Transition-Metal Derivatives of a Functionalized Cyclopentadienyl Ligand. 15.† Synthesis and Structures of Amino Cyclopentadienyl Derivatives of Rhodium(I) and Rhodium(III) Including Water-Soluble Compounds

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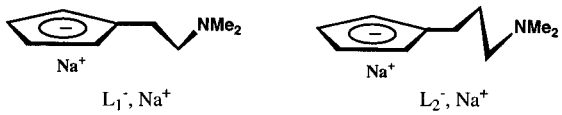
The synthesis of monometallic rhodium(III) and rhodium(I) derivatives of dialkylamino-functionalized cyclopentadienyl using the corresponding cyclopentadiene as starting material is facilitated by the presence of the basic amino group. This procedure affords the chloro salts of the substituted rhodicinium cation $[(\eta^5\text{-}C_5H_4(CH_2)_2\text{-}NMe_2H)_2Rh^{III}]^{3+}$ ([**1**][Cl]$_3$) from the reaction of the [2-(dimethylamino)ethyl]cyclopentadiene with $Na_3Rh^{III}Cl_6\cdot 12H_2O$. Similarly the cationic half-sandwich complexes $[(\eta^5\text{-}C_5H_4(CH_2)_nNMe_2H)Rh^{I}(cod)]^+$ ($n = 2$, [**2**][Cl], $n = 3$, [**5**][Cl]) are obtained from the reaction of the corresponding dialkylamino cyclopentadiene with $[RhCl(cod)]_2$. These types of cationic complexes, **1**, **2**, and **5**, bear pendant ammonium groups. The most classical procedure, starting from the lithium or more efficiently from the sodium cyclopentadienide salt, was used to synthesize neutral complexes $[(\eta^5\text{-}C_5H_4(CH_2)_nNMe_2)Rh^{I}(cod)]$ ($n = 2$, **3**; $n = 3$, **4**). The structure of the chloride bis(hexafluorophosphate) salt, $[(\eta^5\text{-}C_5H_4(CH_2)_2NMe_2H)_2Rh^{III}]^{3+}(Cl^-)(PF_6^-)_2$, ([**1**][Cl][$PF_6$]$_2$) was solved in the triclinic space group $P\bar{1}$ with one molecule in the unit cell, the dimensions of which are $a = 6.617(2)$ Å, $b = 7.436(2)$ Å, $c = 13.965(3)$ Å, $\alpha = 76.39(2)°$, $\beta = 82.31(3)°$, $\gamma = 87.26(2)°$, and $V = 661.8(3)$ Å^3. The noncentrosymmetric character of this solid is attributed to the chloride ion. The tetrafluoroborate salt $[(\eta^5\text{-}C_5H_4(CH_2)_2NMe_2H)Rh^{I}(cod)]^+(BF_4^-)$ ([**2**][BF_4]) crystallizes in the tetragonal space group $P4_2/n$ with eight molecules in the unit cell, the dimensions of which are $a = 21.183(2)$ Å, $b = 21.179(3)$ Å, $c = 8.324(2)$ Å, and $V = 3734(1)$ Å^3. Least squares refinement leads to values for the conventional R index of [**1**][Cl][PF_6]$_2$ (0.0484 for 2191 reflections used) and of [**2**][BF_4] (0.0525 for 1083 reflections used); in both cases $I > 3\sigma(I)$. As expected, compounds like [**2**][Cl]$_3$, [**1**][Cl][PF_6]$_2$, [**2**][Cl], [**2**][BF_4], [**5**][Cl], and [**5**][BF_4] are soluble in water.

1. Introduction

η^5-Cyclopentadienyl derivatives of transition metals represent undoubtedly the most important class of organometallic compounds.[1] The so-called half-sandwich complexes containing one cyclopentadienyl ring with a functionalized side chain have received much attention by numerous research groups.[2] Specific properties of these complexes are expected, namely, in catalysis, likely being tailored by an appropriate choice of the substituents of the ring and of the side chain functions.[3] A functionalized side chain can also temporarily and reversibly coordinate to a metal ion, and this can stabilize reactive intermediates; thus a half-sandwich iron(II) halide complex stabilized by an oxygen donor side chain[4] nicely exemplifies this possibility. On the other hand, functionalized silane as a side chain exemplifies the possibility of immobilizing catalytically active complexes on the surface.[5]

In this paper, we report the use of cyclopentadienes bearing amino-functionalized side chains and of their sodium (Chart 1) and lithium salts, for the preparation of various organometallic rhodium complexes.

Chart 1



L_1^-, Na^+ L_2^-, Na^+

Previous investigations in this area were performed by P. Jutzi et al.,[9] as part of their work on the synthesis of derivatives of the 1-[2-(dimethylamino)ethyl]-2,3,4,5-tetramethylcyclopentadienyl[8a] ligand.

†For previous paper of this series, see ref 28.

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(1) For recent reviews, see: (a) Jutzi, P. *J. Organomet. Chem.* **1990**, *400*, *1*. (b) Janiak, C.; Schumman, H. *Adv. Organomet. Chem.* **1991**, *33*, 291. (c) Okuda, J. *Top. Curr. Chem.* **1991**, *160*, 97. (d) Coville, N. J.; du Plooy, K. E.; Pickl W. *Coord. Chem. Rev.* **1992**, *116*, 1. (e) Okuda, J. *Nachr. Chem., Tech. Lab.* **1993**, *41*, 8.

(2) See: Jutzi, P.; Siemeling, U. *J. Organomet. Chem.* **1995**, *500*, 175 and particularly the included references 4−8 i.

(3) (a) Flores, J. C.; Chien, J. C. W.; Rausch, M. D. *Organometallics* **1994**, *13*, 4140. (b) See also: Brintzinger, H. H.; Fischer, D.; Mülhaupt, R.; Rieger, B.; Waymouth, R. M. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1143.

(4) Siemeling, U. *Chem. Ber.* **1995**, 128, 1135 and references therein.

(5) Jutzi, P.; Heidemann, T.; Neumann B.; Stammler, H. G. *J. Organomet. Chem.* **1994**, *472*, 27.

(6) (a) Kopf-Maier, P.; Kopf, H. *Struct. Bonding* **1988**, *70*, 116. (b) Kuo, L. Y.; Kanadjidis, M. G.; Sabat, M.; Tripton, A. L.; Marks, T. J. *J. Am. Chem. Soc.* **1991**, *113* 9027. (c) Smith, D. P.; Olmstead, M. M.; Noll, B. C.; Maestre, M. F.; Fish, R. H.*Organometallics* **1993**, *12*, 593. (d) Sheldrick, W. S.; Hauck, E.; Korn, S. *J. Organomet.Chem.* **1994**, *467*, 283. (e) Chen, H.; Maestre, M. F.; Fish, R. H. *J. Am. Chem. Soc.* **1995**, *117*, 3631.

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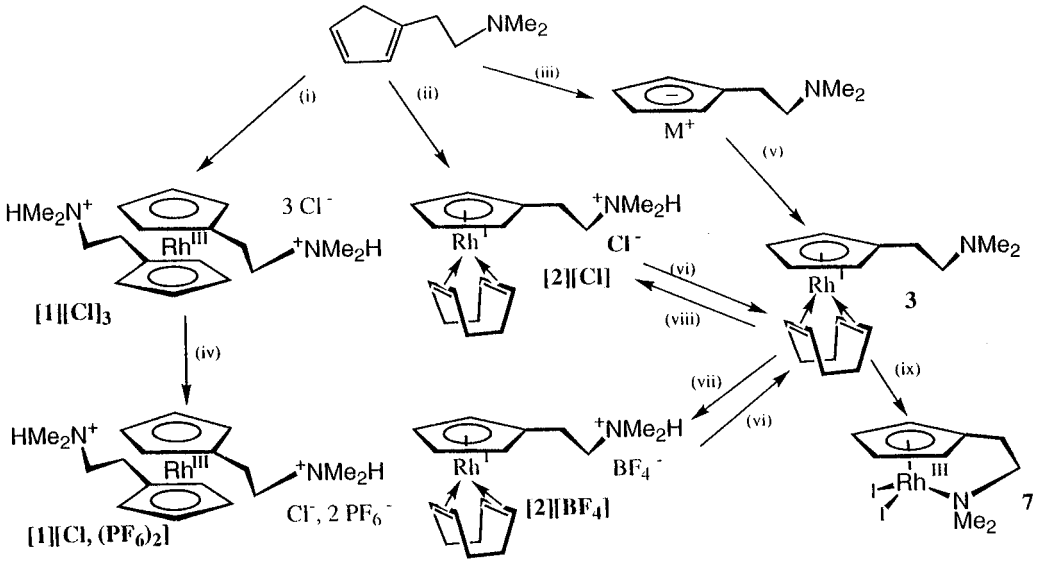


Figure 1. Pathways toward the monometallic rhodium(III) and -(I) derivatives of the dimethylamino-functionalized cyclopentadienyl ligand: (i) $Na_3RhCl_6 \cdot 12H_2O$ in MeOH, reflux, 1 h; (ii) $[Rh(cod)Cl]_2$ in MeOH, room temperature, 1 h; (iii) NaH (*n*-BuLi) in THF, 0 °C; (iv) NH_4PF_6, 1 h, room temperature; (v) $[Rh(cod)Cl]_2$, THF, room temperature; overnight; (vi) *n*-BuLi, in CH_2Cl_2, 0 °C; (vii) HBF_4 in Et_2O, 0 °C, overnight; (viii) HCl, room temperature, 1 h; (ix) I_2 in Et_2O, 0 °C, 1 h.

In addition, several metallocene dihalides (e.g., V, Ti, Nb, Mo, etc.) possess antitumor properties against a variety of tumors.[6] In this field, solubility in biological media is an important parameter; it can be particularly enhanced by the presence of an amino group on the side chain and by its quaternization.[7] For this reason, we were interested in such complexes bearing an amino or ammonio group on a pendant arm.[2−8] In fact, the present report is part of a larger project we have undertaken for the study of the interactions of these and other transition metal cyclopentadienyl derivatives with DNA or RNA constituents. It is also planned that all of the complexes prepared will be screened for antitumor activity.

The complexes were synthesized by using [2-(dimethylamino)ethyl]cyclopentadiene (HL^1) and [3-(dimethylamino)propyl]-cyclopentadiene (HL^2) derivatives or their lithium or sodium salts. The preparative procedures for compounds HL^1 and HL^2, as well as their use for the *in situ* preparation of the cyclopentadienide anions $[L^1]^-$ and $[L^2]^-$, are well-known.[10] In addition, the synthesis and reactivity of their sodium salts have been investigated recently.[11] Obtained as pure, tractable materials, these sodium cyclopentadienides often allow better, higher yielding routes. The reactions studied are summarized in Figure 1 for the case of [2-(dimethylamino)ethyl]cyclopentadiene as starting material.

2. Experimental Section

General Methods and Materials. All reactions (unless otherwise noted) were carried out under nitrogen, by standard Schlenk techniques. Solvents and reagents were purified and dried by standard methods and were distilled under nitrogen immediately prior to use. The starting materials $C_5H_5(CH_2)_nN(CH_3)_2$ ($n = 2$;[12] $n = 3$[11]) and the complex $[Rh(cod)Cl]_2$ (cod = 1,5-cyclooctadiene)[13] were prepared according to literature methods. Nevertheless, the preparation of the well-characterized compounds HL^1 and HL^2 and of their sodium salts according to ref 11 is given hereafter. The conductivity measurements were performed in an E 365 Conductoscope, Metrohm Ltd., Herisau, Switzerland. Microanalyses were performed by the Service de Microanalyse of the Laboratoire de Chimie de Coordination, du CNRS. Mass spectra were recorded on a Varian MAT 311 A instrument. Infrared spectra were recorded on a Perkin-Elmer Model 983 grating spectrophotometer as KBr pellets or in Nujol mulls. ^1H and ^{13}C NMR spectra were obtained on Bruker AC 200 FT and AMX 400 MHz spectrometers of the Laboratoire de Chimie de Coordination and the University of Ioannina, respectively.

2.1. Synthesis of the Amino-Substituted Cyclopentadienes and of Their Sodium Salts. The two compounds HL^1 and HL^2 and their salts were synthesized by the same methods.[11] According to these methods, the hydrochloride of respectively 2-chloro-1-(dimethylamino)-ethane ($ClCH_2CH_2NMe_2 \cdot HCl$) or 3-chloro-1-(dimethylamino)propane ($ClCH_2(CH_2)_2NMe_2 \cdot HCl$) was reacted with excess sodium cyclopentadienyl in THF, yielding a mixture of approximately equal amounts of two regioisomers of the dienes and sodium chloride.[12]

To obtain the salts of these cyclopentadienes, deprotonation of the cyclopentadiene ring was carried out with sodium hydride in THF. A typical preparation is as follows: To a solution of ice-cooled NaH (1.4 g, 0.058 mol) in THF (50 mL) (the NaH was prewashed and dried as before) was added 1 equiv of free ligand (8 g, 0.058 mol). A white solid immediately formed. After several hours the THF was removed under vacuum the salt washed twice with pentane (40 mL) and then dried under vacuum. Yield = 7.5 g, 81%.

Spectral Data of Sodium [2-(Dimethylamino)ethyl]cyclopentadienide (NaL^1). ^1H NMR (in CD_3CN): 5.57, 5.50 (2 × s, 4H, $C_5H_4CH_2CH_2NMe_2$), 2.65 (m, 2H, $CH_2CH_2NMe_2$), 2.43 (m, 2H, $CH_2CH_2NMe_2$), 2.14 (s, 6H, $CH_2CH_2NMe_2$).

$^{13}C\{^1H\}$ NMR (in CD_3CN): 117.0 [s, $C(CH_2)_2NMe_2$], 102.8 [m, $C_4H_4C(CH_2)_2NMe_2$], 64.1 (s, CH_2NMe_2), 45.5 (s, $CH_2CH_2NMe_2$), 29.2 (s, $CH_2CH_2NMe_2$).

Spectral Data of Sodium [3-(Dimethylamino)propyl]cyclopentadienide (NaL^2). ^1H NMR (in CD_3CN): 5.50, 5.48 (2 × s, 4H, $C_5H_4CH_2CH_2CH_2NMe_2$), 2.51−2.44 (m, 2H, $CH_2CH_2CH_2NMe_2$), 2.34−2.19 (m, 2H, $CH_2CH_2CH_2NMe_2$), 2.19 (s, 6H, $CH_2CH_2CH_2NMe_2$), 1.72−1.69 (m, 2H, $CH_2CH_2CH_2NMe_2$).

(7) (a) Avey, A.; Weakley, T. J. R.; Tyler, D. R. *J. Am. Chem. Soc.* **1993**, *115*, 7706. (b) Jutzi, P.; Redeker, T.; Neumann B.; Stammler, H. G. *J. Organomet. Chem.* **1994**, *498*, 127. (c) Jutzi, P.; Redeker, T.; Neumann B.; Stammler, H. G. *Organometallics* **1996**, *15*, 4153.

(8) (a) Macomber, D. W.; Hart, W. P.; Rausch, M. D. *Adv. Organomet. Chem.* **1982**, *21*, 1. (b) Okuda, J. *Comments Inorg. Chem.* **1994**, *16*, 185. (c) Jutzi, P.; Dahlaus, J. *Coord. Chem. Rev.* **1994**, *137*, 179. (d) Jutzi, P.; Siemeling, U. *J. Organomet. Chem.* **1995**, *500*, 175.

(9) (a) Jutzi, P.; Kristen, M. O.; Dahlaus, J.; Neumann, B.; Stammler, H. G. *Organometallics* **1993**, *12*, 2980. (b) Jutzi, P.; Kristen, M. O.; Dahlaus, J.; Neumann, B.; Stammler, H. G. *Organometallics* **1994**, *13*, 3854.

(10) (a) Bernheim, M.; Boche, G. *Angew. Chem., Int. Ed. Engl.* **1980**, *19*, 1010. (b) Hermann, W. A.; Anwander, R.; Muk, C. F.; Scherer, W. *Chem. Ber.* **1993**, *126*, 331.

(11) Mc Gowan, P. C.; Hart, C. E.; Donnadieu, B.; Poilblanc, R. Accepted for publication.

(12) Wang, T. F.; Lee, T. Y.; Chou, J. W.; Ong, C. W. *J. Organomet. Chem.* **1992**, *423*, 31.

(13) Giordano, G.; Crabtree, R. H.; Heintz, R. M.; Forster, D.; Morris, D. E. *Inorg. Synth.* **1990**, *28*, 88.

$^{13}C\{^1H\}$ NMR (in CD_3CN): 120.2 [s, $C(CH_2)_3NMe_2$], 102.8, 102.3 [2 × s, CH of $C_5H_4(CH_2)_3NMe_2$], 61.6 (s, $CH_2CH_2CH_2NMe_2$), 45.9 [s, $C_5H_4(CH_2)_3NMe_2$], 32.0 (s, $CH_2CH_2CH_2NMe_2$), 29.8 (s, $CH_2CH_2CH_2$-NMe_2).

Remarkably, in both salts an exchange was observed between the protons of the cyclopentadienyl ring and the deuterons of the NMR solvent.[11]

2.2. Preparation of [{η^5-$C_5H_4(CH_2)_2NH(CH_3)_2$}$_2$$Rh^{III}$]$^{3+}$($Cl^-$)$_3$ ([1][Cl]$_3$). To a suspension of $Na_3RhCl_6 \cdot 12H_2O$ (110 mg, 0.183 mmol) in methanol (5 mL) was added dropwise the diene $C_5H_5(CH_2)_2N(CH_3)_2$ until complete dissolution occurred. During the addition of the ligand the color changed from violet-red to orange. The mixture was then heated gently to boiling and refluxed for *ca*. 1 h. After cooling, the orange solution was filtered and evaporated to dryness and the residue redissolved in cold methanol. After being filtered, the solution was evaporated *in vacuo* and the yellow-brown solid was washed with diethyl ether (2 × 5 mL) and dried at 50 °C under vacuum. Yield: 85%.

A second fraction was obtained after evaporation of the filtrate, washing with diethyl ether, and drying *in vacuo.* Total yield: 94% (*ca*. 70.8 mg). Anal. Calcd for $C_{18}H_{30}N_2Cl_3Rh$ (483.7 g/mol): C, 44.70; H, 6.26; N, 5.79; Cl, 22.00. Found: C,45.00; H, 6.31; N, 5.76; Cl, 21.98. Mass spectrum (CI): *m*/*e* = 375 ([**1**][Cl]$_3$ − HCl − Cl^-). Mp = 169 °C

IR (KBr): 3090, 3050, 3020 (m, >CH), 2940 (w, −CH), 2670 (s, N^+H), 1470 (m, C═C), 1000, 970, 850 cm^{-1}, and other less characterized bands.

^1H NMR (in D_2O) [using 3-(trimethylsilyl)propanesulfonic acid (TSP) as internal standard]: 6.07, 5.95 [2 × t, 4H, $C_5H_4(CH_2)_3NMe_2$], 3.36 (t, 2H, CH_2N), 2.99−2.95 [m, 8H, CH_2CH_2N and $N(CH_3)_2$. ^1H NMR (in DMSO-d_6): 10.7 (br sh, N^+H), 6.22 [d, 2H, $C_5H_4(CH_2)_3$-NMe_2], 6.00 [d,2H, $C_5H_4(CH_2)_3NMe_2$], 2.96 (m, 2H, CH_2CH_2N), 2.80 [m, 8H, $CH_2N(CH_3)_2$).

^{13}C NMR (in D_2O): 110.7 (s), 110 (d), 109.6 (d), 109 (d), (C_5H_4-CH_2), 79.6 (s, CH_2N), 65.5 [$N(CH_3)_2$], 45.0 (s, CH_2CH_2N). ^{13}C NMR (in DMSO-d_6): 106.3 [d, *J* = 7.0 Hz, $C(CH_2)_2N(CH_3)_2$], 86.7, 86.6 (2 × d, *J* = 7.04 Hz, C_5H_4), 55.3 (s, CH_2N), 41.4 [s, $N(CH_3)_2$], 21.6 (s, CH_2CH_2N).

(The differences in δ values in D_2O are due to thermal and concentration dependence.)

2.3. Preparation of [{η^5-$C_5H_4(CH_2)_2NH(CH_3)_2$}$_2$$Rh^{III}$]$^{3+}$($Cl^-$)-($PF_6^-$)$_2$ ([1][Cl] [PF_6]$_2$). To a stirred solution of [**1**][Cl]$_3$ (100 mg, 0.20 mmol) in H_2O (3 mL) was added dropwise an aqueous solution (2 mL) of NH_4PF_6 (140 mg, 0.858 mmol). A yellow-brown precipitate was immediately formed. The suspension was stirred for 1 h and centrifuged, and the residue was filtered off and washed with ethanol and diethyl ether. Then, it was recrystallized from acetonitrile (2 mL) by addition of diethyl ether (10 mL). This product was dried *in vacuo* at 60 °C. Yield: 47% (60 mg). Anal. Calcd for $C_{18}H_{30}N_2P_2F_{12}Rh$ (702.5): C, 30.77; H, 4.27; N, 3.98. Found: C, 31.69; H, 3.99; N, 4.38. Mp = 195 °C

IR (KBr): 3140 (m, CH of Cp), 2940 (m, CH), 2680 (v s, N^+H), 1460 (m, C═C), 1005, 965, 840 (br sh vs, PF_6^-), 520 cm^{-1}.

^1H NMR (in D_2O): 6.02, 5.92 (2 × t, 4H, Cp H), 3.29−3.25 (t, 2H, *J* = 8.0 Hz, CH_2N) 2.94−2.88 [m, 8H, $CH_2CH_2N(CH_3)_2$]. ^1H NMR (in DMSO-d_6): 9.46 (br s, N^+H), 6.07, 6.02 [m, 4H, $C_5H_4(CH_2)_3NMe_2$], 3.20 (t, 2H, *J* = 8.0 Hz, CH_2N) 2.83 [s, $N(CH_3)_2$], 2.77 (t, 2H, CH_2-CH_2N).

^{13}C NMR (in D_2O): 95 [d, $C(C_5H_4)$], 89 (m, C_5H_4), 56 (s, CH_2N), 42.0 [s, $N(CH_3)_2$], 21.2 (s, CH_2CH_2N). ^{13}C NMR (in DMSO-d_6): 105.6 [d, *J* = 6.04 Hz, $C(CH_2)_2N(CH_3)_2$], 86.9, 86.8, 86.7 (t, *J* = 6.04 Hz, C_5H_4), 55.9 (s, CH_2N), 42.4 [s,-$N(CH_3)_2$], 26.2 (s, CH_2CH_2N).

2.4. Preparation of [{η^5-$C_5H_4(CH_2)_2NH(CH_3)_2Cl$}Rh(cod)]$^+$($Cl^-$) ([2][Cl]). [Rh(cod)Cl]$_2$ (197 mg, 0.40 mmol) was suspended in methanol (5 mL) at room temperature. The ligand $C_5H_5(CH_2)_2N(CH_3)_2$ was added dropwise with stirring until complete dissolution. After 1 h the solvent was removed under reduced pressure. The solid residue was dissolved in small volumes of methanol (5−10 mL). The yellow orange solid was recrystallised twice in a mixture of CH_2Cl_2: pentane (1:4) A pale yellow solid was finally obtained in 95% yield (290 mg). Anal. Calcd for $C_{17}H_{27}NRhCl$ (383.7): C, 53.20; H, 7.09; N, 3.65. Found: C, 53.29; H, 7.01; N, 3.89. Mass spectrum (CI): *m*/*e* = 348 ([**2**][Cl] − Cl^-). Λ_M: 25 $\Omega^{-1}\cdot cm^2\cdot mol^{-1}$.

IR (KBr): 3079 (w, CH), 2994 (m, CH), 2901−2820 (br sh, CH bands of cod), 2627−2436 (vs, N^+H), 1468, 1446, 1323, 1241, 963, 874, 808, 792, 384 (cod coordinated to Rh).

^1H NMR ($CDCl_3$): 5.04 [br s, $C_5H_4CH_2CH_2N(CH_3)_2$], 3.77 (br s, 4H of cod), 3.25−3.17 (m, 2H, CH_2N), 2.88−2.71 [m, 8H, CH_2CH_2N-$(CH_3)_2$], 2.15 (br d, 4H, cod aliphatic), 1.90 (br d 4H, cod aliphatic).

2.5. Preparation of [η^5-$C_5H_4(CH_2)_2N(CH_3)_2$]Rh(cod) (3). To a solution of [Rh(cod)Cl]$_2$ (215 mg, 0.43 mmol) in THF (10 mL) was added dropwise a solution of [$C_5H_4(CH_2)N(CH_3)_2$]Li in THF (10 mL) [prepared from the ligand (120 mg, 0.874 mmol) and *n*-BuLi (0.6 mL, 0.96 mmol) in THF], *via* a double-ended needle at room temperature. The reaction mixture was stirred for *ca*. 20 h, and the resulting brown solution was evaporated to dryness. The residue was dissolved in toluene (2 mL) and eluted through a silica gel column with a mixture of toluene/THF (3:1). The solvents were removed *in vacuo*, leading to a yellow oily liquid. Yield: 47% (60 mg). Anal. Calcd for $C_{17}H_{26}$-NRh (347.3): C, 58.79; H, 7.34; N, 4.03. Found: C, 58.81; H, 7.89; N, 4.09. Mass spectrum (CI): *m*/*e* = 348 (MH^+).

This compound was also synthesized by the reaction of the sodium salt of the above ligand with [Rh(cod)Cl]$_2$. To a stirred solution of [RhCl(cod)]$_2$ (1 g, 2.03 mmol) in THF (10 mL) was added 2 equiv of the sodium salt of [2-(dimethylamino)ethyl]cyclopentadiene (0.646 g, 4.06 mmol) in THF (10 mL). The solution was left to stir overnight. The THF was then removed under reduced pressure and the product extracted in ether (10 mL). The ether was then removed under reduced pressure to leave a yellow oil.

IR (NaCl): 3090 (m, CH), 2971−2762 (br s, CH bands of cod), 1552, 1460, 1446, 1038, 869, 790, 384 (m, cod coordinated to Rh).

^1H NMR (in C_6D_6): 5.05 [t, *J* = 1.9 Hz, 2H, $C_5H_4(CH_2)_3NMe_2$], 4.85 [t, 2H, *J* = 1.9 Hz, $C_5H_4(CH_2)_3NMe_2$], 3.88 (br s, 4H, cod vinylic), 2.49−2.43 (m, 2H, CH_2N), 2.32−2.25 (m, 6H, cod aliphatic + CH_2-CH_2N), 2.14 [s, $N(CH_3)_2$], 2.03 (d, 4H, *J* = 7.7 Hz, cod). ^1H NMR (in $CDCl_3$): 5.03 (t, 2H), 4.91 (t, 2H), 3.71 (br, s, 4H, cod), 2.94 (m, 2H, CH_2CH_2N), 2.44 (m, CH_2N), 2.19 [s, 6H, $N(CH_3)_2$], 2.12 (m, 4H, CH_2 of cod), 1.85 (m, 2H, CH_2 of cod aliphatic).

^{13}C NMR (in $CDCl_3$): 103 [s, $C(C_5H_4)$], 85.6, 84.1 (2 × d, *J* = 4 Hz, C_5H_4), 62.7 (d, $J^{103}_{Rh-^{13}C}$ = 14.3 Hz, CH of cod), 60.1 (s, CH_2-CH_2N), 44.5 [s, $N(CH_3)_2$], 31.5 (s, CH of cod), 25.1 (s, CH_2N).

2.6. Protonation of 3 with HCl or with HBF_4: Preparation of [2][Cl] and [2][BF_4]. Complex **3** (70 mg, 0.20 mmol) was dissolved in a mixture of toluene (2 mL) and CH_2Cl_2 (3 mL). HCl (0.1N,1.5 mL) was then added dropwise with stirring. The organic yellow phase was evaporated to dryness, affording [**2**][Cl] as a pale yellow solid. It was then recrystallized from a mixture of CH_2Cl_2/pentane (1:5). Similarly, the protonation of **3** with HBF_4 was carried out in ether at room temperature, affording [**2**][BF_4].

2.7. Deprotonation of [2][Cl] (or [2][BF_4]) with *n*-BuLi. The salt [**2**][Cl] (50 mg, 0.13 mmol) was dissolved in CH_2Cl_2 (4 mL). A solution of *n*-BuLi (0.09 mmol, 1.6 M in hexane) was added dropwise at −80 °C. The yellow solution was stirred for 1 h at this temperature and then warmed gently to ambient temperature. Solvents were removed *in vacuo*, and the residue was extracted with toluene (3 × 5 mL). The toluene extracts were evaporated to a small volume. The yellow-brown solution was eluted through a silica gel column with a mixture of toluene/THF (3:1). Evaporation of the solvents gave **3** as a yellow waxy liquid.

2.8. Preparation of the [3-(dimethylamino)propyl]cyclopentadienyl Derivatives 4, [5][Cl], and [5][BF_4]. The three complexes were all prepared similarly to complexes **3**, [**2**][Cl], and [**2**][BF_4].

Characterization of [η^5-$C_5H_4(CH_2)_3N(CH_3)_2$]Rh^I(cod) (4). Anal. Calcd for $C_{18}H_{28}NRh$ (361.3): C, 59.84; H, 7.81; N, 3.87. Found: C, 58.89; H, 8.09; N, 3.71.

^1H NMR (in C_6D_6): 5.08, 4.88 (2t, 4H, $C_5H_4CH_2CH_2CH_2NMe_2$), 3.90 (br s, 4H, CH of cod), 2.35−2.10 (m, 14H, $CH_2CH_2CH_2NMe_2$ and CH_2 of cod), 2.05 (m, 4H, CH_2 of cod), 1.70 (quintet, 2H, CH_2CH_2-CH_2NMe_2).

$^{13}C\{^1H\}$ NMR (in C_6D_6): 107.3 [s, $C(CH_2)_3NMe_2$], 87.5, 85.8 [2 × s, CH of $C_5H_4(CH_2)_3NMe$], 59.7 (s, $CH_2CH_2CH_2NMe_2$), 64.4 (d, $J^{103}_{Rh-^{13}C}$ = 14.0 Hz, CH of cod), 46.0 [s, $C_5H_4(CH_2)_3NMe_2$], 33.4 (s, CH_2 of cod), 30.0 (s, $CH_2CH_2CH_2NMe_2$), 26.0 (s, CH_2NMe_2).

Characterization of [{η^5-$C_5H_4(CH_2)_3NH(CH_3)_2Cl$}Rh(cod)]$^+$($Cl^-$) ([5][Cl]). The product was identified by NMR.

^{1}H NMR (in $CDCl_3$): 5.10, 4.98 (2 × t, 4H, $C_5H_4CH_2CH_2CH_2NMe_2$), 4.22 (br s, NH of $C_5H_4CH_2CH_2CH_2NMe_2H^+$), 3.75 (br s, 4H, CH of cod), 2.95 (m, 2H, $CH_2CH_2CH_2NMe_2$), 2.66 (s, 6H, $CH_2CH_2CH_2NMe_2$), 2.44 (m, 2H, $CH_2CH_2CH_2NMe_2$), 2.25−1.65 (m, 10H, $CH_2CH_2CH_2$-NMe_2 and CH_2 of cod).

^{13}C{^{1}H} NMR (in $CDCl_3$): 104.1 [s, $C(CH_2)_3NMe_2$], 86.3, 85.3 (2 × s, CH of $C_5H_4(CH_2)_3NMe_2$], 63.9 (d, $J_{^{103}Rh-^{13}C}$ = 13.6 Hz, CH of cod), 57.8 [s, $CH_2CH_2CH_2NMe_2$], 43.4 (s, $C_5H_4(CH_2)_3NMe_2$), 32.2 (s, CH_2 of cod), 30.8 (s, $CH_2CH_2CH_2NMe_2$), 24.8 (s, $CH_2CH_2CH_2NMe_2$).

Characterization of [{η^5-$C_5H_4(CH_2)_3NH(CH_3)_2Cl$}$Rh(cod)]^+$-($BF_4^-$) ([5][$BF_4$]). Anal. Calcd for $C_{18}H_{29}NBF_4Rh$ (449.1): C, 48.14; H, 6.51; N, 3.12. Found: C, 47.72; H, 6.40; N, 3.19.

^{1}H NMR (in $CDCl_3$): 6.00 (br s, NH of $C_5H_4CH_2CH_2CH_2NMe_2H^+$), 5.09, 4.93 (2 × t, 4H, $C_5H_4CH_2CH_2CH_2NMe_2$), 3.73 (br s, 4H, CH of cod), 2.95 (m, 2H of $CH_2CH_2CH_2NMe_2$), 2.73 (s, 6H, CH_2CH_2-CH_2NMe_2), 2.18 (m, 6H, $CH_2CH_2CH_2NMe_2$ and CH_2 of cod).

^{13}C{^{1}H} NMR (in $CDCl_3$): 103.9 [s, $C(CH_2)_3NMe_2$], 86.6, 85.5 [2 × s, CH of $C_5H_4(CH_2)_3NMe_2$], 64.0 (d, $J_{^{103}Rh-^{13}C}$ = 14.0 Hz, CH of cod), 57.9 (s, $CH_2CH_2CH_2NMe_2$), 43.3 [s, $C_5H_4(CH_2)_3NMe_2$], 32.4 (s, CH_2 of cod), 26.1 (s, $CH_2CH_2CH_2NMe_2$), 24.5 (s, $CH_2CH_2CH_2NMe_2$).

2.9. Preparation of [η^5-$C_5H_4(CH_2)_2N(CH_3)_2$]$Rh^I(coe)_2$ (6). To a stirred solution of $[RhCl(coe)_2]_2$ (coe = cyclooctene) (0.25 g, 0.34 mmol) in THF was added 2 equiv of the sodium salt of [2-dimethylamino)ethyl]cyclopentadiene (0.108 g, 0.68 mmol) in THF (5 mL). There was a color change from bright orange to brown/orange. The solution was left to stir overnight and the THF removed under reduced pressure. The product was extracted in ether, which was subsequently removed under vacuum to leave a yellow oil, which was identified by NMR.

^{1}H NMR (in C_6D_6): 4.92, 4.40 (2 × t, 4H, $C_5H_4CH_2CH_2CH_2NMe_2$), 2.52 (m, 2H, $CH_2CH_2CH_2NMe_2$), 2.29 (m, 8H, $CH_2CH_2NMe_2$ and CH_2-CH_2NMe_2), 1.64−1.20 (m, 28H, CH_2 and CH of coe).

2.10. Preparation of [η^5:η^1-$C_5H_4(CH_2)_2N(CH_3)_2$]$Rh^{III}I_2$ (7). To a stirred solution of compound **3** (1.4 g, 4.06 mmol) in ether (10 mL) was added 1 equiv of I_2 (1.03 g, 4.06 mmol) in ether (15 mL). A purple precipitate immediately formed. The reaction mixture was left to stir overnight. The product was then filtered off, washed twice with ether, and dried under reduced pressure to leave a deep purple solid. Yield: ca. 80%. Anal. Calcd for $C_9H_{14}NRhI_2$: C, 21.92; H, 2.86; N, 2.84. Found: C, 22.10; H, 2.81; N, 2.70.

^{1}H NMR [in $(CD_3)_2SO$]: 6.25, 6.15 (2 × s, 4H, $C_5H_4CH_2CH_2NMe_2$), 3.50 (m, 2H, $CH_2CH_2NMe_2$), 2.99 (m, 8H,$CH_2CH_2NMe_2$ and CH_2CH_2-NMe_2). ^{1}H NMR (in $CDCl_3$): 5.59, 5.63 (2 × s, 4H, $C_5H_4CH_2CH_2$-NMe_2), 3.68 (m, 2H, $CH_2CH_2NMe_2$), 3.00 (s, 6H,$CH_2CH_2NMe_2$), 2.46 (s, 6H,$CH_2CH_2NMe_2$). ^{13}C{^{1}H} NMR (in $CDCl_3$): 105.2 [s, $C(CH_2)_2$-NMe_2], 92.3, 89.5 [2 × d, $J_{^{103}Rh-^{13}C}$ = 5.8 Hz, CH of $C_5H_4(CH_2)_2$-NMe_2], 56.8 (s, $CH_2CH_2NMe_2$), 44.2 [s, $C_5H_4(CH_2)_2NMe_2$], 24.3 (s, $CH_2H_2NMe_2$).

2.11. Preparation of [η^5:η^1-$C_5H_4(CH_2)_3N(CH_3)_2$]$Rh^{III}I_2$ (8). This purple product was synthetized similalry to compound **7** by starting from **4**. It was identified by NMR.

^{1}H NMR [in $(CD_3)_2SO$]: 6.19, 6.15 (2 × t, 4H, $C_5H_4CH_2CH_2CH_2$-NMe_2), 3.50 (m, 2H, $CH_2CH_2CH_2NMe_2$), 3.23 (m, 2H, $CH_2CH_2CH_2$-NMe_2), 2.89 (s, 6H, $CH_2CH_2CH_2NMe_2$), 2.63 (m, 2H, $CH_2CH_2CH_2$-NMe_2).

^{13}C{^{1}H} NMR [in $(CD_3)_2SO$]: 111.2 [d, $J_{^{103}Rh-^{13}C}$ = 5.7 Hz, $C(CH_2)_3$-NMe_2], 91.3, 89.4 [2 × d, $J_{^{103}Rh-^{13}C}$ = 6.2 Hz, $C_4H_4C(CH_2)_3NMe_2$], 57.4 (s, CH_2NMe), 43.9 [s, $C_5H_4(CH_2)_3NMe_2$], 26.1 (s, $CH_2CH_2CH_2$-NMe_2), 24.9 (s, $CH_2CH_2CH_2NMe_2$).

Collection of X-ray Diffraction Data of [(η^5-$C_5H_4(CH_2)_2NMe_2H)_2$-$Rh^{III}]^{3+}(Cl^-)(PF_6^-)_2$ ([1][Cl][$(PF_6)_2$]) and [(η^5-$C_5H_4(CH_2)_2NMe_2H$)-$Rh^I(cod)]^+$(BF_4^-) ([2][BF_4]). A most well shaped crystal of [**1**][Cl]-$[PF_6]_2$, suitable for X-ray analysis, was selected from a pile of similar crystals obtained by slow evaporation of a solution in an ethanol/diethyl ether mixture of the salt analyzing as [**1**][Cl]$[PF_6]_2$ (preparation 2.3).

Crystals of [**2**][BF_4] suitable for X-ray crystallography were grown by slow diffusion of ether into a dichloromethane solution.

Data Collection. The diffraction data for [**1**][Cl]$[PF_6]_2$ and [**2**][BF_4]-were collected at room temperature (293 K) on a four-circle Enraf-Nonius diffractometer using Mo Kα radiation and a graphite monochromator. The lattice parameters having been determined from the least-squares refinement of the setting angles of 25 well-centered reflections, three standard reflections were checked periodically; they show no change during data collection. Details of the data collection, least-squares refinement, and crystal parameters are summarized in Table 1.

Table 1. Crystallographic Data for [**1**][Cl]$[PF_6]_2$ and [**2**][BF_4]

	[**1**][Cl]$[PF_6]_2$	[**2**][BF_4]
chemical formula	$[Rh(C_9NH_{15})_2][Cl][PF_6]_2$	$[RhC_{17}H_{27}][BF_4]$
formula wt	674.7	434.1
space group	*P*1 (No. 1)	$P4_2/n$ (No. 86)
T (°C)	20	20
λ (Å)	0.710 73	0.710 73
a (Å)	6.617(2)	21.183(2)
b (Å)	7.436(2)	21.179(3)
c (Å)	13.965(3)	8.324(2)
α (deg)	76.39(2)	90
β (deg)	82.31	90
γ (deg)	87.26	90
V (Å^3)	661.8(3)	3734(1)
Z	1	8
ρ (g·cm^{-3})	1.69	1.54
μ (cm^{-1})	9.43	9.43
R^a	0.0440	0.0472
$R_w{}^b$	0.0484	0.0525

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

Corrections for Lorentz and polarization effects were made, and absorption corrections using DIFABS[14] were applied; a weighting scheme[15] was adopted for [**2**][BF_4].

3. Results

The ^{1}H and ^{13}C NMR spectra of [**1**][Cl]$_3$ in D_2O are in agreement with the proposed structure. Both the (*β*) CH_2-N triplet and the $N(CH_3)_2$ singlet are shifted downfield compared to the free ligand, by 0.80 and 0.68 ppm, respectively. The coupling constants J_{H-H} are of the order of 6 Hz in all cases. In DMSO-d_6, the protonated amino (NH^+) group is observed as an additional broad peak at 10.7 ppm. In the mass spectrum (CI) of [**1**][Cl]$_3$ a peak is found at m/e = 375 that can be assigned to the nonprotonated cationic fragment {[$Cp(CH_2)_2N$-$(CH_3)_2]_2Rh$}$^+$. However, it is clear from both the IR and the ^{1}H NMR spectra and from the elemental analysis that in the complex [**1**][Cl]$_3$ the $N(CH_3)_2$ group is protonated.

Addition of NH_4PF_6 to an aqueous solution of [**1**][Cl]$_3$ produces a brown yellow solid, proven to be the hexafluorophosphate salt of the bis(dimethylamino) rhodicinium compound [**1**][Cl]$[PF_6]_2$ (Figure 1). The relatively high solubility of this compound in water makes difficult the complete recovering of the product and reduced the overall yield to about 47%.[16] The IR spectrum of [**1**][Cl]$[PF_6]_2$ is similar to that of complex [**1**]-[Cl]$_3$, except for the characteristic frequencies of the PF_6^- anion at 840 cm^{-1} observed as a strong and broad band. Furthermore, both ^{1}H and ^{13}C NMR spectra in D_2O of [**1**][Cl]$[PF_6]_2$ are similar to those of [**1**][Cl]$_3$.

Reaction of [2-(dimethylamino)ethyl]cyclopentadiene with the $[Rh(cod)Cl]_2$ dimer in methanolic solution produced in high yield (95%) the chloride salt [(η^5-$C_5H_4(CH_2)_2NMe_2)Rh^I(cod)]^+$-($Cl^-$) ([**2**][Cl]) (Figure 1). The IR spectrum of [**2**][Cl] shows a broad band at *ca*. 2700 cm^{-1}, indicative of the protonation of the dimethylamino group of the side chain. An IR band characteristic for the cyclooctadiene coordinated to rhodium was observed at 384 cm^{-1}.[17] Elemental analysis and molecular

(14) Walker, N.; Stuart, D. *Acta Crystallogr.* **1983**, *A39*, 158.
(15) Prince, E. *Mathematical Techniques in Crystallography*; Springer-Verlag: Berlin, 1982.
(16) Cotton, P. A.; Whipple, R. O.; Wilkinson, G. *J. Am. Chem. Soc.* **1953**, *75*, 3586.
(17) (a) Bennett, M. A.; Clark, R. J. H.; Milner, D. L. *Inorg. Chem.* **1967**, *6*, 1647. (b) Herrmann, W. A.; Kohlpainter, C. W. *Angew. Chem., Int. Ed. Engl.* **1996**, *32*, 1524.

weight determination agree with the empirical formula. The molar conductance value indicates also a 1:1 electrolyte in methanolic solution.[18] In the ^{1}H NMR spectrum of [**2**][Cl] at 225 K, two triplets for the ring were observed at 5.08 and 5.03 ppm; however, at room temperature, only one singlet at 5.04 ppm was observed for the cyclopentadienyl protons.

In accordance with the 18-electron rule, all these data exclude the coordination of the amino group with the metal atom.

At room temperature, the ethylenic side chain protons (CH_2N and CH_2CH_2N) appeared at 0.70 and 0.30 ppm downfield compared with the free ligand, overlapping with the singlet of the dimethylamino protons at 2.82 ppm. As shown by the presence of aliphatic protons at 2.09 and 1.90 ppm and olefinic protons at 3.79 ppm, the cyclooctadiene ligand coordinates in a bidentate fashion with rhodium(I). The aliphatic protons of the side chain were assigned on the grounds of NOE experiments at $T = 225$ and 193 K. Thus, saturation of the aliphatic signal at *ca*. 3.20 ppm in $CDCl_3$ at 225 K revealed another resonance at 2.63 ppm due to CH_2CH_2N overlapping with the protons of the N$(CH_3)_2$ group. Consequently, these protons must be adjacent to the aliphatic protons of the side chain.

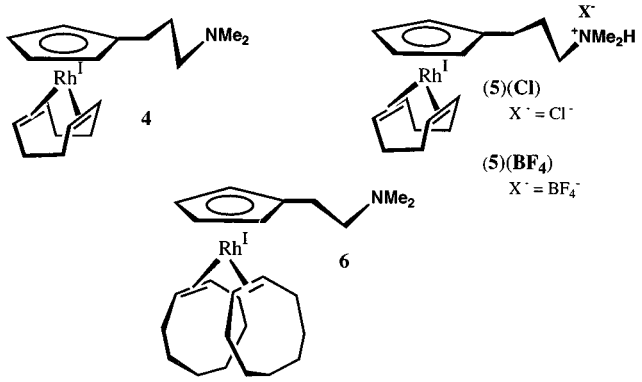
The protonation of nitrogen was confirmed by the downfield shift (*ca*. 0.6 ppm)[9b] of the protons of the two methyl groups attached to it, observed at 2.82 ppm in the complex and at 2.27 ppm in the free ligand. Similar observations have been made in the titanium[3a] and the molybdenum[7] complexes of similar ligands. It is noteworthy that reversible transformation can be achieved upon treatment of [**2**][Cl] with a slight excess of *n*-BuLi in CH_2Cl_2, the deprotonated complex [(η^5-$C_5H_4(CH_2)_2$-NMe_2)Rh$^{(I)}$(cod)] (**3**) was produced as a yellow waxy liquid, in a 49% yield. The opposite transformation was observed by reacting **3** with HCl (Figure 1). Complex **3** was also prepared from the reaction of sodium [2-(dimethylamino)ethyl]cyclopentadienide with [RhCl(cod)]$_2$ in THF, which affords it as an analytically pure yellow oil on extraction with ether (Figure 1).

The ^{1}H NMR spectrum of **3** shows an AA′BB′ pattern for the C_5H_4 ring, a singlet (integrated for 6H) for the N$(CH_3)_2$ protons, and two multiplets for the CH_2 protons of the side chain. In order to assign the aliphatic protons of the cyclooctadiene ligand,[19] we carried out NOE experiments at room temperature. Saturation of the aliphatic signal at 2.32 ppm caused a decrease of the double resonance at 2.08 ppm, which was assigned to the aliphatic cyclooctadiene protons. Consequently, this aliphatic unit must be adjacent to this proton. Saturation of the olefinic signal at 3.88 ppm caused a small decrease in the double resonance at 2.08 ppm. This confirms that the olefinic proton is also adjacent to this proton.

The ^{13}C and the ^{13}C J-MOD spectra of **3** are in agreement with the proposed structure and have been fully assigned (see Experimental Section). The ^{13}C spectra show a ^{103}Rh−^{13}C coupling between the rhodium atom and the CH_2 groups of the cod that has a coupling constant of *ca*. 14 Hz. Finally, in the IR spectrum of **3** typical bands for the cyclooctadiene ligand are observed in the region 2760−2970 cm^{-1} and at 384 cm^{-1} for cyclooctadiene coordinated to Rh, while the strong and broad band in the region 2700−2400 cm^{-1}, indicating nitrogen protonation, is absent.

Protonation of **3** was also carried out by reaction with HBF_4 (Chart 1) in diethyl ether at ambient temperature to form a pale yellow solid, [**2**][BF_4], which is insoluble in ether. In solution, the ^{1}H NMR spectrum of the compound [**2**][BF_4] is similar to that of the neutral compound **3** except that a broad singlet for the NH at 7.75 ppm can be seen, confirming the protonation of nitrogen and therefore the non coordination in solution of the side chain to the rhodium(I) atom. The broadness of the signal is attributed to the quadrupolar effect of ^{14}N.

Chart 2



As expected, the reaction of sodium [3-(dimethylamino)-propyl]cyclopentadienide with [RhCl(cod)]$_2$ in THF gives also as a yellow oil, on extraction with ether, the corresponding [3-(dimethylamino)propyl]cyclopentadienyl complex **4** (Chart 2). The ^{1}H NMR spectrum of this compound is similar to that of **3** except that two of the CH_2 groups of the side chain and one set of cod signals are overlapping thereby making it difficult to assign individual parts of a multiplet stretching from 2.3 to 2.1 ppm. Characterization was more easily achieved by way of ^{13}C J-MOD spectra where the three peaks due to the CH_2 groups point down, as well as the peak due to the quaternary carbon center. As in the case of **3**, the protonation of **4** was carried out by reaction with HBF_4 in ether at ambient temperature to form a pale yellow solid, [**5**][BF_4], which is practically insoluble in ether.

By way of comparison, starting material [RhCl(cod)]$_2$ was also reacted with the free ligand [3-(dimethylamino)propyl]-cyclopentadiene itself by addition to a THF solution and was left to stir overnight, during which time a pale yellow solid, [**5**][Cl], was formed. The ^{1}H NMR spectrum of the compound is similar to that of the neutral complex **4** (see above) except for a broad singlet for NH at $\delta = 4.1$ ppm. Subsequent NMR and IR analysis showed these salts [**5**][Cl] and [**5**][BF_4] to be identical except, of course, for the counterion. The ^{1}H and ^{13}C NMR spectra are very similar. It is noticeable that in the proton spectrum the NH peak for [**5**][Cl] can be seen at 6.0 ppm.

A rhodium cyclooctene (coe) compound, **6**, can also be made that is analogous to **4** (Chart 2). The crystal structure of this molecule has already been reported.[11] The ^{13}C spectrum shows ^{103}Rh−^{13}C coupling for the CH groups of both the coe ligands and the Cp ring and for the quaternary carbon of the cyclopentadienyl ring.

Both compounds **3** and **4** in ether can be reacted with a solution of iodine in ether to give compounds **7** and **8**.

The ^{1}H spectra of these compounds show that the two CH_2 multiplets and the singlet for the methyl groups have all been shifted significantly downfield (by at least 0.5 ppm) in comparison with the ^{1}H spectra of compounds **1** and **4**, showing a profound change in environment for these groups. Interestingly, in these compounds, ^{103}Rh−^{13}C coupling can also be seen in the signals due to the Cp. In all cases, the coupling constants are in the region of 6 Hz.

The change in environment that caused the shift in the ^{1}H signals of the side chain of the ligand must be that the nitrogen is now coordinated to the rhodium atom.

Wang *et al.* have reported intramolecular coordination for the [2- (dimethylamino)ethyl]cyclopentadienyl ligand in man-

(18) Geary, W. J. *Coord. Chem. Rev.* **1971**, *7*, 81.
(19) Wehman-Doyevaar, I. C. M.; Kapteijn, M. G.; Grove, M. D.; Smeets, J. J. W.; Spek, L. A.; Kosen, B. *J. Chem. Soc., Dalton Trans.* **1994**, 703.

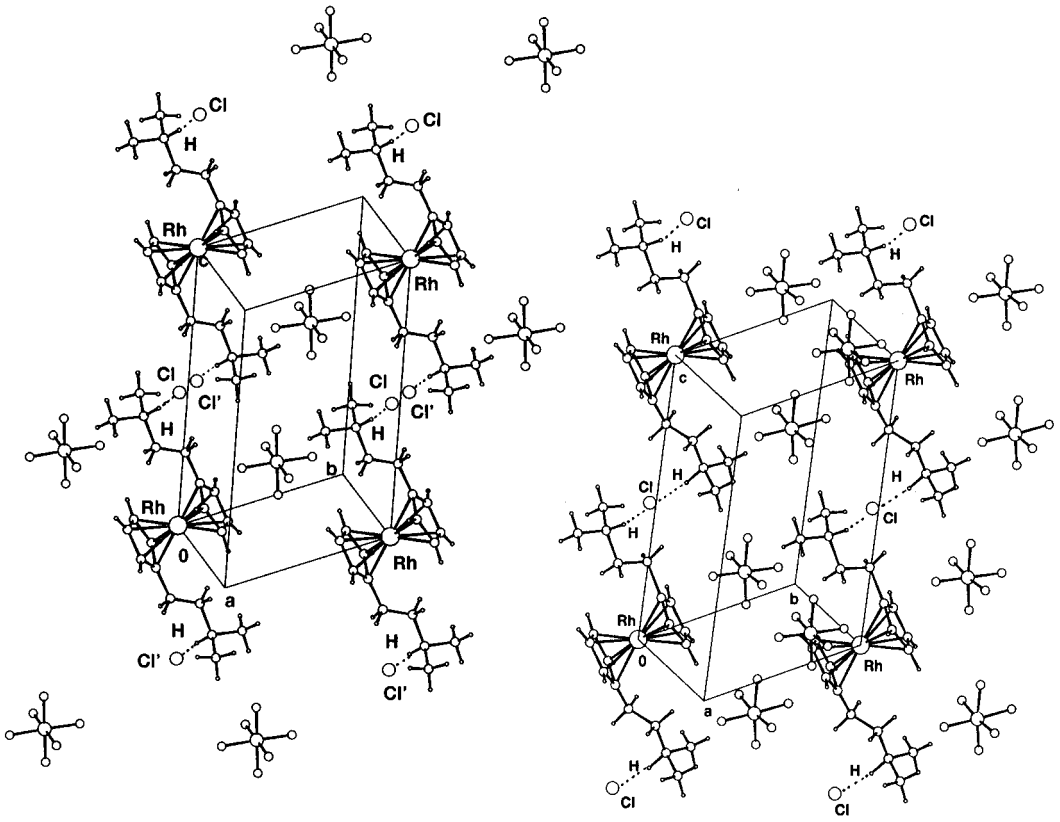


Figure 2. (a, left) Crystal packing obtained by tentatively solving the structure of [**1**][Cl][PF_6]$_2$ in the centrosymmetric $P\bar{1}$ space group. (b, right) Crystal packing in the noncentrosymmetric *P*1 space group showing the arrangement of the [(η^5-$C_5H_4(CH_2)_2NMe_2H)_2RhCl$] asymmetric units and the short distance $Cl^-\cdots H^+-N<$ of interaction. Part of the cell content has been omitted for clarity.

ganese,[20a] molybdenum[12,20b] and rhenium[20c] complexes. The nitrogen is also coordinated in several titanium and zirconium complexes.[21] X-ray investigations of the [[(dialkylamino)alkyl]-2,3,4,5-tetramethylcyclopentadienyl]cobalt,[9a] -rhodium, and -iridium[9b] derivatives have been published already.

4. Resolution, Refinement, and Discussion of the Molecular Structures of [2][BF_4] and [1][Cl][PF_6]$_2$

Computations were performed by using the program CRYSTALS[22] adapted on a PC. The atomic scattering factors for all atoms were taken from literature.[23] The structure of [**2**][BF_4] was solved by direct methods in accordance with the package SIR92[24] whereas the heavy atom method (PATTERSON) was used for [**1**][Cl][PF_6]$_2$; in addition, subsequent difference Fourier maps were necessary for both structures.

Molecular Structure of [1][Cl][PF_6]$_2$. Attempts to refine this structure in the centrosymmetric $P\bar{1}$ space group result in a disordered distribution of three atoms: apparently, the two C atoms of the $(CH_2)_2NMe_2$ chain and the chloride anion appear distributed each on two sites with a statistic probability of 50:50. At this stage of the resolution, the significance of a statistic distribution of the chloride anion along the infinite arrangement of rhodicinium−chloride pairs (Figure 2a) had to be considered. Indeed a distribution for which two sites Cl and Cl′ are randomly occupied in half would imply that *some* rhodicinium cations were more closely associated with two anions at short distances and other cations with two anions at longer distances. From an electrostatic consideration, this statistic distribution seemed less probable than a regular repartition, implying the association of *each* rhodicinium cation with, on one side, a chloride anion at a short distance and, on the other side, a chloride anion at a longer distance. But clearly such a regular distribution does imply a noncentrosymmetric space group.

The refinement was therefore carried out using the noncentrosymmetric space group *P*1. Both models, based either on the centrosymmetric $P\bar{1}$ space group with the motive [(η^5-$C_5H_4(CH_2)_2NMe_2H)Rh_{0.5}Cl_{0.5}$] as asymmetric unit or on the noncentrosymmetric space group *P*1 with the motive [(η^5-$C_5H_4(CH_2)_2NMe_2H)_2RhCl$] as asymmetric unit, were tested starting from the mean values of the molecular distances obtained after the first refinement in the non centrosymmetric hypothesis. In spite of a relatively low data:parameters ratio, all non-hydrogen atoms have been anisotropically refined. The hydrogen atoms attached to the C atoms of hydrocarbon chains and cyclopentadienyl rings were not located by difference Fourier synthesis; their coordinates were only introduced in the refinement as fixed contributors and recalculated after each cycle with isotropic thermal parameters fixed 20% higher than those of the carbons to which they were attached. The atoms H1 and H2 attached to the nitrogen atoms were located by difference Fourier maps and refined with a *U*(iso) fixed. The refinement was carried out in four blocks by minimizing the function $\sum w(|F_o| - |F_c|)^2$,where F_o and F_c are the observed and calculated structure factors. Finally, the intensity statistics for normalized factors favor the acentric model.

(20) (a) Wang, T. F.; Lee, T. Y.; Wen, Y. S.; Liu, L. K. *J. Organomet. Chem.* **1991**, *403*, 353. (b) Wang, T. F.; Wen, T. Y. *J. Organomet. Chem.* **1992**, *439*, 155. (c) Wang, T. F.; Lai, C. Y.; Wen, Y. S. *J. Organomet. Chem.* **1996**, *523*, 187.
(21) (a) Hermann,W. A.; Morowietz, J. A.; Priermeir, T.; Mashima, K. *J. Organomet. Chem.* **1995**, *485*, 291. (b) Van der Zeijden, A. A. H. *J. Organomet. Chem.* **1996**, *518*, 147.
(22) Watkin, D. J.; Carruthers, J. R.; Betteridge, P. W. *User Guide*; Chemical Crystallography Laboratory, University of Oxford: Oxford, U.K., 1985.
(23) *International Tables for X-Ray Crystallography*; Kynoch Press: Birmingham, England, 1974; Vol. IV.
(24) Altomare, A.; Cascarano, G.; Burla, A.; Polidori, M. C.; Camailli, G. SIR 92. *J. Appl. Crystallogr.* **1994**, *27*, 435.

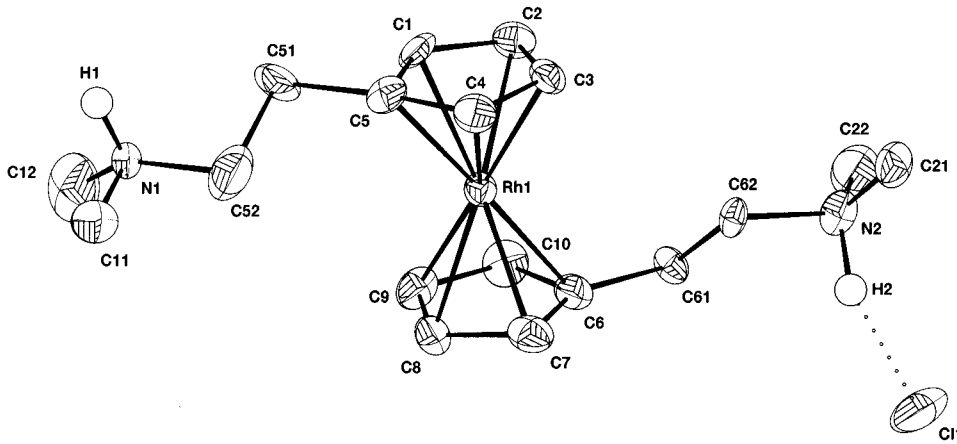


Figure 3. ORTEP view of the rhodicinium cation $[(\eta^5\text{-}C_5H_4(CH_2)_2NMe_2H)_2Rh]^{3+}$ together with the proximal chloride anion in [**1**][Cl][PF_6]$_2$.

Table 2. Selected Bond Lengths (Å) and Angles (deg) of [**1**][Cl][PF_6]$_2$[a]

Mean Value of Rh1−C(Cp) Distances: 2.16(1)			
Rh1−C5	2.22(1)	Rh1−C10	2.19(1)
Mean Value of the Cyclopentadienyl Ring C−C Distances: 1.40(2)			
C5−C5	1.574(9)	C6−C61	1.63(1)
C51−C52	1.533(9)	C61−C62	1.52(1)
Mean Value of the N−C Distances: 1.47(2)			
N1−H1	1.02(5)	N2−H2	1.05(6)
H1′−Cl1	2.06(2)	H2−Cl1	1.962(4)
C−N−H Angles			
C52−N1−H1	110.8(64)	C11−N1−H1	97.4(69)
Counteranion $[PF_6]^-$			
P−F	1.56(1)	F−P−F	89.90(9)
			172.91(9)

[a] Esd's in parentheses refer to the last significant digit.

An ORTEP view of [**1**][Cl][PF_6]$_2$ is shown in Figure 3. Crystal parameters are given in Table 1. Important distances and angles are included in Table 2. Figure 3 emphasizes the diametrically opposed positions of the two $(CH_2)_2N(CH_3)H$ nonequivalent chains and the rather short distance of interaction [(1.962(4) Å] between the ammonium proton H2 and the proximal chloride Cl. The distance of the proton H1′ to another rhodicinium cation (Cl−H1) is 2.06(2) Å. Thus the crystal structure can be described as an assembly of chains of ammonium-disubstituted rhodicinium cations bound through H···Cl···H bridges. In this structure, it is difficult to specify the possible role of the PF_6^- anions in the local charge neutralization of the second ammonium function, but by contrast, the packing appears to be structured by the smaller anion.

As usually observed, the cyclopentadienyl ring is slightly distorted from the corresponding least-squares plane (C1, C2, C3, C4, C5), the maximum distance between the carbon atoms and the mean plane being *ca*. 0.025 Å. The rhodium atom is centered exactly at the C_5 axis of the cyclopentadienyl rings, the small deviations from the mean value of the Rh−C distances being insignificant. As expected, the angular deviations of the C5−C51 and C6−C61 axis from the planes of the cyclopentadienyl ring (Table 2) show that the lateral chains are tilted back from the metal.

Molecular Structure of [2][BF_4]. The refinement for the structure [**2**][BF_4] was more easily performed than that of [**1**][Cl][PF_6]$_2$. All non-hydrogen atoms were easily located and well fitted, except for the counteranion $[BF_4]^-$ and the lateral arm $(CH_2)_2N(CH_3)_2$,which shows unusually high anisotropic thermal parameters. A least-squares refinement of factors of occupation of these atoms associated with a subsequent difference Fourier synthesis showed that BF_4^- and $(CH_2)_2N(CH_3)_2$ appeared to have a statistic arrangement on two sites, with ratios of statistic probability of 50:50 for the counteranion and 60:40 for $(CH_2)_2N(CH_3)_2$; restraints were applied on the interatomic lengths and bond angles of $[BF_4]^-$ close to chemically reasonable values (B−F = 1.30 Å and F−B−F = 109°). All hydrogen atoms were located by difference Fourier synthesis, and the method of refinement was the same as that used for [**1**][Cl][PF_6]$_2$, except for the hydrogen atom attached to the nitrogen N1 which, on account of the thermal disorder, was not found. The refinement was carried out in three blocks minimizing the function $\sum w(|F_o| - |F_c|)^2$.

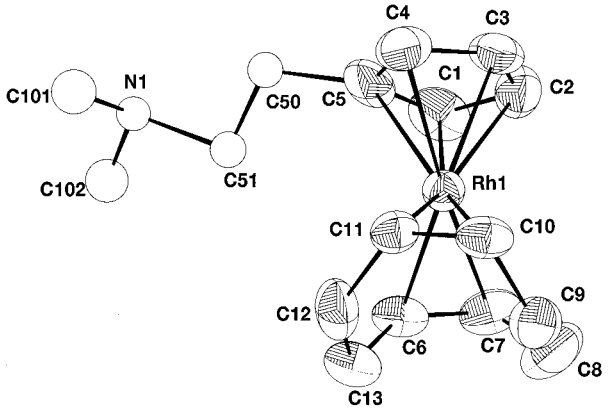


Figure 4. ORTEP view of the ammonium-substituted cyclopentadienylrhodium (I) complex [**2**][BF_4].

Table 3. Selected Bond Lengths (Å) and Angles (deg) of [**2**][BF_4][a]

Mean Value of the Rh−C(Cp) Distances: 2.25(1)			
Rh1−C6	2.12(1)	Rh1−C7	2.11(1)
Rh1−C10	2.11(1)	Rh1−C11	2.11(1)
C11−C10	1.39(2)	C6−C7	1.39(2)
C5−C50	1.64(3)	C50−C51	1.46(4)
C51−N1	1.64(4)	C51′−N1′	1.60(5)
C101−N1	1.50(3)	C102−N1	1.34(2)
C−N−C Angles			
C51−N1−C101	115.5(17)		
C51−N1−C102	98.4(11)		
C101−N1−C102	114.9(16)		

[a] Esd's in parentheses refer to the last significant digit.

The ORTEP diagram of [**2**][BF_4] is shown in Figure 4. Crystal parameters are given in Table 1. Important distances and angles are included in Table 3.

Compound [**2**][BF_4] is the first crystallographic example of an ammonium-substituted cyclopentadienyl rhodium(I) complex. The nitrogen atom lies far from the metal center, and while the NMR evidence in solution (see above) indicates that it is protonated, the hydrogen was not localized from the residual electron density of the difference density map. The nitrogen

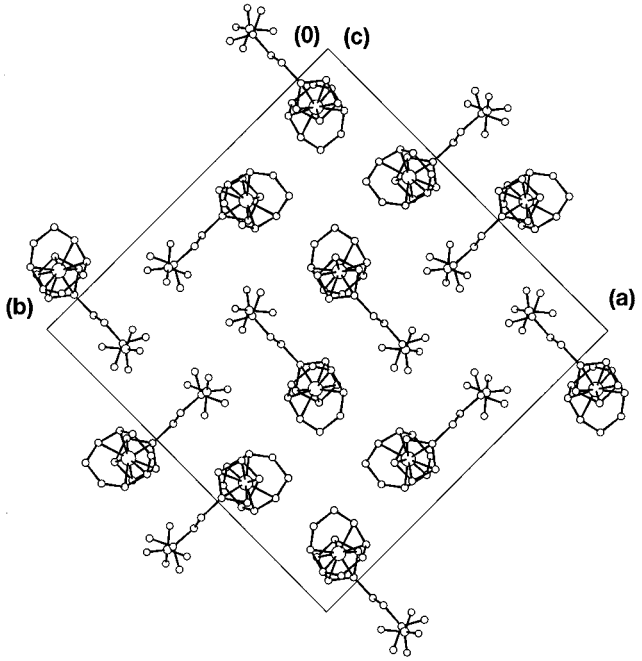


Figure 5. Projection along the c axis showing the helical arrangement of the asymmetric units [**2**][BF_4] along this 4-fold screw axis.

atom shows apparently an almost planar configuration [the sum of the C−N−C angles around it being 354.9(47)°], but we can explain it by the superposition of two opposite pyramidal configurations in accordance with the positional disorder. Close equivalences of the Rh−C distances with respect to the cyclopentadienyl ligand (C_1 to C_5) and the cyclooctadiene (C6, C7, C10, and C11) are also observed.

As in the preceding case, the cyclopentadienyl ring is slightly distorted from the corresponding least-squares plane C3, C4, C5, C6, C7) and the rhodium atom is centered on the C_5 axis of the cyclopentadienyl ring. Interestingly, the mean value of the Rh^{I}−C distance [2.25(1) Å] is significantly longer than the mean value for the Rh^{III}−C distance [2.16(1) Å] observed in the rhodicinium compound. The tilting of the lateral chain is also observed. No interaction was observed between the positively charged nitrogen atom and the [BF_4] counterion, which was found to be disordered equally over two sites.

The arrangement of the [**2**][BF_4] unit in the solid is shown in Figure 5. Apparently the electric neutralization of the charge of the ammonium group is obtained by the presence of the BF_4 anion in the same space portion. Except for this aspect of the crystal organization, the packing seems to be controlled mainly by ordinary van der Waals interactions between the asymmetric units.

5. Conclusions

(i) The described synthesis of [**1**][$Cl]_3$ starting from the amino-substituted cyclopentadiene contrasts with the hitherto published preparation of the rhodicinium salts.[25] More generally, most syntheses of bis(cyclopentadienyl) transition-metal complexes require previous deprotonation of the weakly acidic cyclopentadiene. Only the most electropositive metals (Li, Na, K, Mg) react easily with the cyclopentadiene. Therefore cyclopentadienyl sodium and lithium are the most common reagents for the introduction of cyclopentadienyl ligands.

Starting from a transition-metal salt, an auxiliary base is required to deprotonate the cyclopentadiene.[26] During the easy preparations of [**1**][$Cl]_3$ and [**2**][Cl], the role of an auxiliary basic reagent is probably assured by the free amino group attached to the cyclopentadiene. The same direct procedure has been used to obtain rhodium and iridium derivatives of the (*S*)-1-(2-(dimethylamino)ethyl)-2-(2,3,4,5-tetramethylcyclopenta-1,3-dienyl)benzene ligand.[27] The generalization of the procedure for the synthesis of other cyclopentadienyl transition-metal salts is now being tested.

(ii) The easy crystallization of the salt [**1**][Cl][$PF_6]_2$ from a solution containing both the chloride and the hexafluorophosphate anions is possibly due to the stabilization of the corresponding crystal by the H−Cl···H hereupon described bridging unit. This suggests a practical trick to obtain noncentrosymmetric organometallic solids.

(iii) In agreement with the results of Jutzi *et al.*[9] the intramolecular chelation of the [[(*N*,*N*-dimethylamino)ethyl]-cyclopentadienyl] ligand depends on the oxidation state of the metal. Thus in complexes of the type $L_2MCp(CH_2)_2N(CH_3)_2$ (M = Rh,Ir,Co), where the metals are in low oxidation states and L is a π-electron acceptor ligand (cyclooctadiene and cyclooctene in the present case), coordination of L is preferred over intramolecular chelation of the side chain amino nitrogen. Oxidation toward rhodium(III) complexes, however, results in the formation of the chelate with concomitant loss of L and the creation of a stable 18-electron complex. In the case of the sandwich complexes, chelation is not allowed with rhodium-(III). As well as the other water-soluble compounds bearing a pendant amine or ammonium group that we have obtained, this easily prepared functionalized rhodicinium complex offers interesting potentialities as a ligand.

Further details of the crystal structure investigation are available on request from the Director of the Cambridge Crystallographic Data Centre, 12 Union Road, GB-Cambridge CB21EZ (U.K.),on quoting the full journal citation.

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Supporting Information Available: X-ray crystallographic files in CIF format for compounds [**1**][Cl][$PF_6]_2$ and [**2**][BF_4] are available on the Internet only. Access information is given on any current masthead page.

IC960395G

(25) (a) Baghurst, D. R.; Mingos D. M. P.; Watson M. J. *J. Organomet. Chem.* **1989**, *368*, C43. (b) Cotton, F. A.; Wipple, R. O.; Wilkinson, G. *J. Am. Chem. Soc.* **1953**, *75*, 3586.

(26) (a) Jolly, W. L. *Inorg. Synth.* **1968**, *11*, 113. (b) Jolly, W. L.; Carrey, N. A. D.; Clark H. C. *Inorg. Synth.* **1968**, *11*, 120. (c) Jolly, W. L.; Carrey, N. A. D.; Clark H. C.; Chazan D. J. *Inorg. Synth.* **1968**, *11*, 120.

(27) Adams, H.; Bailey, N. A.; Colley, M.; Schofield, P. A.; White, C. *J. Chem. Soc., Dalton Trans.* **1994**, 1445.

(28) Lee, I.; Dahan, F.; Maisonnat, A.; Poilblanc, R. *J. Organomet. Chem.* **1997**, in press.