

Cobalt Complexes with the 1-[2-(*N,N*-Dimethylamino)ethyl]-2,3,4,5-tetramethylcyclopentadienyl Ligand

Peter Jutzi,* Marc O. Kristen, Jürgen Dahlhaus, Beate Neumann, and Hans-Georg Stammler

Fakultät für Chemie, Universität Bielefeld, Universitätsstrasse 1,
D-W 4800 Bielefeld 1, Germany

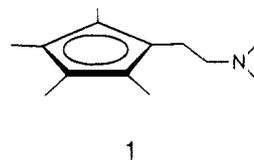
Received March 19, 1993

Some new Co(I), Co(II), and Co(III) complexes containing the 1-[2-(*N,N*-dimethylamino)ethyl]-2,3,4,5-tetramethylcyclopentadienyl ligand (Cp^A) are described. Dicobalt octacarbonyl reacts with $Cp^A H$ to give dicarbonyl(η^5 -1-[2-(*N,N*-dimethylamino)ethyl]-2,3,4,5-tetramethylcyclopentadienyl)cobalt(I) ($Cp^A Co(CO)_2$) with a noncoordinating dimethylamino function. Addition of iodine to $Cp^A Co(CO)_2$ leads to the formation of the diiodocyclopentadienylcobalt complex $Cp^A CoI_2$ with intramolecular dimethylamino coordination. $Cp^A CoI_2$ is formed via the diiodocarbonylcyclopentadienylcobalt complex $Cp^A Co(CO)I_2$. Under ordinary conditions $Cp^A CoI_2$ and $Cp^A Co(CO)I_2$ can easily be interconverted. $Cp^A CoI_2$ does not react with ethylene. Reduction of $Cp^A CoI_2$ with sodium amalgam under a CO atmosphere yields $Cp^A Co(CO)_2$; under an ethylene atmosphere $Cp^A Co(C_2H_4)_2$ with a noncoordinating dimethylamino group is formed. $Cp^A Co(C_2H_4)_2$ can also be synthesized by a different route: Reaction of $CoCl_2$ with $Cp^A Li$ yields the paramagnetic Co(II) dimer [$Cp^A CoCl$] $_2$, which is subsequently reduced with sodium amalgam to $Cp^A Co(C_2H_4)_2$. Structure investigations on $Cp^A CoI_2$ confirm the intramolecular coordination of the dimethylamino group (crystal system: triclinic; space group $P\bar{1}$; $a = 7.903(3)$ Å, $b = 12.802(7)$ Å, $c = 14.067(5)$ Å, $\alpha = 106.94(4)^\circ$, $\beta = 92.12(3)^\circ$, $\gamma = 107.55(4)^\circ$; $Z = 2$).

Introduction

Cyclopentadienyl systems with additional donor ligands are attracting increased interest in the chemistry of metal complexes.¹⁻¹⁰ Under appropriate conditions, the donor atom can coordinate to the metal center in addition to the cyclopentadienyl system. As a result, it seems possible to verify new types of complexes, to stabilize highly reactive intermediates and to influence the selectivity of catalytic processes. Very recently, we have introduced the 1-[2-(*N,N*-dimethylamino)ethyl]-2,3,4,5-tetramethylcyclopentadienyl ligand¹¹ (1) into the chemistry of s-, p-, d-, and f-block elements with some typical examples.^{12a} The corresponding ligand derived from the parent cyclopentadiene has been used by Wang et al. in the chemistry of manganese^{7a} and molybdenum.^{7b,c} Ligand 1 combines the advantages of a peralkylated cyclopentadienyl system with those of a bi(poly)dentate ligand possessing at the same time both a hard and a soft donor function, following Pearson's¹³ concept of hard and soft acids and bases. In this work, we describe the synthesis of cobalt complexes containing 1. Special emphasis is put on the coordination mode of the ligand.

Chart I



(1) Miguel-Garcia, J. A.; Adams, H.; Bailey, N. A.; Maitlis, P. M. *J. Organomet. Chem.* **1991**, *413*, 427.

(2) Miguel-Garcia, J. A.; Maitlis, P. M. *J. Chem. Soc., Chem. Commun.* **1990**, 1472.

(3) Fondors, R.; Meetsma, A.; Teuben, J. H. *Organometallics* **1991**, *10*, 59.

(4) (a) Kettenbach, R. T.; Butenschön, H. *New. J. Chem.* **1990**, *14*, 599. (b) Kettenbach, R. T.; Krüger, C.; Butenschön, H. *Angew. Chem.* **1992**, *104*, 1052; *Angew. Chem., Int. Ed. Engl.* **1992**, *33*, 1066.

(5) (a) Charrier, C.; Mathey, F. *J. Organomet. Chem.* **1979**, *170*, C41. (b) Slawin, A. M. Z.; Williams, D. J.; Crosby, J.; Ramsden, J. A.; White, C. *J. Chem. Soc., Dalton Trans.* **1988**, 2491.

(6) (a) Shapiro, P. J.; Bunel, E.; Schaefer, W. P.; Bercaw, J. E. *Organometallics* **1990**, *9*, 867. (b) Okuda, J. *Chem. Ber.* **1990**, *123*, 1649.

(7) (a) Wang, T.-F.; Lee, T.-Y.; Wen, Y.-S.; Liu, L.-K. *J. Organomet. Chem.* **1991**, *403*, 353. (b) Wang, T.-F.; Lee, T.-Y.; Chou, J.-W.; Ong, C.-W. *J. Organomet. Chem.* **1992**, *423*, 31. (c) Wang, T.-F.; Wen, Y.-S. *J. Organomet. Chem.* **1992**, *439*, 155.

(8) (a) Siemeling, U. *J. Organomet. Chem.* **1992**, *429*, C14. (b) Siemeling, U. *J. Chem. Soc., Chem. Commun.* **1992**, 1335.

(9) Okuda, J.; Zimmermann, K.-H. *J. Organomet. Chem.* **1988**, *344*, C1.

(10) (a) Okuda, J.; Zimmermann, K.-H. *Chem. Ber.* **1989**, *122*, 1645. (b) Okuda, J.; Zimmermann, K.-H. *Chem. Ber.* **1990**, *123*, 1641. (c) Okuda, J.; Zimmermann, K.-H.; Herdtweck, E. *Angew. Chem.* **1991**, *103*, 446; *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 430. (d) Okuda, J.; Zimmermann, K.-H. *Chem. Ber.* **1992**, *125*, 637. (e) Okuda, J.; Herdtweck, E.; Zimmermann, K.-H. In *Organic Synthesis via Organometallics*; Dötz, K. H., Hoffmann, R. W., Eds.; Vieweg: Braunschweig, Germany **1991**; p 207. (f) Zimmermann, K.-H.; Pilato, R. S.; Horváth, I. T.; Okuda, J. *Organometallics* **1992**, *11*, 3935.

tadienyl ligand¹¹ (1) into the chemistry of s-, p-, d-, and f-block elements with some typical examples.^{12a} The corresponding ligand derived from the parent cyclopentadiene has been used by Wang et al. in the chemistry of manganese^{7a} and molybdenum.^{7b,c} Ligand 1 combines the advantages of a peralkylated cyclopentadienyl system with those of a bi(poly)dentate ligand possessing at the same time both a hard and a soft donor function, following Pearson's¹³ concept of hard and soft acids and bases. In this work, we describe the synthesis of cobalt complexes containing 1. Special emphasis is put on the coordination mode of the ligand.

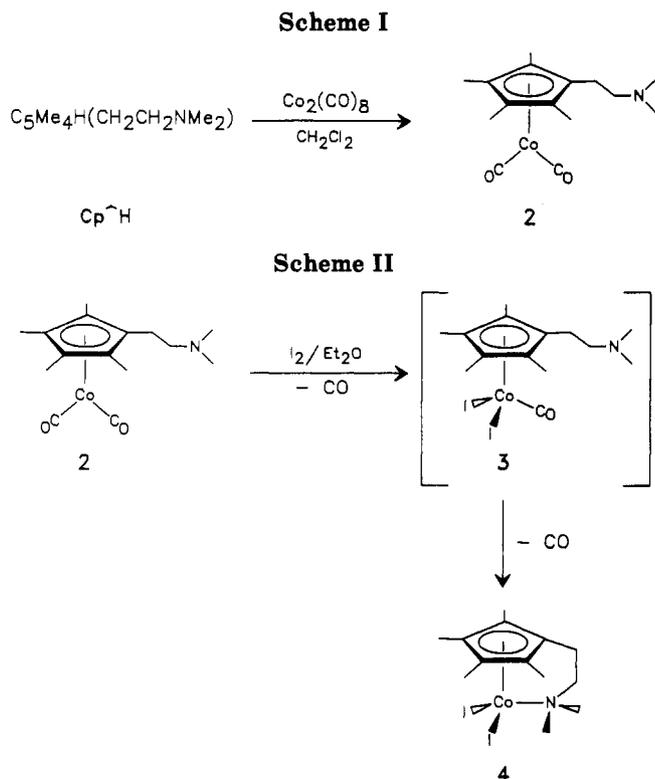
Results

Refluxing a dichloromethane solution of $Co_2(CO)_8$ and the protonated ligand 1 ($Cp^A H$) leads to the formation of the dicarbonyl cobalt complex 2, which can be isolated as an air-sensitive red-brown oil in moderate yields. Performing the reaction in 3,3-dimethyl-1-butene solution following a procedure described by Buzinkai and Schrock¹⁴ does not improve the yield.

(11) Jutzi, P.; Dahlhaus, J. *Synthesis*, in press.

(12) (a) Jutzi, P.; Dahlhaus, J.; Kristen, M. O. *J. Organomet. Chem.* **1993**, *450*, C1. (b) Kristen, M. O. Diploma Thesis, Universität Bielefeld, **1992**3) Pearson, R. G. *J. Am. Chem. Soc.* **1963**, *85*, 3533.

(14) Buzinkai, J. F.; Schrock, R. R. *Organometallics* **1987**, *6*, 1447.



The IR spectrum of **2** shows two absorptions at 1992 and 1929 cm^{-1} , indicating that two terminal carbonyl groups are present and the nitrogen atom of the side chain is not coordinated to the cobalt atom. In addition, the 1H - and ^{13}C -NMR spectra show signals very similar to those of the dimeric molybdenum dicarbonyl complex of **1** where the noncoordination of the side chain has been proved by an X-ray crystal structure analysis.¹²

Photolysis, the general procedure to eliminate carbonyl groups from transition metal centers, does not lead to the corresponding intramolecularly coordinated complex. In analogy to the results of Vollhardt et al.¹⁵ for $CpCo(CO)_2$, formation of multinuclear cobalt complexes is observed when irradiating a THF solution of **2**.¹⁶ An alternative approach to a cyclopentadienylcobalt complex where the donor function of the side chain coordinates intramolecularly has been reported by Okuda and Zimmermann.^{10a} In a first step the dicarbonyl complex is oxidized with iodine, yielding the corresponding diiodo carbonyl complex; subsequent reduction of this complex with sodium amalgam yields the desired carbonyl complex with intramolecular coordination. This route had to be discarded in our case, since the isolation of the diiodocarbonyl cobalt complex (compound **3**) failed. When iodine is added to an ether solution of **2**, the diiodo- $(\eta^5-\eta^1-1-[2-(N,N$ -dimethylamino)ethyl]-2,3,4,5-tetramethylcyclopentadienyl)cobalt(III) complex (**4**) precipitates spontaneously from the reaction mixture as black microcrystals. This intramolecularly coordinated complex **4** is formed via the diiodocarbonyl complex **3** (vide infra). Unlike similar compounds,^{10a,17} **3** loses carbon monoxide already at room temperature. The CO-free molecule **4** precipitates, whereas **3** is still present in solution, as indicated by the dark purple color.

(15) Vollhardt, K. P. C.; Bercaw, J. E.; Bergman, R. G. *J. Am. Chem. Soc.* 1974, 96, 4998.

(16) A detailed analysis of the multinuclear cobalt carbonyl complexes has not been done.

(17) Roe, D. M.; Maitlis, P. M. *J. Chem. Soc. A* 1971, 3173.

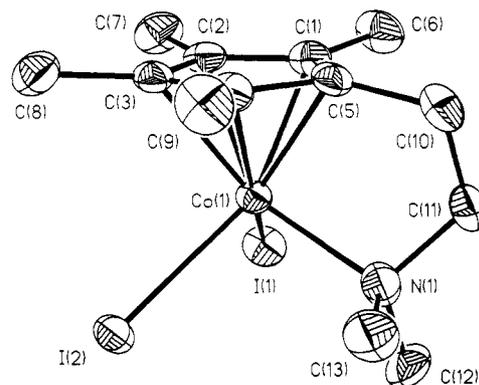


Figure 1. Plot of the solid state structure of **4**, with thermal ellipsoids at the 50% probability level.

The 1H -NMR spectrum¹⁸ of **4** shows some interesting differences in comparison with that of **2** which indicate intramolecular coordination of the dimethylamino group. The signals for one set of methyl groups at the cyclopentadienyl ring and for the methyl groups at the nitrogen are shifted downfield by ca. 0.2 ppm. The most significant change, however, is found for the signal of the methylene group adjacent to the nitrogen atom. It is shifted 1.4 ppm downfield compared with **2**, indicating that a significant change of the environment of the methylene group has occurred. Additional evidence for an intramolecular coordination stems from the ^{13}C -NMR spectrum. While the signal for the dimethylamino group in **2** is found at 45.5 ppm, here it is observed at 57.5 ppm. About the same downfield shift is found for the methylene carbon attached to the nitrogen (61.7 ppm for **2** and 72.7 ppm for **3**). Although these NMR data strongly suggest that a monomeric compound with intramolecular coordination of the dimethylamino group has been formed, one cannot definitely exclude the existence of an iodine bridged dimer without additional intramolecular coordination.¹⁹

Thus, it was of interest to obtain information on the crystal structure of **4**. A crystal suitable for X-ray diffraction analysis was obtained by recrystallization from benzene. The structure analysis shows that **4** forms monomeric molecules where the dimethylamino group is intramolecularly coordinated to the cobalt atom²⁰ (see Figure 1 and Tables I-IV). Both possible enantiomers are present in a 1:1 ratio. The Co-N bond distance is 2.115(6) Å. This distance is only slightly longer than that reported for $[Co(C_5H_{12}N_2)_2Cl_2]Cl \cdot HCl \cdot H_2O$ (1.979(3) Å), another cyclopentadienylcobalt(III) complex with a nitrogen ligand.²¹ The lengths of the Co-I bonds are 2.630(2) and 2.613(2) Å, respectively. Known cyclopentadienyliodocobalt(III) complexes show values slightly shorter (2.556(4) Å; $[CpCo(dppm)]I \cdot CHCl_3$; 2.598(1) and 2.572(1) Å, $CpCo[dppm(O)]I_2$ ^{22,23} but within the same range.

(18) The 1H -NMR spectra are subject to rather large solvent shifts. Comparisons were made from spectra recorded in $CDCl_3$.

(19) The formation of the corresponding dimer is observed for $(C_5Me_5)Co_2(CO)_2$ upon heating (loss of carbon monoxide).¹⁷ Okuda and Zimmermann^{10a} obtained the same result for their system rather than intramolecular coordination of the butenyl group in the side chain of the cyclopentadienyl ligand.

(20) A similar iridium complex of the formula $(C_5Me_4CH_2CH_2CH=CH_2)IrCl_2$ where the double bond coordinates internally has been reported.¹ No crystal structure data are available.

(21) Goto, M.; Ohta, K.; Toriumi, K.; Ito, T. *Acta Crystallogr., Sect. B* 1981, 37, 1189.

(22) Bao, Q.-B.; Landon, S. J.; Rheingold, A. L.; Haller, T. M.; Brill, T. B. *Inorg. Chem.* 1985, 24, 900.

(23) dppm: bis(diphenylphosphino)methane.

Table I. Crystallographic Data for Diffraction Studies for 4^a

empirical formula	C ₁₃ H ₂₂ CoI ₂ N + (C ₆ H ₆) ₂
cryst size, mm ³	0.15 × 0.4 × 0.5
fw	661.3
cryst syst	triclinic
space group	P $\bar{1}$
lattice param	
<i>a</i> , Å	7.903(3)
<i>b</i> , Å	12.802(7)
<i>c</i> , Å	14.067(5)
α, deg	106.94(4)
β, deg	92.12(3)
γ, deg	107.55(4)
<i>V</i> , Å ³	1285.9(10)
<i>Z</i>	2
<i>d</i> _{calc} g/cm ³	1.71
diffractometer	Syntax P2 ₁
<i>F</i> (000)	648
μ (Mo Kα), mm ⁻¹	3.05
temp, °C	-100
2θ _{max} , deg	60
no. data collcd	8022
no. obsd data [<i>F</i> > 5σ(<i>F</i>)]	4818
no. of params refined	262
residuals: <i>R</i> , <i>R</i> _w	0.041, 0.036
largest peak in final diff map, e/Å ³	0.036
abs corr	empirical

^a X-ray Structure Determination: A single crystal was coated with a layer of hydrocarbon oil, attached to a glass fiber and cooled to 173 K for data collection. Crystallographic programs used for structure solution and refinement were from SHELXTL PLUS. The structure was solved by using direct methods and was refined by using full-matrix least squares with anisotropic thermal parameters for all non-hydrogen atoms. All the hydrogen atoms were fixed at the calculated positions with an isotropic *U* value of 0.08 Å².

Table II. Atomic Coordinates (×10⁴) and Equivalent Isotropic Displacement Coefficients (Å² × 10³)

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> (eq) ^a
I(1)	1856(1)	2396(1)	528(1)	36(1)
I(2)	1871(1)	2917(1)	3366(1)	30(1)
Co(1)	4163(1)	2763(1)	2083(1)	22(1)
N(1)	3842(6)	1010(4)	1895(3)	33(2)
C(1)	6371(7)	3342(5)	1379(3)	30(2)
C(2)	5791(7)	4318(5)	1859(3)	28(2)
C(3)	5890(6)	4456(5)	2904(3)	26(2)
C(4)	6518(7)	3581(5)	3081(3)	28(2)
C(5)	6817(6)	2898(5)	2133(4)	28(2)
C(6)	6667(8)	2986(6)	308(4)	42(3)
C(7)	5341(8)	5110(5)	1377(4)	42(3)
C(8)	5558(8)	5426(5)	3681(4)	38(2)
C(9)	7018(8)	3549(6)	4112(3)	40(3)
C(10)	7135(7)	1764(5)	1917(4)	36(2)
C(11)	5401(7)	827(5)	1377(4)	36(2)
C(12)	2162(8)	136(5)	1278(5)	46(3)
C(13)	3961(9)	775(6)	2874(4)	46(3)
C(14)	10185(10)	7018(8)	2062(7)	77(4)
C(15)	10150(10)	7419(7)	3086(7)	70(4)
C(16)	10405(9)	6807(7)	3672(5)	56(3)
C(17)	10701(8)	5790(6)	3269(5)	51(3)
C(18)	10753(8)	5369(6)	2291(5)	51(3)
C(19)	10509(10)	5975(8)	1664(5)	73(4)
C(20)	-1761(11)	89(7)	3910(7)	68(4)
C(21)	-2067(11)	-465(8)	2895(7)	67(5)
C(22)	-3559(13)	-1458(8)	2504(5)	68(4)
C(23)	-4692(10)	-1860(6)	3155(6)	60(3)
C(24)	-4283(12)	-1267(8)	4149(6)	71(4)
C(25)	-2839(13)	-327(8)	4507(6)	78(4)

^a Equivalent isotropic *U* defined as one-third of the trace of the orthogonalized *U*_{*ij*} tensor.

The cobalt ring-carbon bond lengths are in the expected range. A more detailed analysis shows the cobalt atom not to be exactly centered below the cyclopentadienyl unit but shifted to C(5) by a small extent. All methyl groups at the ring are bent away from the cobalt atom by ca. 5°, in contrast to C(10) that is bent by 10° in the opposite

Table III. Bond Lengths (Å)

I(1)-Co(1)	2.630(2)	I(2)-Co(1)	2.613(2)
Co(1)-N(1)	2.115(6)	Co(1)-C(1)	2.086(5)
Co(1)-C(2)	2.137(6)	Co(1)-C(3)	2.130(5)
Co(1)-C(4)	2.075(5)	Co(1)-C(5)	2.049(5)
N(1)-C(11)	1.498(8)	N(1)-C(12)	1.490(6)
N(1)-C(13)	1.497(9)	C(1)-C(2)	1.451(9)
C(1)-C(5)	1.420(9)	C(1)-C(6)	1.491(7)
C(2)-C(3)	1.424(7)	C(2)-C(7)	1.489(10)
C(3)-C(4)	1.432(9)	C(3)-C(8)	1.494(8)
C(4)-C(5)	1.438(7)	C(4)-C(9)	1.504(8)
C(5)-C(10)	1.493(9)	C(10)-C(11)	1.515(7)
C(14)-C(15)	1.385(13)	C(14)-C(19)	1.394(15)
C(15)-C(16)	1.338(14)	C(16)-C(17)	1.354(12)
C(17)-C(18)	1.331(10)	C(18)-C(19)	1.375(14)
C(20)-C(21)	1.372(13)	C(20)-C(25)	1.325(14)
C(21)-C(22)	1.396(11)	C(22)-C(23)	1.401(12)
C(23)-C(24)	1.355(11)	C(24)-C(25)	1.335(11)

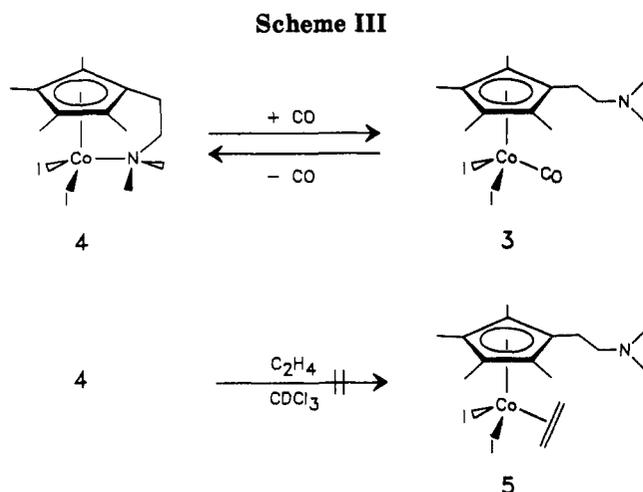
Table IV. Bond Angles (deg)

I(1)-Co(1)-I(2)	94.5(1)	I(1)-Co(1)-N(1)	97.0(1)
I(2)-Co(1)-N(1)	94.9(1)	I(1)-Co(1)-C(1)	93.1(2)
I(2)-Co(1)-C(1)	157.0(2)	N(1)-Co(1)-C(1)	105.7(2)
I(1)-Co(1)-C(2)	90.1(1)	I(2)-Co(1)-C(2)	118.1(2)
N(1)-Co(1)-C(2)	145.6(2)	C(1)-Co(1)-C(2)	40.2(2)
I(1)-Co(1)-C(3)	121.4(2)	I(2)-Co(1)-C(3)	90.8(1)
N(1)-Co(1)-C(3)	140.6(2)	C(1)-Co(1)-C(3)	66.8(2)
C(2)-Co(1)-C(3)	39.0(2)	I(1)-Co(1)-C(4)	156.7(2)
I(2)-Co(1)-C(4)	98.8(1)	N(1)-Co(1)-C(4)	100.8(2)
C(1)-Co(1)-C(4)	67.7(2)	C(2)-Co(1)-C(4)	66.8(2)
C(3)-Co(1)-C(4)	39.8(3)	I(1)-Co(1)-C(5)	128.7(1)
I(2)-Co(1)-C(5)	136.8(1)	N(1)-Co(1)-C(5)	82.4(2)
C(1)-Co(1)-C(5)	40.2(2)	C(2)-Co(1)-C(5)	67.3(2)
C(3)-Co(1)-C(5)	67.4(2)	C(4)-Co(1)-C(5)	40.8(2)
Co(1)-N(1)-C(11)	103.4(4)	Co(1)-N(1)-C(12)	116.7(4)
C(11)-N(1)-C(12)	108.6(4)	Co(1)-N(1)-C(13)	112.7(3)
C(11)-N(1)-C(13)	108.9(5)	C(12)-N(1)-C(13)	106.4(5)
Co(1)-C(1)-C(2)	71.8(3)	Co(1)-C(1)-C(5)	68.5(3)
C(2)-C(1)-C(5)	107.9(4)	Co(1)-C(1)-C(6)	131.2(3)
C(2)-C(1)-C(6)	124.9(6)	C(5)-C(1)-C(6)	126.7(6)
Co(1)-C(2)-C(1)	68.0(3)	Co(1)-C(2)-C(3)	70.2(3)
C(1)-C(2)-C(3)	107.6(5)	Co(1)-C(2)-C(7)	131.5(4)
C(1)-C(2)-C(7)	126.7(5)	C(3)-C(2)-C(7)	125.4(5)
Co(1)-C(3)-C(2)	70.8(3)	Co(1)-C(3)-C(4)	68.0(3)
C(2)-C(3)-C(4)	108.5(5)	Co(1)-C(3)-C(8)	131.4(4)
C(2)-C(3)-C(8)	124.8(6)	C(4)-C(3)-C(8)	126.5(5)
Co(1)-C(4)-C(3)	72.2(3)	Co(1)-C(4)-C(5)	68.6(3)
C(3)-C(4)-C(5)	107.7(5)	Co(1)-C(4)-C(9)	131.8(4)
C(3)-C(4)-C(9)	123.5(5)	C(5)-C(4)-C(9)	128.1(6)
Co(1)-C(5)-C(1)	71.3(3)	Co(1)-C(5)-C(4)	70.6(3)
C(1)-C(5)-C(4)	108.3(5)	Co(1)-C(5)-C(10)	113.7(3)
C(1)-C(5)-C(10)	123.8(4)	C(4)-C(5)-C(10)	126.5(5)
C(5)-C(10)-C(11)	107.6(5)	N(1)-C(11)-C(10)	111.0(4)
C(15)-C(14)-C(19)	118.5(10)	C(14)-C(15)-C(16)	120.4(9)
C(15)-C(16)-C(17)	120.3(7)	C(16)-C(17)-C(18)	121.7(8)
C(17)-C(18)-C(19)	119.8(8)	C(14)-C(19)-C(18)	119.4(7)
C(21)-C(20)-C(25)	120.5(7)	C(20)-C(21)-C(22)	118.6(8)
C(21)-C(22)-C(23)	119.4(7)	C(22)-C(23)-C(24)	118.3(6)
C(23)-C(24)-C(25)	121.3(9)	C(20)-C(25)-C(24)	121.9(8)

direction. The side chain is coordinated to the cobalt in a zigzag fashion. The same results regarding the orientation of the side chain have been found by Wang et al.^{7b} for the molybdenum complex [C₅H₄CH₂CH₂NMe₂]₂Mo(CO)₂I.

On the basis of the above findings complex 4 is expected to be a chiral molecule, showing two enantiomers. On the other hand the NMR spectra show 4 to be symmetric because only one set of signals is observed. The symmetry found in solution is caused by a very fast flip of the side chain, so that only an averaged spectrum of the two enantiomers present is observed. The structural data presented for 4 strongly support the assumption that monomeric molecules are present in solution, too.

When carbon monoxide is bubbled through a solution of 4 the color immediately changes from black-green to

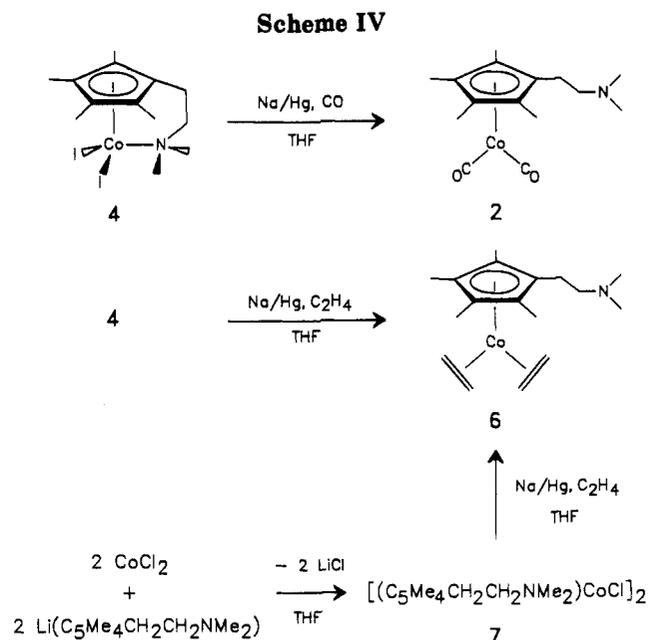


dark purple. The carbon monoxide molecule displaces the dimethylamino group; this leads to the formation of carbonyldiiodo(η^5 -1-[2-(*N,N*-dimethylamino)ethyl]-2,3,4,5-tetramethylcyclopentadienyl)cobalt(III) (3).

Compound 3 has been identified by 1H - and ^{13}C -NMR and IR spectroscopy. The most significant change in the 1H -NMR spectrum is the upfield shift of the methylene group adjacent to the nitrogen atom (compared with the spectrum of 4). The chemical shift of these hydrogen atoms is very similar to that of the corresponding hydrogen atoms in 2; therefore, a noncoordination of the side chain can be assumed. Additional evidence is provided by the ^{13}C -NMR spectrum. Here the characteristic signals (for the methyl and methylene carbon atoms at the nitrogen center) show chemical shifts nearly identical to those of 2. The IR spectrum of 3 in dichloromethane shows one absorption at 2057 cm^{-1} , indicating that the carbon monoxide is weakly bound to the cobalt atom. It is not possible to get further analytical data, because 3 cannot be isolated; 3 is only stable in solution under an atmosphere of carbon monoxide.

Any attempt to remove the solvent or just the carbon monoxide atmosphere, either by applying vacuum or simply by bubbling argon through the solution, immediately leads in a reversible reaction to the formation of 4, as indicated by the color change in the solution back to black-green. Alternate bubbling of carbon monoxide and argon through a solution of 4 for several cycles yields dark purple or black-green solutions, respectively. 1H -NMR spectra recorded from these solutions show that only signals for 4 (black-green solution) or 3 (dark purple solution) are present. At room temperature the equilibrium is not completely on the side of 3, even under a carbon monoxide atmosphere there is still about 10% of 4 present. Performing the reaction at $-50\text{ }^\circ\text{C}$ does not yield a substantial lowering of the portion of 4, as indicated by 1H -NMR spectroscopy. If a similar experiment is performed with ethylene instead of carbon monoxide, no reaction to complex 5 occurs, as confirmed by 1H -NMR spectroscopy.

The reduction of 4 with sodium amalgam under an atmosphere of carbon monoxide yields the carbonyl complex 2 in high yields besides a small amount of free ligand (Cp^*H). Immediately after adding a THF solution of 4 to the amalgam, the color changes to dark purple, indicating that 3 has been formed. Thus, 3 is the actual complex that will be reduced. The two iodine atoms are removed from the cobalt atom, leaving a 16-electron



complex with a vacant coordination site. The exclusive formation of 2 by occupation of two coordination sites with carbon monoxide is observed. The species $Cp^*Co(CO)$ with intramolecular coordination of the dimethylamino group could not be detected.

Performing the reduction of 4 with sodium amalgam under an atmosphere of ethylene leads to (η^5 -1-[2-(*N,N*-dimethylamino)ethyl]-2,3,4,5-tetramethylcyclopentadienyl)bis(η^2 -ethene)cobalt(I) (6). The formation of 6 is proved by 1H -NMR data. The spectrum shows two multiplets at 0.71 and 1.52 ppm, respectively, for the inner and outer (relative to the cobalt atom) hydrogen atoms of the ethylene molecules. The integral clearly demonstrates that two molecules of ethylene are coordinated to the cobalt atom. All the other 1H -NMR data are consistent with the proposed structure. The formation of the corresponding intramolecular coordinated complex $Cp^*Co(C_2H_4)$ is excluded. Unfortunately, it was not possible to get additional analytical data. On the one hand an impurity with Cp^*H (10%) could not be removed, on the other hand a ^{13}C -NMR spectrum could not be recorded due to the poor solubility of 6 in standard solvents; furthermore 6 decomposes slowly in solution.

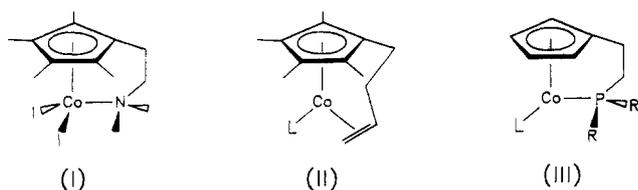
The ethylene complex 6 is also accessible by a different route: The paramagnetic dimer 7 was prepared by an adaptation of the method used by Koelle et al.²⁴ for the synthesis of $[(C_5Me_5)CoCl]_2$. When solid cobalt(II) chloride is added to a solution of the lithiated ligand (Cp^*Li) in THF, 7 is immediately formed, as indicated by a color change of the solution from yellow to dark brown. This solution is used without any workup in the next reaction. Reaction of 7 with sodium amalgam under an atmosphere of ethylene gives 6, impurified with 15% of free ligand (Cp^*H), in 53% yield (based on Cp^*Li).

Discussion

In the cyclopentadienyl chemistry of cobalt the effect of a (dimethylamino)ethyl ligand depends on the formal oxidation state of the cobalt atom. In cobalt(III) complexes

(24) Koelle, U.; Khouzami, F.; Fuss, B. *Angew. Chem.* 1982, 94, 132; *Angew. Chem. Int. Ed. Engl.* 1982, 21, 131; *Angew. Chem. Suppl.* 1982, 232.

Chart II



the dimethylamino group can coordinate to the central atom, whereas in cobalt(I) complexes a coordination has not been observed so far. Compound 4 represents the first example of a cyclopentadienylcobalt(III) complex with intramolecular coordination of a donor function in the side chain.

It is known from the literature that in cyclopentadienylcobalt(III) complexes nitrogen-containing units are better donors than carbon monoxide.^{25a} In these situations the ligand qualities of CO are not determined by its high π -acceptor but by its low σ -donor ability. As a consequence, the corresponding Co(III)-CO bonds are rather weak, as has been demonstrated by the IR spectrum of 3 that shows an absorption at higher wavenumbers compared with 2. Similar absorptions have been found for the compounds CpCoI₂CO^{25a} and Cp*CoI₂CO^{25b} and for a Co(III) carbonyl complex with the 1-(3-butenyl)-2,3,4,5-tetramethylcyclopentadienyl ligand.^{10a}

Surprisingly, in the (1-[2-(*N,N*-dimethylamino)ethyl]-2,3,4,5-tetramethylcyclopentadienyl)cobalt(III) complex 4 described here (type I) the CO coordination still can compete with the coordination of the dimethylamino group, as shown by the equilibrium between 3 and 4. On the other hand, no competition has been observed between the coordination of the dimethylamino group and ethylene. Preliminary results²⁶ show that the dimethylamino group in 4 can be displaced irreversibly by stronger donating ligands such as phosphines and *tert*-butyl isocyanide. Thus, the dimethylamino group seems to be bound strong enough to the cobalt(III) center to form stable complexes but weak enough to be displaced by a variety of donor reagents.

In the cyclopentadienyl complexes of Okuda¹⁰ (type II) and Butenschön⁴ (type III) an intramolecular coordination of the side chain is achieved at cobalt(I) centers. The displacement of the intramolecular coordinating ligand is only successful under very drastic conditions (ethylene: 36 atm, 10 days, ~50%)^{10f} or with chelating ligands such as 1,5-cyclooctadiene^{10f,4b} 1,2-bis(diisopropylphosphino)ethane,^{4b} or 2,2'-bipyridyl.^{4b} This contrasts with our observations in cobalt(III) chemistry where the displacement of the protecting side chain can be observed already at mild conditions both irreversibly and reversibly.

The completely different coordination behavior of cobalt(I) and cobalt(III) complexes with the 1-[2-(*N,N*-dimethylamino)ethyl]-2,3,4,5-tetramethylcyclopentadienyl ligand strengthens the expectation that complexes with this ligand may find application in catalytic or stoichiometric oxidative addition/reductive elimination processes. It seems that a very fine tuning of additional ligands is necessary because a small change of their donor and/or acceptor abilities might result in a dramatic change of the chemistry of the entire system.

Experimental Section

All experiments were carried out under an atmosphere of dry argon. When carbon monoxide or ethylene was used as a reagent, the gas provides a protective atmosphere. Solvents were dried by using standard procedures and distilled prior to use. All other reagents were used as purchased. All NMR spectra were obtained using a Bruker AM 300 spectrometer on solutions in CDCl₃ or C₆D₆ as noted. The spectra were calibrated using signals of residual protons from the solvents referenced to SiMe₄. The mass spectra were determined by using a VG AutoSpec. Only characteristic fragments and isotopes of the highest abundance are listed. Melting points were determined in sealed capillaries with a Büchi 510 Schmelzpunktbestimmungsapparatur and are uncorrected. IR spectra were recorded on CH₂Cl₂ solutions on a Perkin-Elmer 598 infrared spectrophotometer. Only characteristic frequencies (CO) are listed. The CHN analyses were performed by Analytisches Labor der Fakultät für Chemie der Universität Bielefeld.

[2-(*N,N*-Dimethylamino)ethyl]tetramethylcyclopentadiene (Cp[∧]H) was prepared as described in the literature.¹¹

Dicarbonyl(η^5 -1-[2-(*N,N*-dimethylamino)ethyl]-2,3,4,5-tetramethylcyclopentadienyl)cobalt(I) (2). A solution of 3.42 g (10.0 mmol) of Co₂(CO)₈, 3.87 g (20.0 mmol) of Cp[∧]H, and 3.3 mL (35.0 mmol) of 1,3-cyclohexadiene in 50 mL of dichloromethane was heated to gentle reflux for 7 h. The solvent was removed in vacuo, and the red-brown oily residue was extracted with 70 mL of *n*-hexane. The *n*-hexane solution was filtered through Florisil and the oily residue washed with additional 20-mL portions of *n*-hexane, until the washings were bright yellow. The combined *n*-hexane extracts were evaporated in vacuo leaving 2.76 g (45%) of 2 as a very air-sensitive red-brown oil.

¹H-NMR (CDCl₃): δ = 1.85, 1.89 (2s, 2 \times 6H, CH₃), 2.22–2.28 (m, 2H, CH₂), 2.26 (s, 6H, N-CH₃), 2.41–2.46 (m, 2H, CH₂-N). ¹³C{¹H}-NMR (C₆D₆): δ = 10.38 (CH₃), 23.93 (CH₂), 45.49 (N-CH₃), 61.74 (CH₂-N), 96.60, 97.16, 100.26, (ring C), 208.57 (CO). IR (CH₂Cl₂): ν = 1992, 1929 cm⁻¹. MS [*m/z* (relative intensity %)]: 307 (M⁺ 3), 279 ([M - CO]⁺, 56), 249 ([M - 2CO - 2H]⁺, 100), 58 (Me₂NCH₂⁺, 96). Anal. Calcd for C₁₅H₂₂CoNO₂ (307.3): C, 58.63; H, 7.22; N, 4.56. Found: C, 58.82; H, 7.30; N, 4.93.

Diiodo(η^5 -1-[2-(*N,N*-dimethylamino)ethyl]-2,3,4,5-tetramethylcyclopentadienyl)cobalt(III) (4). A solution of 1.31 g (5.10 mmol) of iodine in 30 mL of ether was added dropwise to a solution of 1.74 g (5.66 mmol) of 2 in 30 mL of ether at 0 °C. During the addition the color of the solution changed from red-brown to dark purple and the formation of a black precipitate was observed. The solution was allowed to warm to room temperature and then stirred for 2 h. When the reaction mixture was filtered, its color changed to black-green, leaving black-green microcrystals. The microcrystals were washed with 15 mL of ether and then dried in vacuo, yielding 2.47 g (96%) of air-stable 4. Mp: >300 °C.

¹H-NMR (CDCl₃): δ = 1.67, 2.21 (2s, 2 \times 6H, CH₃), 2.23 (t, *J* = 6.5 Hz, 2H, CH₂), 2.48 (s, 6H, N-CH₃), 3.86 (t, *J* = 6.4 Hz, 2H, CH₂-N). ¹H-NMR (C₆D₆): δ = 1.04 (t, *J* = 6.4 Hz, 2H, CH₂), 1.41, 1.74 (2s, 2 \times 6H, CH₃), 2.10 (s, 6H, N-CH₃), 2.92 (t, *J* = 6.4 Hz, CH₂-N). ¹³C{¹H}-NMR (CDCl₃): δ = 10.92, 14.00 (CH₃), 22.50 (CH₂), 57.46 (N-CH₃), 72.73 (CH₂-N), 86.58, 92.19, 102.47 (ring C). MS [*m/z* (relative intensity %)]: 378 ([M - I]⁺, 7), 58 (Me₂NCH₂⁺, 100). Anal. Calcd for C₁₃H₂₂CoI₂N (505.1): C, 30.92; H, 4.39; N, 2.77; I, 50.25. Found: C, 30.69; H, 4.47; N, 2.56; I, 50.60.

Carbonyldiiodo(η^5 -1-[2-(*N,N*-dimethylamino)ethyl]-2,3,4,5-tetramethylcyclopentadienyl)cobalt(III) (3). A solution of 4 in CDCl₃ was prepared in an NMR tube. Carbon monoxide was bubbled through this solution for 10 min. The color of the solution immediately changed from black-green to dark purple. The NMR spectra were recorded using this sample. The IR spectrum was recorded on a CH₂Cl₂ solution prepared as described above.

¹H-NMR (CDCl₃): δ = 2.21, 2.26 (2s, 2 \times 6H, CH₃), 2.32 (s, 6H, N-CH₃), 2.40–2.48 (m, 2H, CH₂), 2.72–2.80 (m, 2H, CH₂-N). ¹³C-

(25) (a) Heck, R. F. *Inorg. Chem.* 1965, 4, 855. (b) King, R. B.; Efraty, A.; Douglas, W. M. *J. Organomet. Chem.* 1973, 56, 345.

(26) Jutzi, P.; Kristen, M. O. Unpublished results.

1H -NMR ($CDCl_3$): δ = 11.55, 11.92 (CH_3), 24.11 (CH_2), 45.11 ($N-CH_3$), 58.62 (CH_2-N), 101.41 (ring C), 181.24 (CO). IR (CH_2Cl_2): ν = 2057 cm^{-1} .

Reaction of 4 with Ethylene. A solution of 4 in $CDCl_3$ was prepared in an NMR tube. Ethylene was bubbled through this solution for 10 min. No change in color could be observed. Except for dissolved ethylene, no change in the 1H -NMR spectrum was detected.

Reduction of 4 with Na/Hg under a CO Atmosphere. A solution of 0.13 g (0.26 mmol) of 4 in 10 mL of THF was prepared under an atmosphere of carbon monoxide. The color immediately changed from black-green to dark purple. This solution was added to sodium amalgam (0.7%, 16 g, 4.8 mmol) at room temperature. Within seconds the color changed to amber. After the reaction mixture was stirred at room temperature for 2 h, it was decanted from the amalgam. The solvent was removed in vacuo and the residue extracted with 10 mL of *n*-hexane. After filtration the solvent was removed in vacuo leaving 0.06 g of a red-brown oil. The 1H -NMR spectrum showed only signals of 2 (85%) and free ligand (15%).

$(\eta^5-1-[2-(N,N\text{-Dimethylamino)ethyl}]-2,3,4,5\text{-tetramethylcyclopentadienyl})bis(\eta^2\text{-ethene})cobalt(I)$ (6). **Route A.** A solution of 0.75 g (1.5 mmol) of 4 in 35 mL of THF was prepared under an atmosphere of ethylene. This solution was added to sodium amalgam (1%, 70 g, 30 mmol) at room temperature. The reaction mixture was stirred for 2 h, during which time the color changed from black-green to tan. The solution was decanted from the amalgam, the solvent was removed in vacuo, and the residue was extracted with 20 mL of *n*-hexane. After filtration, the *n*-hexane was removed in vacuo leaving 0.40 g (87%) of 6 as a green oil that forms brown solutions in $CDCl_3$ and C_6D_6 . The 1H -NMR spectrum showed the presence of free ligand (10%), which could not be removed.

Route B. *n*-Butyllithium (1.8 mL, 2.9 mmol) in *n*-hexane (1.6 M) was added to a solution of 0.57 g (2.9 mmol) of Cp^*H in 20

mL of THF at -30 °C. After stirring for 30 min at this temperature, 0.38 g (2.9 mmol) of cobalt(II) chloride was added at -60 °C. The reaction mixture was allowed to warm to room temperature within 2 h, during which time the green-blue suspension changed to a dark brown solution.²⁷ This solution was added to sodium amalgam (0.8%, 120 g, 42 mmol) under an atmosphere of ethylene at -40 °C. Again the reaction mixture was allowed to warm to room temperature and then stirred for 2 h. After the solution was decanted from the amalgam, the solvent was evaporated and the residue extracted with 50 mL of *n*-hexane. Filtration of the *n*-hexane extracts and removal of the volatiles in vacuo afforded 0.47 g (53% based on Cp^*H) of 6 as a green-brown oil. The 1H -NMR spectrum showed the presence of Cp^*H (15%), which could not be removed.

1H -NMR ($CDCl_3$): δ = 0.71 (m, 4H, inner 2H of C_2H_4), 1.47 (s, 6H, CH_3), 1.52 (m, 4H, outer 2H of C_2H_4), 1.61 (s, 6H, CH_3), 1.82–1.91 (m, 2H, CH_2), 2.17–2.32 (m, 2H, CH_2-N), 2.27 (s, 6H, $N-CH_3$).

Acknowledgment. M.O.K. thanks the Fritz ter Meer Stiftung for a scholarship. This work was further supported by the Fonds der Chemischen Industrie and the BASF AG. We thank J. Nierle for his experimental work.

Supplementary Material Available: Tables of anisotropic displacement coefficients and hydrogen coordinates and isotropic displacement coefficients for 4 (2 pages). Ordering information is given on any current masthead page.

OM9301703

(27) When a small sample of this solution is worked up, the paramagnetic dimer 7 can be isolated as black-brown crystals. It is identified by its EI mass spectrum. MS [m/z (relative intensity %)]: 286 ($[M/2]^+$, 16), 251 ($[M/2 - Cl]^+$, 7), 58 ($Me_2NCH_2^+$, 100).