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Structure and reactivity of paramagnetic cyclopentadienyl cobalt complexes with bulky alkyl substituents

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Abstract

Sodium tetraisopropylcyclopentadienide or lithium tri(*tert*-butyl)cyclopentadienide reacts with cobalt(II) chloride in THF to give the corresponding dimers $[(C_5HR_4)Co(\mu\text{-}Cl)]_2$ (**1a**, R = $CHMe_2$) or $[(C_5H_2R_3)Co(\mu\text{-}Cl)]_2$ (**1b**, R = CMe_3) in good yield. The nitrosyl complexes $[(C_5HR_4)Co(\mu\text{-}NO)]_2$ (**2a**), $[(C_5HR_4)Co(\mu\text{-}Cl)(\mu\text{-}NO)Co(C_5HR_4)]$ (**3a**), and $[(C_5HR_4)Co(NO)Cl]$ (**4a**) (R = $CHMe_2$) or the tri(*tert*-butyl)cyclopentadienyl derivatives **2b**, **3b**, and **4b** have been obtained from $CoCl_2$, the respective cyclopentadienide, and nitric oxide. From the disproportionation of **1a** or **1b** with carbon monoxide, the salt $[(C_5HR_4)Co(\mu\text{-}Cl)_3Co(C_5HR_4)]_2^+[Cl_2Co(\mu\text{-}Cl)]_2^{2-}$ (**5a**, R = $CHMe_2$) and the dicarbonyl complex $[(C_5HR_4)Co(CO)_2]$ (**6a**, R = $CHMe_2$) or the tri(*tert*-butyl)cyclopentadienyl derivatives **5b** and **6b** have been isolated. Compounds **6a** and **6b** were converted to the carbonyl-bridged dimers $[(C_5HR_4)Co(\mu\text{-}CO)]_2$ (**7a**, R = $CHMe_2$) or $[(C_5H_2R_3)Co(\mu\text{-}CO)]_2$ (**7b**, R = CMe_3) by UV irradiation. Compound **1a** was cleaved with acetonitrile to yield the novel 17 valence electron cation $[(C_5HR_4)Co(MeCN)_2]^+$ (**8**, R = $CHMe_2$), which in acetonitrile solution could be further oxidized to $[(C_5HR_4)Co(MeCN)_3]^{2+}$ (**9**, R = $CHMe_2$) by electrochemical means or chemically with ferrocenium hexafluorophosphate. Compound **1a** gave the neutral 17 VE complex $[(C_5HR_4)Co(PMe_3)Cl]$ (**10**, R = $CHMe_2$) with trimethylphosphane, which could be converted to the methyl-substituted odd-electron compound $[(C_5HR_4)Co(PMe_3)CH_3]$ (**11**, R = $CHMe_2$) by treatment with methyllithium. Hydrolysis of complex **11** proceeded with phosphane loss and resulted in formation of the hydroxo-bridged dimer $[(C_5HR_4)Co(\mu\text{-}OH)]_2$ (**12**, R = $CHMe_2$). Crystal structure analyses have been carried out for **1a**, **3b**, **5a**, **7a**, **7b**, **8**, **10**, and **12**. For growth of single crystals tetraisopropylcyclopentadiene turned out to be a well-suited solvent. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: Cobalt complexes; Tetraisopropylcyclopentadienyl; Tri(*tert*-butyl)cyclopentadienyl; Crystallization; Magnetism; Crystal structure

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1. Introduction

Introduction of extreme steric bulk into peralkylated cyclopentadienyl ligands by means of tertiary butyl or isopropyl instead of methyl groups significantly alters the structure and reactivity of the respective complexes. The novel high-spin iron(II) halides $[(C_5R_4R')FeBr]_2$ (R = $CHMe_2$, R′ = H, $CHMe_2$), for example, not only displayed interesting magnetic properties and high reactivity, but also enabled us to synthesize the first example of a stable dicarbonyl(cyclopentadienyl)iron radical in solution [1]. These findings prompted us to test the impact of strongly electron-donating and extremely bulky tetraisopropyl- or tri(*tert*-butyl)cyclopentadienyl on similar complexes of third row transition metals other than iron. Cyclopentadienylcobalt(II) halide dimers are reactive and easily accessible starting compounds for a wide variety of cyclopentadienylcobalt complexes. Following the generation of ethylte-

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tramethylcyclopentadienylcobalt(II) chloride dimer in solution as a starting compound for the preparation of ethyltetramethylcyclopentadienylcobalt(III) complexes [2], seminal work has been done especially for pentamethylcyclopentadienylcobalt(II) halides [3].

The work presented here was directed towards two different goals: first, the impact of the tetraisopropylcyclopentadienyl ring on known cobalt complexes with other cyclopentadienyl derivatives should provide insight into the changes in structure and reactivity brought about by steric bulk. Secondly, we expected the synthetic potential of tetraisopropyl- and tri(*tert*-butyl)cyclopentadienylcobalt(II) halides to reach beyond that of the known derivatives.

2. Experimental

2.1. General procedures

All manipulations were carried out under argon or nitrogen using standard Schlenk techniques or a glove box (MBraun) and carefully dried solvents. NMR spectra were recorded on a Bruker AMX 400 spectrometer with the protiosolvent signal (^{1}H-NMR) or solvent signals (^{13}C-NMR) used as a reference; chemical shifts are quoted on the δ scale (downfield shifts are positive) relative to tetramethylsilane. Elemental analyses were performed on an elemental analyzer 240 (Perkin–Elmer), IR spectra were recorded on the spectrometer 881 (Perkin–Elmer). Starting compounds were prepared according to literature procedures: sodium tetraisopropylcyclopentadienide and 1,3,5-tri(*tert*-butyl)cyclopentadiene [4], lithium 1,2,4-tri(*tert*-butyl)cyclopentadienide [5], and trimethylphosphane [6]. All column chromatography was carried out using deactivated silica gel or alumina containing 3% water.

2.2. Chloro(tetraisopropylcyclopentadienyl)cobalt(II) dimer; $[\{C_5H(CHMe_2)_4\}Co(\mu\text{-}Cl)]_2$ (**1a**)

A suspension of 1.09 g (8.39 mmol) $CoCl_2$ in 30 ml of THF was cooled to −20°C and a solution of 2.16 g (8.42 mmol) sodium tetraisopropylcyclopentadienide in 20 ml THF was added dropwise at that temperature. The resulting brown–black solution was then allowed to warm up to room temperature (r.t.), stirred for another 30 min and evaporated to dryness. After extraction of the black residue with 80 ml of petroleum ether, centrifugation and reduction in volume to ca. 10 ml, the product was crystallized at −78°C to yield 2.04 g (3.11 mmol, 74%) brown–black crystals, which decompose on heating above 245°C. The most beautiful crystals were obtained during work-up of one early experiment where the THF solvent must have contained traces of residual water. In addition to a low yield of **1a**, a toluene extract contained the tetraisopropylcyclopentadiene resulting from partial hydrolysis of sodium tetraisopropylcyclopentadienide. In the oily solution of **1a** in tetraisopropylcyclopentadiene, with traces of toluene resulting from almost complete evaporation, well-shaped crystals formed during 2 weeks with one very large individual and several small crystals suitable for X-ray diffraction. Anal. Calc. for **1a** ($C_{17}H_{29}ClCo$; fw = 327.80): C, 62.29; H, 8.92. Found: C, 62.30; H, 8.80. EI MS: *m*/*z* 654 (25; M^+), 327 (35; $M/2^+$), 284 (7; $M/2^+ - CHMe_2$), 249 (51; $M/2^+ - CHMe_2$–Cl), 233 (43; $C_{17}H_{29}^+$), 190 (17; $C_{14}H_{22}^+$), 147 (27; $C_{11}H_{15}^+$), 43 (79; $C_3H_7^+$).

2.3. Chloro{1,2,4-tri(tert-butyl)cyclopentadienyl}-cobalt(II) dimer; $[(C_5H_2(CMe_3)_3\text{-}1,2,4\}CoCl]_2$ (**1b**)

A suspension of 1.08 g (8.32 mmol) $CoCl_2$ in 30 ml of THF was cooled to −45°C and a solution of 2.13 g (8.31 mmol) lithium tri(*tert*-butyl)cyclopentadienide in 20 ml THF was added dropwise at that temperature. Treatment of the resulting brown–black solution as above gave brown–black crystals in 1.47 g (2.24 mmol, 54%) yield, m.p. 155–156°C. Anal. Calc. for **1b** ($C_{17}H_{29}ClCo$; fw = 327.80): C, 62.29; H, 8.92. Found: C, 61.76; H, 8.82. CI MS (150 eV, 200°C): *m*/*z* 654 (13; M^+), 327 (38; $M/2^+$), 292 (7; $M/2^+ - Cl$), 235 (100; $M/2^+ - Cl\text{–}CMe_3$), 233 (26; $C_{17}H_{29}^+$), 178 (39; $C_{13}H_{22}^+$), 121 (26; $C_9H_{13}^+$).

2.4. Nitrosyl complexes **2a**, **3a**, and **4a**

In a 250 ml flask from 1.16 g (8.93 mmol) anhydrous cobalt(II) chloride and 2.27 g (8.85 mmol) of sodium tetraisopropylcyclopentadienide, a THF solution of **1a** was prepared at −20°C and immersed in an acetone/dry-ice bath. At −78°C the flask was partially evacuated and 160 ml (7.1 mmol) of nitrous oxide was admitted with concomitant color change of the brown–black solution to dark-green. After 5 min of stirring, the cool bath was removed and the solution was allowed to warm up to r.t. The solvent was removed in vacuo and the residue dissolved in 5 ml of methylene chloride, mixed with the same volume of silica and evaporated to dryness. Chromatographic separation on silica gel gave four fractions.

The first fraction was eluted with petroleum ether and toluene (10:1), looked faintly yellow and contained a small amount of tetraisopropylcyclopentadiene identified by ^{1}H-NMR spectroscopy.

*2.5. Nitrosyl(tetraisopropylcyclopentadienyl)cobalt dimer, $[\{C_5H(CHMe_2)_4\}Co(\mu\text{-}NO)]_2$ (**2a**)*

With petroleum ether and toluene (2:1) a brown fraction was collected giving a black, microcrystalline powder in 120 mg (0.19 mmol, 4%) yield, m.p. 133–135°C. Anal. Calc. (found) for **2a** ($C_{17}H_{29}CoNO$; fw = 322.31): C, 63.33; H, 9.07; N, 4.35. Found: C, 61.10; H, 8.80; N, 4.10. EI MS (70 eV, 200°C): *m/z* (relative intensity) 644 [M^+, 100%], 322 [$M/2^+$, 12%], 279 [$M/2^+ - C_3H_7$, 24%], 233 ($C_{17}H_{29}^+$, 2%), 190 ($C_{14}H_{22}^+$, 2%), 147 ($C_{11}H_{15}^+$, 2%), 43 ($C_3H_7^+$, 2%), 30 (NO^+, 1%). ^{1}H-NMR in C_6D_6, δ: 4.29 (s, 2H, ring-*H*), 2.88–2.91 (2 sep, superimposed, 8H, C*H*Me$_2$), 1.37 (d, 12H, C*H*$_3$, $^3J_{HH} = 7.2$ Hz), 1.34 (d, 12H, C*H*$_3$, $^3J_{HH} = 7.2$ Hz), 1.21 (d, 12H, C*H*$_3$, $^3J_{HH} = 7.0$ Hz), 1.02 (d, 12H, C*H*$_3$, $^3J_{HH} = 6.6$ Hz). $^{13}C\{^1H\}$-NMR in C_6D_6, δ: 106.5 (s, 4C, ring *C*CHMe$_2$), 106.2 (s, 4C, ring *C*CHMe$_2$), 78.9 (d, 2C, ring *C*H, $J_{CH} = 169.5$ Hz), 25.2–23.1 (2d and 4q superimposed, *C*H$_3$ and *C*HMe$_2$ signals). IR (pentane solution, cm^{-1}): ν_{NO} 1559 (s), 1506 (vs, br).

*2.6. μ-Chloro,μ-nitrosylbis(tetraisopropylcyclopentadienyl)dicobalt $[\{C_5H(CHMe_2)_4\}Co(\mu\text{-}NO)(\mu\text{-}Cl)Co\{C_5H(CHMe_2)_4\}]$ (**3a**)*

With toluene a dark-red fraction was obtained which on evaporation gave a dark-red oil. At r.t. the oil slowly crystallized to yield 230 mg (0.35 mmol, 8%) black microcrystals of **3a**, m.p. 188–191°C. Anal. Calc. for **3a** ($C_{34}H_{58}ClCoNO$; fw = 650.16): C, 62.81; H, 8.99; N, 2.15. Found: C, 63.07; H, 8.40; N, 1.74. CI MS (150 eV, 200°C): *m/z* (relative intensity) 649 [M^+, 23%], 644 (**2a**$^+$, 100%), 614.2 [$M^+ - Cl$, 1%], 327 ([$(C_5HR_4)CoCl]^+$, 8%), 322 ([$(C_5HR_4)CoNO]^+$, 25%), 292 ([$(C_5HR_4)Co]^+$, 1%), 233 ($C_{17}H_{29}^+$, 7%). IR (pentane solution, cm^{-1}): ν_{NO} 1492 (vs, br).

*2.7. Chloro(nitrosyl)tetraisopropylcyclopentadienylcobalt $[\{C_5H(CHMe_2)_4\}Co(NO)Cl]$ (**4a**)*

With toluene and diethyl ether (10:1) a green fraction was eluted and gave a dark-green oil which crystallized at r.t. Recrystallization from hexane gave 220 mg (0.61 mmol, 7%) black crystals of **4a**, m.p. 103–105°C. Anal. Calc. for **4a** ($C_{17}H_{29}ClCoNO$; fw = 357.81): C, 57.05; H, 8.17; N, 3.91. Found: C, 56.90; H, 8.20; N, 4.00. EI MS (70 eV, 200°C): *m/z* (relative intensity) 644 (**2a**$^+$, 17%), 357.2 [M^+, 5%], 327 ([$(C_5HR_4)CoCl]^+$, 100%), 322 ([$(C_5HR_4)CoNO]^+$, 5%), 284 ([$(C_5HR_3)CoCl]^+$, 48%), 241 ([$(C_5HR_2)CoCl]^+$, 1%), 233 ($C_{17}H_{29}^+$, 4%). 190 ($C_{14}H_{22}^+$, 2%), 147 ($C_{11}H_{15}^+$, 3%), 43 ($C_3H_7^+$, 5%), 30 (NO^+, 2%); R = CHMe$_2$. ^{1}H-NMR in C_6D_6, δ: 4.89 (s, 2H, ring-*H*), 2.38–2.50 (2 sep, superimposed, 8H, C*H*Me$_2$), 1.25 (br, 12H, C*H*$_3$), 1.14 (d, 12H, C*H*$_3$, $^3J_{HH} = 6.9$ Hz), 1.08 (d, 12H, C*H*$_3$, $^3J_{HH} = 6.2$ Hz), 0.87 (d, 12H, C*H*$_3$, $^3J_{HH} = 6.3$ Hz). IR (petroleum ether solution, cm^{-1}): $\nu_{NO} = 1809$ (vs).

Alternative procedure for more selective production of **4a**. In a 250 ml flask a solution of 1.13 g (1.75 mmol) **1a** in 60 ml petroleum ether is cooled to −78°C. The flask is evacuated, nitric oxide is admitted and the NO uptake of the stirred solution is replenished during the next 5 min. The solution is allowed to warm to r.t. and evaporated to dryness. Chromatography as described before gives a small orange–brown fraction and a dark-green main fraction. Evaporation to dryness yields 657 mg (1.84 mmol, 52%) **4a**.

*2.8. Nitrosyl complexes **2b**, **3b**, and **4b***

In a 250 ml flask a solution of 3.23 g (12.6 mmol) sodium tri(*tert*-butyl)cyclopentadienide in 30 ml of THF was added dropwise to a suspension of 1.64 g (12.7 mmol) of anhydrous cobalt(II)chloride at −20°C. The so-formed solution of **1b** was cooled to −78°C and after evacuation, nitric oxide (180 ml; 8.0 mmol) was admitted to the brown–black solution with an immediate color change to dark-green and to red–brown within a few minutes. The solvent was evaporated, the residue dissolved in 5 ml of methylene chloride, mixed with the same volume of silica and evaporated to dryness. Chromatographic separation on silica gel gave a pale-yellow fraction of 1,3,5-tri(*tert*-butyl) cyclopentadiene and was followed by three metal-containing product fractions.

*2.9. Nitrosyl{1,2,4-tri(tert-butyl)cyclopentadienyl}cobalt dimer, $[\{C_5H_2(CMe_3)_3\text{-}1,2,4\}Co(\mu\text{-}NO)]_2$ (**2b**)*

With petroleum ether and toluene (1:2) a dark-brown fraction was collected which on evaporation of the solvents left 280 mg (0.43 mmol, 7%) of **2b** as a black, microcrystalline powder, m.p. 209–211°C. Anal. Calc. for **2b** ($C_{17}H_{29}CoNO$; fw = 322.31): C, 63.33; H, 9.07; N, 4.35. Found: C, 62.70; H, 9.10; N, 3.60. EI MS (70 eV, 200°C): *m/z* (relative intensity) 644 [M^+, 100%], 233 ($C_{17}H_{29}^+$, 10%), 176 ($C_{13}H_{20}^+$, 4%), 119 ($C_9H_{11}^+$, 13%), 57 ($C_4H_9^+$, 7%). IR (pentane solution, cm^{-1}): ν_{NO} 1564 (s), 1511 (vs, br).

*2.10. μ-Chloro,μ-nitrosylbis{1,2,4-tri(tert-butyl)cyclopentadienyl}dicobalt $[\{C_5H_2(CMe_3)_3\text{-}1,2,4\}Co(\mu\text{-}NO)(\mu\text{-}Cl)Co\{C_5H_2(CMe_3)_3\text{-}1,2,4\}]$ (**3b**)*

With petroleum ether and toluene (1:3) a dark-red fraction was obtained which on evaporation yielded 520 mg (0.8 mmol, 13%) of **3b** as a black, microcrystalline powder, m.p. 185–188°C. Anal. Calc. for **3b** ($C_{34}H_{58}ClCoNO$; fw = 650.16): C, 62.81; H, 8.99; N, 2.15. Found: C, 62.60; H, 8.50; N, 2.10. EI MS (35 eV, 260°C): *m/z* (relative intensity) 644 (**2b**$^+$, 100%), 233 (C$_{17}$H$_{29}^+$, 6%), 183 ([Co$_2$ClNO]$^+$, 63%), 178 ([(C$_9$H$_{11}$Co]$^+$, 10%), 121 ([(C$_5$H$_5$Co]$^+$, 10%), 57 (C$_4$H$_9^+$, 43%). ^{1}H-NMR in C$_6$D$_6$, δ: 4.56 (s, 4H, ring-*H*), 1.41 (s, 36H, C*H*$_3$), 1.37 (d, 18H, C*H*$_3$). ^{13}C{^{1}H}-NMR in C$_6$D$_6$, δ: 106.3 (s, 4C, ring *C*CMe$_3$), 103.8 (s, 2C, ring *C*CMe$_3$), 81.9 (d, 4C, ring *C*H, $J_{\mathrm{CH}} = 170$ Hz), 33.0 (s, 4C, *C*Me$_3$), 32.6 (q,* 12C, *C*H$_3$), 31.6 (s, 2C, *C*Me$_3$), 30.4 (q,* 6 C, *C*H$_3$). (* = coupling constant not determined due to signal superimposition). IR (pentane solution, cm^{-1}): ν_{NO} 1501 (vs, br).

2.11. Chloro(nitrosyl){1,2,4-tri(tert-butyl)cyclopentadienyl}cobalt [{C$_5$H$_2$(CMe$_3$)$_3$-1,2,4}Co(NO)Cl] (**4b**)

With toluene and diethyl ether (5:1) a green fraction was eluted and evaporated to a dark-green oil which crystallized at r.t. as 110 mg (0.15 mmol, 2%) of black crystals of **4b**, m.p. 101–104°C. Anal. Calc. for **4b** (C$_{17}$H$_{29}$ClCoNO; fw = 357.81): C, 57.05; H, 8.17; N, 3.91. Found: C, 57.90; H, 8.40; N, 3.20. EI MS (35 eV, 260°C): *m/z* (relative intensity) 644 (**2b**$^+$, 24%), 357 [M$^+$, 4%], 327 ([(C$_5$H$_2$R$_3$)CoCl]$^+$, 91%), 322 ([(C$_5$H$_2$R$_3$)CoNO]$^+$, 5%), 270 ([(C$_5$H$_2$R$_2$)CoCl]$^+$, 13%), 265 ([(C$_5$H$_2$R$_2$)CoNO]$^+$, 7%), 233 (C$_{17}$H$_{29}^+$, 6%), 121 (C$_9$H$_{13}^+$, 18%), 57 (C$_4$H$_9^+$, 100%), 30 (NO$^+$, 3%). IR (pentane solution, cm^{-1}): ν_{NO} 1810 (vs).

2.12. Reaction of **1a** and **1b** with carbon monoxide

From CoCl$_2$ suspended in 40 ml of THF solutions of **1a** or **1b** were obtained as described before, input amounts were 1.75 g (13.5 mmol) CoCl$_2$ and 3.46 g (13.5 mmol) sodium tetraisopropylcyclopentadienide for **1a** and 1.62 g (12.5 mmol) CoCl$_2$ and 3.00 g (12.5 mmol) lithium 1,2,4-tri(*tert*-butyl)cyclopentadienide for **1b**. At r.t. the solvent was evaporated, the black residue extracted with 80 ml of pentanes and separated from unsoluble alkali salts by centrifugation. The resulting brown–black solution was transferred into a 500 ml flask and the inert gas atmosphere replaced with carbon monoxide. After a short induction period the mixture turned brown and precipitation of **5** (**a** or **b**) becomes visible. The carbon monoxide absorbed by the solution was replenished from time to time. The reaction flask should be covered to prevent decomposition of light-sensitive **6** (**a** or **b**). The reaction mixture was stirred for 2 h 30 min, then the ionic compound was collected by centrifugation, dissolved in a minimum amount of methylene chloride and precipitated by addition of pentane. Analytically pure **5a** and **5b** are obtained by crystallization from methylene chloride solutions layered with pentane in 0.75 g (0.4 mmol, 18%, **5a**) and 0.62 g (0.33 mmol, 16%, **5b**) yield. Anal. Calc. for **5a** (C$_{70}$H$_{120}$Cl$_{16}$Co$_6$; fw = 1882.57): C, 44.66; H, 6.42. Found: C, 44.15; H, 6.63. ^{1}H-NMR in CD$_2$Cl$_2$, δ: 5.13 (s, 2H, ring-*H*), 2.47 (2 sep, br, 8H, C*H*Me$_2$), 1.29 (d, 12H, C*H*$_3$, $^3J_{\mathrm{HH}} = 6.1$ Hz), 1.17 (d, 12H, C*H*$_3$, $^3J_{\mathrm{HH}} = 6.5$ Hz), 0.86 (d, 12H, C*H*$_3$, $^3J_{\mathrm{HH}} = 6.6$ Hz), 0.45 (d, 12H, C*H*$_3$, $^3J_{\mathrm{HH}} = 6.1$ Hz). Anal. Calc. for **5b** (C$_{70}$H$_{120}$Cl$_{16}$Co$_6$; fw = 1882.57): C, 44.66; H, 6.42. Found: C, 44.34; H, 6.45. EI MS (70 eV, 220°C): *m/z* (relative intensity) 654 ([(C$_5$H$_2$R$_3$)CoCl]$_2^+$, 3%), 327 ([(C$_5$H$_2$R$_3$)CoCl]$^+$, 6%), 177 ([C$_5$H$_3$R$_2$]$^+$, 4%), 121 ([C$_5$H$_4$R]$^+$, 20%), 57 (C$_4$H$_9^+$, 100%). ^{1}H-NMR in CD$_2$Cl$_2$, δ: 5.30 (s, 4H, ring-*H*), 1.15 (s, 36H, C*H*$_3$), 1.09 (d, 18H, C*H*$_3$).

The pentane solution of mononuclear dicarbonyl complexes **6** (**a** or **b**) was evaporated to a small amount of concentrated solution and isolated by column chromatography on alumina (column of 1 cm diameter and 15 cm length covered with aluminum foil) as a red fraction with pentane. Evaporation of pentane leaves **6a** or **6b** as dark-red oils mixed with the respective cyclopentadiene. Attempts to remove this impurity were unsuccessful because of substantial loss and/or decomposition of **6**. Anal. Calc. for **6a** (C$_{19}$H$_{29}$CoO$_2$; fw = 348.37) with 26% (by weight) C$_5$H$_2$(CHMe$_2$)$_4$ impurity: C, 71.12; H, 9.56. Found: C, 71.14; H, 9.43. ^{1}H-NMR in C$_6$D$_6$, δ: 4.57 (s, 1H, ring-*H*), 2.57 (sep, 2H, C*H*Me$_2$), 2.49 (sep, 2H, C*H*Me$_2$), 1.27 (d, 6H, C*H*$_3$, $^3J_{\mathrm{HH}} = 7.3$ Hz), 1.20 (d, 6H, C*H*$_3$, $^3J_{\mathrm{HH}} = 7.3$ Hz), 1.16 (d, 6H, C*H*$_3$, $^3J_{\mathrm{HH}} = 6.8$ Hz), 0.97 (d, 6H, C*H*$_3$, $^3J_{\mathrm{HH}} = 6.8$ Hz). ^{13}C{^{1}H}-NMR in C$_6$D$_6$, δ: 207.9 (s, 2C, CO), 110.1 (s, 2C, ring *C*CHMe$_2$), 109.6 (s, 2C, ring *C*CHMe$_2$), 75.8 (d, 1C, ring *C*H, $J_{\mathrm{CH}} = 171$ Hz). Due to superimposition with signals of the C$_5$H$_2$(CHMe$_2$)$_4$ impurity the alkyl carbon signals could not be observed. IR (pentane solution, cm^{-1}): ν_{CO} 2010 (vs), 1951 (s). Anal. Calc. for **6b** (C$_{19}$H$_{29}$CoO$_2$; fw = 348.37) with 25% (by weight) C$_5$H$_3$(CMe$_3$)$_3$ impurity: C, 70.90; H, 9.52. Found: C, 71.14; H, 9.43. ^{1}H-NMR in C$_6$D$_6$, δ: 4.79 (s, 2H, ring-*H*), 1.26 (s, 18H, C*H*$_3$), 1.10 (d, 9H, C*H*$_3$). ^{13}C{^{1}H}-NMR in C$_6$D$_6$, δ: 207.6 (s, 2C, CO), 115.2 (s, 1C, ring *C*CMe$_3$), 113.6 (s, 2C, ring *C*CMe$_3$), 82.3 (d, 2C, ring *C*H, $J_{\mathrm{CH}} = 171$ Hz), 33.9 (q, 6C, *C*H$_3$, $^1J_{\mathrm{CH}} = 127$ Hz), 31.7 (q, 6C, *C*H$_3$, $^1J_{\mathrm{CH}} = 127$ Hz). Due to superimposition with signals of the C$_5$H$_3$(CMe$_3$)$_3$ impurity the signals of the quarternary *C*(CH$_3$)$_3$ carbon atoms could not be observed. IR (pentane solution, cm^{-1}): ν_{CO} 2013 (vs), 1955 (s).

2.13. Photochemical formation of **7a** and **7b**

Compound **6a** (0.580 g, 1.66 mmol, containing additional tetraisopropylcyclopentadiene) or **6b** (0.530 g, 1.52 mmol, containing additional tri(*tert*-butyl)cyclopentadiene) was dissolved in 100 ml toluene and irradiated until IR spectra showed no further decrease in intensity of the educt signals (4.5 h for **6a** and 6.5 h for **6b**). The green solution was concentrated to a few ml, the residual solution mixed with ca. 3 g aluminum oxide, evaporated to a dry powder and packed on top of a column of 20 g aluminum oxide in petroleum ether. With the same solvent unreacted educt is eluted first, a mixture of petroleum ether with 20% toluene eluted deep-green solutions of **7a** or **7b**. The products were isolated as dark-green crystals by evaporation to dryness and recrystallization from petroleum ether at −20°C, the yield is 0.21 g (0.33 mmol, 40%) **7a** or 0.19 g (0.30 mmol, 39%) **7b**. Anal. Calc. for **7a** ($C_{36}H_{58}Co_2O_2$; fw = 640.72): C, 67.49; H, 9.12. Found: C, 67.12; H, 9.00. EI MS (70 eV, 220°C): *m*/*z* (relative intensity) 640 [M^+, 100%], 525 ($[(C_5HR_4)_2Co]^+$, 3%), 320 [$M/2^+$, 9%], 292 ($[(C_5HR_4)Co]^+$, 12%) ($(C_5HR_4)^+$, 4%); R = $CHMe_2$. ^{1}H-NMR in C_6D_6, δ: 4.93 (s, 2H, ring-*H*), 3.27 (sep, 4H, C*H*Me$_2$), 2.29 (sep, 4H, C*H*Me$_2$), 1.22 (d, 12H, C*H*$_3$, $^3J_{HH} = 7.7$ Hz), 1.21 (d, 12H, C*H*$_3$, $^3J_{HH} = 6.9$ Hz), 1.14 (d, 12H, C*H*$_3$, $^3J_{HH} =$ 6.8 Hz), 1.11 (d, 12H, C*H*$_3$, $^3J_{HH} = 6.7$ Hz). $^{13}C\{^1H\}$-NMR in C_6D_6, δ: 105.9 (s, 4C, ring *C*CHMe$_2$), 105.4 (s, 4C, ring *C*CHMe$_2$), 25.2 (s, 4C, *C*HMe$_2$), 24.9 (s, 4C, *C*HMe$_2$), 24.1 (s, 4C, *C*H$_3$), 24.0 (s, 4C, *C*H$_3$), 23.8 (s, 4C, *C*H$_3$), 23.2 (s, 4C, *C*H$_3$). IR (pentane solution, cm^{-1}): ν_{CO} 1762 (s). Anal. Calc. for **7b** ($C_{36}H_{58}Co_2O_2$; fw = 640.72): C, 67.49; H, 9.12. Found: C, 66.15; H, 9.00. EI MS (70 eV, 220°C): *m*/*z* (relative intensity) 640 [M^+, 75%], 525 ($[(C_5H_2R_3)_2Co]^+$, 14%), 466 ($(C_5H_2R_3)_2^+$, 10%), (320 [$M/2^+$, 8%], 233 ($C_5H_2R_3^+$, 10%); R = CMe_3. ^{1}H-NMR in C_6D_6, δ: 5.19 (s, 4H, ring-*H*), 1.41 (s, 36H, C*H*$_3$), 0.79 (d, 18H, C*H*$_3$). ^{13}C-NMR in C_6D_6, δ: 269.5 (2, 2C, CO), 109.1 (s, 4C, ring *C*CMe$_3$), 104.7 (s, 2C, ring *C*CMe$_3$), 92.9 (d, 4C, ring *C*H, $J_{CH} = 172$ Hz), 33.5 (q, 12C, *C*H$_3$, $^1J_{CH} = 126$ Hz), 32.3 (s, 4C, *C*Me$_3$), 30.7 (q, 6C, *C*H$_3$, $^1J_{CH} = 126$ Hz), 29.0 (s, 2C, *C*Me$_3$). IR (pentane solution, cm^{-1}): ν_{CO} 1767 (s).

2.14. *Bis(acetonitrile)tetraisopropylcyclopentadienylcobalt(II) hexafluorophosphate* (**8**)

A solution of 0.56 g (3.43 mmol) $NH_4^+PF_6^-$ in 15 ml of acetonitrile was added dropwise at r.t. to a solution of 1 g (1.52 mmol) **1a** in 15 ml of acetonitrile. After stirring for 2 h the solution was evaporated to dryness, the solid residue washed with 10 ml of pentane, extracted with 10 ml of methylene chloride and the solution was separated from the ammonium chloride precipitate by centrifugation. The red–brown solution was concentrated in vacuo and **8** was isolated as a microcrystalline precipitate upon addition of pentane and recrystallized from a methylene chloride solution layered with pentane as ruby-red crystals in 1.23 g (2.37 mmol, 78%) yield, m.p. 136–138°C. Anal. Calc. for **8** ($C_{21}H_{35}CoF_6N_2P$; fw = 519.42): C, 48.56; H, 6.79; N, 5.20. Found: C, 48.20; H, 6.80; N, 5.39. ^{1}H-NMR in CD_2Cl_2, δ: 4.75 (s, 1H, ring-*H*), 3.00 (m, C*H*Me$_2$), 2.84 (m, C*H*Me$_2$), 2.82 (m, C*H*Me$_2$), 2.55 (s, CH_3CN), 2.21 (d, C*H*$_3$, $^3J_{HH} = 7.0$ Hz), 1.66 (d, C*H*$_3$, $^3J_{HH} = 6.8$ Hz), 1.64 (d, C*H*$_3$, superimposed), 1.59 (d, C*H*$_3$, $^3J_{HH} = 7.0$ Hz), 1.43 (d, C*H*$_3$, $^3J_{HH} = 6.8$ Hz), 1.30 (d, C*H*$_3$, $^3J_{HH} = 7.3$ Hz),0.96 (d, C*H*$_3$, $^3J_{HH} = 6.8$ Hz), (d, C*H*$_3$, $^3J_{HH} = 6.9$ Hz), 1.14 (d, C*H*$_3$, $^3J_{HH} = 6.8$ Hz), 1.11 (d, C*H*$_3$, $^3J_{HH} = 6.7$ Hz). Due to the paramagnetic nature of the complex all signals are broadened. The reported doublets show different intensity, partial superimposition precluded proper integration of the signals. IR (Nujol suspension, cm^{-1}): ν_{CO} 2360 (w), 2341 (w).

2.15. *Tris(acetonitrile)tetraisopropylcyclopentadienylcobalt(III) hexafluorophosphate* (**9**)

A solution of 204 mg (0.618 mmol) ferrocenium hexafluorophosphate in 10 ml of acetonitrile was added to a solution of 321 mg (0.618 mmol) of **8** in 6 ml of acetonitrile at r.t. The mixture turned red–violet and was evaporated to dryness after 3 h of stirring. The red–violet residue was washed several times with pentane to remove all of the ferrocene formed during the reaction and dried in vacuo. Compound **9** was obtained analytically pure from a methylene chloride solution layered with pentane in 349 mg (0.495 mmol, 80%) yield. Anal. Calc. for **9** ($C_{23}H_{38}CoF_{12}N_3P_2$; fw = 705.43): C, 39.16; H, 5.43; N, 5.96. Found: C, 38.50; H, 5.30; N, 5.60. ^{1}H-NMR in CD_3CN, δ: 6.27 (s, 1H, ring-*H*), 2.99 (sep, 2H, C*H*Me$_2$), 2.88 (sep, 2H, C*H*Me$_2$), 1.95 (s, 9H, C*H*$_3$CN), 1.56 (d, 6H, C*H*$_3$, $^3J_{HH} = 6.6$ Hz), 1.50 (d, 6H, C*H*$_3$, $^3J_{HH} = 7.0$ Hz), 1.37 (d, 6H, C*H*$_3$, $^3J_{HH} = 7.0$ Hz), 1.14 (d, 6H, C*H*$_3$, $^3J_{HH} =$ 6.8 Hz). ^{13}C-NMR in CD_3CN, δ: 134.3 (s, 3C, CD_3CN, coordinated to Co), 119.7 (br, CD_3CN solvent), 112.4 (s, 2C, ring *C*CHMe$_2$), 109.6 (s, 2C, ring *C*CHMe$_2$), 84.8 (d, 1C, ring *C*H, $^1J_{CH} = 179$ Hz), 26.7 (s, 2C, *C*HMe$_2$, $^1J_{CH} = 131$ Hz), 26.4 (d, 2C, *C*HMe$_2$, $^1J_{CH} =$ 133 Hz), 22.2 (q, 2C, *C*H$_3$, superimposed), 20.9 (q, 2C, *C*H$_3$, superimposed), 19.9 (q, 2C, *C*HMe$_2$, $^1J_{CH} = 128$ Hz), 4.2 (sep, 3C, *C*D$_3$CN, coordinated to Co), 1.3 (sep, *C*D$_3$CN solvent). ^{31}P-NMR in $(CD_3)_2CO$, δ: −138 ppm (sep, PF_6^-, $^1J_{PF} = 708$ Hz). IR (Nujol suspension, cm^{-1}): ν_{CN} 2362 (w), 2333 (w), 2305(w).

2.16. *Chloro(trimethylphosphane)tetraisopropylcyclopentadienylcobalt(II)* (**10**)

Trimethylphosphane (1 ml, 9.66 mmol) was added at r.t. to a solution of 2.33 g (3.55 mmol) of **1a** in 60 ml of methylene chloride and the mixture was stirred for 24 h. After evaporation of the solution to dryness the residue was extracted with 100 ml of pentane. Centrifugation, concentration of the purple solution to ca. 20 ml and storage at −78°C gave 2.12 g (5.25 mmol, 74%) yield of purple–red crystals, m.p. 142–143°C. Anal. Calc. for **10** ($C_{20}H_{38}ClCoP$; fw = 403.88): C, 59.48; H, 9.48. Found: C, 58.85; H, 9.36. ^{1}H-NMR in $CDCl_3$, δ: 14–5 ppm (very broad), 2.2 (br), 1.69 (br), 1.19 (br), 0.12 (br), −1.48 (br). Additional signals of low intensity: 4.52 (br), 3.97 (br), 3.19 (br), 2.73 (br). EI MS (120 eV, 180°C): *m/z* (relative intensity) 654 (**1a**$^+$, 82%), 466 ($[C_5HR_4]_2^+$, 8%), 403 [M$^+$, 100%], 368 ($[(C_5HR_4)CoPMe_3]^+$, 18%), 327 ($[(C_5HR_4)CoCl]^+$, 70%), 284 ($[(C_5H_2R_3)CoCl]^+$, 7%), 233 ($C_{17}H_{29}^+$, 17%). 77 ($HPMe_3^+$, 17%), 76 ($HPMe_3^+$, 17%); R = $CHMe_2$.

2.17. *Methyl(trimethylphosphane)tetraisopropylcyclopentadienylcobalt(II)* (***11***)

A 1.9 molar solution (1.1 ml) of methyllithium in diethyl ether (2.09 mmol) was added dropwise to a solution of 845 mg (2.09 mmol) **10** in 40 ml of diethyl ether and stirred 24 h at r.t. After evaporation of the mixture the solid residue was extracted with 20 ml of pentane. Centrifugation, evaporation to ca. 3 ml residual volume and storage at −30°C gave **11** as a brown, microcrystalline solid in 138 mg (0.36 mmol, 17%) yield, which decomposes above 104°C. Anal. Calc. for **11** ($C_{21}H_{41}CoP$; fw = 383.46): C, 65.78; H, 10.78. Found: C, 63.88; H, 10.35. ^{1}H-NMR in C_6D_6, δ: 1.38 (br), 1.37 (br), 0.97 (br), 0.69 (br). Additional signals of low intensity: 13.3 (br), 2.70 (br), 2.48 (br), 2.38 (br). EI MS (120 eV, 180°C): *m/z* (relative intensity) 383 [M$^+$, 90%], 368 ($[(C_5HR_4)CoPMe_3]^+$, 18%), 340 [M$^+$ − C_3H_7, 100%], 297 [M$^+$ − 2C_3H_7, 14%], 325 ($[(C_5HR_3)CoPMe_3]^+$, 12%), 233 ($C_5HR_4^+$, 17%), 191 ($C_5H_2R_3^+$, 54%), 149 ($C_5H_3R_2^+$, 44%), 107 ($C_5H_4R^+$, 46%), 43 (R$^+$, 46%); R = $CHMe_2$.

2.18. *Bis{μ-hydroxy(tetraisopropylcyclopentadienyl)cobalt}* (***12***)

To a solution of 663 mg (1.73 mmol) of **11** in 10 ml of pentane, 30 μl of degassed water were added and the mixture was stirred for 72 h at r.t. The brown solution was separated from a blue precipitate by centrifugation, reduced in volume to ca. 3 ml and stored at −30°C. The microcrystalline product was recrystallized from pentane at −20°C to give 126 mg (0.21 mmol, 12%) of **12**, which decomposes on heating above 125°C. Anal. Calc. for **12** ($C_{34}H_{60}Co_2O_2$; fw = 618.71): C, 66.00; H, 9.77. Found: C, 64.81; H, 9.90. ^{1}H-NMR in C_6D_6, δ: 3.66 (br), 2.31 (br), 1.29 (br), 0.05 (br). Additional signals of low intensity: 2.86 (br), 1.93 (br), 1.72 (br), 0.68 (br), 0.29 (br), −11.3 (br). EI MS (70 eV, 220°C): *m/z* (relative intensity) 636 [M$^+$ + H_2O, 5%], 618 [M$^+$, 36%], 601 [M$^+$ −OH, 39%], 600 [M$^+$ −H_2O, 81%], 368 ($[(C_5HR_4)CoPMe_3]^+$, 18%), 340 [M$^+$ − C_3H_7, 100%], 297 [M$^+$ − 2C_3H_7, 14%], 325 ($[(C_5HR_3)CoPMe_3]^+$, 12%), 233 ($C_5HR_4^+$, 17%), 191 ($C_5H_2R_3^+$, 54%), 149 ($C_5H_3R_2^+$, 44%), 107 ($C_5H_4R^+$, 46%), 43 (R$^+$, 46%); (R = $CHMe_2$).

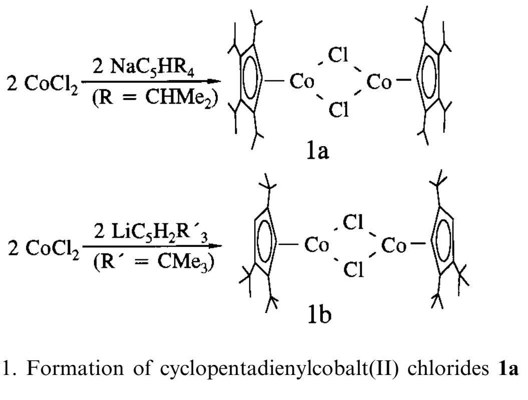
3. Results and discussion

If $CoCl_2$ is reacted with sodium tetraisopropylcyclopentadienide or lithium tri(*tert*-butyl)cyclopentadienide in tetrahydrofuran at low temperature (Scheme 1) a black–brown color indicates formation of the respective cyclopentadienyl cobalt halides, which can be obtained as crystalline, air sensitive solids in good yield.

The tetraisopropylcyclopentadienyl derivative **1a** and the tri(*tert*-butyl)cyclopentadienyl derivative **1b** dissolve well in pentane and diethyl ether and even better in methylene chloride, toluene or acetonitrile.

Proton NMR spectra of **1a** and **1b** show broad signals extending from −0.5 to 11 ppm for **1a** and from −7 to 19 ppm for **1b**. Neither the number of NMR signals nor integral ratios nor the chemical shift permit unambiguous assignment of signals except for the *tert*-butyl groups of **1b**, which give rise to singlets at 9.16 and 6.16 ppm with 93 and 112 Hz half width and an integral ratio of approximately 1:2. These values closely resemble the signals observed by Schneider et al. for the bromo derivative $[\{C_5H_2(CMe_3)_3\}CoBr]_2$ δ = 9.55/6.20 ppm; $\nu_{1/2}$ = 130/95 Hz) [7].

Mass spectra show the molecular ion in 37% (**1a**) or 100% (**1b**) intensity and fragment ions originating from symmetric cleavage of the dimeric unit, metal–ligand



Scheme 1. Formation of cyclopentadienylcobalt(II) chlorides **1a** and **1b**.

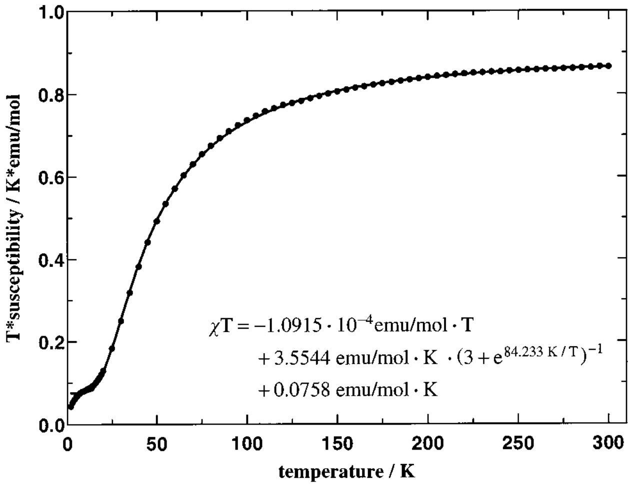


Fig. 1. Product of magnetic susceptibility and absolute temperature of **1a** plotted against temperature [K].

bond cleavage or olefin elimination from the organic ligands (for details see Section 2). Interesting is the occurrence of the $C_{34}H_{58}^{+}$ ion (466 u, 20% relative intensity) in mass spectra of **1a**, probably originating from octaisopropyldihydrofulvalene radical cation, while in mass spectra of **1b** the respective cation (both tetraisopropyl- and tri(*tert*-butyl)-cyclopentadienyl are linkage isomers of $C_{17}H_{29}$) is not detected. The reverse is true outside of the mass spectrometer, where octaisopropyldihydrofulvalene is as yet unknown, while hexa(*tert*-butyl)dihydrofulvalene is an isolable compound [8].

The magnetic susceptibility of **1a** as a function of the absolute temperature reveals an effective magnetic moment of 2.26 μ_B at 300 K and an antiferromagnetic exchange interaction $\Theta = -85.8 \pm 1.6$ K with a Néel temperature of 48 K. The antiferromagnetic coupling in **1a** is much weaker than the -238 cm^{-1} found for $[(C_5Me_5)Co(\mu\text{-}Cl)]_2$ [3] indicating a shorter Co···Co distance and more acute Co–Cl–Co angles in the latter (Cp*) derivative [9]. At very low temperature the product of susceptibility and absolute temperature for **1a** shows an unexpected curvature (Fig. 1) indicating than not all spins present in the probe are coupled antiferromagnetically.

A second sample, which had been recrystallized several times to assure the required purity, displayed the same effect even slightly stronger. The experimental data can be rationalized assuming as much as 22% defect spins ($\rho = 0.22$) following the equation

$$\chi T = \chi_{\mathrm{Dia}}T + (2Ng^2\mu_B^2/k)(3 + e^{-J/kT})^{-1}](1-\rho) + [Ng^2\mu_B^2/2k]\rho$$

given in Ref. [10]. The magnetic behavior of **1a** resembles that of diaquatetra(μ-acetato)dicopper(II) [11]. A possible explanation could be a phase transition at very low temperatures with partial formation of a second phase with much smaller or no antiferromagnetic exchange interaction. Dimeric tetraisopropylcyclopentadienyl cobalt complexes with bridging groups other than chloride ions are currently under investigation in order to obtain more information on magnetic exchange interaction in these systems.

Crystallization of **1a** was most successful with tetraisopropylcyclopentadiene as a solvent. This procedure was discovered adventitiously (see Section 2) and its success is probably based on the viscosity of such solutions. Whereas crystallization in gels is well known [12], deliberate use of oily solvents for that purpose is much less common. We are currently exploring other viscous media like paraffins or toluene solutions of polystyrene as solvents. The crystal structure of **1a** (Fig.

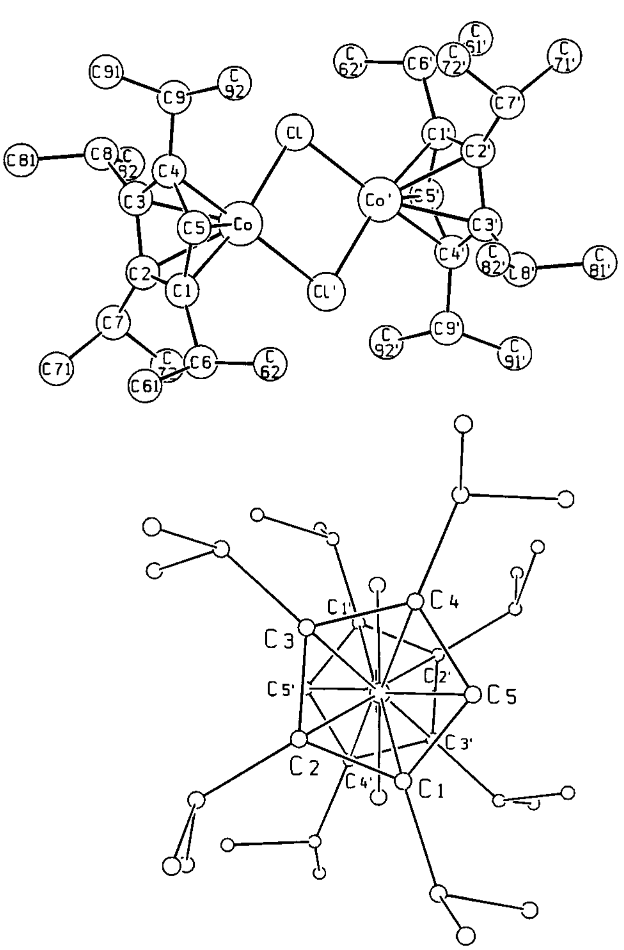
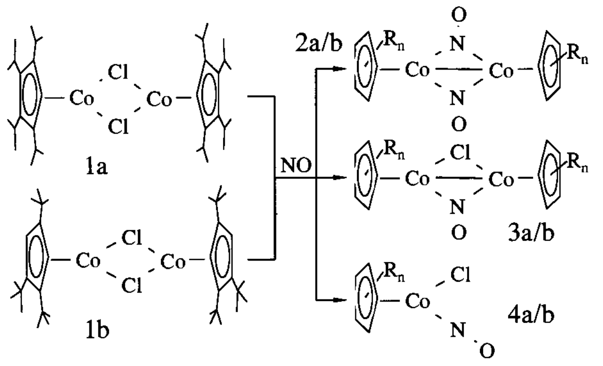


Fig. 2. Molecular structure and numbering scheme for **1a**. Hydrogen atoms have been omitted for clarity. Selected bond distances (Å) and angles (°) for dimer **1a**: Co···Co 3.183(2), Co–Cl 2.232(2), Co–Cl′ 2.225(2), Co–C1 2.060(4), Co–C3 2.067(4), Co–C4 2.038(4), Co–C5 2.080(4), Co-ring plane 1.678, ring C–C from 1.396(5) to 1.446(5), mean value 1.422; Cl–Co–Cl 88.84(6), Co–Cl–Co 91.16(6).



Scheme 2. Reaction of dimers **1a** and **1b** with nitric oxide.

2, Table 1) shows the dimeric unit on a center of symmetry with a nearly square–planar Co_2Cl_2 ring, Co–Cl distances of 2.232(2) and 2.225(2) Å, and a non-bonding Co–Co distance of 3.183(2) Å. With respect to the parallel five-membered rings, the chloride bridges are not close to the only ring CH moiety as could be expected for steric reasons. Instead, the isopropyl neighbors at ring C3 and C4 are rotated away from each other in order to accommodate the chloride ligand. So each of the two chloride bridges is repelled by two gear-meshed isopropyl groups of one ring and is accommodated between two isopropyl groups of the other ring, which are rotated away from each other. The molecular structure of **1a** differs from $[(C_5Me_5)Co(\mu\text{-}Br)]_2$, which according to a preliminary crystal structure determination displays a fold angle of 123° between the two Co_2Br planes and a significantly shorter Co–Co bond length of 2.77 Å [3c]. The less symmetric butterfly complex $[(C_5Me_5)Co\mu\text{-}Cl)(\mu\text{-}NMe_2)Co(C_5Me_5)]$ shows a short Co–Co bond length of 2.49 Å (0.71 Å shorter than the Co–Co distance found in **1a**) and a fold angle of 117° between the Co–N–Co and the Co–Cl–Co planes [3c].

Addition of nitric oxide to solutions of in situ generated **1a** or **1b** at low temperature quickly converts the starting compounds to a mixture of NO addition and Co(II) → Co(I) redox products (Scheme 2). Chromatographic separation gives the dinuclear nitrosyl complexes $[(C_5HR_4)Co(\mu\text{-}NO)]_2$ (**2a**, R = $CHMe_2$) or $[(C_5H_2R_3)Co(\mu\text{-}NO)]_2$ (**2b**, R = CMe_3), the unsymmetric substitution products $[(C_5HR_4)Co(\mu\text{-}NO)(\mu\text{-}Cl)Co(C_5HR_4)]$ (**3a**, R = $CHMe_2$) or $[(C_5H_2R_3)Co(\mu\text{-}NO)(\mu\text{-}Cl)Co(C_5H_2R_3)]$ (**3b**, R = CMe_3) and the mononuclear NO addition products $[(C_5HR_4)Co(NO)Cl]$ (**4a**, R = $CHMe_2$) or $[(C_5H_2R_3)Co(NO)Cl]$ (**4b**, R = CMe_3) in poor to moderate yields.

If isolated **1a** is used instead of generating **1a** in solution, the reaction is much more selective and produces the half-sandwich compound **4a** in more than 50% yield. The procedure is a fast one-pot reaction and does not require the use of carbonyl complex precursors, which is the most common synthetic approach to cyclopentadienyl nitrosyl complexes [13].

Solution IR spectra of complexes **2**–**4** show two absorptions in the region typical for nitrosyl bridges for each of the dinitrosyl complexes corresponding to the symmetric and antisymmetric NO bond stretch vibration, one absorption at 1501 cm^{-1} for **3a** and at 1492 cm^{-1} for **3b** (NO bridge) and one absorption in the region typical for terminal nitrosyl ligands for **4a** (1807 cm^{-1}) and **4b** (1810 cm^{-1}, see Section 2).

Black crystals of **3b** suitable for X-ray diffraction (Table 1) were grown from concentrated toluene/tetraisopropylcyclopentadiene solution. The structure shows disorder of chloro and nitrosyl bridges, which are found both in each of two bridging positions with 50% probability. In Fig. 3 this feature has been omitted

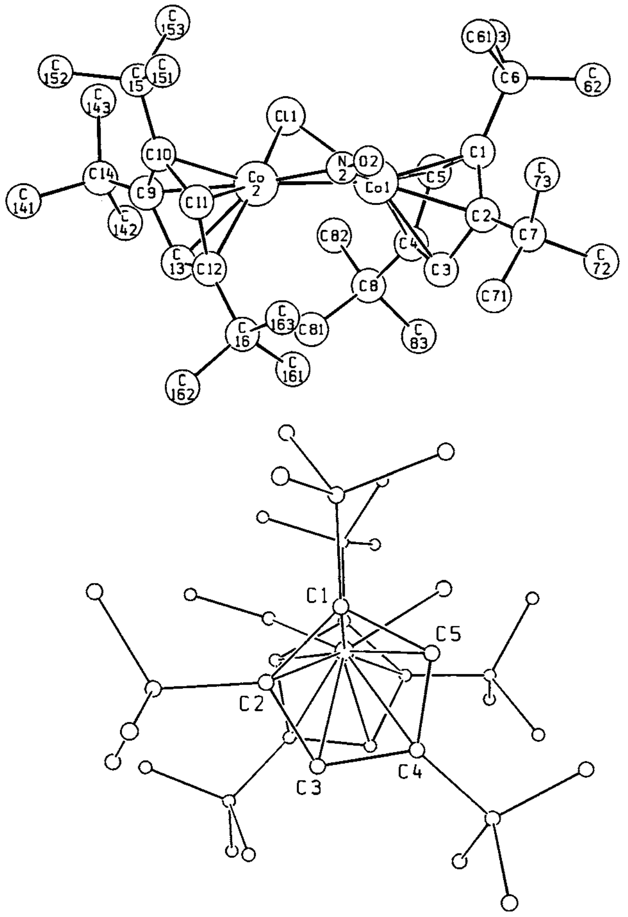
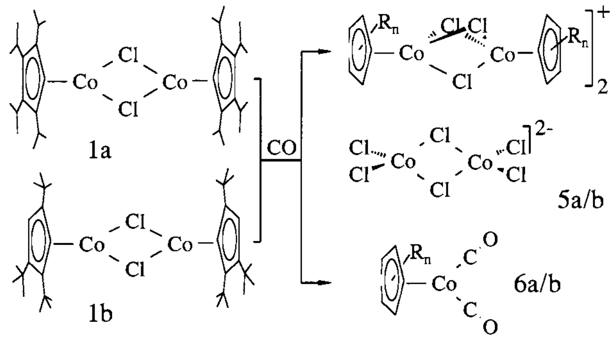


Fig. 3. Molecular structure and numbering scheme for **3b**. Hydrogen atoms have been omitted for clarity. Selected bond distances (Å) and angles (°) for complex **3b**: Co1–Co2 2.4997(12), Co1–Cl1 2.236(2), Co2–Cl1 2.242(2), Co1–N2 1.783(6), Co2–N2 1.776(5), N2–O2 1.278(6), Co1-ring C distance range 2.074(2)–2.117(2), mean value 2.102, distance Co1-ring plane 1.713, Co2-ring C distance range 2.068(2)–2.125(2), mean value 1.432; N2–Co1–Cl1 86.7(2), N2–Co2–Cl1 86.7(2), Co1–N2–Co2 89.2(3), Co1–Cl1–Co2 67.87(6), interplanar angle between planes defined by Co1–Co2–N2 and Co1–Co2–Cl1 124.5, between Cp ring planes 140.9.

Table 1
Crystal data and summary of X-ray data collection for complexes **1a**, **3b**, **5a**, **7a**, **7b**, **8**, **10** and **12** [a]

Complex number	**1a**	**3b**	**5a**	**7a**	**7b**	**8**	**10**	**12**
Empirical formula	$C_{34}H_{58}Cl_2Co_2$	$C_{34}H_{58}ClCo_2NO$	$C_{70}H_{120}Cl_{14}Co_6$	$C_{36}H_{58}Co_2O_2$	$C_{36}H_{58}Co_2O_2$	$C_{21}H_{35}CoF_6N_2P$	$C_{20}H_{38}ClCoP$	$C_{34}H_{60}Co_2O_2$
Formula weight (g mol^{-1})	655.606	650.160	1811.660	640.722	640.722	521.420	403.881	618.716
Crystal size (mm)	0.3 × 0.2 × 0.1	0.5 × 0.4 × 0.4	0.70 × 0.40 × 0.22	0.3 × 0.2 × 0.2	0.65 × 0.3 × 0.25	0.5 × 0.5 × 0.4	0.8 × 0.15 × 0.15	0.6 × 0.4 × 0.4
Space group	$C2/c$ (No. 15)	$P1$ (No. 2) quer	$P2_1/m$ (No. 11)	$P2_1/m$ (No. 11)	$P2_1$ (No. 4)	$Pbca$ (No. 61)	$P2_1/c$ (No. 14)	$C2/c$ (No. 15)
Unit cell dimensions								
a (Å)	18.907(7)	9.833(2)	20.793(2)	11.310(1)	10.4833(8)	15.982(3)	14.796(3)	19.020(2)
b (Å)	17.775(6)	11.303(2)	9.619(1)	8.611(1)	14.5754(8)	17.460(4)	8.436(2)	17.737(3)
c (Å)	11.446(4)	17.038(3)	21.936(2)	18.739(1)	11.4943(9)	17.653(4)	18.118(5)	11.380(1)
α (°)	90	71.28(3)	90	90	90	90	90	90
β (°)	115.88(3)	87.88(3)	94.21(1)	106.91(1)	93.464(8)	90	94.00(1)	115.75(1)
γ (°)	90	73.61(3)	90	90	90	90	90	90
V (Å^3)		1717.6(6)	4375.6(7)	1746.1(3)	1753.1(2)	4926(2)	2256.0(9)	3457.9(8)
Z	4	4	4	2	4	8	4	4
Temperature (K)	293(2)	183(2)	293(2)	293(2)	293(2)	153(2)	183(2)	293(2)
$D_{calc.}$ (g cm^{-3})	1.258	1.257	1.429	1.219	1.214	1.401	1.189	1.188
μ (cm^{-1})	10.60	10.69	16.36	9.78	9.74	8.17	9.49	9.85
Transmission factors	0.903–1.000	0.62–0.67	0.27–0.49		0.523–0.772	0.2361–0.2608	0.507–0.612	0.428–0.483
Theta limits (°)	1.66–27.46	2.16–30.00	3.03–30.47	2.47–30.00	2.71–25.49	4.16–22.55	2.25–25.00	2.30–30.00
Total reflections	4220	11 798	31 959	6459	15 504	4446	5116	5713
Unique reflections	3963	9809	12 402	5061	6411	3214	3968	4988
Structure solution	Direct methods	Direct methods	Direct methods	Direct methods	Direct methods	Direct methods	Direct methods	Direct methods
Program used	SHELXS-97	SHELXL-97	SHELXTL	SHELXTL	SHELXS-97	SHELXTL	SHELXTL	SHELXTL
Refinement	SHELXL-97	SHELXL-97	SHELXTL	SHELXTL	SHELXL-97	SHELXTL	SHELXTL	SHELXTL
Data/restraints/parameters	3963/0/180	9808/0/397	12400/0/431		6411/176/379	3211/0/296	3968/0/219	4988/1/183
R_1, wR_2 [$I > 2\sigma(I)$]	0.0606, 0.1389	0.0426, 0.0878	0.0432, 0.1116	0.053, 0.099	0.0433, 0.1061	0.0410, 0.0868	0.0385, 0.0725	0.0406, 0.0891
R_1, wR_2 (all data)	0.1266, 0.1497	0.0764, 0.0986	0.0620, 0.1296	0.112, 0.121	0.0642, 0.1160	0.0642, 0.1516	0.0698, 0.0841	0.0731, 0.1039
GOF (all data)	1.220	1.035	1.036	1.008	0.942	1.048	1.015	1.018
Max./min. difference peak (e Å^{-3})	0.775, −0.656	0.430, −0.354	0.453, −0.484	0.484, −0.327	0.565, −0.453	0.478, −0.234	0.259, −0.259	0.348, −0.294

[a] For all crystal structure determinations Mo–K_α radiation ($\lambda = 0.71073$ Å) was used.



Scheme 3. Disproportionation of dimers **1a** and **1b** with carbon monoxide.

for clarity. The Co–Co bond length of 2.500(2) Å corresponds to the metal–metal single bond required to fulfill the 18 valence electron rule for a cyclopentadienyl cobalt dimer with two bridging three electron donor ligands.

Solutions of **1a** or **1b** react with an excess of carbon monoxide under disproportionation to a complex salt **5a** or **5b** and the mononuclear dicarbonyl cyclopentadienyl complex **6a** or **6b** (Scheme 3).

If the reaction is carried out in pentane, the salt precipitates as a green powder and the black solution turns brown. The green salt of analytical composition $C_{70}H_{120}Cl_{16}Co_6$ consists of $[(C_{17}H_{29})_2Co_2(\mu\text{-}Cl)_3]^+$ cations, $[Co_2(\mu\text{-}Cl)_2Cl_2]^{2-}$ anions and contains two molecules of methylene chloride per formula unit after recrystallization from this solvent. Analogous cations with pentamethyl– or ethyltetramethyl–cyclopentadienyl ligands are well known and have been obtained by oxidation of $[(C_5Me_5)CoCl]_2$ [14] or $[(C_5Me_4Et)CoCl]_2$ [15] with $FeCl_3$ in aqueous solution or from the radical anion $[(C_5Me_4Et)Co(\mu\text{-}CO)]_2^-$ and Me_2GeCl_2 [16]. The $[Co_2Cl_6]^{2-}$ dianion has been discussed by Dahl [16]. NMR spectra show the expected signals for the ring protons and alkyl groups of both **5a** and **5b** with only the methine septets of **5a** being strongly affected by signal broadening due to the influence of the paramagnetic counterion. The molecular structure of **5a** has been determined by X-ray crystallography and shows a cation without crystallographic symmetry (Fig. 4(a), Table 1).

The Co···Co distance of 2.9483(5) Å is non-bonding and slightly longer than in $[\{(C_5Me_5)Co\}_2(\mu\text{-}Cl)_3]^+$ (2.914(2) Å) [16] or $[\{(C_5Me_4Et)Co\}_2(\mu\text{-}Cl)_3]^+$ (2.887(2) Å) [15]. This is in agreement with both Co atoms having a formal electron count of 18 valence electrons. While the symmetry of the central Co_2Cl_3 moiety is close to C_{3v} with Co–Cl–Co angles of 79.13(2), 78.50(2), and 79.50(2)° for Cl1-3, the tetraisopropylcyclopentadienyl ligands are inclined by 2.7° towards each other and deviate by a 6.8° torsion about the Co_2 axis from an ecliptic conformation. All Co–C bonds are within a small range from 2.049(2)–2.094 Å (the mean value of 2.068 Å is even slightly shorter than the 2.077 Å found for the pentamethylcyclopentadienyl derivative $[\{(C_5Me_5)Co\}_2(\mu\text{-}Cl)_3]^+$ [16]) and the Co–ring center distance is 1.665 Å for Co1 and 1.667 Å for Co2. The anion (Fig. 4(b)) displays a non-bonding Co···Co distance of 3.182(1) Å. This is unexpectedly short compared to 3.277(6) Å in the $[Co\{N_6P_6(NMe_2)_{12}\}Cl]^+$ salt [17] or even 3.366(3) Å in the $[Co_2(C_5Me_5)_2(\mu\text{-}Cl)_3]^+$ salt of the same anion [16]. The significant difference, especially for the two $Co_2Cl_6^{2-}$ salts with trichlorobis(alkylcyclopentadienyl)dicobalt(III) cations, indicates a strong impact of crystal packing forces on the geometry of the four-membered Co_2Cl_2 ring and evokes an impression of the core of this anion readily undergoing distortion along the Co···Co direction.

Most dicarbonyl(cyclopentadienyl)cobalt derivatives have been synthesized from dicobalt octacarbonyl using cyclopentadiene or substituted cyclopentadiene derivatives in the presence of a hydride acceptor as a source for the cyclopentadienyl ligand. This method has been shown to work very cleanly also for dicarbonyl(tetraisopropylcyclopentadienyl)cobalt, which was used subsequently to generate $[\{(C_5H_2R_3)Co\}_3P_8]$ and $[\{(C_5H_2R_3)Co\}_3P_{12}]$ $(R = CMe_3)$ [18]. The dicarbonyl complexes **6a** and **6b** generated in a one-pot reaction from cobalt(II) chloride, sodium tetraisopropylcyclopentadienide, and carbon monoxide could be isolated only as oily mixtures with the respective cyclopentadiene, which cannot be easily separated. These mixtures are suitable for further reactions, however, and have been converted to the corresponding dinuclear species $[(C_5HR_4)Co(\mu\text{-}CO]_2(Co{=}Co)$ (**7a**, $R = CHMe_2$) and $[(C_5H_2R_3)Co(\mu\text{-}CO]_2(Co{=}Co)$ (**7b**, $R = CMe_3$) by UV irradiation of **6a** or **6b** in a quartz apparatus. Compounds **7a** and **7b** could be isolated as thermally stable, emerald-green crystals (Scheme 4).

Mass spectra show a strong signal for the molecular ion (100% intensity for **7a** and 75% for **7b**) as well as the symmetric cleavage product with 12% (**7a**) and 10% intensity (**7b**) as well as a small signal for the corresponding cobaltocenium cations $[Co(C_{17}H_{29})_2]^+$, which are obviously generated in the mass spectrometer [19]. IR spectra of compounds **7a** and **7b** exhibit only one absorption for the asymmetric CO bond stretch indicating an angle close to linearity between the two CO vectors [20]. The observed IR signals reflect the well known trend to lower wavenumbers for higher degrees of cyclopentadienyl ring alkylation. ^1H-NMR spectra show the typical, well resolved 1:2:2:6:6:6:6 signal pattern for one ring proton, two sets of two symmetry-related methine protons, and four pairwise diastereotopic sets, each consisting of two symmetry-equivalent methyl groups for the tetraisopropylcyclopentadienyl ligand of **7a** or the 2:9:18 pattern for two ring protons and three *tert*-butyl groups of the 1,2,4-tri(*tert*-butyl)cyclopentadienyl ligand of **7b**. Both compounds were subjected to X-ray diffraction [21] (Figs. 5 and 6, Table 1).

The tetraisopropylcyclopentadienyl derivative **7a** is centrosymmetric implying a planar Co_2C_2 unit and parallel five-membered rings. The bridging carbonyl ligands show slightly different Co–C distances, the difference being approximately equal to the two-fold standard deviation (Co1–C6′ = 1.855(3) Å and Co1′–C6′ = 1.868(3) Å) and seemingly counterintuitive in so far as the shorter Co–C bond connects C6′ to the site of greater steric hindrance. The respective isopropyl groups are turned away from each other so as to accommodate the carbonyl ligand in between. Since the corresponding ring atoms are staggered with respect to the carbonyl C atom, this conformation provides at least as much space as the ring CH moiety on the other side, which is located in an ecliptic position. The Co–Co bond length of 2.3385(8) Å is in good agreement with the double-bond character required to fulfil the 18-electron rule for **7a** and with the value of 2.327(2) Å found for the pentamethylcyclopentadienyl derivative [22]. For **7b** the metal–metal bond is very similar (2.3538(6) Å) and the fold angle of the four-membered Co_2C_2 ring along the Co–Co axis is 169.7°. It is not inter-ring interactions, but the necessity to find a gap for each of two carbonyl bridges that dictates the staggered conformation of the two tri(*tert*-butyl)cyclopentadienyl rings (Fig. 6). Interesting is a comparison with the octaisopropyl- and hexa(*tert*-butyl)-substituted cyclopentadienyl(μ-carbonyl)nickel dimers, which are almost superimposable on **7a** and **7b** except for their Ni–Ni single bonds being about 2%

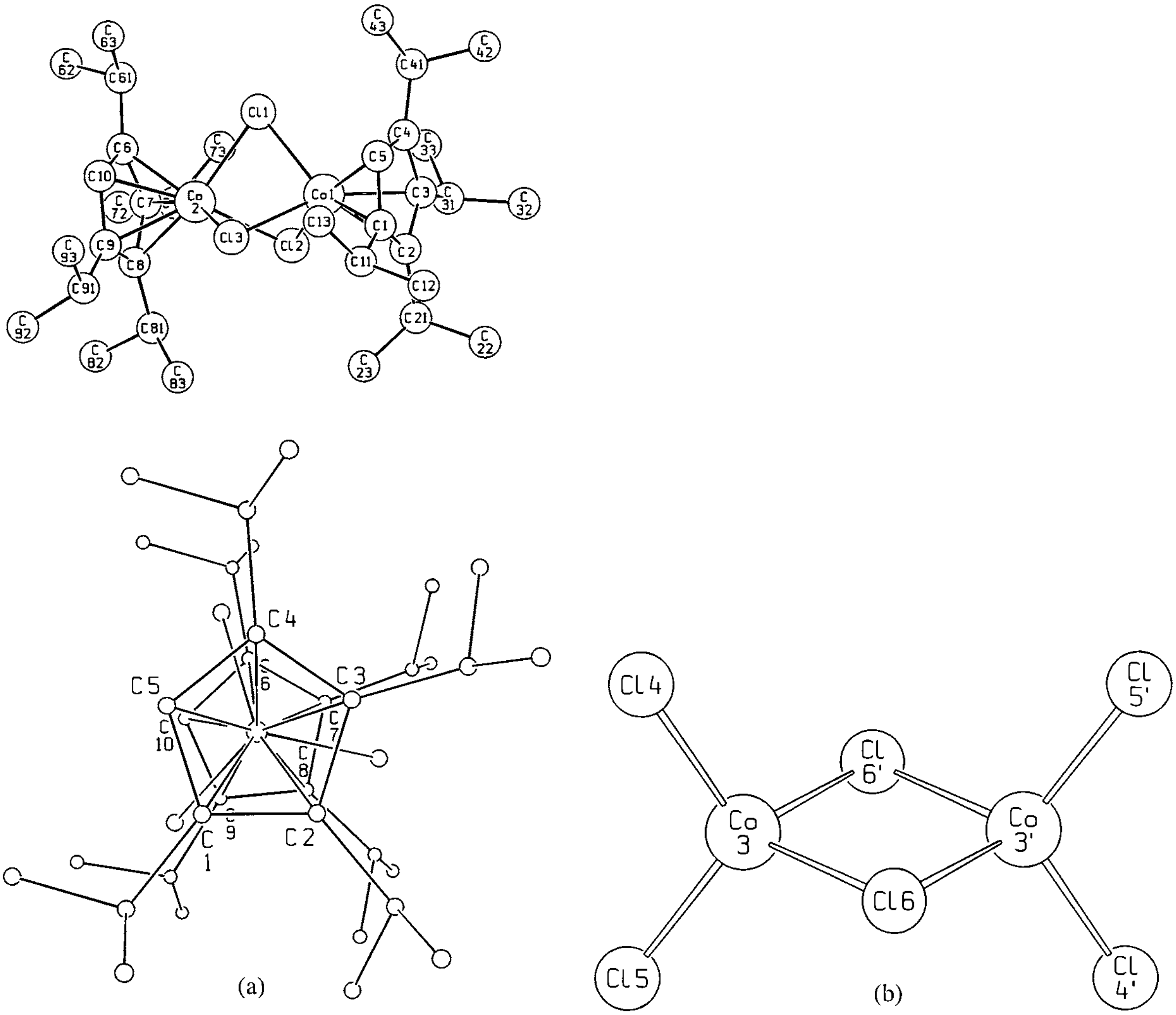
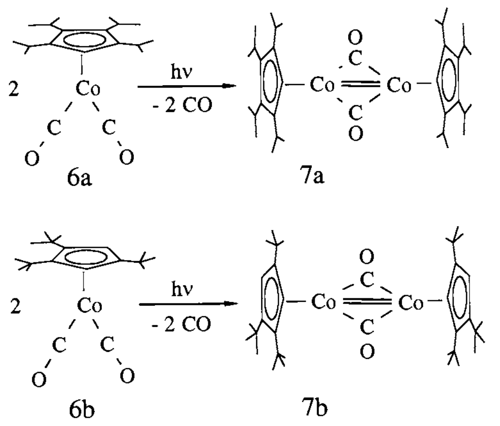


Fig. 4. (a) Molecular structure and numbering scheme for the cation of **5a**. Hydrogen atoms have been omitted for clarity. Selected bond distances (Å) and angles (°) for the cation of **5a**: Co···Co 2.9483(5), Co–Cl range from 2.2900(7) to 2.3326(7), mean value 2.3165, Co–C range from 2.049(2) to 2.094(2), mean value 2.068, ring C–C from 1.424(3) to 1.479(4), mean value 1.441, Cl–Co–Cl from 83.49(3) to 84.60(3), mean value 83.83, Cp_{cent}–Co1 1.665. Cp_{cent}–Co2 1.667; Co–Cl–Co 79.13(2) (Cl1), 78.50(2) (Cl2), 79.50(2) (Cl3), angle between ring planes 2.7. (b) Molecular structure and numbering scheme for the hexachlorodicobaltate anion of **5a**. Selected bond distances (Å) and angles (°) for the anion of **5a**: Co3···Cl5 2.225(1), Co3–Cl6 2.340(1), Co3–Cl6′ 2.341(1); Co3–Cl6–Co3′ 85.71(3), Cl6–Co3–Cl6′ 94.29(3), Cl4–Co3–Cl5 113.78(4), Cl4–Co3–Cl6 110.67(4), Cl5–Co3–Cl6 112.93(4), Cl4–Co3–Cl6′ 111.71(4), Cl5–Co3–Cl6′ 111.93.



Scheme 4. Irradiation of mononuclear carbonyl complexes **6a** and **6b**.

longer than the Co=Co double bonds and the bend angle of the central dicarbonyl dinickel core of $[\{C_5H_2(CMe_3)_3\text{-}1,2,4\}Ni(\mu\text{-}CO)]_2$ being more acute by almost 12° (157.9°) [23].

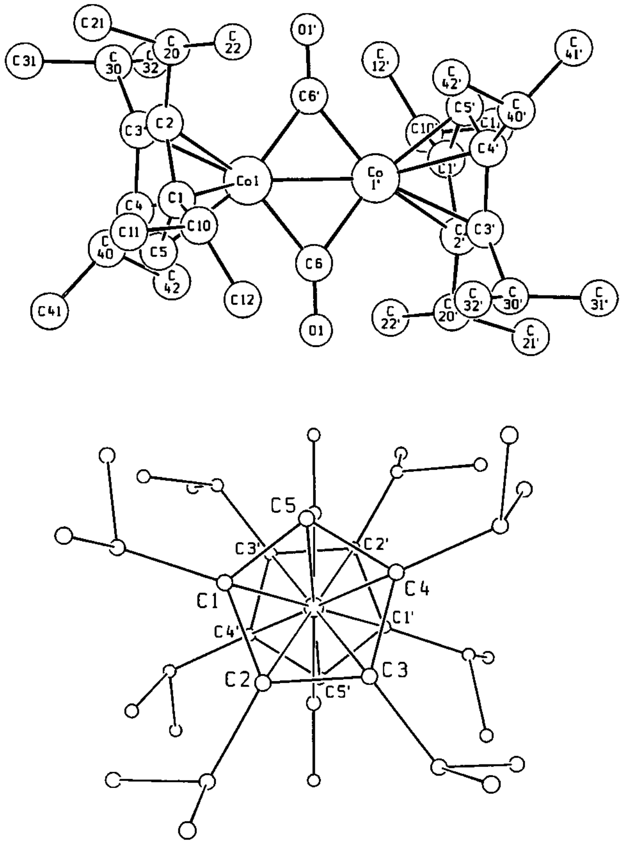


Fig. 5. Molecular structure and numbering scheme for dimer **7a**. Hydrogen atoms have been omitted for clarity. Selected bond distances (Å) and angles (°) for dimer **7a**: Co–Co 2.3385(8), Co1–C1 2.076(3), Co1–C2 2.091(3), Co1–C3 2.106(3), Co1–C4 2.110(3), Co1–C5 2.071(3), Co1–Cp_{cent} 1.701, Co1–C6 1.868(3), Co1–C6′ 1.855(3), C6–O1 1.182(4), ring C–C from 1.414(4) to 1.446(4); Co1–C6–Co1′ 77.82(12), C6–Co1–C6′ 102.18(12), Co1–C6–O1 141.3(3), Co1′–C6–O1 140.9.

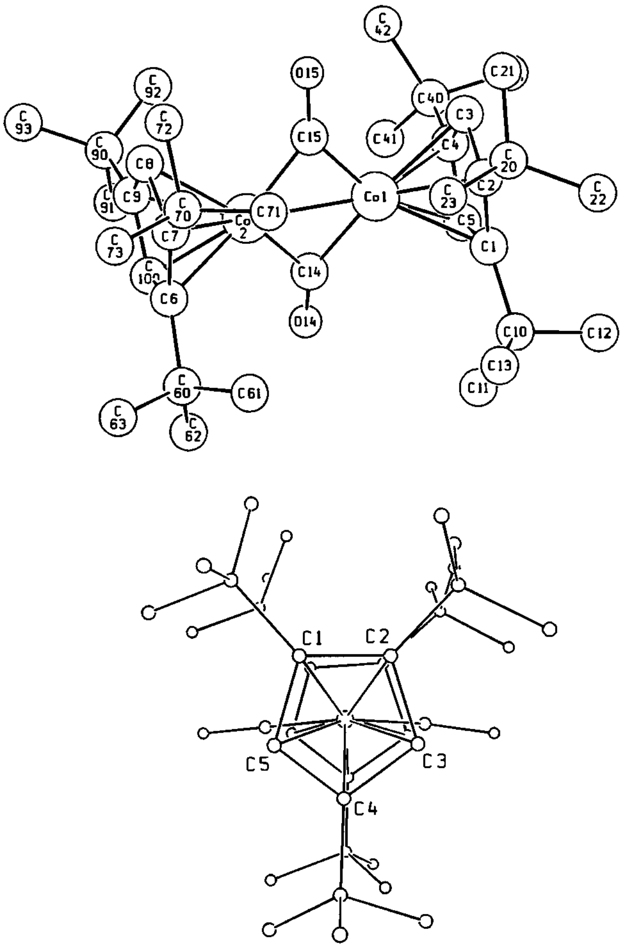
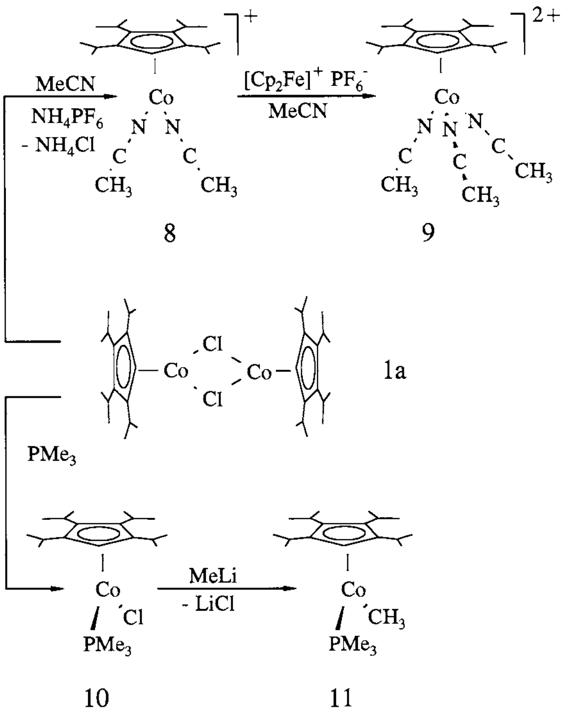


Fig. 6. Molecular structure and numbering scheme for dimer **7b**. Hydrogen atoms have been omitted for clarity. Selected bond distances (Å) and angles (°) for dimer **7b**: Co1–Co2 2.3538(6), Co1–C1 2.129(11), Co1–C2 2.118(9), Co1–C3 2.095 (11), Co1–C4 2.101(3), Co1–C5 2.075(11), Co1–Cp_{cent} 1.717, Co2–Cp_{cent} 1.711, Co1–C14 1.907(12), Co1–C15 1.798(13), C14–O14 1.108(14), C15–O15 1.281(16), ring C–C from 1.376(15) to 1.456(15); Co1–C14–Co2 76.5(5), Co1–C15–Co2 81.1(7), C14–Co1–C15 100.8(2), C14–Co2–C15 100.5(2), Co1–C14–O14 141.3(9), Co2–C14–O14 142.1(9), Co1–C15–O15 140.8(9), Co2–C14–O14 138.1(8), angle between ring planes 1.3.

With cleavage of the chloro bridges, **1a** adds acetonitrile to form the 17-valence-electron cation $[(C_5HR_4)Co(NCMe)_2]^+$ ($R = CHMe_2$), which could be isolated as hexafluorophosphate **8** (Scheme 5).

IR spectra show two weak absorptions at 2360 and 2341 cm^{-1} comparable to those of the 18 valence electron tris(acetonitrile)cobalt(III) complex $[(C_5Me_4\text{-}Et)Co(NCMe)_3]^{2+}[PF_6^-]_2$ (2330, 2305 cm^{-1}) [24]. Proton NMR spectra show some broadening but still allow $^3J_{HH}$ coupling constants to be observed (see Section 2).

The EPR spectrum of solid **8** (Fig. 7) at 4 K shows a strong signal with $g_x = 2.083$, $g_y = 1.990$, $g_z = 2.281$, and a medium value $<g>$ [25] of 2.121. The uncommon observation of missing ^{59}Co coupling has also been noted for $[(C_5H_5)Co(CO)\{P(C_6H_{11})_3\}]^+PF_6^-$ [26].



Scheme 5. Cleavage of dimer **1a** with donor ligands.

Cyclovoltammetry in acetonitrile/$(n\text{-Bu})_4N^+PF_6^-$ gave a reversible oxidation wave at -0.35 V versus ferrocene/ferrocenium and an irreversible reduction at -1.64 V (Fig. 8).

In dichloromethane solution, the respective redox processes occur at $+0.11$ and -1.71 V and are both irreversible. Oxidation of **8** can be assumed to yield the unstable dication $[(C_5HR_4)Co(NCMe)_2]^{2+}$, which coordinates one additional donor ligand in acetonitrile solution or decomposes in the absence of such stabilization. While tris(acetonitrile)cyclopentadienyl cobalt(III) dications are well known [24,27], stable 17-valence-electron cations of type **8** have not been found before. Electrochemical reduction of $[(C_5H_5)Co(NCMe)_3]^{2+}(ClO_4^-)_2$, for example, does not result in formation of the unsubstituted derivative of **8**, but leads to dismutation and redox reactions instead [28]. The remarkable stabilization of the 17-valence-electron complex **8** could therefore result from the prevention of dismutation by sterically demanding tetraisopropylcyclopentadienyl. A similar effect allowed the cyclopentadienyliron(II)halides $[(C_5R_4R')Fe(\mu\text{-}Br)]$ ($R = CHMe_2$, $R' = H$, $CHMe_2$) to be isolated as the first derivatives of this class of iron complexes, because the dismutation with formation of ferrocene and iron(II)halide could be blocked using tetra- or pentaisopropylcyclopentadienyl ligands [1]. The X-ray crystal structure of **8** (Table 1) proves the expected half-sandwich geometry as shown in Fig. 9.

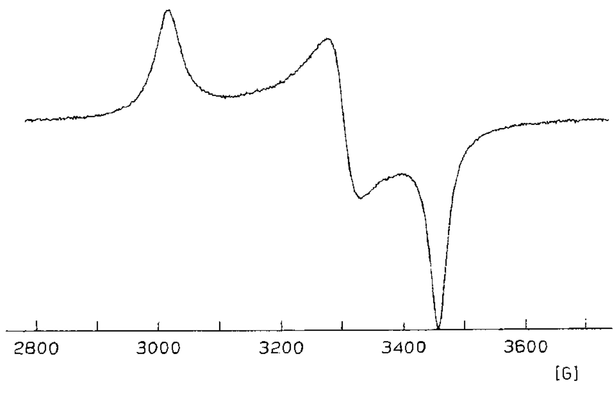


Fig. 7. EPR spectrum of salt **8** as a solid at 4 K.

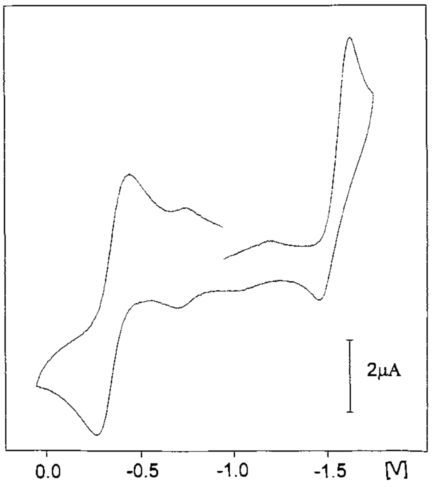


Fig. 8. Cyclic voltammogram of **8** in acetonitrile. Criteria for reversibility are $\delta(E) \approx 60$ mV for reduction and oxidation wave and $i(a)/i(c) \approx 1.0$. The scan rate was 100 mV s^{-1} and the sample concentration ca. 1 mM. 0.1 mol l^{-1} tetrabutylammonium hexafluorophosphate was used as supporting electrolyte and ferrocene/ferrocenium served as external reference.

The Co–N and Co–C bond distances of 1.911 and 2.084 Å (average values for **8**) compare very well with those found for the pyridine complex $[(C_5Me_5)Co(C_5H_5N)Cl]$ (1.917(2) and 2.076 Å) and the N–Co–X angles of 93.65(13)° for **8** (X = N) and 94.36(5)° for $[(C_5Me_5)Co(C_5H_5N)Cl]$ (X = Cl) are in good agreement [29]. The isopropyl groups attached to ring atoms C3 and C4 are turned away from each other and allow a somewhat closer approach of one acetonitrile ligand (N50–C50–C51) towards the ring plane with the angle between the ring plane and the C–N vector being 44.6° for N50–C50 and 49.2° for N60–C60. Steric congestion does not play a significant role, however, since the conformation of **8** is obviously not designed to use the space provided by the only ring CH moiety to accommodate one of the acetonitrile ligands. Comparison with neutral 17-valence-electron cyclopentadienyl iron dicarbonyl fragments shows that the tetraisopropylcyclopentadienyl [30] and even the pentaphenylcyclopentadienyl derivative of these two-legged 'piano stool' complexes are not overcrowded and still able to dimerize [31] and that the unbroken bulk of the pentaisopropylcyclopentadienyl derivative is necessary to prevent the $[(C_5R_5)Fe(CO)_2]^•$ radical from dimerization in solution [1].

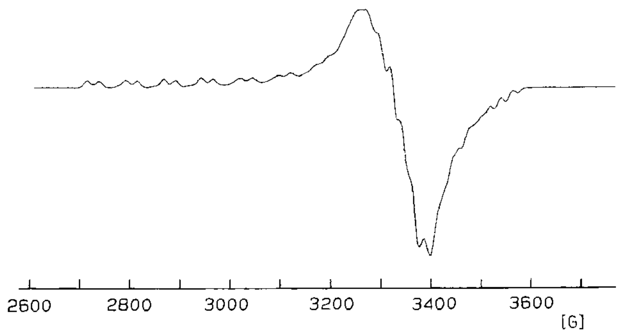


Fig. 10. EPR spectrum of phosphane complex **10** in toluene glass at 3.4 K.

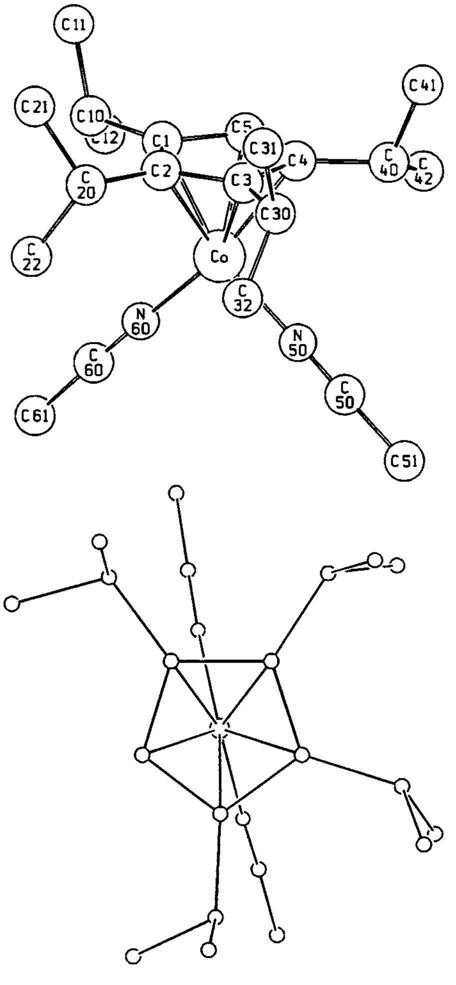


Fig. 9. Molecular structure and numbering scheme for the cation of **8**. Hydrogen atoms have been omitted for clarity. Selected bond distances (Å) and angles (°) for the cation of **8**: Co–N50 1.912(3), Co–N60 1.910(3), Co–C1 2.07193), Co–C2 2.112(3), Co–C3 2.092(3) Co–C4 2.058(3), Co1–C5 2.086(4), Co–Cp_{cent} 1.690, N50–C50 1.139(3), N60–C60 1.143(4), C50–C51 1.450(6), C60–C61 1.451(6), ring C–C from 1.408(5) to 1.466(5), medium value 1.430; N50–Co–N60 93.65(13), N50–C50–C51 179.3(4), N60–C60–N61 179.0(4).

As suggested by the electrochemical investigation, chemical oxidation of **8** with ferrocenium hexafluorophosphate in acetonitrile affords the corresponding tris(acetonitrile) dication $[(C_5HR_4)Co(NCMe)_3]^{2+}$ as red–violet hexafluorophosphate **9** in high yield. As has been observed for $[(C_5Me_4Et)Co(NCMe)_3]^{2+}$ [24], ^{1}H-NMR spectra of **9** show exchange of coordinated CH_3CN with the solvent CD_3CN, which in the case of **9** took about two days at r.t. to reach equilibrium. ^{13}C-NMR spectra show a broad signal at 119.6 ppm and a septet at 1.3 ppm with $^1J_{CD} = 20$ Hz for free CD_3CN and signals at 134.3 and 4.2 ppm ($^1J_{CD} = 20$ Hz) for coordinated CD_3CN. Compound **9** is also formed by disproportionation of **8** during its reaction with carbon monoxide:

$$2[(C_5HR_4)\underset{\mathbf{8}}{C}o(NCMe)_2]^+$$
$$+\ 2Co \xrightarrow[-\ MeCn]{CH_2Cl_2} [(C_5HR_4)\underset{\mathbf{6a}}{C}o(CO)_2]$$
$$+\ [(C_5HR_4)\underset{\mathbf{9}}{C}o(NCMe)_3]^{2+}$$

The products have been identified by IR (**6a**) and ^{1}H-NMR spectroscopy (**9**).

In 1986 Koelle et al. reacted $[(C_5Me_5)CoX]_2$ with phosphanes and isolated the 17-valence-electron radicals $[(C_5Me_5)CoX(PMe_2R]$ (X = Cl: R = Me, Ph; X = Br: R = Ph), which were characterized by elemental analysis, EPR spectroscopy and mass spectrometry [3c]. Similarly, **1a** adds trimethylphosphane with cleavage of the chloro bridges to form the tetraisopropylcyclopentadienyl derivative $[(C_5HR_4)CoCl(PMe_3)]$ (**10**). Mass spectra show the molecular ion with 100% intensity and a remarkably strong signal at $m/e = 654$ for $(\mathbf{1a})^+$ formed in the mass spectrometer as well as signals for the Co-containing fragments $M^+ - Cl$ (18%) and $M^+ - PMe_3$ (70%). The EPR spectrum of **10** in toluene glass at 4 K is well resolved with couplings a_1 (^{59}Co) = 76.2, a_2 (^{59}Co) = 21.3, and a_3 (^{59}Co) = 24.5 G to one ^{59}Co nucleus ($I = 7/2$). The hyperfine coupling to ^{31}P is 23.3 G (Fig. 10).

The components of the anisotropic g tensor are in good agreement with those of $[(C_5Me_5)CoCl(PMe_3)]$, $[(C_5Me_5)CoCl(py)]$ [3a], and **8** Table 2. The molecular

Table 2
EPR data for some 17-valence-electron cobalt(II) complexes, including **8** and **10**

	Conditions		g Factors					
Complex (R = CHMe$_2$)	Temperature [K]	Solvent	g_z	g_y	g	$<g>$	Δg	Ref.
[(C$_5$HR$_4$)Co(PMe$_3$)Cl] (**10**)	4	Toluene	2.296	1.970	2.066	2.115	0.326	
[(C$_5$Me$_5$)Co(PMe$_3$)Cl]	54	THF	2.290	1.970	2.060	2.110	0.320	[3c]
[(C$_5$HR$_4$)Co(NCMe)$_2$]$^+$PF$_6^-$ (**8**)	4	(Solid)	2.281	1.990	2.083	2.121	0.291	
[(C$_5$Me$_5$)Co(pyridine)Cl]	77	Toluene	2.290	1.970	2.079	2.117	0.320	[3c]

structure of half-sandwich **10** is shown in Fig. 11 (for details on the structure solution see Table 1).

The Co–Cl bond distance of 2.2018(10) Å is rather short, compared with [(C$_5$Me$_5$)CoCl(py)] (2.223(1) Å) [29] or [(C$_5$Me$_4$Et)CoCl$_2$(PPh$_3$)] (2.263(2) and 2.288(2) Å); the same holds for the Co–P distance of 2.2070(9) Å in **10**, compared with [(C$_5$Me$_4$Et)CoCl$_2$(PPh$_3$)] (Co–P = 2.289(2) Å) or [(C$_5$Me$_5$)Co(PEt$_3$)$_2$]$^+$ [32]. The P–Co–Cl angle is 90.37(4)° and the plane defined by these three atoms intersects the least-squares plane of the cyclopentadienyl ring at an angle of 87.60°. In contrast to the acetonitrile ligands of **8**, the trimethylphosphane for obvious steric reasons chooses the substitution gap of the tetraisopropylcyclopentadienyl ring to reside at. Even with the slim acetonitrile substituents of **8** such an orientation should be preferred for steric reasons; from the experimentally observed conformation of **8** we may think of electronic reasons in favor of a conformation with the local symmetry plane of the tetraisopropylcyclopentadienyl ring perpendicular to the X–Co–Y plane (**8**: N–Co–N), which is overridden by steric reasons in **10**.

Complex **10** reacts with an equimolar amount of methyllithium to give the corresponding methyl complex [(C$_5$HR$_4$)CoCH$_3$(PMe$_3$)] (**11**) as a very air-sensitive microcrystalline solid, which is extremely soluble in all common aprotic solvents and can be crystallized only from very concentrated solutions. The broad ^{1}H-NMR signals of **11** do not allow proper signal assignment. In mass spectra of **11** five signals of metal complex fragments including the molecular ion (90%), M$^+$ − CH$_3$ (88%), M$^+$ − C$_3$H$_7$ (100%), and cleavage products with two missing alkyl groups could be detected. Complex **11** can be viewed as a radical derived from homolytic Co–C bond cleavage of the known complex type [(C$_5$H$_5$)CoMe$_2$(PPh$_3$)] [33,34], and resembles the [(C$_5$H$_5$)Co(CO)CH$_3$]$^\bullet$ radical intermediate involved in acetone formation from the dimer [(C$_5$H$_5$)Co-(μ-CO)CH$_3$]$_2$ [34]. Repeated attempts to obtain crystals of **11** suitable for X-ray diffraction finally led to the isolation of brown–black crystals of a dinuclear complex, which turned out to be the hydrolysis product

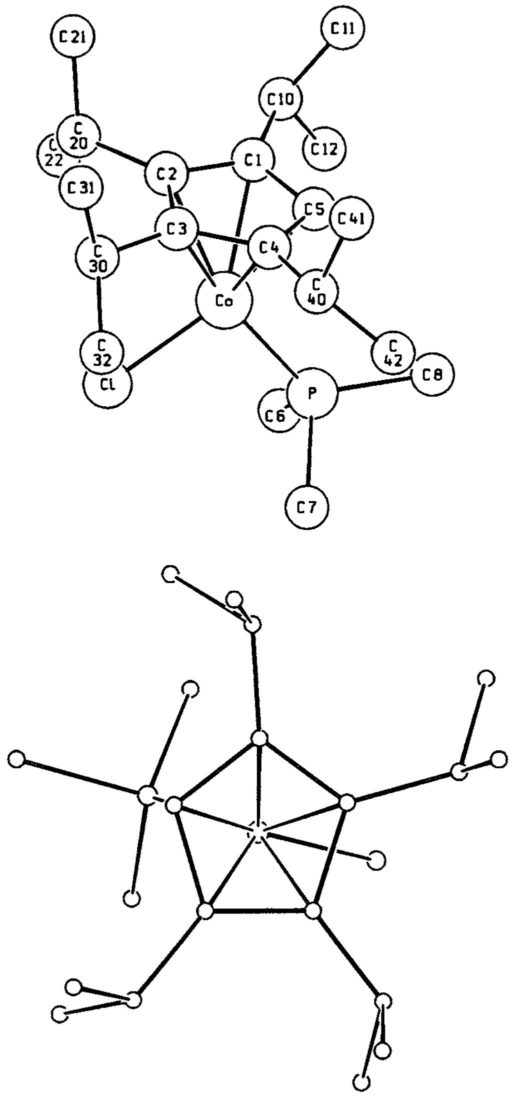


Fig. 11. Molecular structure and numbering scheme for the trimethylphosphane complex **10**. Hydrogen atoms have been omitted for clarity. Selected bond distances (Å) and angles (°) for complex **10**: Co–Cl 2.202(1), Co–P 2.2070(9), Co–C1 2.129(3), Co–C2 2.113(3), Co–C3 2.103(3), Co–C4 2.119(3), Co1–C5 2.046(3), Co–Cp$_{\text{cent}}$ 1.712; Cl–Co–P 90.37(4).

$[(C_5HR_4)Co(\mu\text{-}OH)]_2$ (**12**). Mass spectra show the molecular ion (36% relative intensity), $M^+ - OH$ (39%), $M^+ - H_2O$ (81%), and $M/2^+$ (15%) and deliberate hydrolysis of **11** gave reproducibly complex **12**, albeit in low yields.

By X-ray crystal structure investigation (Fig. 12, Table 1) **12** was shown to be a centrosymmetric dimer with a non-bonding Co–Co distance of 2.9560(6) Å, remarkably similar to the value of 2.932(5) Å found for the hydroxo-bridged Co(III) dimer $[(H_3N)_4Co(\mu\text{-}OH)]_2^{4+}$ [35]. The Co–O bond lengths are virtually identical and make up a Co_2O_2 rhombus with Co–O–Co angles of 100.99(2)° and O–Co–O angles of 79.02(8)°, which deviate by less than 1° from the corresponding values for the Co(III) ammine complex mentioned above. In contrast to the chloro(phosphane) complex **10** and in accordance with the bis(acetonitrile) cation **8**, the plane defined by the Co_2O_2 ring of **12** is approximately perpendicular to the local plane of symmetry of the tetraisopropylcyclopentadienyl ligands. Like the terminal acetonitrile ligands of **8**, the hydroxo bridges of **12** do not need the space provided by the ring CH moiety and the geometry of the complex follows the presumed electronic preference.

4. Conclusions

Among all cyclopentadienylmetal(II) halides of third row transition metals [36], the cobalt derivatives have been most widely studied owing to their ready availability [37]. Introduction of extremely bulky cyclopentadienyl rings with secondary and tertiary alkyl substituents is straightforward and yields useful starting compounds for the synthesis of cobalt half-sandwich complexes with favorable solubility and crystallinity. The synthetic utility of these starting compounds has been demonstrated by facile introduction of carbonyl, nitrosyl, acetonitrile or trimethylphosphane ligands. The acetonitrile complex **8** and the methyl complex **11** prove the ability of bulky alkylcyclopentadienyl rings to stabilize previously unknown types of 17-valence-electron cobalt(II) complexes. Advantages of tetraisopropylcyclopentadiene as a viscous solvent for slow growth of beautiful single crystals have been documented.

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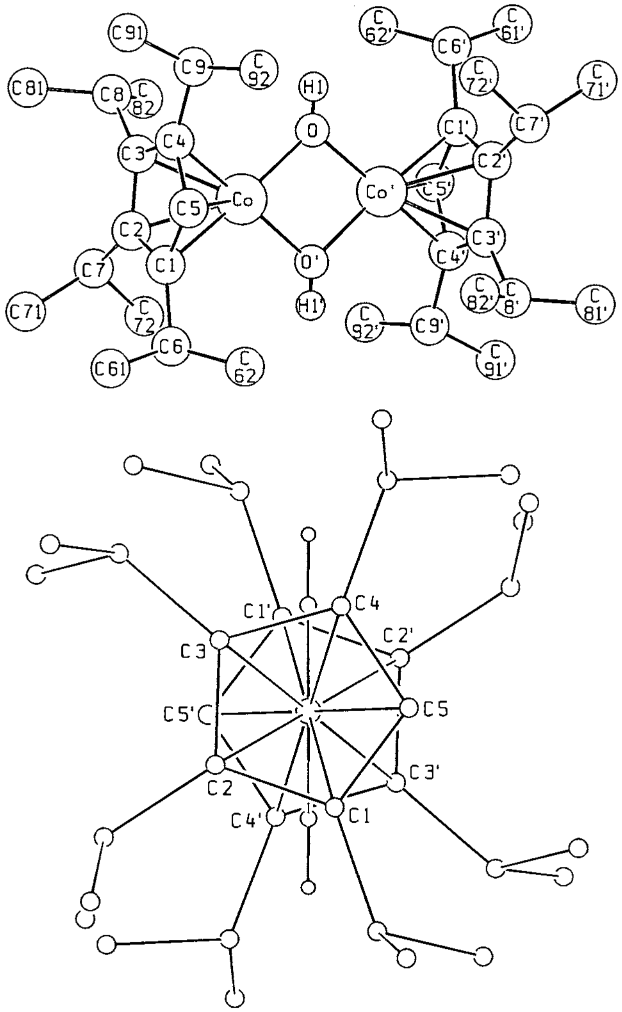

Fig. 12. Molecular structure and numbering scheme for dimeric hydroxide **12**. Hydrogen atoms other than those of the two bridging hydroxy groups have been omitted for clarity. Selected bond distances (Å) and angles (°) for complex **12**: Co···Co 2.9560(6), Co–O 1.916(2), Co–O′ 1.915 (2), Co–C1 2.052(2), Co–C2 2.083(2), Co–C3 2.107(2), Co–C4 2.080(2), Co–C5 2.103 (2), Co–Cp_{cent} 1.694, ring C–C from 1.409(3) to 1.449(3), mean value 1.430; O–Co–O′ 79.02(8), Co–O–Co′ 100.99(8).

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