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Transition Metal Derivatives of a ((Dimethylamino)ethyl)cyclopentadienyl Ligand. Synthesis and Structures of Amino-Containing Cyclopentadienyl Derivatives of Cobalt(I) and -(III) Including Water-Soluble Compounds

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The synthesis of monometallic cobalt(III) and -(I) complexes of ((dimethylamino)ethyl)cyclopentadienyl are reported. The presence of the basic amino group facilitates these synthesis using the corresponding cyclopentadiene complexes as starting material. A cobaltocenium green complex $[\{\eta^5\text{-}C_5H_4(CH_2)_2N(H)Me_2\}_2Co^{III}]^{3+}(Cl^-)_3$ (**3**) was obtained from $C_5H_5(CH_2)_2NMe_2$ (**1**) or from its salt $M[C_5H_4(CH_2)_2NMe_2]$ (M = Na, Li) (**2**) upon reaction with $Co^{II}Cl_2$ in THF. The structure of the complex $[\{(\eta^5\text{-}C_5H_4(CH_2)_2NMe_2)(\eta^5\text{-}C_5H_4(CH_2)_2N(H)Me_2)\}Co^{III}](PF_6)_2$ (**4**), prepared from **3** by treatment with NH_4PF_6 in aqueous solutions, was solved in the triclinic space group $P\bar{1}$ with one molecule in the unit cell, the dimensions of which were $a = 6.314(2)$ Å, $b = 7.137(2)$ Å, $c = 13.452(2)$ Å, $\alpha = 103.66(2)°$, $\beta = 90.25(2)°$, $\gamma = 92.89(2)°$, and $V = 588.2(3)$ Å^3. Adjacent molecules in the unit cell of **4** are hydrogen bonded via a H^+ through their $-NMe_2$ side chains. The reaction of $Co_2(CO)_8$ with $C_5H_5(CH_2)_2NMe_2$ (**1**) leads to the formation of $[\{\eta^5\text{-}C_5H_4(CH_2)_2NMe_2\}Co^I(CO)_2]$ (**5**). Treatment of **5** with HBF_4 in ether solutions yielded $[\{\eta^5\text{-}C_5H_4(CH_2)_2N(H)Me_2\}Co^I(CO)_2]^+BF_4^-$ (**6**). Oxidation of **5** with I_2 or Cl_2 gas yielded $[\{\eta^5\text{-}C_5H_4(CH_2)_2NMe_2\}Co^{III}I_2]$ (**7a**) and $[\{\eta^5\text{-}C_5H_4(CH_2)_2NMe_2\}Co^{III}Cl_2]$ (**7b**). Addition of HBF_4 to complex **7a** resulted in the breaking of the Co^{III}-NMe_2 bond, producing the dimeric complex $[\{(\eta^5\text{-}C_5H_4(CH_2)_2N(H)Me_2)Co^{III}I_2\}_2]^{2+}(BF_4^-)_2$ (**9**). The bridged diiodo dimer **10**, $[\{(\eta^5\text{-}C_5H_4(CH_2)_2NMe_2)CoI\}_2]^{2+}(BF_4^-)_2$, on the other hand, could be obtained from complex **7a** upon addition of $AgBF_4$ in CH_2Cl_2.

Introduction

The cyclopentadienyl group, C_5H_5 (Cp), is one of the most important ligands in the organometallic chemistry of the transition metals, more than 80% of which are known to form complexes containing Cp or related ligands.[1,2] Such ligands can stabilize metals in low and high oxidation states, while the easy change of hapticity (η^1, η^3, or η^5) of the Cp ligand allows it to be readily adaptable to changes in the electronic and steric requirements of the central atom.

Among the cyclopentadienyl ligands, those with an additional functionalized side chain, which can reversibly coordinate to the metal centers, have attracted much interest in recent years.[3−6] Thus, by temporarily blocking a vacant coordination site, it is possible to stabilize highly reactive intermediates and find applications in catalytic processes.[7] In addition, an amino group in the side chain may enhance water solubility of the corresponding metal complexes via quaternization[8−10] and contribute to the development of organometallic chemistry in aqueous solutions.[11]

In addition, it has been shown that several metallocene dihalides (e.g V, Ti, Nb, Mo, etc.) exhibit anticancer activity against a variety of tumors.[12−14] Solubility in aqueous media is a very important factor for an organometallic complex to possess antitumor activity.[5] Consequently, one can speculate that cyclopentadienylmetal complexes with a pendant side chain containing an amino group might have a better chance of exhibiting antitumor properties than neutral metal−Cp complexes. In this respect, we recently reported[5] the syntheses of organometallic complexes of Rh(I) and Rh(III) with the cyclopentadienyl ligand bearing such an amino side chain, specially tailored to be water soluble.

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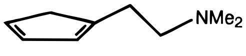
In the present paper, we report on organometallic complexes of Co(I) and Co(III) with the same ligand, synthesized by using either the functionalized cyclopentadiene $C_5H_5(CH_2)_2NMe_2$ (**1**)- or its Li[15] or Na[16] salts (**2**). The results are compared to those obtained with Rh(I) and Rh(III). The use of the cyclopentadienyl (Cp) ligand for these cobalt complexes may also allow comparisons with complexes of the tetramethylcyclopentadienyl (η^5-C_5Me_4R) analogues.[17] Usually the latter complexes show greater air and water stability compared to the former.



(**1**)

(**2**)

Results and Discussion

Most of the syntheses of cyclopentadienyl transition metal complexes require a prior deprotonation of the weakly acidic cyclopentadiene. Cyclopentadienyllithium or -sodium salts are therefore the most common reagents for the introduction of cyclopentadienyl ligands. In addition, starting from a transition metal salt generally requires an auxiliary base to deprotonate the cyclopentadiene. It has recently been shown in the case of various rhodium derivatives that the role of this auxiliary basic reagent can probably be filled by the free amino group attached to the cyclopentadiene.[5,16]

In this paper we report that the addition of an excess of $C_5H_5(CH_2)_2NMe_2$ to a suspension of $Co^{II}Cl_2$ in THF affords after 4 h reflux a green product (**3**). In view of the extremely easy oxidation of the cobaltocenes,[18] we considered **3** to be more as a cobaltocenium salt than as a cobaltocene derivative. In other words, we supposed that, after the initial formation of an ammonium cobaltocene derivative (similar to the previously reported formation of a rhodocenium salt[5]), a second process of oxidation of this primary product occurred, possibly involving traces of water or oxygen as oxidants.

Originally, we thought that complex **3** may be monoprotonated or biprotonated at the two $-NMe_2$ side chains. Later, we found that its elemental analysis and its molar conductance value (Λ_M=350 $\Omega^{-1}\cdot cm^2\cdot mol^{-1}$) were more consistent with a 1:3 electrolyte, corresponding to a biprotonated derivative (**3**) as the major product.

In the ^1H NMR spectrum of **3** in D_2O, the cyclopentadienyl pseudotriplets are observed at 5.78 and 5.75 ppm, the (b)-CH_2N triplet of the side chain is at 3.27 ppm, the (a)-CH_2 triplet is at 2.95 ppm, and the $-NMe_2$ singlet is at 3.21 ppm. Due to protonation, both the (b)-CH_2N triplet and the $-NMe_2$ singlet are downfield-shifted by 0.81 and 1.06 ppm, respectively, compared to those of the free ligand. In DMSO-d_6 an additional broad signal is observed at 8.91 ppm, assigned to the protonated amino group (N^+H). On the other hand, the ^{13}C NMR spectrum in D_2O shows the quaternary carbon of the cyclopentadienyl ring at 105.38 ppm, two peaks at 87.04 and 86.83 ppm for the other four carbons of the ring, a peak at 59.60 ppm for the $-NCH_2$ carbon, a peak at 25.94 ppm for the $-CH_2$ carbon of the side chain, and one peak for the two methyl carbons of $-NMe_2$ at 45.60 ppm.

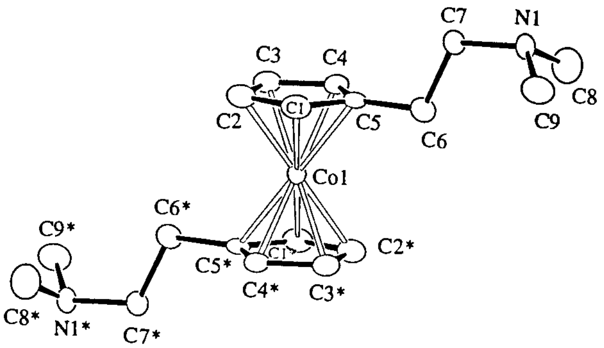


Figure 1. ORTEP diagram of the cation 4^{2+}. The cobalt atom is situated on a crystallographic inversion center.

Related complexes were reported by El Murr,[19] $[(C_5H_4NH_2)_2Co]^+$, Boche *et al.*,[20] $[(C_5H_4NMe_2)_2Co]^+$, and Rees *et al.*,[21] $[C_5H_4(CH_2)_2NMe_2]_2Fe$. Similar results were obtained by us using the rhodocenium salt $[\{\eta^5\text{-}C_5H_4(CH_2)_2N(H)Me_2\}_2Rh^{III}]^{3+}$-(Cl)$(PF_6^-)_2$.[5]

Addition of NH_4PF_6 in a powdered form, to an aqueous solution of **3** produced a brown yellow solid that was subsequently shown to be the bis(hexafluorophosphate) salt of the ((dimethylamino)ethyl)((dimethylammonio)ethyl)cobaltocenium ion (**4**) by an X-ray crystal structure determination (vide infra) and other evidence.

The IR spectrum of the yellow monoprotonated complex **4** is similar to that of the green diprotonated precursor **3**, showing the typical metallocene skeletal vibrations at 3110, 3000, 2950, 1465, 1030, 1015, and 990 cm^{-1},[22,19] except that the characteristic frequencies of the PF_6^- anion at 830 cm^{-1} are now observed as a strong and broad band, while the broad and strong band expected for the N^+H group was not detected.

In the ^1H NMR spectrum of **4** in CD_3CN and DMSO-d_6 solutions, at ambient temperatures (298 K), the signals of the CH_2 protons of the side chain and the $-N^+H$ signal coincide into two broad signals at 2.80, 2.70 ppm (in CD_3CN) and 2.83, 2.67 ppm (in DMSO-d_6), respectively. However, at 284 K (in CD_3CN), the $-N^+H$ signal is broadened and shifted to 3.30 ppm. The two $-CH_2CH_2N$ triplets at 2.70 ppm ($-CH_2-$) and 2.82 ppm ($-CH_2N$) are now clear and sharp signals. The coupling constants for the side chain protons were of the order of 6−7 Hz as expected. The situation is similar also at lower temperatures. This can be explained by the slow flipping of the H^+ hydrogen bonded to the $-NMe_2$ groups of adjacent molecules. (See the crystal structure of **4**.)

The ^{13}C NMR spectrum of **4** at 298 K, however, is very similar to that of **3**. Finally, in the mass spectrum (CI) of **4** two peaks were found at m/e = 623 and 477 that could be assigned to the fragments $[\{[Cp(CH_2)_2N(H)Me_2]_2Co\}(PF_6)_2]^+$ and $[\{[Cp(CH_2)_2N(H)Me_2][Cp(CH_2)_2NMe_2]Co\}(PF_6)]^+$, respectively.

Crystals of **4** suitable for X-ray crystallography were grown by slow diffusion of ether into a saturated acetonitrile solution. An ORTEP diagram of **4** is shown in Figure 1, and a unit cell plot is shown in Figure 2. Crystal parameters are given in Table 1. Selected distances are included in Table 2.

Compound **4** is the first crystallographic example of an aminoethyl−ammonioethyl-substituted cobaltocenium complex.

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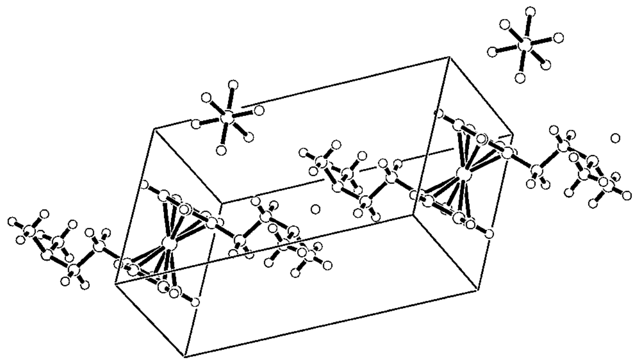


Figure 2. Crystal packing of **4**. The bridging H atom, which was crystallographically located, is seen at the very center of the unit cell.

Table 1. Crystallographic Data for **4**

chem formula	$C_{18}H_{29}CoF_{12}N_2P_2$	V	588.2(3) Å^3
fw	622.3	Z	1
space group	$P\bar{1}$ (No. 2)	ρ_{calcd}	1.757 g/cm^3
a	6.314(2) Å	T	−120 °C
b	7.137(2) Å	λ	1.541 78 Å
c	13.452(2) Å	μ	8.011 cm^{-1}
α	103.66(2)°	$R(F_o)^a$	0.0401
β	90.25(2)°	$R_w(F_o)^b$	0.0423
γ	92.89(2)°		

[a] $R = \Sigma(|F_o| - |F_c|)/\Sigma|F_o|$. [b] $R_w = [\Sigma_w(||F_o| - |F_c||)^2/\Sigma(|F_o|)^2]^{1/2}$.

Table 2. Selected Bond Lengths of Complex **4** in Å[a]

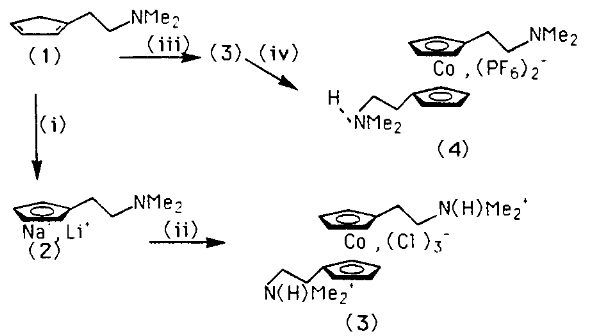
Co(1)−Cl(1)	2.028(5)	Co(1)−C(2)	2.024(5)
Co(1)−C(3)	2.035(5)	Co(1)−C(4)	2.036(5)
Co(1)−C(5)	2.036(5)	Co(1)−C(1*)	2.029(5)
Co(1)−C(2*)	2.024(5)	Co(1)−C(3*)	2.035(5)
Co(1)−C(4*)	2.036(5)	Co(1)−C(5*)	2.036(5)
P(1)−F(1)	1.580(4)	P(1)−F(2)	1.592(3)
P(1)−F(3)	1.589(3)	P(1)−F(4)	1.588(3)
P(1)−F(5)	1.594(4)	P(1)−F(6)	1.576(4)
N(1)−C(7)	1.485(6)	N(1)−C(8)	1.482(6)
N(1)−C(9)	1.456(6)	N(1)−H(15*)	1.318(4)
C(1)−C(2)	1.431(7)	C(1)−C(5)	1.429(6)
C(2)−C(3)	1.402(6)	C(5)−C(6)	1.491(6)
C(3)−C(4)	1.421(6)	C(6)−C(7)	1.531(8)
C(4)−C(5)	1.408(6)	H(15)−N(1*)	1.318(4)

[a] Asterisk indicates equivalent atomic position.

Interestingly, in the unit cell a symmetric hydrogen bond between two atoms on neighboring molecules N···H···N was formed (Figure 2), with N−H = 1.318(5) Å and N−H−N = 180°, the latter of which is required to be linear by symmetry. This bridging hydrogen atom was crystallographically located and was in fact the largest feature in the difference Fourier map after all the calculated H atom positions for the Cp, Me, and methylene groups were included in a structure factor calculation. Due to this intermolecular hydrogen bond, the crystal is stabilized further. Thus, the structure of **4** consists of one Co(III) atom, two formally anionic $C_5H_4(CH_2)_2NMe_2$ ligands, two PF_6^- anions, and one unique bridging H^+ atom. The distances between the respective metal and the ring carbons lie in the range of 2.024−2.036 Å, which is characteristic of a Co(III)−C(cyclopentadienyl) bond (in the cobaltocenes the Co(II)−C distances are longer, around 2.096 Å).

The rhodocenium (bis)hexafluorophosphate salt $[\{\eta^5\text{-Cp}(CH_2)_2N(H)Me_2\}_2Rh^{III}](Cl)(PF_6)_2$ structure was also solved and reported by us earlier.[5] In that case both $-NMe_2$ groups were protonated, with an additional Cl^- ion present. That crystal was stabilized by an H···Cl···H bridge. Also Koch *et al.*[23] reported the structure of complex $[(CpCHPh_2)_2Co]^+(PF_6)^-$.

Scheme 1



[a] Key: (i) **1** + NaH, in THF; (ii) **2** + $CoCl_2$ (1:1), in THF reflux for ca. 3 h; (iii) **1** + $CoCl_2$ (4:1), in THF reflux for ca. 3 h; (iv) **3** + NH_4PF_6 (1:3), in H_2O.

The diprotonated complex $[\{\eta^5\text{-}C_5H_4(CH_2)_2N(H)Me_2\}_2Co^{III}]^{3+}(Cl^-)_3$ (**3**) could also be obtained by another method, the reaction of **2** with anhydrous $CoCl_2$ in 1:1 or 1:2 molar ratio (Scheme 1). Following Kölle[24,25] and Butenschön,[26] we have tried to prepare the paramagnetic dimeric complex $[\{Cp(CH_2)_2NMe_2\}Co^{II}Cl]_2$ by reacting **2** with anhydrous $CoCl_2$ at temperatures ranging from −40 to 65 °C (refluxing THF). Evidence for the presence of Co(II) in a possible dimeric species was detected by a broad ESR signal of the brown product obtained from the above reaction, at a ligand/Co molar ratio of 2:1. By comparison with nonfunctionalized or with phosphino-functionalized cyclopentadienyl, the reagents **1** or **2** seem to favor the formation of **3** instead of a dimeric species.

Refluxing a dichloromethane solution of $Co_2(CO)_8$ and $C_5H_5(CH_2)_2NMe_2$ leads to the formation of the dicarbonyl complex $[Cp(CH_2)_2NMe_2]Co(CO)_2$ (**5**) which could be isolated as an air-sensitive orange oil, in high yield (ca. 90%) (Scheme 2). Its infrared spectrum (in CH_2Cl_2) shows two absorptions at 2025 and 1966 cm^{-1} typical of two terminal carbonyl groups. These frequencies are 33−37 cm^{-1} higher than those of the corresponding tetramethylcyclopentadienyl analogue (η^5-C_5Me_4R),[27] in accord with other reports comparing unsubstituted cyclopentadienyl with (η^5-C_5Me_4R)Co dicarbonyls.[28,29]

In the ^{1}H NMR spectrum of **5** in $CDCl_3$, the cyclopentadienyl proton signals are observed at 4.97 and 4.89 ppm, the (b)-CH_2N side chain protons at 2.41, and the (a)-CH_2 ones at 2.31 ppm, respectively. The singlet at 2.19 ppm is due to the methyl groups on nitrogen.

The ^{13}C NMR spectrum, on the other hand, shows the quaternary carbon of the cyclopentadienyl (Cp) ring at 105.40 ppm, two peaks at 85.09, 82.84 ppm for the four carbon atoms of the ring, two singlets at 26.38 and 60.60 ppm for the (a)-CH_2 and (b)-CH_2N carbons of the side chain, and a singlet at 45.41 ppm for the two methyl groups on nitrogen. Also a singlet at 205.60 ppm was assigned to the two CO groups.

Generally, reactions with Me_3NO and heating are the most common methods for the elimination of CO ligands.[30,31]

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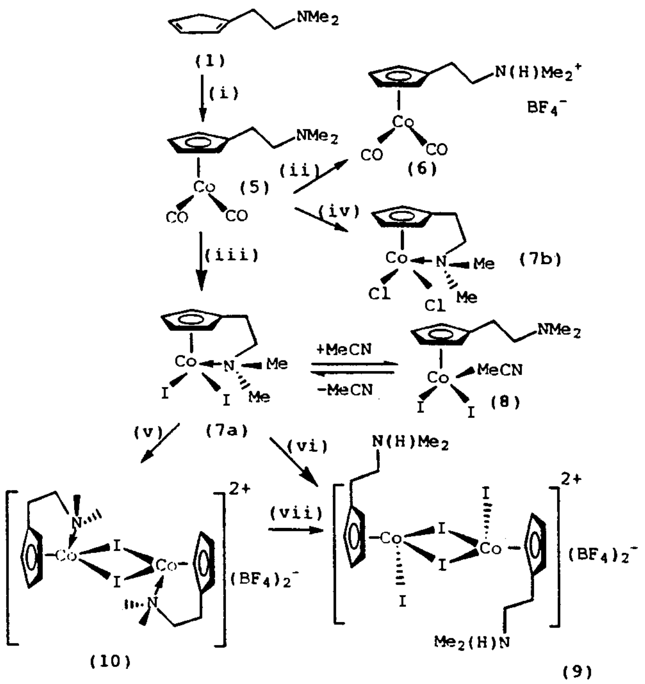
Scheme 2



[a] Key: (i) **1** + $Co_2(CO)_8$, in CH_2Cl_2 reflux for ca. 6 h; (ii) **5** + $HBF_4{\cdot}Et_2O$; (iii) **5** + I_2 in Et_2O; (iv) **5** + Cl_2 in Et_2O; (v) **7a** + $AgBF_4$ (1:1) in CH_2Cl_2; (vi) **7a** + $HBF_4{\cdot}Et_2O$ in CH_2Cl_2; (vii) **10** + HI in CH_2Cl_2.

However, when compound **5** is treated with 1 equiv of trimethylamine oxide (Me_3NO) in CH_3CN, it decomposes to CoO and $C_5H_5(CH_2)_2N^+(H)Me_2$, the free ligand in protonated form.

The inconvenience of handling the oily complex **5** led us to the preparation of its salt, $[\{Cp(CH_2)_2N(H)Me_2\}Co(CO)_2]^+(BF_4)^-$ (**6**). Thus, addition of HBF_4 to a solution of **5** in ether at ambient temperature resulted in the formation of the yellow solid **6**, which is very hygroscopic.

The ^1H NMR spectrum of **6** in methanol-d_4 is similar to its neutral precursor **5**. However, in DMSO-d_6 a broad signal at 4.02 ppm, due to N^+H, was observed. The ^{13}C NMR spectrum of **6** is also very similar to that of **5**. In the IR spectrum of **6**, two ν_{CO} frequencies appear as very strong bands at 2023 and 1962 cm^{-1}. Though very hygroscopic, compound **6** gave a satisfactory elemental analysis. It is also very soluble in polar solvents such as MeOH, CH_3CN, and H_2O.

The low melting and highly air and light sensitive dicarbonyl derivative **5** could be easily oxidized with elemental iodine in ether solutions, affording the air-stable diiodocobalt(III) complex $[\{\eta^5\text{-}C_5H_4(CH_2)_2NMe_2\}Co^{III}I_2]$ (**7a**) in moderate yields (ca. 62%). Complex **7a** is a black-green microcrystalline compound, and it was fully characterized by elemental analysis and NMR and IR spectroscopic methods. The intermediate product $[\{\eta^5\text{-}C_5Me_4(CH_2)_2NMe_2\}Co(CO)I_2]$[27] detected during the preparation of $[\{\eta^5\text{-}C_5Me_4(CH_2)_2NMe_2\}CoI_2]$ could not be detected in the preparation of **7a**. The intermediate $C_5H_5Co(CO)I_2$ was also first isolated[17,31,32] as a stable compound, in the course of the preparation of $(C_5H_5CoI_2)_n$.

Complex **7a** contains a chelate of Co^{III} involving the cyclopentadienyl ring and the amino side chain, thus obeying the $18e^-$ rule, similar to the corresponding rhodium(III) complex.[5] In the IR spectrum of **7a** the skeletal vibrations of the cyclopentadienyl ring (Cp) are observed[22,33] at 3090, 1470, 1030, and 1000 cm^{-1}. No band assignable to ν_{CO} could be observed. The compound is insoluble in Et_2O and soluble in $CHCl_3$, CH_2Cl_2, CH_3CN, DMSO, etc. Upon standing for several hours, solutions of **7a** in donor solvents such as MeOH, THF, or DMSO change color, presumably indicating decomposition.

The ^1H NMR spectrum of **7a** in $CDCl_3$ shows two sets of pseudotriplets for the cyclopentadienyl protons at 5.39 and 5.11 ppm, a singlet for the $-NMe_2$ protons at 2.70 ppm, and two triplets for the (a)-CH_2 and (b)-CH_2N protons at 2.48 and 4.08 ppm, respectively. Both the (a)-CH_2 triplet at 2.48 ppm and the $-NMe_2$ singlet at 2.70 ppm are downfield-shifted compared to those of complex **5**, by ca. 0.2 and 0.5 ppm, respectively. The most significant shift (1.67 ppm), however, is observed for the (b)-CH_2N protons adjacent to nitrogen coordination site of the metal.

The ^{13}C NMR spectrum of **7a** gives additional evidence for an intramolecular coordination of the $-NMe_2$ group with Co(III). Thus, the signal for the (b)-CH_2N group of **7a** appears at 75.23 ppm while that of complex **5** appears at 60.60 ppm. Also, the $-NMe_2$ group of **7a** appears at 56.65 ppm, and the one of **5**, at 45.41 ppm. The two signals expected for the cyclopentadienyl ring protons of a freshly prepared solution of **7a** in CD_3CN are indeed observed, besides four additional ones, that could be assigned to a product like **8**, possessing no symmetry plane.[34] All other proton signals are duplicated. This can be explained by the equilibrium shown in Scheme 2.

This equilibrium is taking place at approximately the 50% level, as integration of the ^1H NMR spectrum suggests. Therefore, the dimethylamino group is bound weakly to Co(III) and can be reversibly displaced by a variety of donor reagents, like CD_3CN in the case of compound **8**. Similar results were also found in the compound observed by Jutzi[27,35] whereby strong donating ligands such as ^tBuCN and CO were found to reversibly add to the metal center. In both cases the equilibrium constant was estimated to be close to unity at room temperature. A general survey concerning the displacement reactions mentioned above is given in detail by Okuda.[36]

The chloro derivative **7b**, analogous to complex **7a**, was obtained as a green solid in an almost quantitative yield by the passage of gaseous Cl_2 through an ethereal solution of **5**. Complex **7b** had a Λ_M (molar conductance) value of about 256 $\Omega^{-1}{\cdot}mol^{-1}{\cdot}cm^2$ in aqueous solutions, indicating hydrolysis of the two chloride ions. The elemental analysis of **7b** and other spectroscopic results suggested that **7b** might be contaminated with a slight amount of its protonated analogue (protonated at the $-NMe_2$ group).

In the IR spectrum of **7b**, typical bands for the cyclopentadienyl ring were observed at 3040, 2940, 1470, and 960 cm^{-1}. The ν_{Co-Cl} symmetric and asymmetric terminal frequencies were also observed[37] at 310 and 325 cm^{-1} as a shoulder. Also a broad and strong band at 2740 cm^{-1} assigned to the N^+H stretching vibration was observed.

In the ^1H NMR spectrum of a freshly prepared solution of complex **7b** in DMSO-d_6, signals at 5.18 and 5.15 ppm were found, due to the cyclopentadienyl protons. A multiplet at 3.21

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ppm is due to the (b)-CH_2N, while the other eight protons are observed as a multiplet at 2.69 ppm [(a)-CH_2 + NMe_2]. The $-N^+H$ signal was observed at 9.92 ppm. The ^{13}C NMR spectrum of **7b** also shows the expected signals (see Experimental Section).

It should be noted here that previous investigations on the isolation of complex $C_5H_5Co^{III}Cl_2$ had suggested a polymeric species of rather unknown structure.[32] In our case however, a monomeric chelated complex **7b** is the main product formed, besides a minor impurity of unknown structure with a protonated side chain. A chelated monochloro Co(II)/Cp complex, $Cp(CH_2)_2P^tBu_2Co^{II}Cl$, was recently reported[38] by Butenschön with the ligand $Cp(CH_2)_2P^tBu_2$. Results on the isolation and characterization of the analogous complex [{η^5-$C_5H_4(CH_2)_2NMe_2$}$Rh^{III}Cl_2$] will be published elsewhere.[39]

The dimeric complex **9** (Scheme 2), which is formed upon addition of HBF_4 to **7a**, has a formula which obeys the 18e$^-$ rule, as indicated by elemental analysis. The existence of the BF_4^- counteranions was also confirmed by ^{19}F NMR (−27.50 ppm) and by IR spectroscopy (1084 cm^{-1}, broad shoulder).

Further reaction of **7a** with $AgBF_4$ in CH_2Cl_2 produces another bridged diiodo dimer (**10**) in high yield. The ^1H NMR spectrum of (**10**) indicates the coordination of the $-NMe_2$ group to Co(III) forming a chelate. Both complexes **7a** and **10** show comparable chemical shift values (δ) of various protons in $CDCl_3$ solutions. Also the Λ_M (molar conductance) value of **10** in CH_3CN (170 $\Omega^{-1}\cdot mol^{-1}\cdot cm^2$) is consistent with a 1:2 electrolyte[40] and confirms the proposed dimeric structure.

It is noteworthy that addition of HI to a dichloromethane solution of **10** leads to the formation of the dimer **9** in a good yield (Scheme 2). Thus, the characterization of both complexes becomes evident.

Experimental Section

General Methods and Materials. All reactions (unless otherwise noted) were carried out under a nitrogen atmosphere, using standard Schlenk techniques. Gaseous Cl_2 was prepared from the oxidation of HCl by $KMnO_4$. Solvents and reagents were purified and dried by standard methods and were distilled immediately prior to use. The ligand $C_5H_5(CH_2)_2NMe_2$ (**1**) and its salt $M[C_5H_4(CH_2)_2NMe_2]$ (M = Na, Li) (**2**) were prepared according to literature methods.[15,16] Conductivity measurements were performed using a E365B conductoscope, Metrhom Ltd., Herisau, Switzerland. Microanalyses were performed by the Service de Microanalyses, Laboratoire de Chimie de Coordination, and by the Microanalysis Center of the University of Ioannina. Mass spectra were recorded on a Varian MAT 311 A instrument. Infrared spectra were recorded on a Perkin-Elmer model 783 grating spectrophotometer, as KBr pellets, neat, or in Nujol mulls. ^1H and ^{13}C NMR spectra were obtained on Bruker AMX 400 MHz and AC 200FT spectrometers of the University of Ioannina and the Laboratoire de Chimie de Coordination, respectively.

Preparation of [{η^5-$C_5H_4(CH_2)_2N(H)Me_2$}$_2Co^{III}$]$^{3+}$(Cl^-)$_3$ (3). Method i Using $C_5H_5(CH_2)_2NMe_2$ (1). To a suspension of $CoCl_2$ (300 mg, 2.31 mmol) in THF (10 mL) was added a solution of the ligand $C_5H_5(CH_2)_2NMe_2$ (1.14 g, 8.32 mmol) in THF (10 mL) via a double-ended needle. The resulting blue-green suspension was heated to reflux for ca. 4 h. After being cooled to room temperature, the solution was filtered off. The green complex was washed with THF (5 mL) and Et_2O (10 mL) and dried *in vacuo*. Yield: 710 mg (70%).

Method ii Using $M[C_5H_4(CH_2)_2NMe_2]$ (M = Na, Li) (2). To a suspension of $CoCl_2$ (0.4 g, 3.08 mmol) in THF (10 mL), the sodium salt of the ligand $NaC_5H_4(CH_2)_2NMe_2$ (0.5 g, 3.14 mmol) in THF (20 mL) was added via a double-ended needle. The resulting green-blue suspension was heated to a gentle reflux for ca. 3 h. After being cooled at room temperature, the solution was evaporated to dryness. Dry CH_3CN (5 mL) was added, and after filtration, the green solution was precipitated with an excess of Et_2O (30 mL). The green solid was washed twice with diethyl ether (2 × 25 mL) and dried at 50−60 °C under *vacuo*. Yield: 510 mg (50%). Anal. Calcd for $C_{18}H_{30}N_2Cl_3Co$ (439.74 g/mol): C, 49.16; H, 6.87; N, 6.37. Found: C, 48.86; H, 6.77; N, 5.92. Λ_M (H_2O) = 350 $\Omega^{-1}\cdot cm^2\cdot mol^{-1}$. IR (KBr): 3080, 3040, 3020 (m, =CH of C_5H_4 ring), 2930 (m, −CH aliphatic), 2680 (s, $-N^+H$), 1465 (m, C=C), 1410, 1260, 1025, 1000, 965, 875, 530 cm^{-1}. ^1H NMR (D_2O) (using 3-(trimethylsilyl)propanesulfonic acid (TSP) as internal standard): 5.78, 5.75 (2 × t, C_5H_4), 3.27 (t, J = 6.9 Hz, CH_2N), 3.21 (s, NMe_2), 2.95 (t, J = 6.9 Hz, CH_2). ^1H NMR (DMSO-d_6): 8.91 (br s, $-N^+H$) and 5.71, 5.68 (2 × t, 4H, C_5H_4), 2.70 (t, 2H, J = 7 Hz, CH_2N), 2.40 (m, 8H, CH_2 and NMe_2). ^{13}C NMR (D_2O): 105.38 (s, $C(CH_2)_2NMe_2$), 87.04, 86.83 (d, C_5H_4), 59.60 (s, CH_2N), 45.60 (s, NMe_2), 25.94 (s, CH_2).

$Li[C_5H_4(CH_2)_2NMe_2]$ could also be used for this reaction instead of the Na salt.

Preparation of [{η^5-$C_5H_4(CH_2)_2N(H)Me_2$}{η^5-$C_5H_4(CH_2)_2NMe_2$}-Co^{III}]$^{2+}$(PF_6^-)$_2$ (4). To a stirred solution of complex **3** (49.5 mg, 0.11 mmol) in H_2O (10 mL) was added solid NH_4PF_6 (68.03 mg, 0.38 mmol). Immediately, a yellow precipitate was formed. The solution was stirred for ca. 1 h, centrifuged, washed with cold ethanol and diethyl ether, and dried *in vacuo*. The yellow solid was redissolved in CH_3CN (2 mL) and precipitated with an excess (15 mL) of Et_2O. After filtration it was dried in vacuo at 50−60 °C. Yield: 28.19 mg (41%). Anal. Calcd for $C_{18}H_{29}N_2CoP_2F_{12}$ (622.320 g/mol): C, 34.75; H, 4.69; N, 4.50. Found: C, 34.64; H, 4.68; N, 4.16. Mass spectrum (CI): *m/e* 623 (**4**), 477 [**4** − (PF_6^-)]. Λ_M (CH_3CN) = 350 $\Omega^{-1}\cdot cm^2\cdot mol^{-1}$. IR (KBr): 3110 (m, =CH), 3000, 2950, 2910 (m, −CH), 1465 (m, C−C), 1400, 1030, 1015, 990, 830 (broad shoulder, PF_6^-), 555, 510, 465, 450 cm^{-1}. ^1H NMR (CD_3CN, 284 K): 5.57, 5.55 (2 × t, 4H, C_5H_4), 3.30 (br s, $-N^+H$), 2.82 (t, J = 6.6 Hz, CH_2N), 2.70 (t, J = 6.6 Hz, CH_2), 2.51 (s, 6H, NMe_2). ^1H NMR (DMSO-d_6, 298 K): 5.75 (broad d, 4H, C_5H_4), 2.83 (broad s, 2H, CH_2N), 2.67 (broad s, 2H, CH_2), 2.60 (s, 6H, NMe_2). ^1H NMR (CD_3CN, 298 K): 5.57, 5.55 (2 × t, 4H, C_5H_4), 2.80 (br s, 3H, $-N^+H$ and CH_2N), 2.70 (br s, 2H, CH_2), 2.50 (s, 6H, NMe_2). ^{13}C NMR (DMSO-d_6, 298 K): 104.44 (s, $C(CH_2)_2NMe_2$)), 84.13, 83.99 (2 × s, C_5H_4), 56.95 (s, CH_2N), 43.67 (s, NMe_2), 23.67 (s, CH_2).

Preparation of [{η^5:η^1-$C_5H_4(CH_2)_2NMe_2$}$Co^I(CO)_2$] (5). To a solution of $Co_2(CO)_8$ (0.56 g, 1.64 mmol) in CH_2Cl_2 (10 mL) was added a solution of $C_5H_5(CH_2)_2NMe_2$ (0.45 g, 3.29 mmol) in CH_2Cl_2 (10 mL) via a doubled-ended needle, followed by the addition of 1,3-cyclohexadiene (0.56 mL, 5.74 mmol). The solution was heated to a gentle reflux for ca. 6 h. After removal of the solvent in vacuo, the orange-red oily residue was extracted with Et_2O (20 mL). The ethereal solution was then filtered through a small pad of alumina and the residue washed with an additional 20 mL of Et_2O. The combined extracts were evaporated to dryness affording **5** as a red-brown air-sensitive oil. Yield: 376 mg (91%). Anal. Calcd for $C_{11}H_{14}CoNO_2$ (251.17 g/mol): C, 52.60; H, 5.62; N, 5.58. Found: C, 52.50; H, 5.49; N, 5.41. IR (CH_2Cl_2): 2025, 1966 (ν_{CO}) cm^{-1}. IR (neat): 2019, 1954 (ν_{CO}) cm^{-1}. ^1H NMR ($CDCl_3$): 4.97, 4.89 (2 × s, 4H, C_5H_4), 2.41 (t, 2H, J = 6.6 Hz, CH_2N), 2.31 (t, 2H, J = 6.5 Hz, CH_2), 2.19 (s, 6H, NMe_2). ^1H NMR (C_6D_6): 4.67, 4.44 (2 × t, 4H, C_5H_4), 2.26 (t, 2H, J = 6.20 Hz, CH_2N), 2.16 (t, 2H, J = 6.42 Hz, CH_2), 2.04 (s, 6H, NMe_2). ^{13}C NMR ($CDCl_3$): 205.60 (s, CO), 105.40 (s, $C(CH_2)_2NMe_2$) 85.09, 82.84 (2 × s, C_5H_4), 60.60 (s, CH_2N), 45.41 (s, NMe_2), 26.38 (s, CH_2).

Preparation of [{η^5:η^1-$C_5H_4(CH_2)_2N(H)Me_2$}$Co^I(CO)_2$]$^+$(BF_4^-) (6). To a stirred solution of **5** (0.358 mg, 1.425 mmol) in Et_2O at 0 °C was added dropwise a solution of $HBF_4\cdot Et_2O$ (0.21 mL, 85% in Et_2O). Immediately an orange-brown solid was precipitated, and the reaction mixture was stirred for ca. 1 h. After filtration, the yellow-brown solid was washed twice with diethyl ether (2 × 25 mL) and dried *in vacuo*. Yield: 390 mg (81%). Anal. Calcd for $C_{11}H_{15}NO_2CoBF_4$ (338.98 g/mol): C, 38.97; H, 4.46; N, 4.13. Found: C, 38.79; H, 4.06; N, 4.16. IR (Nujol): 2561 (s, $-N^+H$), 2023 (ν_{CO}), 1962 (ν_{CO}), 1065 (BF_4^-)

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cm^{-1}. ^{1}H NMR (MeOH-d_4): 5.23, 5.13 (2 × t, 4H, C_5H_4), 3.30 (t, J = 8.64 Hz, 2H, CH_2N), 2.93 (s, 6H, NMe_2) 2.74 (t, J = 8.28 Hz, 2H, CH_2). ^{1}H NMR (DMSO-d_6): 5.17, 5.03 (2 × t, 4H, C_5H_4), 4.02 (br s, N^+H, 1H), 2.83 (t, 2H, J = 7.96 Hz, CH_2N), 2.52 (d, 6H, J = 8.16 Hz, NMe_2), 2.23 (t, 2H, J = 7.44 Hz, CH_2). ^{13}C NMR (MeOH-d_4): 205.60 (s, CO), 104.45 (s, $C(CH_2)_2NMe_2$), 87.6, 87.7 (2 × s, C_5H_4), 61.19 (s, CH_2N), 45.47 (s, NMe_2), 26.12 (s, CH_2).

Preparation of $[\{\eta^5{:}\eta^1\text{-}C_5H_4(CH_2)_2NMe_2\}Co^{III}I_2]$ (7a). A solution of iodine (95.4 mg, 0.37 mmol) in Et_2O (5 mL) was added dropwise to a solution of (**5**) in Et_2O (5 mL) at 0 °C. During the addition, the color changed from red-brown to dark green and the formation of a black precipitate was observed. The solution was allowed to warm to room temperature and then stirred overnight. After filtration the black-green solid was washed with diethyl ether (2 × 10 mL) and dried in vacuo. Yield: 104 mg (62%). Anal. Calcd for $C_9H_{14}NCoI_2$ (448.95 g/mol): C, 24.07; H, 3.14; N, 3.12. Found: C, 24.31; H, 3.12; N, 3.20. IR (KBr): 3090 (m, $=$CH), 2900 (m, $-$CH), 1470 (m, $-$C$-$C), 1400, 1385, 1315, 1260, 1210, 1100, 1030, 1000, 950, 920, 810, 780 cm^{-1}. ^{1}H NMR ($CDCl_3$): 5.39, 5.11 (2 × t, 4H, C_5H_4), 4.08 (t, J = 6.4 Hz, 2H, CH_2N), 2.70 (s, 6H, NMe_2), 2.48 (t, J = 6.4 Hz, 2H, CH_2). ^{13}C NMR ($CDCl_3$): 82.85, 80.21 (2 × s, C_5H_4), 75.23 (s, CH_2N), 56.65 (s, NMe_2), 25.12 (s, CH_2).

Preparation of $[\{\eta^5{:}\eta^1\text{-}C_5H_4(CH_2)_2NMe_2\}Co^{III}Cl_2]$ (7b). To an ice-cold solution of **5** (72 mg, 0.288 mmol) in Et_2O (10 mL) was bubbled gaseous Cl_2 over 10 min. A blue-green precipitate was formed and after filtration was dried in vacuo. The crude material was washed thoroughly with CH_3CN (2 × 5 mL) giving an intense blue solution as well as a green insoluble solid. This was washed further with diethyl ether (2 × 5 mL) and then dried in vacuo. Yield: 62%. Anal. Calcd for $C_9H_{14}NCoCl_2$ (266.05 g/mol): C, 40.63; H, 5.30; N, 5.26; Cl, 26.65. Found: C, 39.98; H, 5.36; N, 5.10; Cl, 29.29. Λ_M (H_2O) = 256 $\Omega^{-1}\cdot cm^2\cdot mol^{-1}$. IR (CsBr): 3040 (m, $=$CH), 2940, 2920 (m, $-$CH), 2740 (s, N^+H), 1470 (m, C$-$C), 1265, 960, 875, 820, 575, 325, 310 (s, ν_{Co-Cl} terminal) cm^{-1}. ^{1}H NMR (DMSO-d_6): 9.92 (br s, N^+H), 5.18, 5.15 (2 × t, 4H, C_5H_4), 3.21 (m, 2H, CH_2N), 2.69 (m, 8H, CH_2-NMe_2). ^{1}H NMR (D_2O): 5.82, 5.75 (2 × t, 4H, C_5H_4), 3.39 (t, 2H, J = 8.4 Hz, CH_2N), 3.03 (t, 2H, J = 8.3 Hz, CH_2N), 2.95 (s, 6H, NMe_2). ^{13}C NMR (DMSO-d_6): 108.47 (s, $C(CH_2)_2NMe_2$), 93.31, 92.31 (2 × s, C_5H_4), 65.58 (s, CH_2N), 52.08 (s, NMe_2), 30.61 (s, CH_2).

Preparation of $[\{\eta^5\text{-}C_5H_4(CH_2)_2N(H)Me_2\}Co^{III}I_2]_2{}^{2+}(BF_4{}^-)_2$ (9). To an ice-cooled solution of **7a** (64 mg, 0.14 mmol) in CH_2Cl_2 (5 mL) was added 1 equiv of $HBF_4\cdot Et_2O$ (21 mL, 85% in Et_2O). A green solid was precipitated, and the mixture was stirred for ca. 2 h. After filtration, it was washed twice with diethyl ether (2 × 10 mL) and dried in vacuo. Yield: 96 mg (80%). Anal. Calcd for $C_{18}H_{30}N_2Co_2I_4B_2F_8$ (1073.539 g/mol): C, 20.14; H, 2.81; N, 2.61. Found: C, 20.56; H, 2.59; N, 2.53. IR (KBr): 3068, 2950, 2670 (s, $-N^+H$), 1476, 1084 ($BF_4{}^-$), 844 cm^{-1}. ^{1}H NMR (MeOH-d_4): 5.65, 5.15 (2 × t, C_5H_4), 4.10 (t, 2H, J = 6.4 Hz, CH_2N), 2.80 (s, 6H, NMe_2), 2.62 (t, 2H, J = 6.4 Hz, CH_2). ^{1}H NMR (CD_3CN): 7.50 (br s, $-N^+H$), 5.50, 5.45 (2 × t, C_5H_4), 3.52 (t, 2H, J = 6.6 Hz, CH_2N), 3.02 (t, J = 6.6 Hz, CH_2), 2.89 (d, J = 5.1 Hz, 6H, N^+HMe_2).^{19}F NMR (DMSO-d_6): -27.5 ppm. ^{13}C NMR (CD_3CN): 107.5 (s, $C(CH_2)_2NMe_2$), 88.13, 82.32 (2 × s, C_5H_4), 57.15 (s, CH_2N), 44.47 (s, NMe_2), 25.29 (s, CH_2).

Preparation of $[\{\eta^5\text{-}C_5H_4(CH_2)_2NMe_2\}Co^{III}I]_2{}^{2+}(BF_4{}^-)_2$ (10). In a Schlenk tube, complex **7a** (97 mg, 0.216 mmol) and 1 equiv of $AgBF_4$ (42 mg, 0.216 mmol) were mixed in the dark and dried for ca. $^1/_2$ h. Dry CH_2Cl_2 (15 mL) was added and the deep green solution was stirred for ca. 3 h. After filtration through a small pad of Celite and removal of about half of the solvent by evaporation, diethyl ether was added in excess (15 mL). A black-green solid was precipitated, and after filtration it was dried *in vacuo*. Yield: 142 mg (80%). Anal. Calcd for $C_{18}H_{28}N_2Co_2I_2B_2F_8$ (817.7 g/mol): C, 26.43; H, 3.45; N, 3.42. Found: C, 25.89; H, 3.10; N, 3.36. Λ_M (CH_3CN): 170 $\Omega^{-1}\cdot cm^2\cdot mol^{-1}$. IR (KBr): 3070, 2850, 1455, 1390, 1305, 930, 910, 840 cm^{-1}. ^{1}H NMR($CDCl_3$): 5.45, 5.15 (2 × t, C_5H_4), 4.12 (t, 2H, J = 6.4 Hz, CH_2N), 2.75 (s, 6H, NMe_2), 2.52 (t, 2H, J = 6.4 Hz, CH_2N). ^{13}C NMR ($CDCl_3$): 82.82, 80.21 (2 × s, C_5H_4), 75.23 (s, CH_2N), 56.64 (s, NMe_2), 25.11(s, CH_2).

Protonation of 10 with HI: Preparation of 9. Complex **9** (66 mg, 0.08 mmol) was dissolved in CH_2Cl_2 (5 mL). HI (20 mL, 55% in H_2O) was then added dropwise with stirring at 0 °C. A green precipitate was immediatedly formed. The suspension was stirred for 1 h at this temperature and then warmed gently to room temperature. Then the residue was filtered off and washed with CH_2Cl_2 and diethyl ether. This product was dried in vacuo. Yield: 55 mg (64%). (An authentic sample, prepared this way, gave the same spectroscopic data (NMR, IR) as those reported for **9** prepared from **7a** (above)).

Conclusions

The present paper demonstrates the following:

(1) It is possible to synthesize metallocene-type complexes, as well as half-sandwich compounds of cobalt, containing the ((dimethylamino)ethyl)cyclopentadienyl ligand. The amino group attached to the cyclopentadienyl ring plays the role of an auxiliary basic reagent that helps the deprotonation of the ring proton and the formation of the metal complex.[3,5] The use of an external base is thus avoided.

(2) The protonated cobalt^{III} complexes as well as the chelated chloro complexes are characterized by a special solubility in water and polar solvents such as MeOH, DMSO, etc. In addition, they show an exceptional stability to air and moisture, making them preferred candidates (starting materials) for reactions in aqueous media. Thus, they are of special interest in aqueous organometallic chemistry.[10,41,42] In water, hydrolysis of the dichloro units takes place leading to the diaquo species $[Cp(CH_2)_2NMe_2Co(H_2O)_2]^{2+}(Cl^-)_2$.

(3) The structure of **4** is stabilized by a hydrogen bonding of the type N···H···N, in contrast to the H···Cl···H bridge found in the structure of a related rhodocenium complex.

Supporting Information Available: For the structure of complex **4**, tables of (a) the structure determination summary, (b) atomic coordinates and equivalent isotropic displacement coefficients, (c) complete bond lengths, (d) complete bond angles, (e) anisotropic displacement coefficients, and (f) H coordinates (7 pages). Ordering information is given on any current masthead page.

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