Metal Atoms in the Synthesis of Metal Clusters, VIII[◇]

On the Reaction of Sterically Demanding Cyclopentadiene Ligands with Cobalt Atoms: Synthesis, Crystal Structure, Spectroscopic Behavior, and Reactivity of Di-, Tri- and Tetranuclear Hydrido Clusters of Cobalt[☆]

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The metal-vapor reactions of Co atoms with 1,3-$t\mathrm{Bu_2CpH}$ (**1a**), 1,3-$t\mathrm{Bu_2CpH}$ (**1a**), 1,2,4-$t\mathrm{Bu_3CpH}$ (**1b**) and $\mathrm{EtMe_4CpH}$ (**1c**) are described. With **1a** the two mononuclear complexes $[(\eta^5\text{-}t\mathrm{Bu_2Cp})(\eta^4\text{-}t\mathrm{Bu_2}\text{-1,3-cyclopentadiene})\mathrm{Co}]$ (**2a**) and $[\{\eta^5\text{-}t\mathrm{Bu_2Cp}\}_2\mathrm{Co}]$ (**3a**) were isolated, together with the dinuclear cobalt cluster $[\{(\eta^5\text{-}t\mathrm{Bu_2Cp})\mathrm{Co}\}_2\mathrm{H_3}]$ (**4a**) and trace amounts of the tetranuclear cluster $[\{(\eta^5\text{-}t\mathrm{Bu_2Cp})\mathrm{CoH}\}_4]$ (**5a**). The molecular structures of **3a** and **4a** were determined by X-ray diffraction. Reaction of **1b** with Co atoms afforded a single product, the dinuclear cluster $[\{(\eta^5\text{-}t\mathrm{Bu_3Cp})\mathrm{Co}\}_2\mathrm{H_3}]$ (**4b**), whose molecular structure was determined by single-crystal X-ray diffraction. Both, **4a** and **4b** exhibit extremely short Co–Co distances [2.244(1) (**4a**) and 2.242(1) Å (**4b**)], as found for the $\mathrm{Me_5Cp}$ analog $[\{(\eta^5\text{-}\mathrm{Me_5Cp})\mathrm{Co}\}_2\mathrm{H_3}]$ (**4c**). Reaction of an isomeric mixture of $\mathrm{Me_4EtCpH}$ (**1c**) with Co atoms furnished the mononuclear sandwich $[(\eta^5\text{-}\mathrm{Me_4EtCp})(\eta^4\text{-}\mathrm{Me_4Et}\text{-1,3-cyclopentadiene})\mathrm{Co}]$ (**2b**), the trinuclear hydridocobalt cluster $[\{(\eta^5\text{-}\mathrm{Me_4EtCp})\mathrm{Co}\}_3\mathrm{H_4}]$ (**6a**) and the tetranuclear hydridocobalt cluster $[\{(\eta^5\text{-}\mathrm{Me_4EtCp})\mathrm{Co}\}_4\mathrm{H_4}]$ (**5c**). The molecular structure of **5c** was determined by X-ray crystallography and revealed a tetrahedral arrangement of the cobalt atoms. The electrochemical behavior of the dinuclear complexes **4a**–**4c** was studied by cyclic voltammetry. Reversible redox couples were found for all three compounds, with a correlation between the degree of alkyl substitution and their respective cathodic shifts. Compounds **4a** and **4b** react with CO to yield the mononuclear and dinuclear complexes $[(\eta^5\text{-}\mathrm{Cp^R})\mathrm{Co(CO)_2}]$ (R = 1,3-$t\mathrm{Bu_2}$, 1,2,4-$t\mathrm{Bu_3}$) (**7a** and **7b**) as well as $[\{(\eta^5\text{-}\mathrm{Cp^R})\mathrm{Co}\}_2(\mathrm{CO})_2]$ (**8a** and **8b**). Reaction of the trinuclear hydridocobalt cluster **6a** and its $\mathrm{Me_5Cp}$ analog **6b** with $\mathrm{AgBF_4}$ in the presence of $\mathrm{PEt_3}$ yielded the heteronuclear clusters $[(\eta^5\text{-}\mathrm{Me_4Cp^R})\mathrm{Co}\}_3\mathrm{AgP(Et)_3H_4}]^+[\mathrm{BF_4}]^-$ (R = Et, Me) (**9a** and **9b**). **9a** was structurally characterized by X-ray crystallography.

Without doubt the Cp ligand is one of the most versatile ligands in organometallic chemistry. Indeed, the vast majority of known organometallic compounds contain either this ligand or derivatives of it[2,3]. It is surprising therefore that the organometallic chemistry of Cp ligands with sterically demanding groups as ring substituents on the C_5 skeleton is still relatively unexplored. Most work has been concentrated on the well-known permethylated Cp ring with its extraordinary ability to stabilize novel organometallic structures. Nevertheless, recent years have seen the introduction of a multitude of substituted Cp ligands with various bulky substituents in the ring periphery, which act as useful ligands in organometallic synthesis. Along with other effects such as ring-rotation dynamics[4] and the introduction of chirality[5], an important reason for the use of bulky substituents is the enhanced kinetic stability imparted to the associated organometallic complexes, thus enabling the synthesis of novel organometallic structures[6]. In our previous studies involving naked metal atoms of the late transition metals Fe, Co and Ni, we observed the latter effect to be important in promoting the formation of metal-cluster compounds containing substituted Cp ligands[4,7].

The reactions of the parent cyclopentadiene (CpH) with the late transition metals Fe, Co and Ni were among the first reactions to be studied in metal-vapor chemistry[8], and were found to produce exclusively mononuclear sandwich complexes in which the EAN or 18-VE rule is obeyed. In contrast, we recently reported on the reaction of cobalt and nickel atoms with various alkyl-substituted cyclopentadienes, which led to the formation of a variety of mono- and multinuclear compounds when equivalent amounts of diene and metal atoms were used. As part of our ongoing studies of the synthesis of ligand-stabilized metal clusters using metal atoms, we report in this paper on the reaction of cobalt atoms with the ligands 1,3-$t\mathrm{Bu_2CpH}$ (**1a**), 1,2,4-$t\mathrm{Bu_3CpH}$ (**1b**) and $\mathrm{Me_4EtCpH}$ (**1c**) as well as on the spectroscopic and structural characterization of a series of hydrido clusters formed in these reactions. In addition, we also investigate the reactivity of these clusters.

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[++] X-ray structure analyses.

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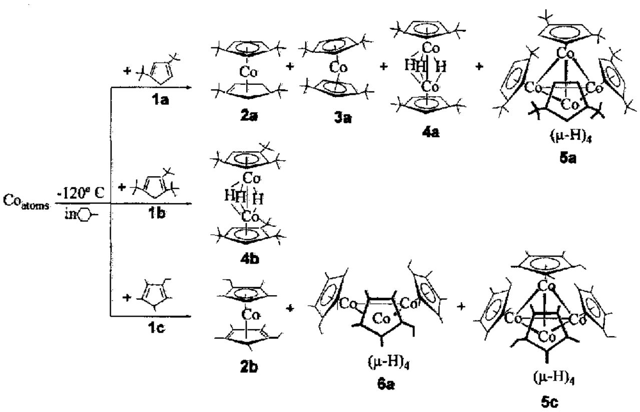
Results and Discussion

Reaction of Co Atoms with $t\mathrm{Bu_2CpH}$ (1a), $t\mathrm{Bu_3CpH}$ (1b) and $\mathrm{Me_4EtCpH}$ (1c)

Co Atoms and **1a**: When cobalt atoms are vaporized into a solution of **1a** in methylcyclohexane at temperatures between −100 and −120 °C, a complex mixture of compounds is obtained, from which **2a**, **3a**, **4a** and **5a** were isolated (Scheme 1).

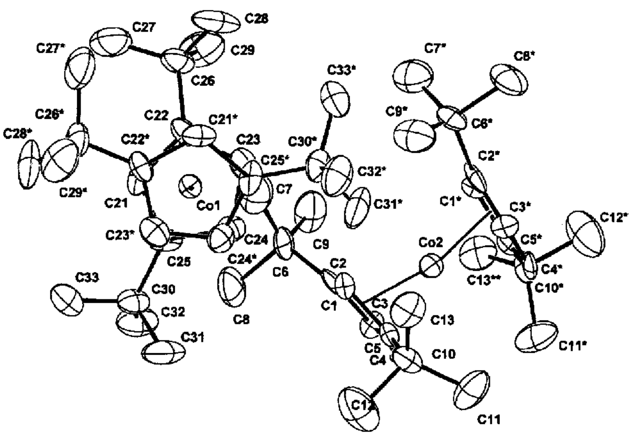
Scheme 1



Except for **3a** and **5a**, the individual compounds can be separated by column chromatography (eluent ether: **3a**, **4a** and **5a**; eluent pentane/ether: **2a**) and recrystallization (0–10 °C from ether: **3a**, **4a** and **5a**; −30 °C from pentane/ethanol (1:1): **2a**). Compound **2a** is obtained as a deep red semicrystalline solid and is the main product of the metal-vapor reaction. In spite of numerous attempts at purification (viz. chromatography followed by recrystallization and vacuum sublimation), it was not possible to obtain well-resolved NMR spectra. This precludes a detailed NMR characterization of **2a**. Despite extremely careful sample preparation (vacuum transfer of predried, oxygen-free solvent and sample sealing before measurement) all signals were broadened to a significant extent. Nevertheless, all signals appeared in the diamagnetic shift region, indicating that no paramagnetic impurities were present in the sample. However, the reason for this has not been clarified yet. Since **2a** belongs to a family of well-known η^4–η^5 sandwich complexes of Co[9], it could be satisfactorily characterized by IR spectroscopy, mass spectrometry and elemental analysis (see Experimental Section). Compounds **3a** and **5a** were isolated in this reaction as brown black crystals in minor quantities after chromatography, followed by recrystallization. The two compounds tend to crystallize and hence are difficult to separate, but single crystals of **3a** suitable for X-ray analysis could be separated manually. Its crystal structure was determined by X-ray crystallography and its molecular structure is given in Figure 1, together with selected bond lengths and angles.

Compound **3a** crystallizes with two almost identical, independent molecules in the asymmetric unit (r.m.s. deviation 0.1 Å). In each molecule the cyclopentadienyl ligands are not parallel as in typical sandwich complexes, but lie at an angle of 9(1)° to one another, in a slightly tilted position.

Figure 1. Molecular structure of $[(\eta^5\text{-}t\mathrm{Bu_2Cp})_2\mathrm{Co}]$ (**3a**) in the crystal, showing the two independent molecules in the asymmetric unit[a]



[a] Selected bond lengths [Å] and angles [°] (D1 is the centroid of the atoms C21–C25, D2 the centroid of C1–C5): Co1–C21 2.14(1), Co1–C22 2.17(1), Co1–C23 2.11(1), Co1–C24 2.11(1), Co1–C25 2.14(1), Co2–C1 2.14(1), Co2–C2 2.16(1), Co2–C3 2.088(9), Co2–C4 2.13(1), Co2–C5 2.11(1); D1–Co1–C1* 174(1), D2–Co2–D2 174(1).

This distortion is presumably a result of intramolecular steric repulsion between the substituents on adjacent rings. The Co–(ring center) distance is 1.75(3) Å (average) and is longer than in the simple sandwich complexes (1.726 Å), probably for the same reason.

To the best of our knowledge, **3a** represents the first case in which a metallocene is formed in a reaction of Co or Ni atoms with a cyclopentadiene derivative. In contrast, mixed Cp/cyclopentadiene complexes are the usual products in this well-investigated type of reaction[8].

Trace amounts of black crystals of the tetranuclear hydride cluster **5a** were manually separated from **3a**, but the crystals were far too small for single-crystal structure analysis.

Compound **5a** was characterized by its ^{1}H-NMR spectrum, which shows a characteristic single μ-H resonance at $\delta = -25.9$ located in the same shift region as observed for the clusters $[\{(\eta^5\text{-Cp})\mathrm{Co}\}_4\mathrm{H_4}]$ (**5b**)[10,11] ($\delta = -23.16$) and $[\{(\eta^5\text{-EtMe_4Cp})\mathrm{Co}\}_4\mathrm{H_4}]$ (**5c**) ($\delta = -27.7$) (see Table 1; this work). The highest peaks in the mass spectrum (EI, 70 eV) of **5a** can be assigned to $[(\eta^5\text{-}t\mathrm{Bu_2Cp})\mathrm{Co_3H}_x]^+$ ($x = 2-4$) fragments of *m/z* 710–712, indicating initial loss of hydrogen and a $\{\eta^5\text{-}t\mathrm{Bu_2CpCo}\}$ unit from the parent molecule $[\{(\eta^5\text{-}t\mathrm{Bu_2Cp})\mathrm{Co}\}_4\mathrm{H_4}]$ (see Experimental Section).

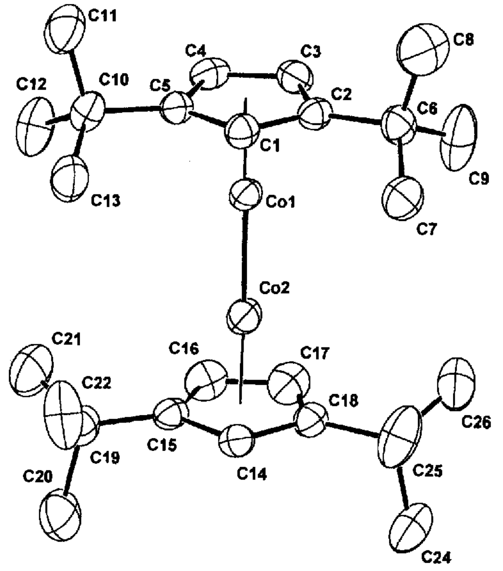
In the high-resolution mass spectrum (EI, 70 eV) of **4a**, a molecular peak is found at *m/z* 475 (round: *m/z* 475.20169; calcd.: *m/z* 475.2185), which establishes its molecular formula to be $[\{(\eta^5\text{-}t\mathrm{Bu_2Cp})\mathrm{Co}\}_2\mathrm{H_3}]$.

The dinuclear complex $[\{(\eta^5\text{-}t\mathrm{Bu_2Cp})\mathrm{Co}\}_2\mathrm{H_3}]$ (**4a**) was obtained as black crystals suitable for an X-ray analysis by slowly cooling a concentrated ether solution of the compound. The molecular structure of the heavy-atom skeleton of **4a** is shown in Figure 2. Unfortunately, the positions of the H atoms could not be determined unambiguously in the X-ray experiment, but three H atoms are thought to bridge

Table 1. ^{1}H-NMR data of **5a−5c** at 20 °C

Cluster	Solvent	δ [ppm] at 27 °C
5c $[\{(\eta^5\text{-}t\text{Bu}_2\text{Cp})\text{CoH}\}_4]$	[D$_6$]benzene	4.93 (d, 8 H), 4.72 (t, 4 H), 1.38 (72 H), -25.9 (4 H)
5b $[\{(\eta^5\text{-Cp})\text{CoH}\}_4]$	[D$_6$]benzene	4.96 (Cp), -23.16 (4 H)
5a $[\{(\eta^5\text{-EtMe}_4\text{Cp})\text{CoH}\}_4]$	[D$_8$]toluene	3.71 (q, 8 H, CH$_2$), 2.0 (24 H, CH$_3$), 1.95 (24 H, CH$_3$), 0.92 (t, 12 H, CH$_3$), -27.7 (4 H)

Figure 2. Molecular structure of $[\{(\eta^5\text{-}t\text{Bu}_2\text{Cp})\text{Co}\}_2\text{H}_3]$ (**4a**)[a]

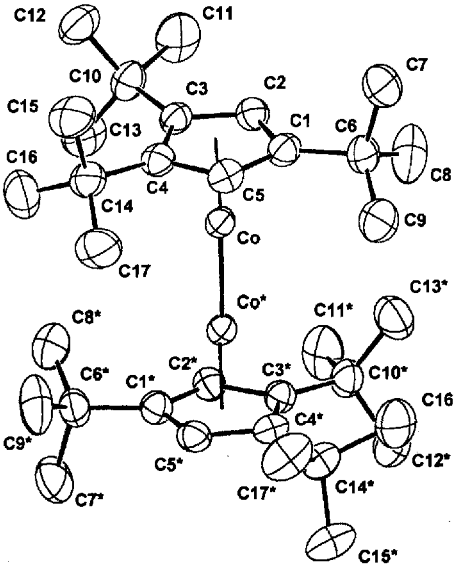


[a] Selected bond lengths [Å] and angles [°] (D1 is the centroid of the atoms C1−C5, D2 the centroid of C14−C18): Co1−Co2 2.244(1), Co1−C1 2.068(5), Co1−C2 2.074(5), Co1−C3 2.073(5), Co1−C4 2.078(5), Co1−C5 2.078(5), Co2−C14 2.084(5), Co2−C15 2.075(5), Co2−C16 2.071(6),Co2−C17 2.067(6), Co2−C18 2.077(5); D1−Co1−Co2 178.8(1), Co1−Co2−D2 179.7(1).

the two Co atoms as revealed by comparion with $[\{(\eta^5\text{-Me}_5\text{Cp})\text{Co}\}_2\text{H}_3]$ (**4c**)[7,12]. The two Co atoms and the midpoints of the two Cp ligands in **4a** are linear within experimental error. The Co1−Co2 distance is 2.244(1) Å, indicating a strong bonding interaction between both Co centers, and is similar to that observed for **4c** [2.253(1) Å][7,11]. The distances from each Co atom to the midpoint of the adjacent Cp ring [average 1.689(6) Å] are also the same as in **4c** [1.689(1) Å].

Co Atoms and **1b**: In order to study the effect of increasing still further the steric bulk of the Cp^R ligand on its interaction with cobalt vapor, we studied the reaction of the sterically highly demanding diene 1,2,4-tBu$_3$CpH (**1b**) with cobalt atoms in methylcyclohexane solution at low temperature (Scheme 1). The crude reaction product obtained from this metal-vapor reaction is a black, highly viscous oil, chromatography of which yields the dimeric Co cluster **4b** as a deep purple oil and a brown oil of as yet unknown composition. Crystals of **4b** were grown from the purple oil by dissolving it in acetonitrile/ether (10:1) and slow cooling to 0 °C over several weeks. Compound **4b** is air-sensitive in solution but moderately air-stable in its crystalline form. The mass spectrum (EI, 70 eV) exhibits the molecular peak at m/z 587 corresponding to the base peak with a molecular formula $[\{(\eta^5\text{-}t\text{Bu}_3\text{Cp})\text{Co}\}_2\text{H}_3]$ for **4b**. Recently, we found that **4b** is also accessible in high yields by a wet chemical synthesis in solution[13].

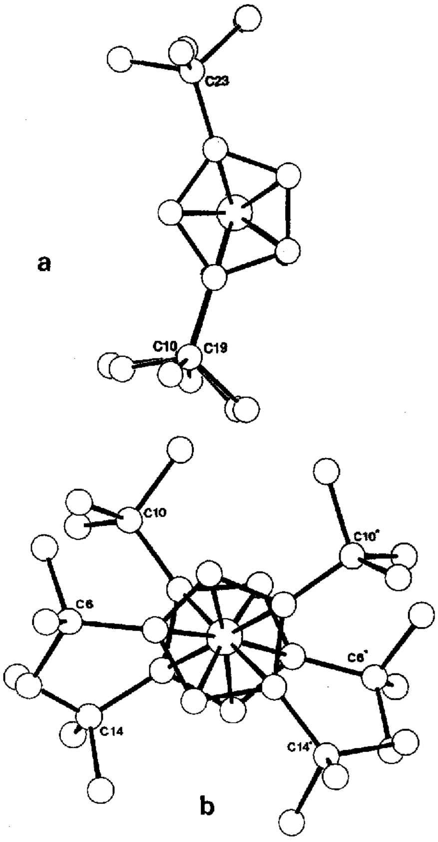
Figure 3. Molecular structure of $[\{(\eta^5\text{-}t\text{bu}_3\text{Cp})\text{Co}\}_2\text{H}_3]$ (**4b**)[a]



[a] Selected bond lengths [Å] and angles [°] (D1 is the centroid of the atoms C1−C5): Co−Co* 2.242(1), Co−C1 2.079(4), Co−C2 2.075(4), Co−C3 2.096(3), Co−C4 2.073(3), Co−C5 2.069(4); D1−Co−Co* 177.8(1).

The molecular structure of **4b**, as determined by X-ray crystallography, is shown in Figure 3. As for **4a**, no hydridic ligands could be located in the X-ray experiment, and the existence of three additional H atoms is inferred on the basis of the molecular mass and the elemental analysis and by comparison of the molecular structure with those of **4a** and **4c**. As for **4a** and **4c**, **4b** displays an exact linear arrangement of the Co atoms and the midpoints of the two Cp rings. The Co atoms are again linked by an extremely short Co−Co bond of 2.242(1) Å, which is nearly identical in length with that determined for **4a**. The distance of the Cp^R ring centroids to the Co atoms in the series of clusters **4a−4c** is 1.689(1) Å for **4c**[7], 1.68(1) Å for **4b**, and 1.689(6) Å for **4a**. It is noteworthy that **4a−4c** have some of the shortest Co−Co bonds observed for dinuclear Co complexes (**4a**, **4b**: see text; **4c**: 2.25(1) Å)[7]. Only $[\{(\eta^5\text{-Cp})\text{Co}\}_2\{\mu\text{-bis(trimethylsilyl)acetylene}\}]$ has a shorter Co−Co distance (2.18 Å)[14]. In contrast to **4a** and **4c**, where the alkyl groups on adjacent Cp rings are eclipsed [torsion angles: 0° (**4a**); 4° (**4c**)], all nine substituents in **4b** are staggered (Figure 4 shows projections of **4a** and **4b** along the Co−Co axis for comparison). This suggests that intramolecular interactions between tBu groups on adjacent Cp rings are small and the Cp rings are freely rotatable, as in other sandwich complexes.

Figure 4. View of the dinuclear clusters **4a** and **4b** along the Co−Co vector in the solid state, showing the eclipsed conformation of the *t*Bu groups for **4a** (a), and the staggered conformation of the *t*Bu groups for **4b** (b)



NMR, UV/Vis and Electrochemical Investigations of 4a−4c

The NMR signals of the ring protons of the Cp rings are subjected to substantial line broadening in the paramagnetic complexes **4a**−**4c** at low temperatures, and they are not observed at all at room temperature. No reliable assignment could be made, even at lower temperatures (Table 2). The same is true for the signals of the hydridic protons, which are presumably directly bonded to the two metal atoms. All three cluster compounds show a variable-temperature T^{-1} dependence (Curie behavior) of the ^{1}H-NMR paramagnetic shifts for both the CH_3 and the *t*Bu groups. Compounds **4a**−**4c** represent a series of mixed valence compounds formally containing two cobalt centers in different oxidation states [Co^{II}-d^7/Co^{III}-d^6]. According to the EAN or 18-VE rule, one metal center is formally an electron deficient Co^{III} with 15 VE, and the other a Co^{II} with an even 16-VE count. The geometries of the molecules are such that the Co atoms appear equivalent, so the unpaired spin density is likely to be delocalized over both metal atoms. There are principally two different ways how this may occur:

- Electron exchange through the hydride H atoms, which in all three compounds are presumed to be bridging the Co atoms, as has been verified for **4c** by X-ray analyxsis[11], IR spectroscopy[12] and most convincingly by neutron diffraction analysis[7].

- Direct exchange via M−M orbital interactions, resulting in delocalization of the unpaired electron over both Co metal centers in the clusters.

MO calculations of a series of hypothetical [{(η^5-Cp)Co}$_2$H$_x$] complexes have been performed[15], but no similar studies of **4a**−**4c** are known. Thus, no quantitative conclusions as to the frontier orbitals involved or the possible exchange pathways for delocalization of the unpaired electron in these cluster systems are yet available.

UV/Vis: The electronic absorption spectra of the clusters **4a**−**4c** are very similar. They are shown in Figure 5 and the absorption maxima are listed in Table 3. The absorption maxima around 540−560 nm are responsible for the purple-to-red color of the clusters **4a**−**4c** in solution. All spectra show characteristic shoulders in the visible region.

Table 2. ^{1}H-NMR paramagnetic shifts of the substituted cobaltocenes [(η^5-tBu$_2$Cp)$_2$Co] (**3a**) and [(η^5-Me$_4$EtCp)$_2$Co] (**3b**) and of the mixed valence compounds [{(η^5-Cp^R)Co}$_2$H$_3$] [R = *t*Bu$_2$ (**4a**), and R = *t*Bu$_3$ (**4b**), Me (**4c**)[7,12]] at 20 °C

Compound	δ_{para}	$\Delta\delta_{para}$	Solvent
[(η^5-Me$_4$EtCp)$_2$Co] (**3b**)	18.9 (s, CH_2CH_3) 46.4 (s, 6 H,CH_3) 46.1 (s, 6 H, CH_3) 5.7 (s, H_2CCH_3)		[D$_8$]toluene
[(η^5-tBu$_2$Cp)$_2$Co] (**3a**)	9.2 (s, *t*Bu, 36 H)		
[{(η^5-tBu$_2$Cp)Co}$_2$H$_3$] (**4a**)	4.1 (s, *t*Bu, 36 H)[c]	+5.1[a]	[D$_8$]toluene
[{(η^5-EtMe$_5$Cp)Co}$_2$H$_3$] (**4c**)	29.3 (s, CH_3)	+16.8[b] +7.1[b]	[D$_6$]benzene
[{(η^5-tBu$_3$Cp)Co}$_2$H$_3$] (**4b**)	3.5 (s, *t*Bu, 54 H)[c]	+5.7[a]	[D$_6$]benzene

[a] $\Delta\delta_{para}$: difference in the paramagnetic shifts compared with the cobaltocene **3a**. − [b] $\Delta\delta_{para}$: difference in the paramagnetic shifts compared with the cobaltocene **3b**[19]. − [c] Only the resonances for the *t*Bu hydrogen atoms are detectable at room temperature.

Electrochemical Investigations: The electrochemical behavior of the clusters **4a**−**4c** was studied by cyclic voltammetry, and the results are summarized in Figure 6 and Table 4. The dinuclear complexes show two reversible one-electron transfer steps. The generated ions are the species resulting from either the loss or gain of one unpaired electron. It is not known whether these ions are also paramagnetic. Attempts to follow the reduction by NMR spectroscopy have been unsuccessful so far. Thus, a deep purple solution of **4b** in [D$_8$]THF reacts immediately at 20 °C with a metallic potassium mirror to give a deep red solution, which exhibits still broad NMR resonances for the *t*Bu groups between $\delta = 5$ and 10 with an observed $\Delta_{\text{line width}} \geqslant 50$ Hz, even after several hours of contact with the potassium mirror. The red color of the solution persists for about 24 h, after which time decomposition occurs with formation of a black residue, presumably Co metal, and a clear colorless THF solution, from which white crystals of [tBu$_3$Cp]$^-$[K]$^+$ precipitate on standing, indicating complete degradation of the Co compound **4b**.

The cathodic shifts for both reversible redox couples of **4a** and **4c** can be understood in terms of the degree of alkyl substitution on the Cp rings. The redox steps **4a**$^{0/+}$ and

Figure 5. Electronic absorption spectra of **4a**–**4c** (in pentane at 293 K)

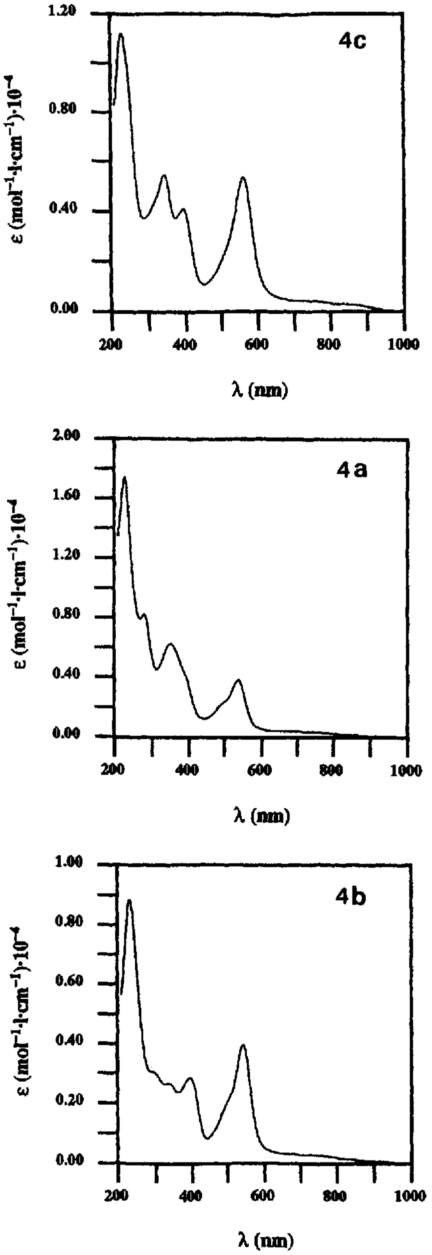
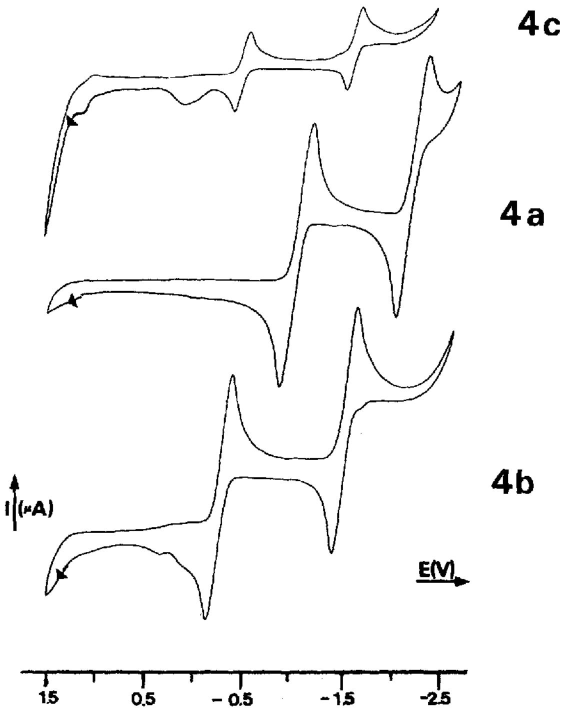


Table 3. UV/Vis data of the hydride clusters **4a**–**4c**

Compound	Absoprtion maxima in nm (molar extinction in $cm^{-1}m^{-1}$) [log ε]		
4a	227	(17408)	[4.24]
	280	(8215)	[3.92]
	350	(6244)	[3.79]
	537	(3802)	[3.58]
	716	(140)	[2.20]
4b	232	(8870)	[3.95]
	290	(3058)	[3.49]
	336	(2764)	[3.43]
	394	(2859)	[3.46]
	542	(3951)	[3.59]
	720	(705)	[2.85]
4c	229	(11234)	[4.05]
	343	(5442)	[3.73]
	392	(4008)	[3.61]
	560	(5340)	[3.72]
	740	(670)	[2.86]
	840	(500)	[2.70]

Figure 6. Cyclic voltammograms of the hydride clusters **4a**–**4c** measured in DME at −40 °C vs. SCE; scan rate 100 mV; supporting electrolyte $[nBu_4N]^+[ClO_4]^-$, 0.1 M in DME



4a$^{0/-}$ vs. **4c**$^{0/+}$ and **4c**$^{0/-}$ are separated by −0.50 V (± 0.02 V), indicating a *cathodic shift* of the corresponding redox couples **4a**$^{0/+}$ vs. **4c**$^{0/+}$ and **4a**$^{0/-}$ vs. **4c**$^{0/-}$ of −0.25 V (± 0.02 V) per additional methyl group in **4a** as compared with **4c** (see Table 4). This effect of increasing cathodic shifts on going from less to more highly alkyl-substituted compounds during oxidation or reduction within a given series seems to be a general one and is known in the literature for organic as well as organometallic compounds[1,16]. Interestingly, the potentials for the observed redox couples **4b**$^{0/+}$ and **4b**$^{0/-}$ for the tBu$_3$-substituted analog **4b** do not follow this scheme when compared with **4c**. They are shifted by +0.31 V (**4b**$^{0/+}$ vs. **4c**$^{0/+}$), +0.82 V (**4b**$^{0/+}$ vs. **4a**$^{0/+}$) and +0.65 V (**4b**$^{0/-}$ vs. **4a**$^{0/-}$) and +0.17 V (**4b**$^{0/-}$ vs. **4c**$^{0/-}$) compared to anodic potential (see Table 4), although the number of CH_3 groups increases from n = 10 for **4c** to n = 12 for **4a** and to n = 18 CH_3 groups in the case of **4b**. Clearly, the increased number of methyl groups in **4a**, **4c** and **4b** has a marked influence on the redox potentials of these dinuclear complexes.

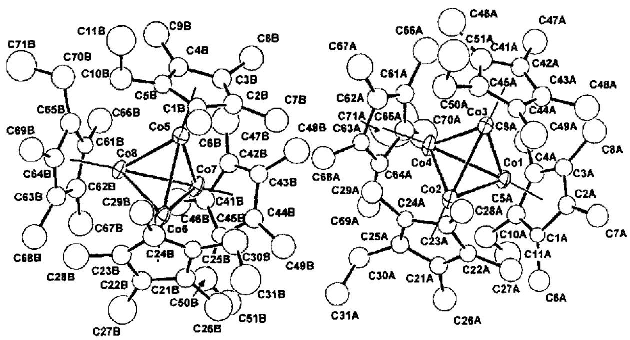
Co Atoms and **1c**: Interestingly, and in contrast to the reaction of **1a** and **1b** with Co atoms[7], we did not observe any formation of the dinuclear complex $[\{(\eta^5\text{-}Me_4EtCp)Co\}_2H_3]$ in the reaction of **1c** with Co atoms (Scheme 1).

Table 4. Cyclovoltammetric data of the hydride clusters **4a**−**4c**

Compound	Temperature	$E_{1/2}$ [V]	$I_{p/a}/I_{p/k}$
4a	-40 °C	-1.03	0.96
		-2.15	0.99
4b	-40 °C	-0.21	1.01
		-1.50	1.07
4c	-40 °C	-0.52	1.18
		-1.67	0.93

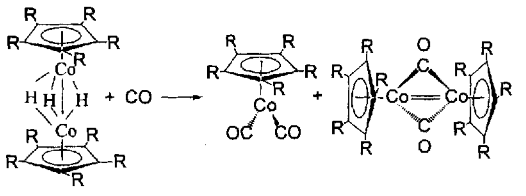
The tetranuclear cluster **5c** was separated from the mononuclear complex **2b**, which is formed as a mixture of *cis*/*trans* isomers, and the trinuclear complex **6a** by chromatography and was further purified by crystallization. Its molecular structure was determined crystallographically (**2b** and **6a** were fully identified by their analytical data, see Experimental Section). Compound **5c** crystallizes with two independent molecules in the asymmetric unit. Their bonding parameters are not significantly different (Figure 7). Here again the positions of the H atoms could not be determined in the X-ray experiment. However, the presence of four additional hydrogen ligands was independently established by mass spectrometry and ^{1}H-NMR spectroscopy (see Experimental Section and Table 1).

Figure 7. Molecular structure of [{(η^5-Me$_4$EtCp)CoH}$_4$] (**5c**), showing the two independent molecules in the unit cell[a]



[a] Selected bond lengths [Å]: Co1−Co2 2.549(3), Co1−Co3 2.523(3), Co1−Co4 2.572(3), Co2−Co3 2.537(3), Co2−Co4 2.516(3), Co3−Co4 2.552(3), Co(5)−Co(6) 2.558(3), Co(5)−Co(7) 2.528(3), Co(5)−Co(8) 2.557(3), Co(6)−Co(7) 2.567(3), Co(6)−Co(8) 2.522(3), Co(7)−Co(8) 2.539(3).

Reaction of **4a**−**4c** *with CO Gas:* All three clusters react with CO at 1 atm at room temperature as shown in eq. 1. In all reactions, we noticed an induction period of up to 10 minutes before a visual color change of the initially black solutions could be detected.



4a $R_{1,3} = C(CH_3)_3$
4b $R_{1,2,4} = C(CH_3)_3$
4c $R_{1\text{-}5} = CH_3$

7a $R_{1,3} = C(CH_3)_3$
7b $R_{1,2,4} = C(CH_3)_3$
7c $R_{1\text{-}5} = CH_3$

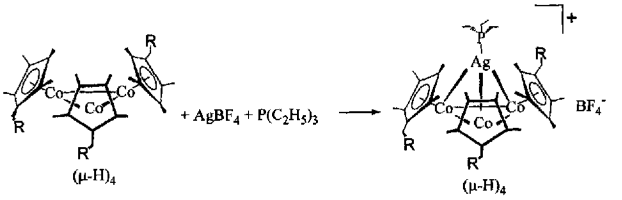
8a $R_{1,3} = C(CH_3)_3$
8b $R_{1,2,4} = C(CH_3)_3$

Compound **4c** gives the known deep red mononuclear Co^I half-sandwich complex **7c**[17] in yields higher than 60%[12]. However, under similar reaction conditions, the clusters **4a** and **4b** form greenish solutions, from which two types of reaction products could be isolated after chromatograpic separation. These are the mononuclear complexes **7a** and **7b** as well as the dinuclear complexes **8a** and **8b**[18], which were identified as by-products by IR and MS analysis. All the carbonyl complexes, **7a** and **7b** as well as **8a** and **8b**, are initially highly viscous oils, presumably due to the high degree of alkyl substitution on the Cp rings. The dinuclear clusters **8a** and **8b** do, however, solidify to wax-like solids upon prolonged standing at room temperature.

The reactivity of the sterically hindered hydride cluster **4b** towards CO and the formation of the dinuclear carbonyl complex **8b** in this reaction are remarkable considering that the core of the molecule is already surrounded by six *t*Bu groups and therefore by far less sterically accesible. In this context, it should be noted that in the reaction of **4c** with CO, we and others[12] did not observe formation of a dinuclear compound. Instead, only the mononuclear complex **7c** was formed, even though the open structure of **4c** would lead one to expect formation of the dinuclear complex **7c** to be favored.

Reaction of **6a** *and* **6b** *with AgBF$_4$/PEt$_3$:* Since the trinuclear tetrahydrido cluster **6a** was expected to be reactive due to its paramagnetic nature and its 46-electron configuration, we and others have recently examined its reactivity in some detail[12,20]. In our earlier studies we had observed that **6a** undergoes exclusively cluster degradation reactions with a variety of organic and inorganic ligands to give various half-sandwich complexes of Co. In this paper we report on the addition of a [AgPEt$_3$]$^+$ cluster fragment to the Co$_3$ metal core of **6a** and its Me$_5$Cp derivative **6b**[7] to give the clusters **9** (eq. 2).

Formel 3



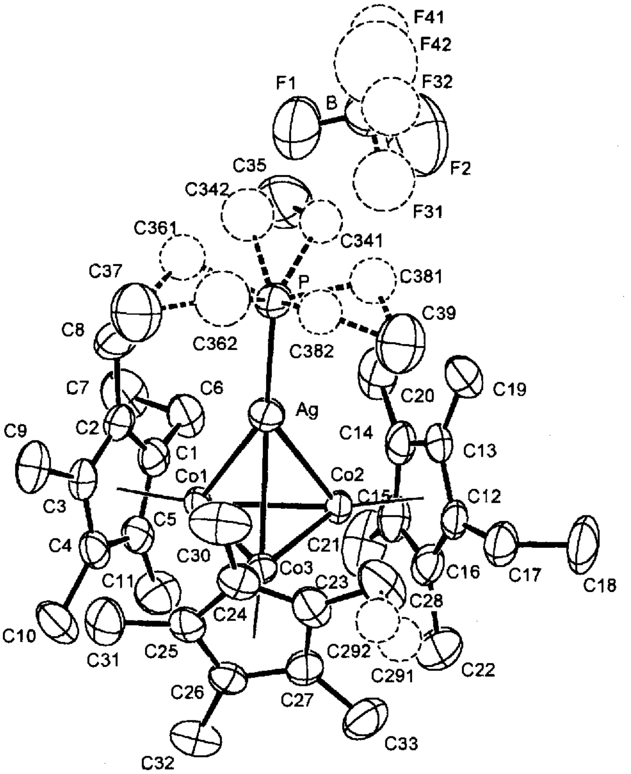
R = H **6b**
R = CH$_3$ **6a**

R = H **9b**
R = CH$_3$ **9a**

Thus, addition of triethylphosphane followed by AgBF$_4$ to a THF solution of **6a** or **6b** results in the formation of the heteronuclear tetrahydrido clusters **9**, which can be isolated as black crystals. To our surprise reports of structurally characterized Co/Ag organometallic clusters are still rare[22,23]. The molecular structure of the EtMe$_4$ derivative **9a** was determined by a single-crytal structure analysis (Figure 8). The Co$_3$ cluster core of **9a** is capped by an [AgPEt$_3$]$^+$ unit, resulting in a distorted tetrahedral arrangement of the four metal atoms.

Whereas the Co−Co bond lengths [mean 2.518(3) Å] are equal within the experimental error, the Ag−Co bond

Figure 8. Molecular structure of $[\{(\eta^5\text{-}Me_4EtCp)Co\}_3Ag(PEt_3)H_4]^+[BF_4]^-$ (**9a**); the atoms C29, C34, C36, C38, F3, and F4 are disordered (1/2)[a]



[a] Selected bond lengths [Å] and angles [°] (D1 is the centroid of the atoms C1−C5, D2 the centroid of C12−C16, D3 the centroid of C23−C27, and D4 the centroid of Co1−Co3): Ag−Co1 2.722(1), Ag−Co2 2.747(1), Ag−Co3 2.745(1), Co1−Co2 2.520(1), Co2−Co3 2.520(1), Co1−Co3 2.515(1), Ag−P 2.379(1), Co1−D1 1.725(5), Co2−D2 1.728(7), Co3−D3 1.726(4); P−Ag−D4 176.7(3), D4−Co1−D1 170.9(5), D4−Co2−D2 170.6(4), D4−Co3−C3 170.1(6).

lengths show some variation [2.722(1)−2.747(1) Å]. Nevertheless, the midpoint of the three Co atoms (D4), the Ag atom and the P atom are almost colinear [P−Ag−D4 176.7(3)°]. The Co−Ag bond lengths lie at the longer end of the observed range of Co−Ag distances {2.59 Å $[\{AgCo(CO)_4\}_3]$[22]; 2.66(1) Å $[As(CH_3)\{C_6H_4As(CH_3)_2\}_2Co(CO)_4\}$[22]; 2.600(2)−2.724(2) Å $[\{AgCo[CN(2,6\text{-}C_6H_3\{CH_3\}_2)]_4\}_3]$[23]} but this cannot be attributed to interligand repulsions since the ethyl groups attached to P are directed towards the other ligands.

The mass spectra of **9a** and **9b** (see Experimental Section) confirm that these compounds are tetrahydrido clusters since the hydrogen ligands are still present in the cluster cations **9a**$^+$ and **9b**$^+$. For both compounds, molecular fragments of the tetrahydrido cluster **6**$^+$ corresponding to a loss of the $[AgP(Et)_3]^+$ unit from **9**$^+$ were observed in the FAB MS (see Experimental Section).

Conclusion

As is well-known, unsubstituted CpH reacts with Co atoms to give mostly mononuclear products. However, we found that the bulkier tBu$_2$CpH and tBu$_3$CpH ligands react with Co atoms to give moderate yields of dinuclear as well as cluster complexes. As a result, a series of isostructural $[\{(\eta^5\text{-}Cp^R)Co\}_2H_3]$ complexes **4a**−**4c** are accesible by metal-atom synthesis for the first time. Our studies of these novel trishydrido complexes revealed that the degree of substitution on the Cp ring exerts a noticeable effect on the electrochemical properties of these complexes. In contrast to **4c**, **4a** and **4b** react with CO gas to form the mono- and dinuclear complexes **7a**, **7b**, **8a** and **8b**. Unusual mixed Co$_3$Ag hydrido clusters **9a** and **9b** can be obtained by capping reactions of **6a** and **6b** with triethylphosphane and AgBF$_4$.

We thank Prof. Dr. *G. Wilke* and Prof. Dr. *M. T. Reetz* for support of this work. J. J. S. acknowledges support of the *Deutsche Forschungs-Gemeinschaft* through a Heisenberg Fellowship and the *Fonds der Chemischen Industrie* for additional financial support.

Experimental Section

General: Unless stated otherwise, all experiments were carried out in Schlenk-type glassware under argon with solvents that were thoroughly dried and deoxygenated. − The ligands 1,3-tBu$_2$CpH (**1a**), 1,2,4-tBu$_3$CpH (**1b**) and Me$_4$EtCpH (**1c**) were prepared according to published procedures[23,24]. − Al$_2$O$_3$ was deactivated by adding 5% H$_2$O and homogenizing the mixture for several hours. − NMR: Bruker AM-200 and WH-400 (^{1}H), sealed tubes, the signal of the solvent as internal reference, paramagnetic chemical shifts are reported on the δ scale. − IR: Nicolet 7199 FT-IR, KBr pellets or CH$_2$Cl$_2$ solutions. − UV/Vis: Carry 2300 spectrophotometer, room temperature. − MS: Varian MAT-5, fractional sublimation technique. − Cyclic voltammograms were recorded at −40°C under argon in 1,2-dimethoxyethane with a stationary platinum working electrode with a PAR electrochemical system and referenced vs. SCE, tetrabutylammonium perchlorate (0.1 M in DME) was the supporting electrolyte. − Metal-vapor reactions were conducted in 6-l glass vessels connected to a rotating metal-vapor reactor system based on that published by Timms[20], metal vaporization was performed from alumina-coated tungsten crucibles (GTE Sylvania, USA, or Balzers Hochvakuum, Lichtenstein) which were heated resistively. − Cobalt metal (Aldrich) was 99.6% pure. − Microanalyses were performed by Dornis & Kolbe microanalytical laboratory Mülheim/Ruhr, Höhenweg, Germany.

Preparation of $[(\eta^5\text{-}1,3\text{-}tBu_2Cp)(\eta^4\text{-}1,3\text{-}tBu_2\text{-}cyclopenta\text{-}1,3\text{-}diene)Co]$ (**2a**), $[\{(\eta^5\text{-}1,3\text{-}tBu_2Cp)_2Co]$ (**3a**), $[\{(\eta^5\text{-}1,3\text{-}tBu_2Cp)Co\}_2H_3]$ (**4a**), *and* $[\{(\eta^5\text{-}1,3\text{-}tBu_2Cp)CoH\}_4]$ (**5a**): During 2 h 3.5 g (59 mmol) of cobalt metal was vaporized in a rotating metal-vapor reactor (80 r min^{-1}) at −120°C into 150 ml of methylcyclohexane, containing 6 g (34 mmol) of 1,3-tBu$_2$CpH (**1a**). Towards the end of the vaporization a brown-black solution had formed. Isolation, filtration and prolonged pumping under vacuum afforded a highly viscous black residue which was dissolved in a minimum amount of THF, adsorbed on Al$_2$O$_3$ (5% H$_2$O) and dried. Chromatography yielded three different eluates.

1st Zone (ether/ethanol): Red crystals, 920 mg (37%) of **2a**. − MS (EI, 70 eV); m/z (%): 415 (12) [M$^+$ + 1], 413 (38) [M$^+$], 357 (100), 301 (82). − IR (KBr): ṽ = 780 cm^{-1} (s), 820 (s), 910 (s), 1020 (s), 1040 (s), 1060 (s), 1195 (s), 1295 (vs), 1360 (vs), 1390 (s), 1460 (s), 1480 (s), 2960 (vs), 3180 (w), 3190 (w). − C$_{26}$H$_{43}$Co (414.56): calcd. C 75.33, H 10.45, Co 14.21; found C 75.26, H 10.70, Co 14.09.

2nd Zone (pentane): Brown crystals, 100 mg (1%) of a mixture of **3a** and **5a**, which were further separated manually. − **3a**: MS

(EI, 70 eV); m/z (%): 413 (100) [M^+]. – $C_{26}H_{42}Co$ (413.56): calcd. C 75.51, H 10.30, Co 14.25; found C 74.42, H 10.13, Co 15.53. – ^1H NMR: Table 2. – **5a**: ^1H NMR ([D_6]benzene): δ = 4.93 (d, 8H), 4.71 (d, 4H), 1.39 (s, 72H), −25.9 (s, 4H). – MS (EI, 70 eV); m/z (%): 712 (16), 710 (15) {[(η^5-1,3-*t*BuCp)Co]$_3H_x$]$^+$ (x = 2–4)}, 413 (100), 57 (19).

3rd Zone (ether): Black crystals, 480 mg (2%) of **4a**. – MS (EI, 70 eV, HR MS); m/z (%): calcd. 475.2185, found 475.20619 (23) [M^+], 455 (14), 441 (8), 413 (100), 399 (29), 57 (21). – $C_{26}H_{45}Co_2$ (475.52): calcd. C 65.67, H 9.54, Co 24.79; found C 65.74, H 9.38, Co 24.92.

Preparation of [(η^5-EtMe$_4$Cp)(η^4-Me$_4$Et-cyclopenta-1,3-diene)Co] (**2b**), *[{(η^5-Me$_4$EtCp)CoH}$_4$]* (**5c**), *and [{(η^5-Me$_4$EtCp)Co}$_3$H$_4$]* (**6a**): 4 g (67.8 mmol) of cobalt metal was vaporized into a solution of 6 g (25.6 mmol) of EtMe$_4$CpH (**1c**) in 150 ml of methylcyclohexane in a rotating metal-vapor reactor (80 r min^{-1}) at −120°C. The resulting brown-black solution was isolated, filtered and pumped under vacuum until all volatile components had been removed. The remaining black residue was dissolved in THF, adsorbed on Al_2O_3 and dried. Chromatography (eluent: pentane) yielded [(η^5-EtMe$_4$Cp)(η^4-1,2,3,4-Me$_4$-5-Et-cyclopenta-1,3-diene)Co] (**2b**) as a red oil (2.4 g, 10%, isomeric mixture) which was purified further by threefold sublimation at 60°C/10^{-3} Torr to give a waxy red solid. – MS (EI, 70 eV); m/z (%): 358 (12) [M^+], 343 (47), 329 (100). – IR (KBr): $\tilde{\nu}$ = 1025 (s), 1050 (m), 1305 (m), 1370 (vs), 1460 (vs, br.), 2720 (w, ν_{exo}), 2900 (vs, vbr.). – ^1H NMR ([D_6]benzene): δ = 0.21 (d), 0.26 (d), 0.35 (t), 0.71 (m), 0.88 (d), 0.94 (m), 1.10 (t), 1.35 (m), 1.45–1.60 (m), 1.67 (s), 1.79 (m), 1.80 (t), 1.84 (d), 1.89 (s), 1.95 (m), 2.05–2.15 (m) (no detailed assignment possible, since an isomeric mixture of at least four of totally six possible isomers was obtained). – $C_{22}H_{35}Co$ (358.21): calcd. C 73.21, H 9.85, Co 16.45; found C 73.20, H 9.83, Co 16.81.

2nd Zone (eluent: pentane): Black crystals from ethanol/ether, −30°C, of {[(η^5-Me$_4$EtCp)CoH}$_4$] (**5c**) (150 mg, 2.7%). – MS (EI, 70 eV); m/z (%): 836 (1) [M^+], 682 (1), 628 (6), 560 (2), 418 (11), 357 (100). – ^1H NMR: Table 1. – IR (KBr): $\tilde{\nu}$ = 870 (vs, br.), 1015 (s), 1150 (s), 1360 (s, br.), 1445 (vs, br.), 2900 (s, vbr.). – $C_{44}H_{72}Co$ (836.78): calcd. C 63.15, H 8.67, Co 28.17; found 63.06, H 8.61, Co 28.32.

3rd Zone (eluent: pentane/ether): Black crystals from ethanol/ether, −78°C, of [{η^5-Me$_4$EtCp)Co}$_3$H$_4$] (**6b**) (1.5 g, 4%). – MS (EI, 70 eV); m/z (%): 628 (32) [M^+], 618 (99), 462 (28), 357 (100). – ^1H NMR ([D_6]benzene, 27°C): δ = −65.0 (s, 18H), −50.5 (s, 18H), −36.5 (s, 6H, CH_2), −4.9 (s, 9H, CH_3). – IR (KBr): $\tilde{\nu}$ = 755 (s, vbr.), 1015 (s), 1050 (w), 1260 (m, vbr.), 1355 (s), 1370 (s), 1400 (s), 1450 (vs, br.), 2890 (vs, br.), 2960 (s). – $C_{33}H_{55}Co_3$ (628.60): calcd. C 63.05, H 8.82, Co 28.12; found C 62.85, H 8.84, Co 28.40.

Preparation of [{(η^5-1,2,4-tBu$_3$Cp)Co}$_2$H$_3$] (**4b**): 4 g (67.8 mmol) of cobalt metal was vaporized into a solution of 6 g (25.6 mmol) of 1,2,4-*t*Bu$_3$CpH (**1b**) in 150 ml of methylcyclohexane in a rotating metal-vapor reactor (80 r min^{-1}) at −120°C. The resulting brown-black solution was isolated, filtered and pumped under vacuum until all volatile components had been removed. The remaining black residue was dissolved in THF, adsorbed on Al_2O_3 and dried. Chromatography (pentane) yielded traces of a red oil which was discareded. Further elution (pentane) yielded 1.1 g of a deep purple oil. Dissolution of this oil in a mixture of acetonitrile/ether (10:1, total volume 80 ml), filtration and slow cooling of the solution to −3°C over several days afforded 620 mg (1.6%) of purple crystals of **4b**. – MS (EI, 70 eV); m/z (%): 587 (100) [M^+], 523 (18), 413 (27), 57 (59). – $C_{34}H_{61}Co_2$ (587.73): calcd. C 69.48, H 10.46, Co 20.05; found C 69.71, H 10.25, Co 20.09. – Further elution with ether yielded a brown oil which has not yet been further identified. A considerable amount of black residue remained at the top of the column after the chromatography was finished.

Reaction of [{(η^5-1,3-tBu$_2$Cp)Co}$_2$H$_3$] (**4a**), *[{(η^5-1,2,4-tBu$_3$Cp)Co}$_2$H$_3$]* (**4b**) *and [{(η^5-Me$_5$Cp)Co}$_2$H$_2$]* (**4c**) *with CO:* CO was bubbled into solutions of **4a**–**4c** (each 0.25% in THF). After 10 min, the color of the initially black or purple solutions changed to red (for **4c**) or green (for **4a** and **4b**). Bubbling was continued for 30 min, after which time all volatile components had been removed. The crude reaction products resulting from the reactions of **4a** and **4b** with CO were further purified by chromatography (Al_2O_3, 5% H_2O; pentane) and the mononuclear complexes **7a** and **7b** as well as the dinuclear complexes **8a** and **8b** were isolated from the eluates. – IR [KBr; ν(CO)]: $\tilde{\nu}$ = 1960, 2005 cm^{-1} (**7a**); 1960, 2005 cm^{-1} (**7b**); 1720 cm^{-1} (**8a**); 1700 cm^{-1} (**8b**). – **8b**: MS (EI, 70 eV); m/z (%): 640 (100) [M^+], 583 (12), 525 (22), 320 (16), 276 (21), 57 (14).

Reaction of [{(η^5-Me$_4$Cp^R)Co}$_3$H$_4$] [R = Et (**6a**), Me (**6b**)] *with AgBF$_4$/PEt$_3$:* A solution of 0.5 g of **6a** or **6b**[7] in 80 ml THF was cooled to −60°C. After addition of 2.4 mmol of PEt$_3$ and 0.8 mmol of AgBF$_4$, each at −60°C, the reaction mixture was warmed to room temperature over 12 h. During that time the silver salt dissolved. The reaction mixture was pumped to dryness and the semicrystalline residue was washed with pentane and ether. Dissolution of the crude material in THF and cooling of the solution to −30°C afforded black rectangular-shaped crystals of **9a** (380 mg, 50%) and black star-like crystals of **9b** (220 mg, 30.5%).

9a: MS [FAB(+), matrix 3,4-dimethoxybenzyl alcohol]; m/z (%): 855 (44) [**9a**$^+$], 735 (31), 656 (28), 628 (1) [**9a**$^+$ – {AgPEt$_3$}]. – IR (KBr): $\tilde{\nu}$ = 760 (s, br.), 1050 (vw, vbr.), 1090 (s, br.), 1190–1290 (m, vbr.), 1370 (m), 1405 (s), 1450 (m, br.), 2870 (m), 2900 (vs, br.), 2960 (s). – $C_{39}H_{70}AgBCo_3F_4P$ (941.4): calcd. C 49.87, H 7.51, Ag 11.48, Co 18.62; found C 49.60, H 7.60, Ag 13.68, Co 18.52.

9b: MS [FAB(+), matrix 3,4-dimethoxybenzyl alcohol]; m/z (%): 811 (100) [**9b**$^+$], 693 (42) [**9b**$^+$ – PEt$_3$], 586 (43) [**6b**$^+$], 329 (47); [FAB(−)]; m/z (%): 87 [BF_4^-] (100). – IR (KBr): $\tilde{\nu}$ = 760 (s, br.), 1050 (vw, vbr.), 1090 (s, br.), 1180–1290 (m, vbr.), 1350 (m), 1450 (m, br.), 2870 (m), 2900 (vs, br.), 2960 (s). – $C_{36}H_{64}AgBCo_3F_4P$ (899.17): calcd. C 48.08, H 7.17, Co 19.66, P 3.44; found C 48.04, H 7.15, Co 16.41, P 3.89.

X-ray Structural Solution and Refinement: Enraf-Nonius diffractometer for **3a**, **4a**, **4b**, **5c** and **9a**, Mo-K_α radiation (λ = 0.71069 Å) for **4a** and **9a**, Cu-K_α radiation (λ = 1.54178 Å) for **3a**, **4a**, and **5c**, graphite monochromator, T = 20°C. The structures were solved by heavy-atom methods (SHELXS-86), refined by full-matrix least squares on F (F^2 for **9a**) with a weighting scheme of $w^{-1} = [\sigma^2(F_o)]$ (for **9a**, see below) (SHELXL-92 for **4b**, GFMLX for **3a**, **4a**, **5c** and SHELXL-93 for **9a**), and completed by difference Fourier syntheses[27].

[{(η^5-1,3-tBu$_2$Cp)}$_2$Co] (**3a**): $C_{26}H_{42}Co$, M_r = 413.6 g mol^{-1}, crystal color black, crystal size 0.05 × 0.24 × 0.47 mm; a = 11.795(1), b = 12.419(1), c = 33.059(2) Å; V = 4842.7(5) Å^3, $d_{calcd.}$ = 1.13 g cm^{-3}, μ = 58.39 cm^{-1}, F(000) = 1800 e, Z = 8, orthorhombic, space group *Pccn* [No. 56], scan mode ω-2Θ, $[(\sin\Theta)/\lambda]_{max}$ = 0.56 Å^{-1}, analytical absorption correction (T_{min} = 0.188, T_{max} = 0.500), 3971 measured reflections ($+h$, $+k$, $+l$), 3505 independent reflections, 1545 observed reflections [$I \geqslant 2\sigma(I)$] for 254 refined parameters, H atom positions calculated and not re-

fined in the final least-squares refinement cycles (U_H = 0.05 Å^2), R = 0.073, R_w = 0.084, residual electron density 0.76 eÅ^{-3}.

[{(η^5-1,3-tBu$_2$Cp)Co}$_2$H$_3$] (**4a**): $C_{26}H_{45}Co_2$, M_r = 475.5 g mol^{-1}, crystal color black, crystal size 0.20 × 0.31 × 0.58 mm; a = 6.257(1), b = 12.849(3), c = 15.964(1) Å; α = 89.32(1), β = 82.91(1), γ = 84.21(1)°; V = 1267.1(4) Å^3, $d_{calcd.}$ = 1.25 g cm^{-3}, μ = 13.17 cm^{-1}, F(000) = 510 e, Z = 2, triclinic, space group P1bar [No.2], scan mode ω-2Θ, $[(\sin\Theta)/\lambda]_{max}$ = 0.65 Å^{-1}, analytical absorption correction (T_{min} = 0.667, T_{max}: = 0.786), 5994 measured reflections (+h, +k, +l), 5785 independent reflections, 4236 observed reflections [$I \geqslant 2\sigma(I)$] for 253 refined parameters, H atom positions on the ligands calculated and not refined in the final leastsquares refinement cycles (U_H = 0.05 Å^2), hydridic H atoms were not located, R = 0.069, R_w = 0.079, residual electron density 2.37 eÅ^{-3}.

[{(η^5-1,2,4-tBu$_3$Cp)Co}$_2$H] (**4b**): $C_{34}H_{61}Co_2$, M_r = 587.7 g mol^{-1}, crystal color black, crystal size 0.19 × 0.45 × 0.62 mm; a = 9.143(1), c = 40.491(3) Å; V = 3385.1(3) Å^3, $d_{calcd.}$ = 1.15 g cm^{-3}, μ = 81.73 cm^{-1}, F(000) = 1276 e, Z = 4, tetragonal, space group $P4_32_12$ [No. 96], scan mode ω-2Θ, $[(\sin\Theta)/\lambda]_{max}$ = 0.63 Å^{-1}, analytical absorption correction (T_{min} = 0.032, T_{max} = 0.366), 14537 measured reflections (+h, +k, +l), 3500 independent reflections, 2789 observed reflections [$I \geqslant 2\sigma(I)$] for 163 refined parameters, H atom positions except for bridging H atoms (which were not located) refined by using the riding model [$U_H = xU_C$, x = 1.2 (CH), 1.5 (CH_3)], R = 0.050, R_w = 0.128, residual electron density 0.44 eÅ^{-3}.

[{(η^5-Me$_4$EtCp)CoH}$_4$] 85**c**): $C_{44}H_{72}Co_4$, M_r = 836.8 g mol^{-1}, crystal color black, crystal size 0.15 × 0.36 × 0.37 mm; a = 21.979(2), b = 10.924(1), c = 34.406(2) Å; β = 90.81(1)°, V = 8259.9(8) Å^3, $d_{calcd.}$ = 1.35 g cm^{-3}, μ = 132.0 cm^{-1}, F(000) = 3552 e, Z = 8, monoclinic, space group $P2_1/a$ [No. 14], scanmode ω-2Θ, $[(\sin\Theta)/\lambda]_{max}$ = 0.63 Å^{-1}, analytical absorption correction (T_{min} = 0.009, T_{max} = 0.258), 17773 measured reflections (+h, +k, +l), 16612 independent reflections, 6406 observed reflections [$I \geqslant 2\sigma(I)$] for 425 refined parameters, Co atoms anisotropic, C atoms isotropic, no H atoms, R = 0.108, R_w = 0.086, residual electron density 0.86 eÅ^{-3}.

[{(η^5-Me$_4$EtCp^R)Co}$_3$Ag(PEt$_3$)H$_4$]$^+$[BF$_4$]$^-$ (**9a**): $C_{39}H_{70}AgBCo_3F_4P$, M_r = 941.4 g mol^{-1}, crystal color black, crystal size 0.35 × 0.52 × 0.63 mm; a = 11.302(1), b = 21.030(2), c = 18.308(3) Å; β = 91.34(1)°, V = 4350.3(9) Å^3, $d_{calcd.}$ = 1.44 g cm^{-3}, μ = 16.46 cm^{-1}, F(000) = 1952 e, Z = 4, monoclinic, space group $P2_1/c$ [No. 14], scan mode ω-2Θ, $[(\sin\Theta/\lambda]_{max}$ = 0.65 Å^{-1}, spherical absorption correction (T_{min} = 0.547, T_{max} = 0.553), 10197 measured reflections (±h, +k, +l), 9893 independent reflections, 8228 observed reflections [$I \geqslant 2\sigma(I)$] for refined 436 parameters, disordered C atoms (C29, C34, C36 and C38) and F atoms (F1 and F2) isotropic, H atoms not found, those attached to non-disordered C atoms riding, R = 0.058 (obsd. data), wR = 0.171 (all data, $w = 1/[\sigma^2(F_o^2) + 5.131p + 0.011p^2$ with $p = (F_o^2 + 2F_c^2)/3$), residual electron density +2.08 eÅ^{-3}.

☆ Dedicated to Professor *W. Siebert* on the occasion of his 60th birthday.

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