cr^+ [20], as well as for substituted ferrocenes [21].

3. Experimental details

Unless otherwise stated, experiments were carried out in Schlenk-type glassware under argon with solvents that had been thoroughly dried and deoxygenated. The organocobalt compounds 1–5 [22], as well as 1,2,3,4,5-pentamethylcyclopentadiene Cp^*H [23] and 1,2,3,4-tetramethyl-5-ethylcyclopentadiene $Cp^{Me_4Et}H$ [24], were prepared by published procedures. (η^5-Cp^{Me})$Mn(CO)_3$ was purchased from Alfa and used as received. Al_2O_3 was deactivated by adding 5% H_2O and homogenizing the mixture for several hours. NMR spectra were recorded on Bruker AM-200, WH-400 (^1H, ^{13}C) and Bruker AM-300 (^{13}C) spectrometers in

sealed tubes and the signal of the solvent was used as internal reference. Chemical shifts are reported on the δ scale. IR spectra were recorded with KBr pellets or CH_2Cl_2 solutions on a Nicolet-7199 FT-IR spectrometer. Mass spectra (MS) were recorded on a Varian-MAT-5 by the fractional sublimation technique. Cyclic voltammograms were recorded at −40°C under argon in 1,2-dimethoxyethane (DME) at a stationary platinum working electrode with a Par electrochemical system and referenced vs. SCE. Tetra-n-butylammonium perchlorate (0.1 M in DME) was the supporting electrolyte. Metal vapour reactions in Mülheim were conducted in 6 l glass vessels which were connected to a rotating metal vapour reactor system based on that described by Timms [25] and those at Kansas State University, Manhattan, KS, USA, in 3 l Kontes glass vessels using the co-condensation procedure [26]. Metal vaporization was from alumina-coated tungsten crucibles (GTE-Sylvania, USA), which were heated resistively. Nickel (Merck) was 99.5% pure and cobalt (Aldrich) was 99.6% pure. Microanalyses were performed by Dornis & Kolbe Microanalytical Laboratory, Mülheim/Ruhr, Höhenweg, Germany, or by Gailbraith Microanalytical Laboratories, Sycamore Drive, Knoxville, TN, USA.

3.1. (η^5-$^tBu_2Cp$)$Co(CO)_2$ (3)

This compound was made by the method used for 1 [22] and 3 was then purified by column chromatography (Al_2O_3/H_2O). Red oil (50% yield). MS (EI, 70 eV), m/z (%): 292 (47.80) [$M^\oplus$], 264 (46.5), 236 (100), 220 (57.4), 218 (51.6), 57 (18). ^1H-NMR ([D_6-benzene]): δ = 1.06 (s, 18H); 4.42 (d, 2H); 4.74 (t, 1H). IR (KBr): ν = 1940 (vs, CO), 2010 (vs, CO) cm^{-1}.

3.2. (η^5-$^iPr_2Cp$)$Co(CO)_2$ (4)

This was made and purified as described for 3. Red oil (42% yield). MS (EI, 70 eV), m/z (%): 264 (64.3) [$M^\oplus$], 236 (52.8), 208 (100), 192 (55.3), 190 (51.8), 188 (31.5), 125 (23.0), 59 (27). ^1H-NMR ([D_6-benzene]): δ = 1.85 (d, 12H); 2.13 (sep, 2H); 4.34 (d, 2H); 4.56 (t, 1H). IR (CH_2Cl_2): ν = 1940 (s, CO), 2010 (s, CO) cm^{-1}.

3.3. [(η^5-Cp)$Co]_3(\mu_3$-$CO)_2$ (6)

Co atoms (1.5 g, 0.025 mol), mesitylene (50 ml) and (η^5-Cp)$Co(CO)_2$ (1) (5 g, 0.027 mol), were co-condensed for 2 h onto the walls of a static metal vapour reactor. The reactor was allowed to warm to −40°C, resulting in melting of the deep brown matrix, and the stirred solution was allowed to warm to room temperature during 3 h and then filtered. The solvent was removed under reduced pressure and the solid residue was dissolved in a minimum amount of CH_2Cl_2. The

solution was filtered and kept overnight at $-20°C$ to give 1.4 g (15%, based on metal vaporized) of black crystals of **6**. Analytical and spectroscopic data were reported previously [10b].

3.4. [(η⁶-Mesitylene)Co]₂Co(η⁵-Cp*)(μ₃-CO)₂ (8a), [(η⁶-mesitylene)Co]₂Co(η⁵-ⁱBu₂Cp)(μ₃-CO)₂ (8b) and [(η⁶-mesitylene)Co]₂Co(η⁵-ⁱPr₂Cp)(μ₃-CO)₂ (8c)

Cobalt atoms (3 g, 51 mmol) were vapourized during 3 h into a solution of the appropriate Co carbonyl compound **2** (7.5 g, 30 mmol), **3** (5 g, 18.9 mmol) or **4** (5 g, 17.1 mmol) in a mixture of 40 ml of mesitylene and 150 ml of methylcyclohexane. The reaction mixture was filtered to remove residual metal and the solvent and excess arene were removed under reduced pressure. The black residue was dissolved in tetrahydrofuran (THF) and the solution was adsorbed onto Al_2O_3 (5% H_2O) and chromatographed.

Co atoms/**2**/mesitylene. First band (pentane): 0.5 g **2**. Second band (pentane/ether (3:1)): 2.3 g **7a** (10.4%), green crystals from pentane. MS (EI, 70 eV), m/z (%): 444 (40) [M⊕], 386 (100) [M⊕− Co], 329 (50) [Cp*₂Co⊕]. IR (KBr): ν = 1750 (s), 1800 (s) cm⁻¹. ¹H-NMR ([D₈]THF): δ = 1.62 (s, 30H, CH₃). Third band (ether): 620 mg **8a** (2.5%), red crystals (THF, $-30°C$). MS (EI, 70 eV), m/z (%): 608 (1) [M⊕], 329 (0.5) [Cp*₂Co⊕], 120 (48) [Mes⊕], 105 (100) [Mes⊕− CH₃]. IR (KBr): ν = 1620 (s) cm⁻¹. ¹H-NMR ([D₈]THF): δ = 1.52 (s, 15H, Cp*-CH₃), 1.92 (s, 18H, arene-CH₃), 5.01 (s, 6H, arene-H). $C_{30}H_{39}O_2Co_3$ (608.42): calc.: C, 59.22; H, 6.46; Co, 29.05; found: C, 59.27; H, 6.63; Co, 28.87.

Co atoms/**3**/mesitylene. First band (pentane): traces of **3**. Second band (pentane): green crystals of **7b** (1.1 g, 2.08 mmol, 12%) (pentane/ethanol, $-30°C$). MS (EI, 70 eV), m/z (%): 528 (24) [M⊕], 454 (13), 413 (100). IR (KBr): ν = 1765 (s, μ₂-CO) cm⁻¹. Third band (ether): red crystals of **8b** (360 mg, 0.50 mmol, 3.0%) (ether, $-30°C$). MS (EI, 70 eV), m/z (%): 650 (52) [M⊕], 502 (100), 399 (22), 179 (26), 120 (52), 105 (73). ¹H-NMR ([D₆-benzene]): δ = 1.68 (s, 18H); 1.93 (s, 18H); 4.32 (m, 2H); 4.35 (m, 1H). IR (KBr): ν = 790 (s), 860 (s), 1030 (s), 1370 (s), 1620 (s, μ₃-CO), 2830 (s), 2900 (s), 2960 (s) cm⁻¹. $C_{33}H_{45}O_2Co_3$ (650.50): calc.: C, 60.93; H, 6.97; Co, 27.18; found: C, 60.79; H, 7.16; Co, 27.18.

Co atoms/**4**/mesitylene. First band (pentane): red oil **4**. Second band (pentane): green crystals of **7c** (1.4 g, 2.96 mmol, 15%) (ether/ethanol, $-30°C$). MS (EI, 70 eV), m/z (%): 472 (22) [M⊕], 412 (40), 357 (100). IR (CH_2Cl_2): ν = 1760 (μ₂-CO) cm⁻¹. $C_{24}H_{34}O_2Co_2$ (472.38): calc.: C, 61.02; H, 7.25; Co, 24.95; found: C, 60.94; H, 7.28; Co, 24.97. Third band (ether): red crystals of **8c** (410 mg, 0.65 mmol, 3.4%) (ether, $-30°C$).

MS (EI, 70 eV), m/z (%): 622 (38) [M⊕], 472 (100), 444 (52), 440 (42), 322 (18), 179 (17), 44 (32). ¹H-NMR ([D₆-benzene]): δ = 1.41 (d, 6H); 1.51 (d, 6H); 1.93 (s, 18H); 3.32 (sep, 2H); 4.42 (d, 2H); 4.48 (t, 1H); 4.92 (s, 6H). IR (KBr): ν = 855 (m), 1030 (s), 1150, 1180 (w), 1370 (s), 1450 (s), 1620 (vs, br, μ₃-CO), 2860, 2920, 2960 (s), 3020 (w) cm⁻¹. $C_{31}H_{41}O_2Co_3$ (622.45): calc.: C, 59.82; H, 6.64; Co, 28.40; found: C, 59.91; H, 6.79; Co, 27.70.

3.5. [(η⁵-Cp*)Ni]₂Co(η⁵-CpMe₄Et)(μ₃-CO)₂ (11)

Ni atoms (5 g, 85 mmol) were vapourized during 3 h into a solution of 5 g (37 mmol) of Cp*H and 5 g (18.9 mmol) of **5** in 200 ml of methylcyclohexane. When the reaction was complete the brown solution was siphoned out and filtered. Removal of remaining ligand and solvent was followed by chromatography (Al_2O_3, 5% H_2O) which yielded three compounds.

First band (pentane): **9** (< 1%). Second band (pentane): **10** (120 mg, 0.23 mmol) Cp*₂Ni₂(CO)₂. Third band (pentane): brown crystals, **11** (580 mg, 0.9 mmol, 5%) (ether or CH₃CN, $-20°C$). MS (EI, 70 eV), m/z (%): 650 (22) [M⊕], 384 (61), 343 (100), 338 (19), 40 (21). ¹H-NMR ([D₆-benzene]): δ = 0.95 (t, 3H); 1.6 (s, 30H); 1.63 (s, 6H); 1.72 (s, 6H); 2.23 (q, 2H). ¹³C-NMR ([D₆-benzene]): δ = 9.6 (q); 9.9 (q); 15.4 (q); 18.6 (t); 92.6, 93.2, 101.1. IR (CH_2Cl_2): ν = 1680 (m, μ₃-CO) cm⁻¹. $C_{33}H_{47}O_2CoNi_2$ (652.03): calc.: C, 60.79; H, 7.26; Co, 9.04; Ni, 18.00; found: C, 60.79; H, 7.37; Co, 9.08; Ni, 18.10.

3.6. [(η⁵-Cp*)Ni]₂Ni(η⁵-CpMe)(μ₃-CO)₂ (18)

Ni atoms (2 g, 34 mmol) were vapourized during 2 h into a solution of 8 g (58 mmol) of Cp*H and 15 g (68.8 mmol) of (η⁵-CpMe)Mn(CO)₃ in 200 ml of methylcyclohexane. When the reaction was complete, the brown solution was siphoned out and filtered to remove the residual metallic nickel. Removal of the remaining excess Cp*H and (η⁵-CpMe)Mn(CO)₃ under reduced pressure followed by chromatography (Al_2O_3/5% H_2O) gave trace amounts of the unchanged (η⁵-CpMe)Mn(CO)₃ as a forerun, as well as traces of **9** and **10**. Elution of the column with pentane/ether (1:1) gave **18** as a brown coloured eluate. Recrystallization (ether/− 10°C) afforded 210 mg (ca. 1%) of brown crystals of **18**. MS (EI, 70 eV), m/z (%): 581 (57) [M⊕], 523 (43), 471 (32), 441 (100), 385 (80), 328 (58), 272 (40), 192 (21), 133 (19), 119 (31). ¹H-NMR ([D₆-benzene]): δ = 1.6 (s, 3H); 1.66 (s, 30H); 4.7 (m, 2H); 5.1 (m, 2H); 5.13 (s, 1H). IR (KBr): ν = 780 (s), 855 (m), 1020 (m), 1375 (s), 1420 (m), 1710 (vs), 2860 (s), 2900 (vs), 2970 (m), 3090 (s) cm⁻¹. $C_{28}H_{37}O_2Ni_3$ calc.: C, 57.82; H, 6.41; Ni, 30.27; found: C, 57.88; H, 6.29; Ni, 30.28.

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