Organometallics **2001,** *20,* 827−833

Nitrogen-Functionalized Cyclopentadienyl Ligands with a Rigid Framework: Complexation Behavior and Properties of Cobalt(I), -(II), and -(III) Half-Sandwich Complexes

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Received August 15, 2000

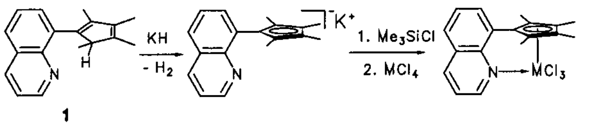
Reaction of 2-lithio-*N*,*N*-dimethylaniline with 2,3,4,5-tetramethylcyclopentenone yields 1-[2-(*N*,*N*-dimethylaminophenyl)-2,3,4,5-tetramethylcyclopentadiene (**2**). As in 1-(8-quinolyl)-2,3,4,5-tetramethylcyclopentadiene (**1**), the N-donor is connected to the Cp ring by a rigid C_2 spacer. $Co_2(CO)_8$ reacts with **1** or **2** to give the Co^I-dicarbonyl half-sandwich complexes **7** and **3**, respectively. Irradiation leads to the binuclear complexes **4** and **8** with a Co−Co double bond. Oxidation of **3** or **7a** is possible with iodine. Whereas **7a** directly forms the Co^{III} complex **9** with coordination of the quinoline to the metal, **3** yields the monocarbonyldiiodo complex **5**. Upon gentle heating in dichloromethane, **5** loses carbon monoxide to give the cobalt complex **6**, displaying intramolecular nitrogen coordination. Reaction of the dimethylaniline-substituted cyclopentadienide **10** with $CoCl_2$ yields the Co^{II} complex **11**. The Co^{III} complex **6** and the Co^{II} complex **11** were treated with methylaluminoxane (MAO) and gave low-activity catalysts for the polymerization of ethylene.

Introduction

During the past decade cyclopentadienyl ligands bearing a sidearm with a donor moiety have attracted a lot of attention in organometallic chemistry.[1] In these hemilabile ligands, the association character and placeholder function of the donor group could steer catalytic processes.[2] Half-sandwich complexes of cobalt with intramolecular phosphorus coordination are known for the cobalt atom in oxidation states +I and +II.[1e] However, the corresponding complexes with pendant nitrogen ligands have only been prepared with Co^{III} centers.[3] Nitrogen donors such as amines or pyridines prefer bonding to transition metals in high oxidation states. Due to their poor acceptor quality, they coordinate only weakly to electron-rich transition metals and labile complexes are built. In contrast, the Cp ligand ($Cp = C_5R_5$, R = H, alkyl, aryl) is known to form strong bonds to many transition metals. Therefore a chelating ligand in which Cp is combined with an amine becomes hemilabile with late transition metals.

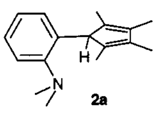
We have synthesized the functionalized cyclopentadiene **1**, where the nitrogen donor atom is incorporated into a rigid aromatic framework.[4] Deprotonation of **1** leads to a chelating ligand which forms stable, crystalline half-sandwich compounds with early transition metals.

Here we report the synthesis of the cyclopentadiene **2**, which is functionalized with an *N*,*N*-dimethylaniline, and the use of **1** and **2** for the preparation of cobalt(I), -(II), and -(III) half-sandwich complexes. In both systems the spacer group between the nitrogen atoms and the cyclopentadiene is a rigid C_2 chain.

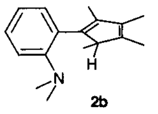


Results

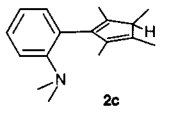
Ligand Synthesis. The synthesis of the new cyclopentadiene **2** follows the route for the preparation of **1**.[4] We treated orthometalated *N*,*N*-dimethylaniline[5] with tetramethylcyclopentenone. After acidic workup and treatment with ammonia, **2** was purified by distillation and a yellow viscous liquid was obtained. The NMR spectra show that a mixture of the three isomers **2a**, **2b**, and **2c** is present. However, the ratio of the isomers changes when the mixture is stored at room temperature. After several weeks, the isomer **2b** becomes the main product and separates as light yellow crystals.



2a



2b



2c

The X-ray structure analysis of **2b** shows that the mainly planar cyclopentadiene forms an angle of 50.7° to the aniline moiety. Because of the conjugation

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[1] Review articles: (a) Okuda, J. *Comm. Inorg. Chem.* **1994**, *16*, 185. (b) Jutzi, P.; Siemeling, U. *J. Organomet. Chem.* **1995**, *500*, 175. (c) Jutzi, P.; Redeker, T. *Eur. J. Inorg. Chem.* **1998**, *6*, 663. (d) Müller, C. Vos, D. Jutzi, P. *J. Organomet. Chem.* **2000**, *600*, 127. (e) Butenschön, H. *Chem. Rev.* **2000**, *100*, 1527. (f) Siemeling, U. *Chem. Rev.* **2000**, *100*, 1495.

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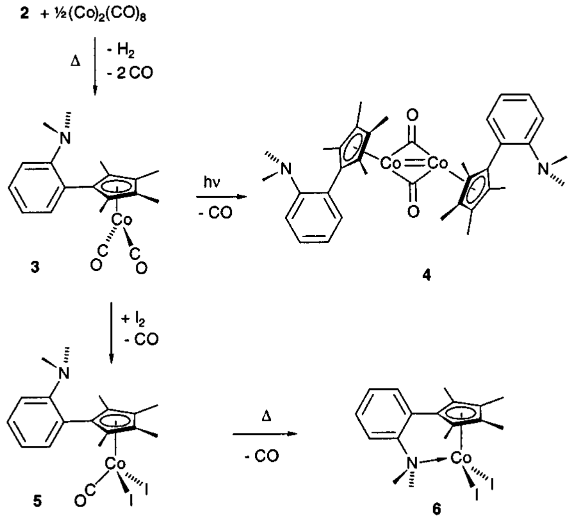
Scheme 1. Preparation of Co^{I} and Co^{III} Complexes Starting with the Dimethylaniline-Substituted Cyclopentadiene 2



between the double bonds in the five-membered ring and the adjacent aniline, isomer **2b** is thermodynamically favored over **2a**. An additional stabilization comes from the interaction of the acidic H atom of the Cp ring and the nitrogen atom. The two ring systems are oriented in a way that the nitrogen lone pair points toward the acidic H atom of the Cp ring. The distance N1−H10 (2.55 Å) is shorter than the sum of the van der Waals radii (2.75 Å), so that the interaction can be described as a C−H···N hydrogen bond.[6] We were also able to obtain crystals from the quinolyl-substituted cyclopentadiene **1**. Similar to **2b**, the orientation of the Cp ring and the quinoline moiety allows interaction of the proton H14 with the nitrogen lone pair, and a H14−N1 distance of 2.59 Å results. The proximity of the heterocyclic system to H14 is also observable in solution: the chemical shift of the H14 atom in the ^{1}H NMR spectrum of **1** (δ(H10) = 4.2[4]) is clearly shifted downfield compared to that of $C_5(CH_3)_5H$.[7]

Cobalt Complexes Starting from 2. It is well known that substituted cyclopentadienes react with $Co_2(CO)_8$ under elimination of hydrogen and formation of dicarbonyl cobalt half-sandwich compounds.[3,8] We treated dicobaltoctacarbonyl with cyclopentadiene **2** in refluxing tetrahydrofuran. After purification by chromatography, the dicarbonyl complex **3** was obtained as red-brown, air-sensitive crystals in good yield (Scheme 1).

The IR spectrum of **3** shows two intense absorptions (1950.7 and 2009.6 cm^{-1}), proving that two CO ligands are present, and therefore no coordination of the nitrogen donor to the saturated cobalt(I) center can occur. In addition we analyzed the solid-state structure of **3** (Figure 2). Two independent molecules are present in the unit cell, and each shows the expected half-sandwich arrangement. The planes of the Cp ring and the aromatic substituent form angles of 69.0° and 69.7°, respectively. Therefore there is no strong interaction between the two π-systems of the ligand. The lone pair of the noncoordinating nitrogen atom points above the plane of the Cp ring opposite the metal center.

Nitrogen donors are weak ligands for low-valent late transition metals. Therefore the aniline group in **3** cannot displace a CO ligand. To create a vacant coordination site, we eliminated one carbon monoxide by irradiation of **3** in hexane. The red-brown solution turns green after a few hours of irradiation with a mercury high-pressure lamp. IR spectroscopy shows that the two absorptions from the terminal carbonyl ligands of **3** become less intense and that a new product is formed (**4**) with a bridging carbonyl group giving a band in the IR at 1770 cm^{-1}. After 4 days the reaction is complete. The NMR spectrum of **4** is very similar to that of the starting compound **3**. The mass spectrum indicates that a dimeric complex was formed. This was not unexpected because it is known that $C_5H_5Co(CO)_2$ and $C_5(CH_3)_5Co(CO)_2$ also form dimers upon irradiation.[9] Complex **4** was analyzed by X-ray crystallography (Figure 3). The solid-state structure shows a bimetallic molecule with bridging CO ligands and pendant *N*,*N*-dimethylaniline groups. Therefore, the loss of one CO ligand in **3** was not compensated by coordination of the free nitrogen donor but by dimerization of the resulting 16-VE fragment. The metal centers in **4** obey the 18-electron rule by interacting via a Co−Co double bond. The distance between the two Co atoms (2.346 Å) lies in the expected range for such molecules.[9]

The donor properties of the chelating nitrogen ligands for cobalt in oxidation state +III have also been investigated. The half-sandwich complex **3** reacts with iodine at room temperature, and dark brown crystals of **5** are formed. The IR spectrum proves that there is still one terminal CO ligand present (2056.7 cm^{-1}). However, the EI mass spectrum shows only an ion without carbon monoxide and with one iodine atom. Jutzi et al. have already demonstrated that oxidation of amino-functionalized Cp−cobaltdicarbonyl complexes with halogens leads to Co^{III} compounds in which one CO ligand remains in the molecule and the nitrogen function does not interact with the metal center.[3] In our case we observed exactly the same behavior. In addition we confirmed the structure of **5** by X-ray crystallography.[10] Gentle heating of **5** in dichloromethane is sufficient to replace the CO ligand by intramolecular coordination of the dimethylamino group to give green, crystalline **6**.

The ^{1}H and ^{13}C NMR signals of the dimethylamino group in **6** are shifted to lower field compared to those of compound **5** ($\Delta\delta = 0.5$ in ^{1}H NMR, $\Delta\delta = 19$ in ^{13}C NMR). The crystal structure analysis of **6** (Figure 4) demonstrates the suitable geometry of the new ligand for chelate complexes.

The aniline ring and the planar Cp ligand are nearly orthogonal (92.9°). This brings the nitrogen donor into an ideal position to coordinate to the metal center with

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(10) The quality of the structure analysis of **5** is poor. In the crystals of compound **5** one I_2 molecule in the bridge interacts with two metal complexes forming an I_4 bridge. A similar arrangement has been found in compound **9** (see Figure 5). Such iodine bridges are known (see ref 11).

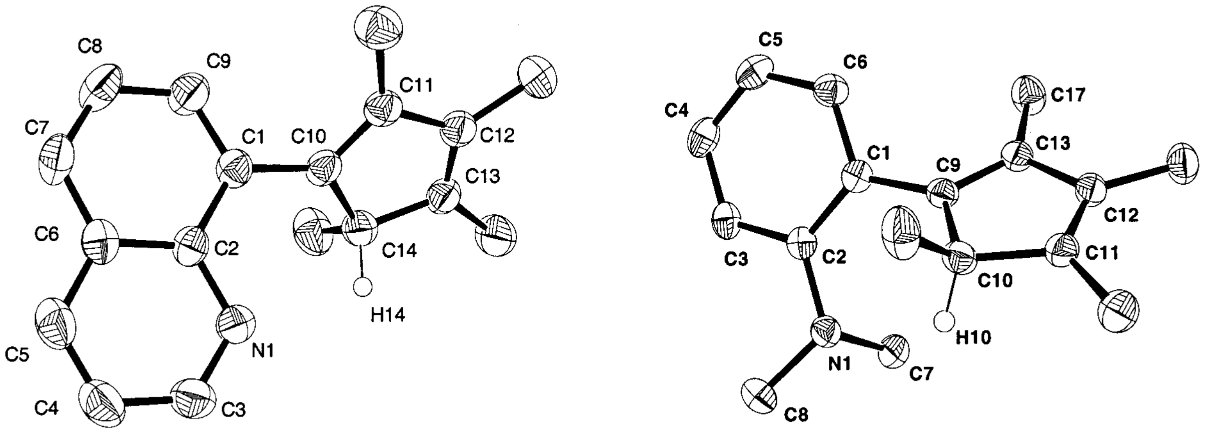


Figure 1. Solid-state structures of **1** (left) and **2b** (right). Selected bond lengths [Å] and angles [deg]: **1**: C1−C10 1.480(4), C10−C11 1.360(4), C11−C12 1.472(4), C12−C13 1.341(4), C13−C14 1.518(4), C10−C14 1.508(4), C14−N1 3.113(5), H14−N1 2.59(3), C14−C10−C1−C2 52.5(4); **2b**: C1−C9 1.482(2), C9−C10 1.513(2), C10−C11 1.509(2), C11−C12 1.342(2), C12−C13 1.478(2), C13−C9 1.355(2), C10−H10 0.98(2), C10−N1 3.120(2), H10−N1 2.55(2), C2−N1−C8 116.78(11), C2−N1−C7 114.37(11), C10−C9−C1−C2 51.1(2).

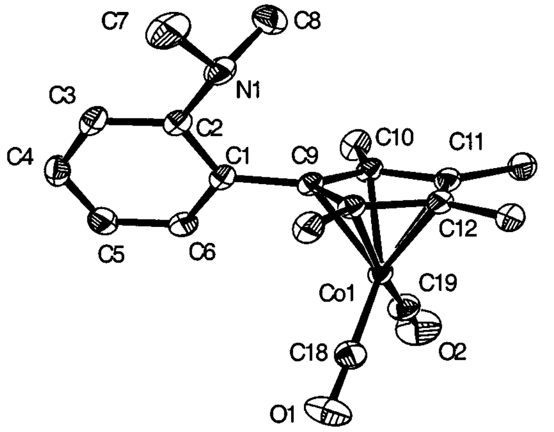


Figure 2. Solid-state structure of **3**, showing one of the two independent molecules in the unit cell. Selected bond lengths [Å] and angles [deg] of the molecule shown: Co−C_{Cp} 2.065−2.097; Co−C_{CO} 1.732−1.740, C−O 1.147−1.151, C2−N1 1.421(1); C7−N1 1.456(2); C2−N1−C7 114.62(12); C2−N1−C8 115.87(12); C7−N1−C8 110.67(14); $plane_{Cp}$−$plane_{dimethylaniline}$ 69.7.

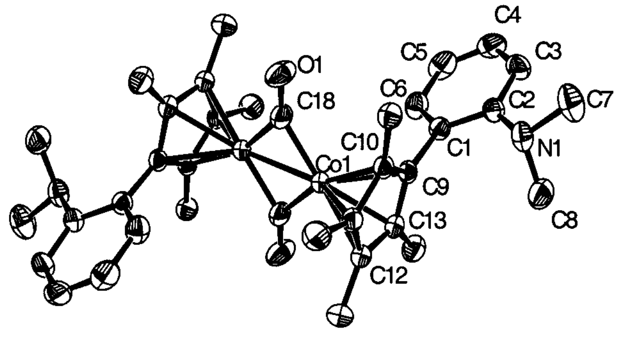


Figure 3. Solid-state structure of **4**. Selected bond lengths [Å] and angles [deg]: Co−C_{Cp} 2.084−2.117; Co1−C18 1.860(2); C−O 1.184(3), Co−Co 2.346(1), C7−N1 1.467(3); C8−N1 1.457(3); C2−N1−C8 113.4(2); C8−N1−C7 110.6(2); C2−N1−C7 115.4(2); $plane_{Cp}$−$plane_{dimethylaniline}$ 67.30.

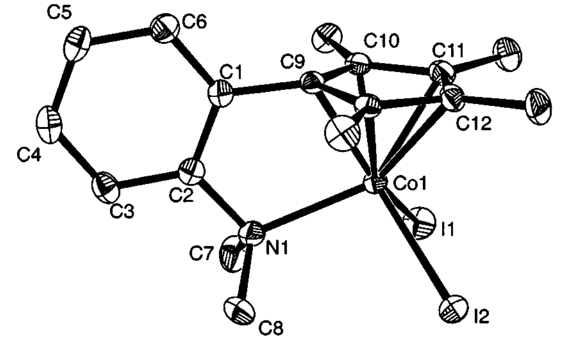


Figure 4. Solid-state structure of **6**. Selected bond lengths [Å] and angles [deg]: Co−C9 2.014(3), Co−C10 2.071(3), Co−C11 2.124(3), Co−C12 2.136(3), Co−C13 2.055(3), Co−I1 2.612(1), Co−I2 2.595(1), Co−N 2.205(2), $plane_{Cp}$−$plane_{aniline}$ 92.9, C2−N−Co 108.8(2), C2−N−C7 107.67(22), C7−N−C8 107.3(3).

a distance of 2.205 Å. The angles at the nitrogen atom (107−109°) are very close to the ideal value for a tetrahedral arrangement. The cobalt atom is not centered below the Cp ring, but shifted toward the *N*,*N*-dimethylaniline substituent. Therefore the Co−C9 distance is 0.12 Å shorter than the average distance from the metal center to C11 and C12. Similar shifts are observed for other donor-functionalized Cp cobalt complexes such as **9** and **11** or examples from the literature.[3]

Cobalt Complexes Starting from 1. We compared the ligand properties of **2** with those of the quinoline-substituted cyclopentadiene **1**. The donor properties of the nitrogen atoms in **1** and **2** are slightly different. Whereas **2** has an sp^3-nitrogen atom without any acceptor properties, the sp^2-nitrogen atom of the quinoline group in **1** is also able to accept electron density because empty π^*-orbitals are available.

1 reacts with $Co_2(CO)_8$ to give the cobalt complex **7a**. In addition we isolated a second complex (**7b**) as a byproduct in up to 5% yield. In **7b** the quinoline is hydrogenated in the heterocyclic moiety. As was the case with **3**, **7a** is transformed to a bimetallic complex (**8**) with bridging CO ligands. However, complex **7a** shows different behavior upon oxidation. Both CO ligands are eliminated by reaction of the red-brown solution in hexane with iodine, leading directly to compound **9**. The observed reactivity shows that the sp^2-nitrogen atom of the quinolyl substituent is able to displace carbon

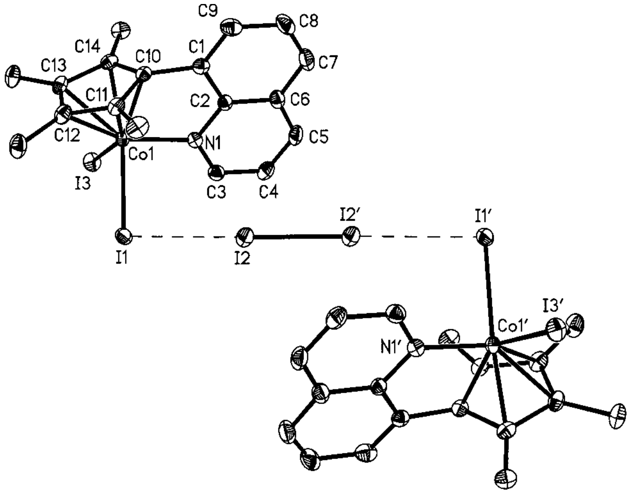


Figure 5. Solid-state structure of **9** with coordinated I_2. Selected bond lengths [Å] and angles [deg]: Co1−C10 2.016(3), Co1−C11 2.082(2), Co1−C12 2.121(3), Co1−C13 2.135(3), Co1−C14 2.047(3), Co−I1 2.608(1), Co−I3 2.595(1), Co−N 1.981(2), I1−I2 3.3625(2), plane$_{Cp}$−plane$_{quinoline}$ 63.0, C10−C1−C9 126.99(24), C10−C1−C2 113.65(21), Co1−I1−I2 97.29(1), I1−I2−I2′ 178.13(1).

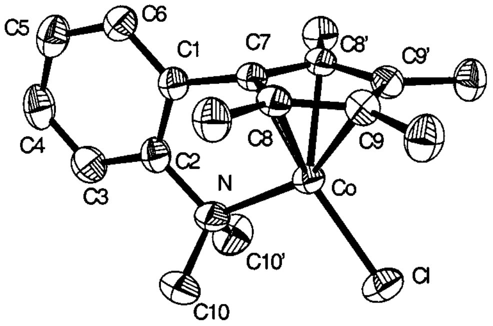


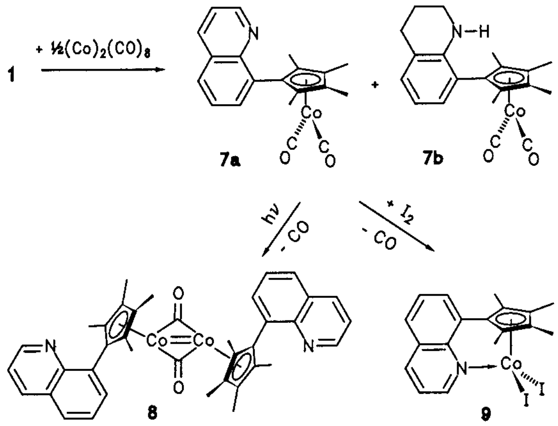
Figure 6. Solid-state structure of **11**. Selected bond lengths [Å] and angles [deg]: Co−C7 1.977(3), Co−C8 2.081(2), Co−C9 2.099(2), Co−Cl 2.224(1), Co−N 2.025(3), plane$_{Cp}$−plane$_{aniline}$ 90.0, C2−N−Co 108.8(2), C2−N−C10 110.0(2), C10−N−Co 109.2(2).

monoxide easily in cobalt(III) complexes, whereas the dimethylaminoaniline ligand binds less strongly to the metal.

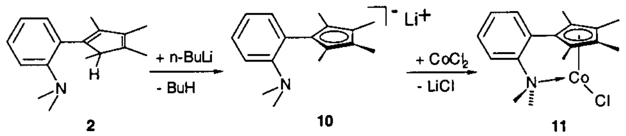
The crystal structure analysis of a charge-transfer adduct of two molecules of **9** with one iodine molecule is shown in Figure 5. The Co^{III} center is coordinated by the nitrogen donor, and the nearly planar quinoline (max. deviation from planarity 0.017 Å) builds an interplanar angle of 83° to the Cp ring. Two half-sandwich complexes are linked by an I_2 molecule, forming a nearly linear I_4 chain. Similar arrangements of iodine chains are known.[11]

Cobalt(II) Complexes. Cyclopentadienyl half-sandwich complexes of cobalt(I) and cobalt(III) are common. The reaction of Co^{II} salts with cyclopentadienides leads preferably to cobaltocene derivatives, because the intermediate half-sandwich complex is electronically unsaturated (15 valence electrons). With the pentamethylcyclopentadienyl ligand, half-sandwich complexes of cobalt(II) have been isolated as dimers. However, in the

Scheme 2. Preparation of Co^{I} and Co^{III} Complexes Starting with the Quinoline-Substituted Cyclopentadiene 1



Scheme 3. Preparation of the Cobalt(II) Half-Sandwich Complex 11



presence of phosphines, or pyridine as external donors, it is possible to isolate compounds of the type $[CpCoL_2]^+$ or CpCoLX (L = phosphine, X = halogen).[12,13] We deprotonated the functionalized cyclopentadiene **2** with n-BuLi and obtained the lithium salt **10**, which was treated with $CoCl_2$ in tetrahydrofuran at room temperature (Scheme 3).

By this route we obtained the Co^{II} complex **11** as a blue powder in 76% yield. The EI mass spectrum shows the molecular ion in 33% abundance. Blue needles that were suitable for X-ray analysis precipitated from a toluene solution (Figure 6).

The molecule has a mirror plane going through the aniline ring as well as the cobalt, chlorine, and one of the carbon atoms of the Cp ring. The distance between the metal center and the plane of the five-membered ring is 1.667 Å and thus significantly shorter than those in Co^{III} complexes **6** (1.684 Å) and **9** (1.683 Å). In addition the Co−N bond in **11** (2.025(3) Å) is much shorter than in **6** (2.205 Å). We conclude that due to the lower coordination number of the cobalt atom, the ligands are more strongly bound in **11** than in **6**.

We recorded an EPR spectrum of **11** in frozen toluene at 110 K (Figure 7). The resonance shows a rhombic *g*-tensor with characteristic ^{59}Co hyperfine structure. Two *g*-values and the corresponding hyperfine coupling constants were directly taken from the spectrum; the values for the third octet in the middle of the spectrum were determined by comparison with a simulated spectrum (see Figure 7 for details).[14]

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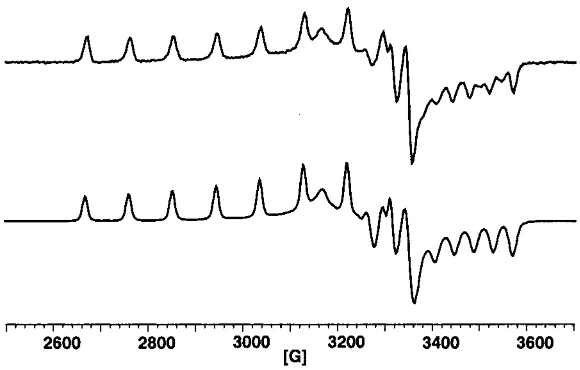

Figure 7. Experimental X-band EPR spectrum of **11** in frozen toluene solution at 110 K (top) and simulated spectrum (bottom). Parameters used for simulation: $A(x,x) = 92.0$ G, $g(x) = 2.265$, line width = 10 G; $A(y,y)$ 18.0 G, $g(y) = 2.090$, line width = 18 G; $A(z,z)$ 41.0 G, $g(z) = 1.975$, line width = 16 G.

To obtain chelated Co(I) complexes, **11** and **9** have been reduced with Na/Hg in the presence of CO. However, only the dicarbonyl complexes **3** and **7a**, respectively, have been obtained. A similar reduction experiment in the presence of ethylene did not lead to isolable products.

Catalytic Olefin Polymerization. Several half-sandwich complexes of transition metals, such as titanium or chromium in oxidation states III or IV, with functionalized Cp ligands show high activity as olefin polymerization catalysts.[15] It is also known that cationic Co^{III} complexes of the type $[C_5Me_5Co(H)L(C_2H_4)]^+$ (L = PR_3, $P(OR)_3$) catalyze the polymerization of ethylene with low activity.[16] Highly active catalysts with late transition metals have been developed with neutral chelating nitrogen ligands.[17]

We tested the Co^{III} complex **6** as well as the Co^{II} complex **11** in catalytic olefin polymerization experiments. Solutions of **6** or **11** in toluene were activated with 1000 equiv of methylaluminoxane, and the mixtures were stirred under an atmosphere of ethylene at room temperature for 1 h. The polymerization was stopped by addition of a mixture of CH_3OH/HCl. Filtration led to small amounts of solid polyethylene. The activity of **6** as well as of **11** lies in the range between 3 and 8 ($g_{(polymer)}$ $mmol^{-1}{}_{(catalyst)}$ h^{-1} bar^{-1}).

Conclusion

We have synthesized a hemilabile chelating ligand in which an amino group is connected to a cyclopentadienyl ring by a rigid C_2 unit. The coordination properties of the new ligand in comparison to the 8-quinolylcyclopentadienyl ligand have been evaluated in terms of the complexation chemistry of Co^I, Co^{II}, and Co^{III} centers. The dimethylamino group as well as the 8-quinolyl group is able to displace CO ligands in Co^{III} compounds, but not in Co^I compounds. The quinolyl substituent shows a greater tendency to bind to the Co^{III} center compared to the *N*,*N*-dimethylamino group. Crystal structure determinations of the cobalt complexes with intramolecular nitrogen coordination prove the tailored fit of the new ligand for the formation of half-sandwich compounds. The paramagnetic Co^{II} complex **11** is stable toward ligand dismutation with formation of a cobaltocene derivative. The EPR spectrum shows a rhombic *g*-tensor and large ^{59}Co electron coupling. In combination with methylaluminoxane complexes **6** and **11** show low activity for the polymerization of ethylene.

Experimental Section

All manipulations were carried out under a nitrogen atmosphere with anhydrous solvents saturated with nitrogen. Glassware was heated under vacuum prior to use. Compound **1** was synthesized according to the reported procedure.[4] NMR spectra were recorded on a Bruker AC200 spectrometer (200.1 MHz for ^1H; 50.3 MHz for ^{13}C). EPR spectra were obtained on a Bruker ESP300 instrument at 9.3 GHz equipped with a frequency counter. Simulation of the anisotropic spectrum of **11** was carried out with the program SimFonia.[14]

1-(2-*N*,*N*-Dimethylaminophenyl)-2,3,4,5,-tetramethylcyclopentadiene (2). *N*,*N*-Dimethylaniline (30.0 g, 0.25 mol) and 80.0 mL (0.20 mol) of 2.5 M n-BuLi in hexane were refluxed for 52 h. At room temperature 27.1 g (0.20 mol) of 2,3,4,5-tetramethylcyclopent-2-enone was added, and the solution was heated to reflux for 48 h. After cooling to room temperature 100 g of ice was added followed by 10 mL of concentrated hydrochloric acid. The mixture was stirred for 30 min, extracted with diethyl ether, and dried over Mg_2SO_4. Distillation at 125–135 °C/10^{-2} mbar gave 21.9 g of **2** (45%) as a yellow oil. Storage of the isomeric mixture at room temperature for several weeks led to the formation of the crystalline isomer **2b**. The spectroscopic data are given for **2b**. ^1H NMR ($CDCl_3$): $\delta = 0.89$ (d, 3 H, $^3J(H,H) = 4.0$ Hz, CH_3); 1.80 (s, 3 H, CH_3); 1.88 (s, 6 H, CH_3); 1.96 (s, 3 H, CH_3); 2.64 (s, 6 H, N-CH_3); 3.5 (q, 1 H, $^3J(H,H) = 4.0$ Hz, CpH); 0.6.97–7.05 (m, 2 H, CH^{Ar}); 7.02–7.35 (m, 2 H, CH^{Ar}). ^{13}C NMR ($CDCl_3$): δ 11.1, 11.9, 12.5, 14.4 (Cp-CH_3); 43.1 (N-CH_3); 51.7 (CH_{Cp}); 117.0, 126.8, 127.4, 131.9 (CH^{Ar}); 121.2, 128.8, 130.0, 132.2, 134.1, 140.0 (C_q). EI MS: *m/z* (%) 241 (100, M^+); 226 (34, $M^+ - CH_3$), 212 (42, $M^+ - 2CH_3$), 196 (30, $M^+ - 3CH_3$), 182 (20, $M^+ - 4CH_3$), 120 (10, $M^+ - Cp^+$), 77 (5, $C_6H_5{}^+$). HR-MS(EI): calcd for $C_{17}H_{23}N$ 241.1830; found 241.1823.

Dicarbonyl-η^5-[1-(2-*N*,*N*-dimethylaminophenyl)-2,3,4,5-tetramethylcyclopentadienyl]cobalt(I) (3). A solution of 0.26 g (0.76 mmol) of $Co_2(CO)_8$ and 0.37 g (1.52 mmol) of **2** in 50 mL of THF was heated to reflux for 5 h. The solvent was removed in a vacuum, and the red-brown oily residue was extracted with 20 mL of hexane. The raw product was purified by chromatography on Al_2O_3 (eluent toluene) to give 0.39 g of **3** (72%). ^1H NMR (C_6D_6): δ 1.76 (s, 6 H, CH_3), 1.62 (s, 6 H, CH_3); 2.87 (s, 6 H, CH_3); 6.92–6.79 (m, 2 H, CH^{Ar}); 7.09–7.13 (m, 1 H, CH^{Ar}); 7.75 (d, 1 H, CH^{Ar}). ^{13}C NMR (C_6D_6): δ 10.5, 10.9 (CH_3); 43.1 (CH_3); 56.3, 97.1, 97.5 (C^{Cp}); 108.5, 118.0, 121.8, 137.7, (CH^{Ar}); 126.4, 154.0 (C^{Ar}); 208.1 (CO). MS: (EI) *m/z* (%) 355 (33, M^+); 327 (18, $M^+ - CO$); 297 (100, $M^+ - 2CO - 2H$); 241 (15, $\mathbf{2}^+$). FT-IR: (hexane) ν (cm^{-1}) 2009.6, 1950.7. Anal. Calcd for $C_{19}H_{22}NO_2Co$ (355.3): C, 64.23; H, 6.24; N, 3.94. Found: C, 63.99; H, 6.32; N, 3.88.

Bis{carbonyl-η^5-[1-(2-*N*,*N*-dimethylaminophenyl)-2,3,4,5,-tetramethylcyclopentadienyl]cobalt(I)} (4). A Pyrex Schlenk tube with a solution of 0.43 g (1.21 mmol) of **3** in 50 mL of hexane was irradiated with a 150 W mercury lamp for 24 h. The color of the solution changed from red-brown to

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Table 1. Crystal Data and Structure Refinement Details for 1−4, 6, 7a, 9, and 11

	1	**2b**	**3**	**4**
empirical formula	$C_{18}H_{19}N$	$C_{17}H_{23}N$	$C_{19}H_{22}CoNO_2$	$C_{36}H_{44}Co_2N_2O_2$
fw	249.34	241.36	355.31	654.60
cryst syst	triclinic	triclinic	triclinic	triclinic
space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
unit cell dimens: *a*, Å	7.100(5)	7.2223(7)	8.4292(1)	8.608(4)
b, Å	9.170(10)	10.3578(10)	14.9784(2)	9.012(4)
c, Å	11.210(10)	10.9185(10)	15.0976(2)	11.470(6)
α, deg	93.36(5)	67.116(2)	107.392(1)	78.02(3)
β deg	102.01(5)	72.827(2)	100.742(1)	68.63(3)
γ, deg	93.27(5)	88.440(2)	92.757(1)	76.88(3)
volume, Å^3	710.9(11)	715.38(12)	1776.15(4)	799.3(7)
Z	2	2	4	1
density (calcd), Mg/m^3	1.165	1.121	1.329	1.360
abs coeff, mm^{-1}	0.067	0.064	0.974	1.072
F(000)	268	264	744	344
cryst size, mm^3	0.35 × 0.25 × 0.10	0.42 × 0.28 × 0.20	0.56 × 0.44 × 0.44	0.8 × 0.6 × 0.15
θ range for data collection, deg	1.86 to 25.03	2.13 to 28.25	1.43 to 28.28	1.92 to 25.00
index ranges	$-8 \le h \le 8$, $-10 \le k \le 10$, $0 \le l \le 13$	$-9 \le h \le 9$, $-12 \le k \le 13$, $0 \le l \le 14$	$-11 \le h \le 10$, $-19 \le k \le 18$, $0 \le l \le 20$	$-9 \le h \le 10$, $-10 \le k \le 10$, $0 \le l \le 13$
no. of reflns collected	2503	4903	23480	2809
no. of ind reflns	2497	3343 [*R*(int) = 0.010]	8588 [*R*(int) = 0.031]	2809
no. of reflns with $I > 2\sigma(I)$	1402	2388	7358	2577
completeness to θ_{max}	99.3%	94.2%	97.4%	99.9%
abs corr	*ψ*-scan	semiemp. from equivalents	semiemp. from equivalents	*ψ*-scan
max. and min. transmn	0.999 and 0.875	0.928 and 0.851	0.831 and 0.639	1.000 and 0.702
no. of data/restraints/params	2497/0/248	3343/0/255	8588/0/591	2809/0/278
goodness-of-fit on F^2	0.985	0.967	1.018	1.044
final *R* indices [$I > 2\sigma(I)$]	R1 = 0.0569, wR2 = 0.1242	R1 = 0.0457, wR2 = 0.1133	R1 = 0.0283, wR2 = 0.0762	R1 = 0.0274, wR2 = 0.0700
R indices (all data)	R1 = 0.1303, wR2 = 0.1502	R1 = 0.0672, wR2 = 0.1230	R1 = 0.0345, wR2 = 0.0792	R1 = 0.0317, wR2 = 0.0725
largest diff peak and hole, e Å^{-3}	0.170 and −0.202	0.280 and −0.195	0.469 and −0.242	0.252 and −0.294

	6	**7a**	**9** with I_2	**11**
empirical formula	$C_{17}H_{22}CoI_2N$	$C_{20}H_{18}CoNO_2$	$C_{18}H_{18}CoI_3N$	$C_{17}H_{22}ClCoN$
fw	553.09	363.28	687.96	334.74
cryst syst	monoclinic	triclinic	monoclinic	monoclinic
space group	*P*2(1)/*c*	$P\bar{1}$	*P*2(1)/*c*	*P*2(1)/*m*
unit cell dimens *a*, Å	8.7194(4)	8.362(5)	13.2848(2)	7.469(4)
b, Å	25.4550(12)	9.119(5)	7.6319(1)	10.662(5)
c, Å	8.2347(4)	12.310(7)	19.7849(3)	10.804(5)
α, deg	90	98.35(4)	90	90
β, deg	97.028(1)	104.25(4)	101.783(1)	109.97(2)
γ, deg	90	105.97(4)	90	90
volume, Å^3	1813.98(15)	851.5(8)	1963.69(5)	808.6(7)
Z	4	2	4	2
density (calcd), Mg/m^3	2.025	1.417	2.327	1.375
abs coeff, mm^{-1}	4.344	1.018	5.589	1.216
F(000)	1056	376	1276	350
cryst size, mm^3	0.32 × 0.20 × 0.11	0.80 × 0.50 × 0.40	0.40 × 0.18 × 0.15	0.45 × 0.45 × 0.15
θ range for data collection	1.60 to 28.29	1.75 to 24.98	1.57 to 28.26	2.01 to 27.99
index ranges	$-11 \le h \le 11$, $0 \le k \le 33$, $0 \le l \le 10$	$-9 \le h \le 9$, $-10 \le k \le 10$, $0 \le l \le 14$	$-17 \le h \le 17$, $0 \le k \le 10$, $0 \le l \le 26$	$-9 \le h \le 9$, $0 \le k \le 14$, $0 \le l \le 14$
no. of reflns collected	12 363	2994	23452	2050
no. of ind reflns	4396 [*R*(int) = 0.023]	2994	4806 [*R*(int) = 0.036]	2050
no. of reflections with $I > 2\sigma(I)$	4011	2917	4373	1534
completeness to θ_{max}	97.8%	99.8%	98.7%	100.0%
abs corr	semiemp. from equivalents	*ψ*-scan	multiscan	*ψ*-scan
max. and min. transmn	0.831 and 0.531	1.000 and 0.915	0.831 and 0.568	1.000 and 0.746
no. of data/restraints/params	4396/0/278	2994/0/247	4806/0/281	2050/0/154
goodness-of-fit on F^2	1.064	1.046	1.051	1.030
final *R* indices [$I > 2\sigma(I)$]	R1 = 0.0246, wR2 = 0.0619	R1 = 0.0245, wR2 = 0.0688	R1 = 0.0196, wR2 = 0.0484	R1 = 0.0374, wR2 = 0.0788
R indices (all data)	R1 = 0.0279, wR2 = 0.0635	R1 = 0.0252, wR2 = 0.0694	R1 = 0.0231, wR2 = 0.0495	R1 = 0.0657, wR2 = 0.0871
largest diff peak and hole, e Å^{-3}	1.577 and −0.876	0.308 and −0.211	0.865 and −0.596	0.270 and −0.408

green. The reaction mixture was concentrated in a vacuum, and at − 30 °C green needles of **4** precipitated (0.31 g, 78%). ^{1}H NMR (C_6D_6): δ 1.47 (s, 12 H, CH_3); 2.15 (s, 12 H, CH_3); 2.38 (s, 12 H, CH_3); 6.06 (d, 2 H, CH^{Ar}); 6.46 (dd, 2H, CH^{Ar}); 6.66 (d, 2 H, CH^{Ar}); 6.96 (dd, 2 H, CH^{Ar}). ^{13}C NMR (C_6D_6): δ 8.8, 9.2 (CH$_3$); 43.1 (CH$_3$); 99.5, 93.4 (C^{Cp}); 117.6, 121.0, 127.6, 136.1 (CH^{Ar}) (some of the quartenary ^{13}C resonances were not detected due to the low solubility of **4**). MS: (EI) *m*/*z* (%) 653 (19, M$^+$); 355 (20, $\mathbf{3}^+$); 327 (23, $\mathbf{3}^+ - $ CO); 299 (100, $\mathbf{3}^+ - $ 2CO); 241 (4, $\mathbf{2}^+$). FT-IR (hexane) ν (cm^{-1}): 1770. Anal. Calcd for $C_{36}H_{44}N_2O_2Co_2$ (654.6): C, 66.05; H, 6.77; N, 4.28. Found: C, 65.79; H, 6.58; N, 4.26.

Carbonyldiiodo-η^5-[1-(2-*N*,*N*-dimethylaminophenyl)-2,3,4,5-tetramethylcyclopentadienyl]cobalt(III) (5). A solution of 0.30 g (1.18 mmol) of I_2 in 30 mL of diethyl ether was added dropwise to a solution of 0.41 g (1.15 mmol) of **3** in 30 mL of diethyl ether at −30 °C. The color of the reaction mixture changed from red-brown to dark violet. After stirring for 16 h at room temperature, the reaction mixture was concentrated to give violet crystals at −30 °C. The crystals were washed with 10 mL of *n*-hexane and dried in a vacuum (yield 0.39 g, 58%). ^{1}H NMR (CD_2Cl_2): δ 2.27, 2.43 (s, 12 H, CH_3); 2.52 (s, 6 H, CH_3); 7.16−7.21 (m, 2 H, CH^{Ar}); 7.38−7.50 (m, 1 H, CH^{Ar}); 8.01−8.05 (m, 1 H, CH^{Ar}). ^{13}C NMR (CD_2Cl_2): δ 10.8, 11.9 (CH$_3$); 42.7 (CH$_3$); 100.5, 101.5, 103.4 (C^{Cp}); 118.3, 121.4, 129.8, 133.6 (CH^{Ar}); 120.4, 153.2 (C^{Ar}). MS: (EI) *m*/*z* (%) 426 (52, M$^+ - $ CO − I); 241 (99, $\mathbf{2}^+$); 28 (100, CO$^+$). FT-IR (CH_2Cl_2): ν (cm^{-1}) 2056.7.

Diiodo-η^5-[1-(2-*N*,*N*-dimethylaminophenyl)-2,3,4,5-tetramethylcyclopentadienyl]cobalt(III) (6). A solution of 0.20 g (0.34 mmol) of **5** in 30 mL of dichloromethane was heated to reflux for 6 h. Removal of solvent and washing with hexane yielded 0.16 g (85%) of green **6**. ^{1}H NMR (CD_2Cl_2): δ 1.71, 2.13 (CH_3); 2.93 (CH_3); 7.42−7.53 (m, 2 H, CH^{Ar}); 7.63−8.00 (m, 2 H, CH^{Ar}). ^{13}C NMR (CD_2Cl_2): δ 11.2, 14.1 (CH$_3$); 61.7 (CH$_3$); 88.4, 91.1, 99.1 (C^{Cp}); 147.5, 160.6 (C^{Ar}); 121.3, 126.2, 127.3, 130.2 (CH^{Ar}). MS (EI) *m*/*z* (%): 426 (5.7, M$^+ - $ I); 241 (100, $\mathbf{2}^+$); 127 (38, I$^+$).

Dicarbonyl-η^5-[1-(8-chinolyl-2,3,4,5-tetramethylcyclopentadienyl]cobalt(I) (7a). A solution of 0.44 g (1.29 mmol) of $Co_2(CO)_8$ and 0.64 g (2.57 mmol) of **1** in 50 mL of tetrahydrofuran was heated to reflux for 16 h. The solvent was removed in vaccum, and the red-brown residue was extracted with 50 mL of *n*-hexane and purified by chromatography on Al_2O_3 (eluent toluene/hexane, 1:1). Yield: 0.28 g (30%). (The hydrogenated derivative **7b** was isolated in up to 5% yield and identified by mass and NMR spectroscopy.) ^{1}H NMR (C_6D_6): δ 1.73, 2.11 (s, 12 H, CH_3); 7.45 (dd,1 H); 7.63 (dd, 1 H); 7.85 (dd, 1 H); 8.18−8.20 (m, 2 H); 8.97 (dd, 1 H). ^{13}C NMR (C_6D_6): δ 10.5, 11.1 (CH$_3$); 97.5, 98.9, 106.6 (C^{Cp}); 121.0, 127.5, 128.2, 133.6, 135.9, 136.6, 148.5, 149.9 (C^{Ar}); 208.7 (CO). MS: (EI) *m*/*z* (%) 363 (12, M$^+$); 335 (20, M$^+ - $ CO); 307 (100, M$^+ - $ 2 CO). FT-IR: (hexane) ν (cm^{-1}) 1948.4, 2007.2. Anal. Calcd for $C_{20}H_{18}NO_2Co$ (363.3): C, 66.12; H, 4.99; N, 3.86. Found: C, 66.06; H, 5.04; N, 3.79.

Bis{carbonyl-η^5-[1(8-chinolyl)-2,3,4,5-tetramethylcyclopentadienyl]cobalt(I) (8). A Pyrex tube with a solution of 0.20 g (0.55 mmol) of **7** in 50 mL of hexane was irradiated with the light of a 150 W mercury lamp for 24 h. The color of the solution changed from red-brown to green. After removal of the solvent in a vacuum, the raw product was washed with hexane to give 0.12 g (65%) of **8** as a green powder. ^{1}H NMR (C_6D_6): δ 1.48, 2.19 (s, 12 H, CH_3); 6.72 (d, 1 H); 6.88 (dd, 1 H); 7.31−7.36 (m, 1 H); 7.57−7.60 (m, 1 H); 7.65 (dd, 1 H); 8.70 (dd, 1 H). ^{13}C NMR (CD_2Cl_2): δ 9.4, 9.9 (CH_3); 87.6, 97.4, 108.1 (C^{Cp}); 123.8, 127.9, 128.6, 129.0, 137.8, 157.5, (CH^{Ar}); 129.0, 129.6, 156.6 (C^{Ar}); 182.4 (CO). MS: (EI) *m*/*z* (%) 670 (21, M$^+$), 614 (5, M$^+ - $ 2 CO), 335 (64, $\mathbf{7}^+ - $ CO), 307 (100, $\mathbf{7}^+ - $ 2CO). FT-IR: (hexane) ν (cm^{-1}) 1770. Anal. Calcd for $C_{38}H_{36}N_2O_2Co_2$ (670.6): C, 68.06; H, 5.41; N, 4.18. Found: C, 67.83; H, 5.49; N, 4.13.

Diiodo-η^5-[1-(8-chinolyl-2,3,4,5-tetramethylcyclopentadienyl]cobalt(III) (9). A solution of 0.18 g (0.71 mmol) of iodine in 20 mL of diethyl ether was added dropwise to a solution of 0.25 g (0.69 mmol) of **7** in 30 mL of diethyl ether at −30 °C. The reaction mixture was stirred at room temperature for 16 h, the solvent was removed in a vacuum, and the brown-violet residue was washed with 20 mL of hexane to give 0.10 g (26%) of brown-violet **9**. In the presence of excess iodine, crystals were obtained from dichloromethane at −30 °C. ^{1}H NMR ($CDCl_3$): δ 2.00, 2.09 (s, 12 H, CH_3); 7.28 (dd, 1 H); 7.74−7.85 (m, 2 H); 7.99 (dd, 1 H); 8.25−8.35 (m, 2 H). ^{13}C NMR ($CDCl_3$): δ 10.5, 12.2 (CH$_3$); 89.9, 93.7, 105.2 (C^{Cp}); 123.0, 126.6, 127.7, 128.2, 136.4, 161.9 (CH^{Ar}); 128.3, 128.4, 155.8 (q, C^{Ar}). MS (FAB$^+$): *m*/*z* (%) 561 (5, M$^+$); 434 (90, M$^+ - $ I); 307 (M$^+ - $ 2I).

Chloro-η^5-[1-(2-*N*,*N*-dimethylaminophenyl)-2,3,4,5,-tetramethylcyclopentadienyl]cobalt(I) (11). A 0.40 g (1.66 mmol) sample of the substituted cyclopentadiene **2** in 30 mL of THF was deprotonated with 0.66 mL (1.65 mmol) of n-BuLi (2.5 M in hexane) at room temperature. After 30 min the orange solution was added dropwise to a suspension of 0.21 g (1.62 mmol) of $CoCl_2$ in 20 mL of THF. The reaction mixture was stirred for 16 h, and the solvent was removed in a vacuum. The blue solid was dissolved in 20 mL of toluene and filtered through a fritted column (G4) to give 0.42 g (77%) of blue **11**. Crystals were obtained from a concentrated solution in toluene at −30 °C. MS (EI): *m*/*z* (%) 334 (19, M$^+$); 296 (21, M$^+ - $ HCl − 2H); 241 (100, $\mathbf{2}^+$); 120 (20, $C_6H_4NMe_2^+$). HR-MS (EI): calcd for $C_{17}H_{22}NCoCl$ 334.0773, found 334.0751. EPR (110 K): $g_1 = 2.265$, $g_2 = 2.090$, $g_3 = 1.975$; $A_1 = 92.0$ G, $A_2 = 18.0$, $A_3 = 41.0$ G.

X-ray Crystal Structure Determinations of 1−4, 6, 7a, 9, and 11. Crystal data for **2**, **3**, **6**, and **9** were collected on a Bruker AXS SMART 1000 diffractometer with a CCD area detector (Mo Kα radiation, graphite monochromator, $\lambda = 0.71073$ Å) at −100 °C, and for **1**, **4**, **7a**, and **11** on a Siemens STOE AED2 (Mo Kα radiation, graphite monochromator, $\lambda = 0.71073$ Å) at −70 °C. The structures were solved by direct methods and refined by full-matrix least squares against F^2 with all reflections using the SHELXTL-programs.[18] All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were located in difference Fourier maps and refined isotropically. Crystal data and experimental details are listed in Table 1.

Acknowledgment. The authors gratefully acknowledge financial support from the Deutsche Forschungsgemeinschaft (Sonderforschungsbereich 247) and the state Baden-Württemberg.

Supporting Information Available: Tables giving X-ray crystal structure data for **1−4, 6, 7a, 9,** and **11**. This material is available free of charge via the Internet at http://pubs.acs.org.

OM0007163

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