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Facial coordination of cyclooctatetraene to a Co_2Ni triangle in a heterometallic trinuclear cluster complex

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Dedicated to Professor Rolf Gleiter on the occasion of his 65th birthday

Abstract

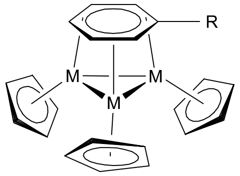
Reaction of $[(\eta\text{-}C_5H_5)NiCo_3(CO)_9]$ (**5**) with 1,3,5,7-cyclooctatetraene or $1,4\text{-}(SiMe_3)_2C_8H_6$, respectively, yields the complexes $[Co_2Ni(CO)_6(\mu_3\text{-}\eta^8\text{-}C_8H_6R_2)]$ (R = H, $SiMe_3$) (**7a**, **b**). Dramatic modifications of the tetrametallic cluster core and the ligand sphere of **5** to give the trinuclear complex **7** are driven by the preference of the cyclopolyenes for facial (μ_3-η^8) coordination. The title complexes are the first examples of facial cyclooctatetraene coordination to a heterometallic (Co_2Ni) triangle. © 2002 Published by Elsevier Science B.V.

Keywords: Cluster complexes; Cyclopolyenes; Facial coordination; Cobalt; Nickel

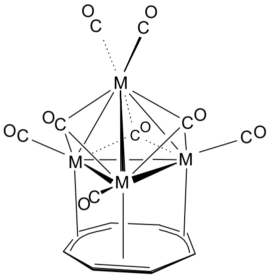
1. Introduction

The cyclic π-perimeters C_nH_n have been shown to facilitate the formation and enhance the stability of oligonuclear molecular transition metal aggregates. This can be attributed to the capability of such ligands to cap a triangular face of a metal cluster. For example, benzene ($n = 6$) may be used as a template to aid the self-assembly of organometal fragments. Three $(\eta\text{-}C_5H_5)Rh$ fragments can be assembled sequentially on a face of benzene, to ultimatively form the trinuclear cluster complex $[\{(\eta\text{-}C_5H_5)Rh\}_3(\mu_3\text{-}C_6H_6)]$ (**1**), with benzene in the facial (μ_3-) coordination mode [1]. Generation of the complexes $[\{(\eta\text{-}C_5H_5)Co\}_3(\mu_3\text{-arene})]$ (**2**) proceeds in a similar and often highly efficient fashion, but not without the additional help of an exocyclic alkenyl group, which guides the metals to the arene nucleus [2].

Facial coordination is a prominent feature of the metal cluster chemistry of cycloheptatrienyl ($n = 7$) and cyclooctatetraene ($n = 8$) [3]. For example, capping of a trimetal face in the binary carbonyls $[M_4(CO)_{12}]$ (M = Co, Rh) by cyclooctatetraene proceeds readily and leads to the formation of cluster complexes like, e.g. $[M_4(CO)_8(\mu_3\text{-}C_8H_8)]$ (**3**, M = Co), [4] (**4**, M = Rh) [5] in very high yield. Recently, evidence was also found for a pronounced template effect due to the cyclopolyolefin when **3** is generated from cyclooctatetraene and dinuclear cobalt carbonyl $[Co_2(CO)_8]$ [6]. These results, along with a now substantial amount of theoretical [7] and experimental [3–5,8] evidence, consistently indicate a high tendency of formation and stability of the $M_3(\mu_3\text{-}C_8H_8)$ moiety.



1 M = Rh, R = H
2 M = Co, R = C(R')=CHR"



3 M = Co
4 M = Rh

In the present paper we report the remarkable formation of *tri*nuclear cyclooctatetraene-capped mixed metal (Co_2Ni) clusters from a *tetra*nuclear precursor, where

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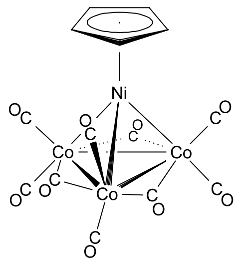
partial destruction of the cluster core and rearrangement of the ligand shell is governed by the preferences of the facial ligands. A preliminary account of part of this work has been given [9].

2. Results and discussion

From a structural point of view, in the complexes **3** and **4** the facial C_8H_8 ligand replaces three axial carbonyl ligands around a trimetal face of the parent carbonyl $[M_4(CO)_{12}]$. However, in order to accommodate the eight electrons donated by a μ_3-η^8-C_8H_8 ligand and keep the total valence electron (v.e.) count at the 'magic number' of 60, [10] a total of four CO molecules have to be displaced, resulting in the formation of an apical [11] $M(CO)_2$ from the original $M(CO)_3$ group. In the complex $[(\eta\text{-}C_5H_5)NiCo_3(CO)_9]$ (**5**) only three (axial) carbonyls can be displaced with ease. Introduction of a facial C_8H_8 ligand in **5** was expected to either result in an only μ_3-η^6 coordination of this ligand, or in the formation of a (potentially paramagnetic) 62 v.e. species with μ_3-η^8-C_8H_8. There is literature precedence for both possibilities. When heated with cyclooctatetraene, the alkylidyne-bridged tricobalt complex $[Co_3(CO)_9(\mu_3\text{-}CPh)]$ was reported to give the species $[Co_3(CO)_6(\mu_3\text{-}CPh)(\mu_3\text{-}C_8H_8)]$ (**6**) [12]. Coordination of only six of the eight ring carbon atoms to the cluster conserves the 60 v.e. count [12]. Electrochemical reduction of $[Co_4(CO)_6(L)(\mu_3\text{-}C_8H_8)]$ (L = η^4-C_8H_8, η^4-C_6H_8, η^4-6,6-$Ph_2C_6H_4$) proceeds in two reversible steps; most likely the η^8 coordination of the facial C_8H_8 ligand is retained in the 61 v.e. monoanion and the 62 v.e. dianion [7,8].



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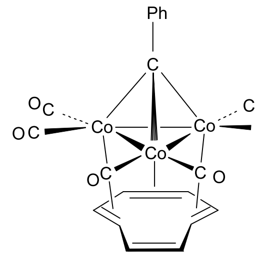

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Reaction of **5** with excess C_8H_8 or 1,4-$C_8H_6(SiMe_3)_2$, respectively, in boiling *n*-heptane gave dark red crystalline products **7a** and **b** in 25 and 38% yield, respectively. The infrared spectra of **7** indicated terminal and bridging carbonyl ligands; the large number of bands (3 terminal and 3 bridging ν_{CO}) points to a rather low molecular symmetry for both derivatives. The NMR spectra were consistent with the presence of facial $C_8H_6R_2$ ligands. Resonances that could have been attributed to a cyclopentadienyl ligand were absent.

Mass spectroscopic analysis and X-ray crystal structure determinations identified the products as the heterotrinuclear cluster complexes $[NiCo_2(CO)_6(\mu_3\text{-}\eta^8\text{-}C_8H_6R_2)]$ (**7a**, R = H; **7b**, R = $SiMe_3$). The metal composition of **7** was unambiguously derived from the mass spectra, where the shapes of the peaks due to the molecular ions were in perfect agreement with the calculated intensities based on the presence of two cobalt atoms and one nickel atom. In addition, XPS analysis of a sample of **7a** also gave an atomic ratio Co:Ni = 2:1.

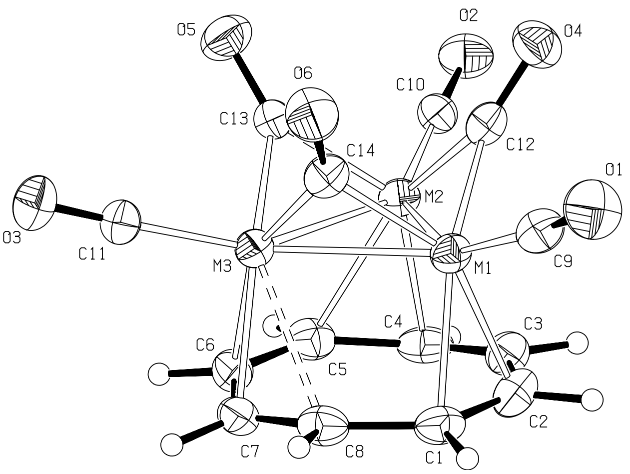
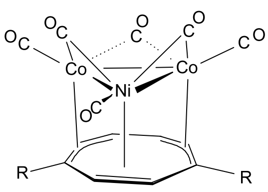
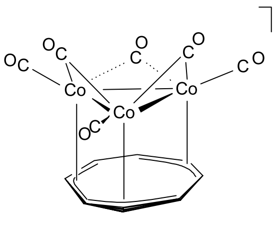


Fig. 1. Molecular structure of $[Co_2Ni(CO)_6(\mu_3\text{-}C_8H_8)]$ (**7a**).



7a R = H
7b R = $SiMe_3$



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The presence of $[(\eta\text{-}C_5H_5)Co(CO)_2]$ (**8**) was spectroscopically detected in the reaction mixtures. It is likely that the reaction involves transfer of a cyclopentadienyl ligand from the nickel to a cobalt atom, which then leaves the cluster in the form of **8**. Related effects have been observed in the course of metal exchange reactions in tri- and tetranuclear cluster complexes [13].

Disregarding the trimethylsilyl groups the two complexes **7a** and **b** have very similar structures. Views of the molecules are depicted in Figs. 1 and 2, respectively; a superposition of the two molecules is shown in Fig. 3. Important bond lengths and angles are summarized in Table 1.

The molecules consist of trimetal triangles, which are capped by the cyclooctatetraene [or 1,4-bis(trimethylsilyl)cyclooctatetraene] in the facial coordination mode. Three terminal and three edge-bridging carbonyls complete the coordination sphere of the clusters.

With complex **7a**, the X-ray data do not allow a distinction to be made between nickel and cobalt. We

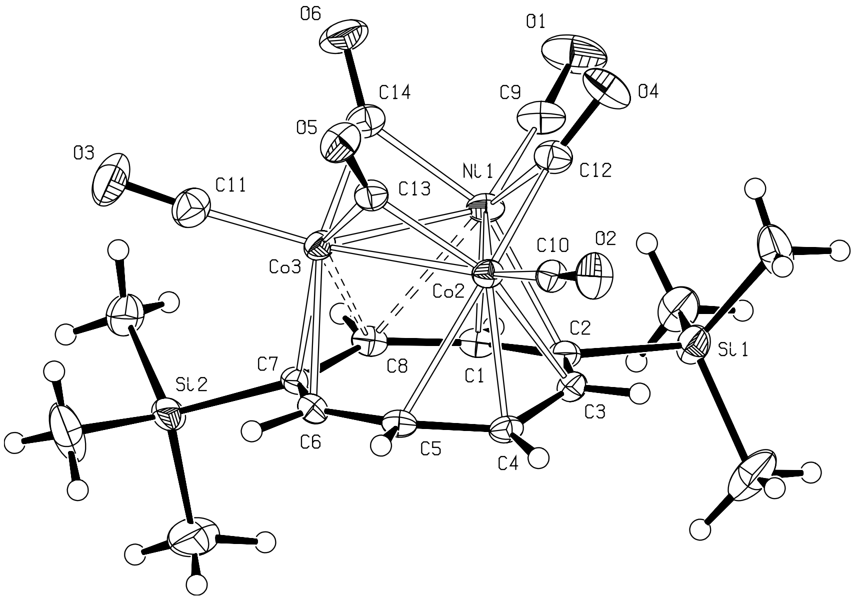

Fig. 2. Molecular structure of [$Co_2Ni(CO)_6\{\mu_3\text{-}C_8H_6(SiMe_3)_2\}$] (**7b**).

can neither completely rule out static disorder of the metal triangles, nor detect definitive signs of it in the shapes and orientations of the anisotropic displacement ellipsoids. In the only structurally characterized comparable Co_2Ni cluster complex, viz. [$NiCo_2(\mu_2\text{-}CO)_3(PMe_3)_6$] (**9**) the metals are disordered, and an average threefold symmetry is imposed upon the molecule by the lattice symmetry [14]. In contrast, the metals could be assigned in the structure of **7b** (Fig. 2). Superposition of the molecular structures of **7a** and **7b** was particularly good in one of the three obvious orientations, which can be generated from permutation of the metals (Fig. 3). This would place the nickel atom on M1 in **7a**.

The metal–metal distances in **7a** and **b** span the range 2.500(1)–2.540(1) Å, comparable to those in the isoelectronic and isostructural anion [$Co_3(CO)_6(\mu_3\text{-}C_8H_8)]^-$ (**10**) (2.507(2), 2.530(2) Å) [8]. Compared to the Co_3 frame in complex **10**, a contraction of the Co_2Ni triangle would have been expected, due to the smaller covalent radius of nickel (compare the metal–metal separation of 2.438 Å in **9**). The bond distances between the metals and the terminal CO ligands show little variation (range 1.774(5)–1.783(5) Å in **7a**; d(Ni–C) = 1.792(2), d(Co–C) = 1.771(2), 1.773(2) Å in **7b**). The carbonyl bridges are somewhat asymmetric in both structures. As expected, metal–C(O) distances are a little longer than those in the tricobalt anion **10** [8].

The cyclooctatetraene ligands exhibit the geometrical features that are typical for the facial coordination mode: [3] a rather flat chair-like ring conformation, with the mean plane through the ring carbons parallel to the trimetal plane, a non-systematic variation of the lengths of the endocyclic carbon–carbon bonds (range: 1.396(8)–1.434(8) Å in **7a**, 1.406(3)–1.451(3) Å in **7b**), and a difficult-to-define hapticity, in between $\mu_3\text{-}\eta^2{:}\eta^3{:}\eta^3$ and $\mu_3\text{-}\eta^3{:}\eta^3{:}\eta^3$ (Figs. 1 and 2). The bulky trimethylsilyl groups do not have much influence on the geometry of the bridging eight-membered ring and on the overall geometry of the molecule (Fig. 3). This was also noted for the tetrarhodium complex [$Rh_4(CO)_6\{\eta^4\text{-}C_8H_6(SiMe_3)_2\}\{\mu_3\text{-}\eta^8\text{-}C_8H_6(SiMe_3)_2\}$] [5].

The NMR spectra of **7** show a high molecular symmetry on the NMR time scale. Only one resonance is observed for the cyclooctatetraene ligand in **7a** both in the ^{1}H- ($\delta = 3.42$) and ^{13}C-NMR spectra ($\delta = 71.8$). Likewise, the proton (one silyl resonance along with a singlet overlaid by an $(AB)_2$ pattern around $\delta = 4.3$) and carbon spectra of **7b** correspond to the highest possible symmetry of the 1,4-$(SiMe_3)_2C_8H_6$ ligand. The

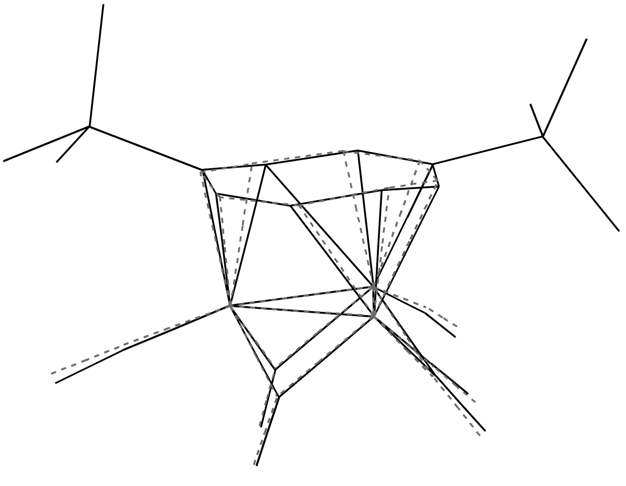

Fig. 3. Superposition of the molecules of **7a** (dashed lines) and **7b** (solid lines).

Table 1
Selected bond lengths (Å) and bond angles (°) for the complex $[Co_2Ni(CO)_6(\mu_3\text{-}C_8H_6R_2)]$ (**7a**, R = H; **7b**, R = $SiMe_3$)

	7a	**7b** [a]		**7a**	**7b** [a]
Bond lengths					
M1–M2	2.512(1)	2.5183(4)	M1–M3	2.503(1)	2.5003(4)
M2–M3	2.526(1)	2.5402(4)	M1–C1	2.118(5)	2.088(2)
M1–C2	2.140(5)	2.198(2)	M1···C8	2.473(5)	2.474(2)
M2–C3	2.333(5)	2.238(2)	M2–C4	2.087(5)	2.070(2)
M2–C5	2.236(5)	2.278(2)	M3–C6	2.190(5)	2.151(2)
M3–C7	2.088(5)	2.109(2)	M3–C8	2.427(5)	2.482(2)
C1–C2	1.396(8)	1.412(3)	C1–C8	1.434(8)	1.426(3)
C2–C3	1.417(8)	1.451(3)	C3–C4	1.418(7)	1.406(3)
C4–C5	1.411(7)	1.409(3)	C5–C6	1.432(8)	1.421(3)
C6–C7	1.412(7)	1.419(3)	C7–C8	1.404(7)	1.424(3)
Bond angles					
C2–C1–C8	133.2(5)	135.1(2)	C1–C2–C3	134.4(5)	129.9(2)
C2–C3–C4	136.5(5)	136.5(2)	C3–C4–C5	131.6(5)	132.2(2)
C4–C5–C6	135.1(5)	136.1(29	C5–C6–C7	134.8(5)	135.7(2)
C6–C7–C8	132.8(5)	128.4(2)	C7–C8–C1	136.5(5)	138.8(2)

[a] M1 = Ni1, M2 = Co2, M3 = Co3.

spectra are consistent with a rapid rotation of the facial ligands on top of the trimetal triangles. The observed ^1H and ^{13}C chemical shifts compare well with those of **10** and other (tetranuclear) $C_8H_6R_2$-capped cluster complexes [3–5,8].

In the chemical shift region typical of terminal carbonyl ligands both **7a** and **7b** show a sharp resonance at $\delta(^{13}C) = 185$. No further low field resonances were found in the spectra of **7a**. Complex **7b** shows an additional rather broad resonance at $\delta(^{13}C) = 247$. There are several possible interpretations of these spectra. In a completely rigid (non-exchanging) system, two resonances each should be present for the terminal and bridging carbonyl ligands. We expect the chemical shift difference between the two groups of resonances (about 70–90 ppm corresponding to 3.5–4.5 kHz) to be much larger than that (a few ppm) within a particular group (i.e. terminal Co- and terminal Ni-bound, or CoCo- and CoNi-bridging, respectively). It is reasonable to assume CO exchange to take place via bridge opening-bridge closing sequences, simultaneously involving all types of terminal and bridging sites [15]. A situation can be envisaged where this exchange process has already merged the individual terminal and individual bridging resonances to give a total of two signals, which are still far from coalescence to a single line. Alternatively, there could be accidental degeneracy of some of the carbonyl resonances. In addition, some resonances may have escaped detection, due to extensive broadening. This is believed to be the case in the carbon spectra of **7a**.

3. Conclusions

Formation of the title complexes **7** from the Co_3Ni cluster complex **5** involves dramatic modifications of both the metal cluster core and the ligand sphere of the starting material. These processes are obviously driven by the needs of the facial η^8-cyclooctatetraene ligand, which cannot be accommodated in a Co_3Ni complex. The high tendency of formation of **7** is also illustrated by our recent observation that complex **7a** can also be generated from $[Co_4(CO)_6(\eta^4\text{-}C_8H_8)(\mu_3\text{-}C_8H_8)]$ and nickelocene [16]. In the terminology of Vahrenkamp these are truly ‘basic cluster reactions’ [17], where the metal core is changed in a very specific way. Heterometallic cluster complexes are often more reactive than their homometallic analogues. This offers a lot of potential for cluster-mediated and cluster-catalyzed reactions [18], but also causes problems due to an enhanced tendency of the cluster to fragment. It has been demonstrated by the present work that facial cyclopolyene ligands are capable of playing an important role in the generation and stabilization of such systems.

Owing to the effort of several research groups in the last 15 years, facial coordination has now become firmly established in the metal complex chemistry of cyclopolyenes [3,19]. Interestingly, apart from the title complexes only one other example of facial coordination involving a *heterometallic* site has so far been reported, with a benzene derivative capping a Ru_2Pt face of a nonanuclear Ru_6Pt_3 cluster [20]. Such complexes may help to understand the sometimes enormous difference between the catalytic properties of metal alloys and supported bimetallic clusters compared to those of the pure metals [21].

4. Experimental

4.1. General procedures

All operations were carried out under an atmosphere of purified nitrogen or argon (BASF R3-11 catalyst) using Schlenk techniques. Solvents were dried by conventional methods. Alumina used as a stationary phase for column chromatography was heated to 180–200 °C under vacuum for several days, deactivated with 5% of degassed water and then stored under nitrogen. 1,4-$(SiMe_3)_2C_8H_6$ (a mixture of the double bond shifted isomers 1,4-$(SiMe_3)_2$-1,3,5,7-C_8H_6 and 1,4-$(SiMe_3)_2$-2,4,6,8-C_8H_6 was prepared according to the literature [22]. NMR spectra were obtained on Bruker AC 200 and AVANCE DRX200 instruments (200.1 MHz for ^1H, 50.3 MHz for ^{13}C). ^1H and ^{13}C chemical shifts are reported versus $SiMe_4$ and were determined by reference to internal $SiMe_4$ or residual solvent peaks. Assignment of the carbon resonances was routinely augmented by $^{13}C-^1H$ DEPT (135°) spectra. Infrared spectra were recorded in CaF_2 cells with a Bruker IFS-28 Fourier transform spectrometer (optical resolution 0.5 cm^{-1}). The XPS analysis of complex **7a** was carried out on a sample film, which was deposited from solution on a gold foil.

Table 2
Crystal data and structure refinement parameters for the complex $[Co_2Ni(CO)_6(\mu_3\text{-}C_8H_6R_2)]$ (**7a**, R = H; **7b**, R = $SiMe_3$)

	7a	**7b**
Empirical formula	$C_{14}H_8Co_2NiO_6 \cdot C_6H_6$	$C_{20}H_{24}Co_2NiO_6Si_2$
Formula weight	526.91	593.14
Temperature (K)	203	173
X-ray, wavelength (Å)	Mo–K_α, graphite monochromated, 0.71073	Mo–K_α, graphite monochromated, 0.71073
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/n$	$P2_1/n$
Unit cell dimensions		
a (Å)	10.203(5)	14.9542(3)
b (Å)	16.674(8)	8.9889(2)
c (Å)	11.902(6)	18.2789(4)
β (°)	101.19(2)	97.256(1)
V (Å^3)	1986(2)	2437.41(9)
Z	4	4
D_{calc} (Mg m^{-3})	1.763	1.616
μ(Mo–K_α) (mm^{-1})	2.62	2.24
F(000)	1056	1208
2ϑ range (°)	4–56	3–57
Index ranges	$-13 \le h \le 13$, $0 \le k \le 22$, $0 \le l \le 15$	$-19 \le h \le 19$, $0 \le k \le 11$, $0 \le l \le 24$
Unique reflections	3454	6013
Reflections observed [$I \ge 2\sigma(I)$]	2261	4607
Parameters refined	319	376
R (observed reflections only)	0.040	0.028
wR_2 (all reflections) ($w = 1/[\sigma^2(F) + (AP)^2 + BP]$)	0.094	0.066
A, B	0.036, 0	0.037, 0
P	$\max((F_o^2, 0)+2F_c^2)/3$	
Goodness-of-fit	1.035	0.943
Largest difference peak and hole (e Å^{-3})	0.28 and −0.36	0.48 and −0.37

*4.2. $[Co_2Ni(CO)_6(\mu_3\text{-}C_8H_8)]$ (**7a**)*

A mixture of 100 mg (0.2 mmol) of **5** and 0.3 ml (2.6 mmol) of 1,3,5,7-cyclooctatetraene in 10 ml of *n*-heptane is heated to reflux for 1 h. After cooling of the mixture to room temperature, the dark red precipitate is collected on a fine frit, washed with several portions of *n*-pentane and recrystallized from benzene. Yield: 20 mg (25%) of dark red microcrystalline $[Co_2Ni(CO)_6(\mu_3\text{-}C_8H_8)]$ (**7a**).

IR (ν_{CO}, in CH_2Cl_2, cm^{-1}): 2059(m), 2020(s), 2003(s), 1883(m), 1853(m), 1834(m). ^1H-NMR (C_6D_6, ppm): δ 3.42 (C_8H_8). $^{13}C\{^1H\}$-NMR (C_6D_6, ppm): δ 71.8 (C_8H_8), 185.1 (CO).

*4.3. $[Co_2Ni(CO)_6\{\mu_3\text{-}C_8H_6(SiMe_3)_2\}]$ (**7b**)*

A mixture of 1.0 g (1.8 mmol) of **5** and 0.5 g (2.0 mmol) of 1,4-$(SiMe_3)_2C_8H_6$ in 400 ml of *n*-heptane is heated to reflux. The course of the reaction is monitored by IR spectroscopy. The mixture is cooled to room temperature when the absorptions of **5** are no longer detectable (ca. 9 h). Solvent is removed under reduced pressure and the dark residue is chromatographed on alumina (4.5 × 15 cm) using *n*-hexane as the mobile phase. Solvent is removed from the deep red eluate and the resulting dark red solid is recrystallized from *n*-pentane. Yield: 420 mg (38%) of dark red microcrystalline $[Co_2Ni(CO)_6\{\mu_3\text{-}C_8H_6(SiMe_3)_2\}]$ (**7b**).

FD-MS (*m*/z, relative intensity [%]): 592.0 (100, [M^+]). IR (ν_{CO}, in *n*-hexane, cm^{-1}): 2059(m), 2023(s), 2008(s), 1882(m), 1857(m), 1843(m). ^1H-NMR ($CDCl_3$, ppm): δ 0.19 (s, 18H, $SiMe_3$), 4.30 (s, 2H, H-2, -3), 4.32 ($(AB)_2$-pattern, 4H, H-5, -8). $^{13}C\{^1H\}$-NMR ($CDCl_3$, ppm): δ −1.0 ($SiMe_3$), 74.0 (CH), 74.3 (CH), 76.0 (CH), 84.1 (*C*–$SiMe_3$), 185.3 (CO), 247 (br, μ-CO).

4.4. Crystal structure determinations

Single crystals of **7a**·C_6H_6 were grown from a benzene solution at 10 °C. These crystals were found to be twinned (two interpenetrating individuals with different orientation). Intensity data were collected using an orientation matrix based on the individual which gave the stronger reflections. Deletion of overlapping reflections resulted in a unique dataset which was used to solve and refine the structure. Crystals of **7b** were obtained from *n*-pentane at 8 °C. Crystal data are compiled in Table 2.

Intensity data were collected at low temperature on a Siemens-Stoe AED2 four circle diffractometer (**7a**) and on a Bruker AXS SMART CCD diffractometer (**7b**). A semi-empirical absorption correction was applied. The structures were solved by direct methods, and refined by full-matrix least-squares based on F^2 using all measured non-overlapping unique reflections. For complex **7a**, all metal atoms were refined as cobalt. All non-hydrogen atoms were given anisotropic displacement parameters. Hydrogen atoms were located from difference Fourier syntheses and refined with isotropic displacement parameters.The calculations were performed using the programs SHELXS-86 and SHELXL-97 [23]. Graphical representations were drawn with PLATON [24]. Anisotropic displacement ellipsoids are scaled to 40% probability. Superposition of structures was carried out with IDEAL [25].

5. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC nos. 182/1148 and 166312 for compounds **7a** and **7b**, respectively. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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