Organometallic Rh(III) complexes with the bifunctional ligand [2-(dimethylamino)ethyl]cyclopentadiene. Crystal structure of the [{η^5:η^1-C$_5$H$_4$(CH$_2$)$_2$NMe$_2$}Rh^{III}Cl$_2$] complex

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Abstract

The preparation of rhodium(III) complexes with [2-(dimethylamino)ethyl]cyclopentadiene is described. Starting from [{η^5-C$_5$H$_4$(CH$_2$)$_2$NMe$_2$}Rh^I(η^4-cod)] (**1**) and [{η^5-C$_5$H$_4$(CH$_2$)$_2$N(H)Me$_2$}Rh^I(η^4-cod)]$^+$·(Cl)$^-$ (**2**) the complexes [{η^5:η^1-C$_5$H$_4$-(CH$_2$)$_2$NMe$_2$}Rh^{III}Cl$_2$] (**3**), [{η^5-C$_5$H$_4$(CH$_2$)$_2$N(H)Me$_2$}Rh^{III}Cl(μ-Cl)]$_2^{2+}$·(Cl)$_2^-$ (**4**), [{η^5-C$_5$H$_4$(CH$_2$)$_2$NMe$_2$}Rh^{III}Cl$_2$(PPh$_3$)] (**5**) and [{η^5-C$_5$H$_4$(CH$_2$)$_2$N(H)Me$_2$}Rh^{III}Cl$_2$(PPh$_3$)]$^+$·(Cl)$^-$ (**6**) were synthesized and characterized by elemental analysis, IR, ^{1}H-, ^{13}C- and ^{31}P-NMR spectroscopy. The X-ray crystal structure of complex **3** has also been determined where Rh(III) chelates through the cyclopentadienyl and the terminal –NMe$_2$ group. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: Organometallic complexes; Cyclopentadienyl ligand; Functionalized; Rhodium complexes

1. Introduction

η^5-Cyclopentadienyl derivatives of transition metals represent one of the most important classes of organometallic compounds, since more than 80% of all known organometallic complexes, of the transition metals, contain the cyclopentadienyl fragment or a derivative thereof [1].

Cyclopentadienyl derivatives with a functionalized side chain like [2-(dimethylamino)ethyl]cyclopentadiene containing both a hard and a soft donor site, form the so-called half-sandwich complexes with metals possessing specific structures and reactivity. Special properties and applications of such complexes are expected, e.g. solubility in unusual solvents including water, antitumour properties [2–4], and catalytic applications [5–7] etc.

Recently Flores et al. [5,6] developed the catalyst precursors [η^5-(2-dimethylaminoethyl)cyclopentadienyl]trichlorotitanium and [η^5-2,3,4,5-tetramethyl-1-(2-dimethylaminoethyl)cyclopentadienyl]trichlorotitanium, for the polymerization of ethylene and propylene. Rausch et al. [7] also reported the use of pendent aminoalkyl-substituted monocyclopentadienyltitanium compounds in the polymerization of ethylene and propylene.

Continuing our work on the use of cyclopentadiene bearing amino functionalized side chain and of its sodium salt, for the preparation of organometallic Rh and Co complexes, we report here the chloro derivatives of Rh(III) with the named ligand, in addition to the iodo ligand already reported [2,4]. In addition, the X-ray crystal structure of [{η^5:η^1-C$_5$H$_4$(CH$_2$)$_2$-NMe$_2$}Rh^{III}Cl$_2$] (**3**) also supports the structure of the corresponding iodo derivative reported earlier [2,4]. Differences in the reactions for the preparation of the chloro complexes, in comparison to those of iodo, are also reported.

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2. Experimental

2.1. General

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-$(CH_2)_2NMe_2$ and its sodium salt $Na[C_5H_4(CH_2)_2NMe_2]$ were prepared according to literature methods [2]. The starting materials $[Rh(cod)Cl]_2$ [8], $[\{\eta^5$-C_5H_4-$(CH_2)_2NMe_2\}Rh^I(\eta^4$-$cod)]$ (**1**) [2] and $[\{\eta^5$-C_5H_4-$(CH_2)_2N(H)Me_2\}Rh^I(\eta^4$-$cod)]^+\cdot(Cl)^-$ (**2**) [2], were also prepared according to published procedures. Conductivity measurements were performed using an E365B Conductoscope, Metrhom Ltd, Herisau, Switzerland. Melting points were determined on a Buchi 510 capillary apparatus and are uncorrected. Microanalyses were performed by the Service de Microanalyses, Laboratoire de Chimie de Coordination and by the Microanalysis Center of the University of Ioannina. For chromatography of organometallic compounds, the silica gel was dried for 48 h at 110°C and then flushed with nitrogen saturated solvent. IR spectra were recorded on a Perkin–Elmer model 783 grating spectrometer, as CsBr pellets. All 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. The spectra were calibrated using signals of residual protons from the solvent referenced to $SiMe_4$. Shifts quoted for the ^{31}P-NMR spectra are relative to 85% H_3PO_4.

2.2. Preparations

2.2.1. $[\{\eta^5{:}\eta^1$-$C_5H_4(CH_2)_2NMe_2\}Rh^{III}Cl_2]$ (3)

To a stirred solution of **1** (70 mg, 0.20 mmol) in Et_2O (5 ml) Cl_2 gas was bubbled over a period of 10 min affording an orange precipitate. After filtration, the solid remaining was extracted with CH_2Cl_2 (2 × 10 ml). Evaporation of the extracts to a small volume, followed by addition of cold diethylether (10 ml) yielded complex **3** as an orange microcrystalline solid. Yield: 35%. M.p. 172–173°C.

Anal. Found: C, 35.04; H, 4.96; N, 4.71. Calc. for $C_9H_{14}NRhCl_2$: C, 34.86; H, 4.56; N, 4.51%.

IR (CsBr): 3100, 3050 (m, =CH), 2930 (m, –CH), 1475, 1455 (m, C=C), 1385, 1320, 1210, 1070, 905, 865, 775, 475, 290 (m, ν_{Rh-Cl}), 260 (m, ν_{Rh-Cl}) cm^{-1}.

^1H-NMR (CDCl$_3$): 5.63, 5.27 (2 × t, 4H, $J = 1.6$ Hz, C_5H_4) [2], 3.63 (t, 2H, $J = 6.4$ Hz, CH_2N), 2.65 (s, 6H, NMe_2), 2.52 (t, 2H, $J = 6.4$ Hz, CH_2).

^{13}C-NMR (CDCl$_3$): 105.20 (s, $\underline{C}(CH_2)_2N$), 92.40, 86.90 (2 × d, $J_{Rh-C} = 6.74$ Hz, C_5H_4), 52.07 (s, CH_2N), 45.40 (s, NMe_2), 29.99 (s, CH_2).

The solid remaining was washed with diethylether (2 × 5 ml) and dried in vacuo, giving **4** as an orange–brown solid. Yield: 55%.

M.p. 221–222°C. Λ_M (H$_2$O): 251 Ω^{-1} cm^2 mol^{-1}. Anal. Found: C, 31.58; H, 4.40; N, 4.14. Calc. for $C_{18}H_{30}N_2Rh_2Cl_6$: C, 31.19; H, 4.36; N, 4.04%.

IR (CsBr): 3050, 3020 (m, =CH), 2930 (m, –CH), 2652 (s, NH$^+$), 1460, 1440 (m, C=C), 1245, 1010, 950, 795, 310 (m, ν_{Rh-Cl}), 282 (m, ν_{Rh-Cl}), 251 (m, ν_{Rh-Cl}) cm^{-1}.

^1H-NMR (D$_2$O): (using 3-(trimethylsilyl)propanesulfonic acid (TSP) as internal standard): 5.88, 5.82 (2 × s, 4H, C_5H_4), 3.56 (t, 2H, $J = 6.4$ Hz, CH_2N), 2.97 (s, 6H, NMe_2), 2.69 (t, 2H, $J = 6.4$ Hz, CH_2). ^1H-NMR (DMSO-d_6): 10.64 (br. s, NH$^+$), 5.99, 5.87 (2 × t, 4H, $J = 1.4$ Hz, C_5H_4) [2], 3.38 (t, 2H, $J = 6.4$ Hz, CH_2N), 2.76 (d, 6H, $J_{NH-CH} = 4.80$ Hz, NMe_2), 2.67 (t, 2H, $J = 6.4$ Hz, CH_2).

^{13}C-NMR (D$_2$O): 101.50 (s, $\underline{C}(CH_2)_2N$), 86.30, 86.20 (2 × s, C_5H_4), 57.31 (s, CH_2N), 45.98 (s, NMe_2), 24.23 (s, CH_2). ^{13}C-NMR (DMSO-d_6): 107.90 (s, $\underline{C}(CH_2)_2N$), 87.70, 86.10 (2 × s, C_5H_4), 53.60 (s, CH_2N), 42.10 (s, NMe_2), 21.10 (s, CH_2).

2.2.2. $[\{\eta^5$-$C_5H_4(CH_2)_2N(H)Me_2\}Rh^{III}$-$Cl(\mu$-$Cl)]_2^{2+}\cdot(Cl)_2^-$ (4)

To a stirred solution of **2** (90 mg, 0.23 mmol) in CH_2Cl_2 (10 ml) Cl_2 gas was bubbled over a period of 10 min affording an orange–brown precipitate. After filtration the solid was washed with CH_2Cl_2 (2 × 5 ml), diethylether (10 ml), and dried in vacuo. Yield: 85%.

Note. An authentic sample prepared in this way gave the same spectroscopic data (i.e. IR, NMR) as those referred to in the preparation in Section 2.2.1.

2.2.3. $[\{\eta^5$-$C_5H_4(CH_2)_2N(H)Me_2\}Rh^{III}$-$Cl_2(PPh_3)]^+\cdot(Cl)^-$ (5)

To a stirred suspension of **4** (84 mg, 0.24 mmol) in CH_3CN (10 ml), solid PPh$_3$ (63.8 mg, 0.24 mmol) was added. Gradually the insoluble solid dissolved affording a clear orange solution, which was stirred for one more hour. After removal of about half of the solvent by evaporation, diethyether was added in excess (15 ml). An orange solid was precipitated and after filtration it was dried in vacuo. The solid was dissolved to the minimum amount of CH_2Cl_2 (3 ml) and was then subjected to flash chromatograph on silica gel (230–400 mesh, 10% MeOH in CH_2Cl_2). A deep red band was collected, giving complex **5** as an orange–red solid and in a 68% yield.

M.p. 188–190°C. Λ_M (CH$_3$CN): 150 Ω^{-1} cm^2 mol^{-1}.

Anal. Found: C, 53.40; H, 4.67; N, 2.25. Calc. for $C_{27}H_{30}NRhCl_3P$: C, 53.28; H, 4.96; N, 2.30%.

IR (CsBr): 3050 (m, =CH), 2950 (m, –CH), 2675 (s, NH^+), 1480, 1435 (m, C=C), 1100, 1035, 750, 700, 530, 280 (m, ν_{Rh-Cl}), 230 (m, ν_{Rh-Cl}) cm^{-1}.

^{1}H-NMR (CDCl$_3$): 10.66 (br, s, NH^+), 7.97–7.34 (m, 15H, Ph), 5.21, 4.81 (2 × s, 4H, C$_5$H$_4$), 3.53 (m, 2H, CH$_2$N), 3.06 (m, 2H, CH$_2$), 2.85 (s, 6H, NMe$_2$).

^{13}C-NMR (CDCl$_3$): 135.44–128.54 (m, Ph), 114.20 (s, C(CH$_2$)$_2$N), 88.68, 84.97 (2 × s, C$_5$H$_4$), 65.86 (s, CH$_2$N), 44.11 (s, NMe$_2$), 22.41 (s, CH$_2$).

^{31}P-NMR (CD$_3$CN): 32.29 (d, J_{Rh-P} = 138.65 Hz).

2.2.4. [{η^5-C$_5$H$_4$(CH$_2$)$_2$NMe$_2$}Rh^{III}Cl$_2$(PPh$_3$)] (6)

2.2.4.1. Method A.
To a stirred solution of complex 3 (70 mg, 0.23 mmol) in CH$_2$Cl$_2$ (10 ml), solid PPh$_3$ (58 mg, 0.22 mmol) was added at room temperature and the solution was stirred for ca. 4 h. After removal of about half of the solvent by evaporation, diethylether was added in excess (15 ml). An orange solid was precipitated and after filtration it was dried in vacuo. The solid was then dissolved with CH$_2$Cl$_2$ (3 ml) and flash column chromatographed on silica gel (230–400 mesh, 10% MeOH in CH$_2$Cl$_2$). An orange band was collected and evaporated to dryness to leave an orange solid in a 40% yield.

Table 1
Summary of crystal and intensity collection data for [{η^5:η^1-C$_5$H$_4$(CH$_2$)$_2$NMe$_2$}Rh^{III}Cl$_2$] (3)

Chemical formula	C$_9$H$_{14}$NCl$_2$Rh
Formula weight (g mol^{-1})	310.03
Crystal size (mm^3)	0.47 × 0.25 × 0.13
Habit	Red needles
Crystal system	Monoclinic
Space group	$P2_1/c$ (no. 14)
a (Å)	11.990(8)
b (Å)	8.213(2)
c (Å)	11.858(2)
β (°)	113.40(2)
V (Å^3)	1067(3)
μ (mm^{-1})	90.47
Diffractometer	Enraf–Nonius CAD-4
Radiation	Mo–K$_\alpha$ (λ = 0.71073 Å)
Temperature (K)	293
Data collection method	$\omega/2\theta$; θ_{max}: 25°
Theta range for cell parameters (°)	11–12
Reflections collected	2091
Independent reflections	1882 (R_m = 0.0155)
Parameters refined	119
Refinement method	Full-matrix least-squares on F
Final R indices [$I > 3\sigma(I)$]	R [a] = 0.0267
R_w [b]	0.0306
GoF [c]	1.12

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

2.2.4.2. Method B.
To an ice-cooled solution of NaH (16 mg, 0.67 mmol) in CH$_3$CN (5 ml) (the NaH was prewashed twice with pentane and dried in vacuo) an equivalent amount of 5 (380.5 mg, 0.63 mmol) in CH$_3$CN (10 ml) was added under nitrogen. The solution was stirred for 30 min at this temperature followed by gentle warming to ambient temperature and was then stirred for another hour. After filtration through a small pad of Celite and removal of about half of the solvent by evaporation, diethylether was added in excess (15 ml). An orange solid was precipitated and after filtration it was dried in vacuo. Yield: 70%. M.p. 174–176°C.

Anal. Found: C, 56.90; H, 4.97; N, 2.25. Calc. for $C_{27}H_{29}NRhCl_2P$: C, 56.66; H, 5.10; N, 2.45%.

IR (CsBr): 3020 (m, =CH), 2900 (m, –CH), 1470, 1425 (m, C=C), 1085, 740, 685, 510, 275 (m, ν_{Rh-Cl}), 235 (m, ν_{Rh-Cl}) cm^{-1}.

^{1}H-NMR (CDCl$_3$): 7.66–7.37 (m, 15H, Ph), 5.10, 4.82 (2 × s, 4H, C$_5$H$_4$), 2.82 (m, 4H, CH$_2$CH$_2$N), 2.33 (s, 6H, NMe$_2$).

^{13}C-NMR (CDCl$_3$): 131.31–128.46 (m, Ph), 110.20 (s, C(CH$_2$)$_2$N), 88.47, 84.94 (2 × s, C$_5$H$_4$), 54.94 (s, CH$_2$N), 43.66 (s, NMe$_2$), 22.27 (s, CH$_2$).

^{31}P-NMR (CDCl$_3$): 32.48 (d, J_{Rh-P} = 133.95 Hz).

2.3. X-ray crystallography and structure solution of complex 3

Crystal data and full details of the data collection and data processing are listed in Table 1. A single crystal of compound 3 was mounted on a four-circle Enraf–Nonius diffractometer using Mo–K$_\alpha$ radiation and a graphite monochromator. Final lattice parameters were determined from the least-squares refinement of the setting angles 25 well centered reflections.

Corrections were made for Lorentz polarization effects, a semi-empirical absorption correction [9], and a scheme of ponderation [10], were applied. Calculations were carried out using the CRYSTALS package [11] adapted on a PC.

Positions of the heavy atoms were determined by direct methods SIR92 [12]. All other non-hydrogen atoms were located from a difference-Fourier synthesis. All non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms were located by Fourier differences, but their coordinates were introduced in processes as fixed contributors with fixed thermal parameters. Refinements converged with $R = 0.0267$ for 1522 observed reflections. Selected bond lengths and bond angles are given in Table 2.

3. Results and discussion

The reactions studied are summarized in Fig. 1 for the case of [{η^5-C$_5$H$_4$(CH$_2$)$_2$NMe$_2$}Rh^I(η^4-cod)] (1) and

Table 2
Selected bond distances (Å) and angles (°) for **3**

Bond distances

Rh(1)–Cl(1)	2.401(1)	C(1)–C(2)	1.419(9)
Rh(1)–Cl(2)	2401(1)	C(1)–C(5)	1.410(9)
Rh(1)–N(1)	2.196(4)	C(2)–C(3)	1.396(9)
Rh(1)–C(1)	2.120(6)	C(3)–C(4)	1.412(9)
Rh(1)–C(2)	2.159(6)	C(4)–C(5)	1.430(9)
Rh(1)–C(3)	2.160(6)	C(5)–C(50)	1.520(8)
Rh(1)–C(4)	2.121(6)	C(5)–C(51)	1.514(8)
Rh(1)–C(5)	2.096(6)	N(1)–C(51)	1.490(7)

Bond angles

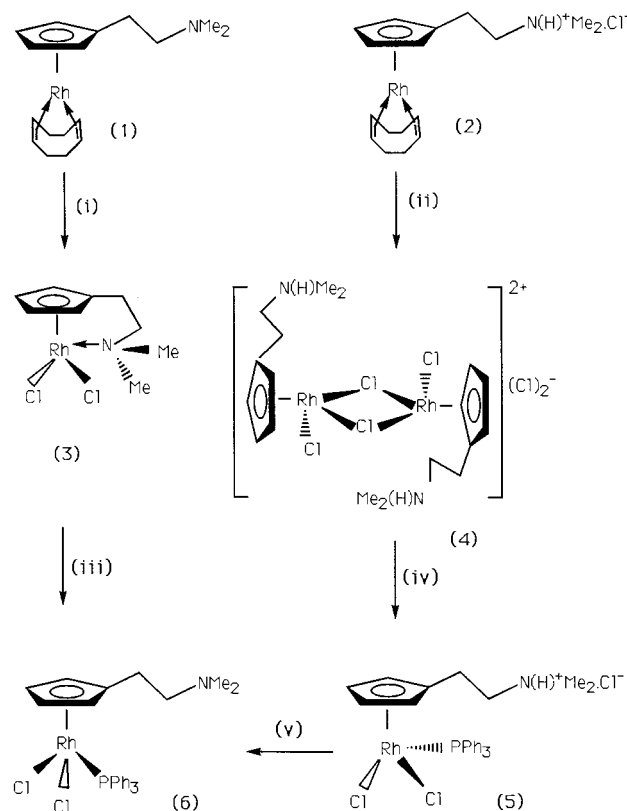|			
Cl(1)–Rh(1)–Cl(2)	89.38(5)	C(5)–C(50)–C(51)	108.2(5)
Cl(1)–Rh(1)–N(1)	91.9(1)	C(51)–N(1)–C(100)	109.4(5)
Cl(2)–Rh(1)–N(1)	95.7(1)	N(1)–C(5)–C(50)	111.8(5)
Rh(1)–N(1)–C(51)	104.3(3)	C(1)–C(5)–C(4)	107.5(5)
C(100)–N(1)–C(101)	106.8(4)	Rh(1)–C(5)–C(50)	113.1(4)

Fig. 1. Pathways towards the rhodium(III) complexes of [2-(dimethyl-amino)ethyl]cyclopentadiene. (i) Cl_2, Et_2O; (ii) Cl_2, CH_2Cl_2; (iii) PPh_3, CH_2Cl_2, 4 h; (iv) PPh_3, CH_3CN, 2 h; (v) NaH, CH_3CN, 0°C.

$[\{\eta^5\text{-}C_5H_4(CH_2)_2N(H)Me_2\}Rh^I(\eta^4\text{-cod})]^+\cdot(Cl)^-$ **(2)** as starting materials.

Both complexes **1** and **2** in ether and in CH_2Cl_2 react with Cl_2 to give compounds **3** and **4**, respectively. Thus, the oxidative addition of gaseous Cl_2 to an etheral solution of **1** yielded a mixture of **3** [13] and **4** in approximately equal proportions. The cationic complex **4** is very soluble in water while the neutral

complex **3** is soluble in CH_2Cl_2. Thus, the two complexes were readily separated after the addition of CH_2Cl_2 to the mixture of **3** and **4**. It should be noted here, that reaction of **1** with I_2 solely produced the corresponding iodo derivative of **3** and not **4** as in the present case [4].

The IR spectrum of **3** shows the typical metallocene skeletal vibrations at 3050, 3045, 2930, 1455, 1070 and 905 cm^{-1} [14]. The far-IR spectrum showed two strong ν_{Rh-Cl} bands at 290 and 260 cm^{-1} [15,16]. The compound is stable under atmospheric conditions and soluble in CH_2Cl_2, $CHCl_3$, $(CH_3)_2CO$, CH_3OH and DMSO. The ^{1}H-NMR spectrum of **3** in $CDCl_3$ shows two sets of pseudotriplets for the cyclopentadienyl protons at 5.63 and 5.27 ppm, a singlet for the $-NMe_2$ protons at 2.65 ppm and two triplets for the (α)-CH_2 and (β)-CH_2N protons at 2.52 and 3.63 ppm, respectively. Both the (α)-CH_2 triplet at 2.52 ppm and the $-NMe_2$ singlet at 2.65 ppm are down field shifted by ca. 0.1 and 0.46 ppm, respectively in comparison to those of complex **1**. The most significant shift ($\Delta\delta = 0.69$ ppm) however, is observed for the (β)-CH_2N protons adjacent to the nitrogen coordination site of the metal. These differences indicate a profound change in the environment of the nitrogen atom in **3**. The change in environment that caused the shift in the ^{1}H-NMR signals of the ligand is undoubtedly due to nitrogen coordination of the rhodium atom. Additional evidence for the intramolecular coordination of the dimethylamino group arises from the change of the multiplicity pattern for the signals of the methylene hydrogen atoms (i.e. $-CH_2CH_2N$). In **1** they appear as multiplets; here they show clear triplets. Corresponding downfield shifts for the methylene and methyl groups adjacent to the nitrogen atom are also observed in the ^{13}C-NMR spectrum on passing from **1** to **3**.

Final proof for the intramolecular coordination of the $-(CH_2)_2NMe_2$ side chain group to the Rh metal in complex **3**, is provided by X-ray crystal structure analysis. Suitable crystals were grown by slow diffusion of ether into a saturated dichloromethane solution of **3** (see Section 3.1). This is the first reported structure of a rhodium chelated compound with a $C_5H_4(CH_2)_2NMe_2$ ligand.

On the other hand, the dimer **4** was obtained as an orange–brown solid in an almost quantitative yield (85%) by the passage of gaseous Cl_2 through a dichloromethane solution of **2**. Complex **4** had a Λ_M (molar conductance) value of about 251 Ω^{-1} cm^2 mol^{-1}, in aqueous solutions [17], indicating possibly hydrolysis of the terminal and bridging chloride anions. The IR spectrum of **4** is similar to that of complex **3** except for the presence of a broad band at ca. 2650

cm^{-1}, indicating protonation of the dimethylamino group at the side chain [2–4]. The far-IR spectrum showed two rather broad bands at 282 and 251 cm^{-1} for both terminal and bridging Rh–Cl bonds [18]. This complex is also stable under atmospheric conditions and soluble in H_2O, DMF and DMSO. In the ^1H-NMR spectrum of **4** in D_2O the cyclopentadienyl triplets are observed at 5.88 and 5.82 ppm, the (β)-CH_2N triplet of the side chain is at 3.56 ppm, the (α)-CH_2 triplet is at 2.69 ppm, and the $-NMe_2$ singlet is at 2.97 ppm. Due to protonation both the (β)-CH_2N triplet and the $-NMe_2$ singlet are downfield shifted by 1.10 and 0.82 ppm, respectively in comparison to those of the free ligand. In DMSO-d_6, a broad singlet can be seen at 10.64 ppm, assigned to the protonated amino group (NH^+), while the $-NMe_2$ group protons appear as a doublet with $J_{NH-CH} = 4.8$ Hz.

The dimer **4** reacted readily with PPh_3 in acetonitrile solution to give the corresponding mononuclear complex **5** in a 68% yield (See Fig. 1). The molar conductance value of 150 Ω^{-1} cm^2 mol^{-1} indicates a 1:1 electrolyte in CH_3CN solution. The IR spectrum of **5** shows the typical metallocene skeletal vibrations at 3050, 2950, 1435 and 1035 cm^{-1}. Moreover, the far-IR spectrum showed two strong bands for terminal v_{Rh-Cl}

at 280 and 230 cm^{-1}. These values are comparable to the ones reported for the $[\eta^5-C_5Me_5Rh^{III}Cl_2(PMe_3)]$ complex [19].

In complex **5** the resonance in the ^{31}P-NMR spectrum is shown at 32.29 ppm, in the expected range, split into a doublet $J_{Rh-P} = 138.65$ Hz by coupling to the rhodium center. On the other hand the ^1H- and ^{13}C-NMR spectra of this compound are similar to those of the dimer **4**.

Upon treatment of the chloride salt **5** with a slight excess of NaH in CH_3CN the deprotonated complex **6** was produced as an orange solid in a 70% yield. Complex **6** could also be prepared but in a lower yield after the addition of PPh_3 to a dichloromethane solution of **3**. The spectroscopic data (i.e. IR, ^1H-, ^{13}C-NMR) are similar to those of complex **5**. Also, the resonance in the ^{31}P-NMR spectrum is shown at 32.48 ppm as a doublet due to coupling to the rhodium center ($J_{Rh-P} = 133.95$ Hz).

3.1. Description of structure

The molecular structure of **3** is shown in Fig. 2. The molecule comprises a dichloro rhodium(III) unit which is bonded to a pentahapto cyclopentadienyl ligand. The
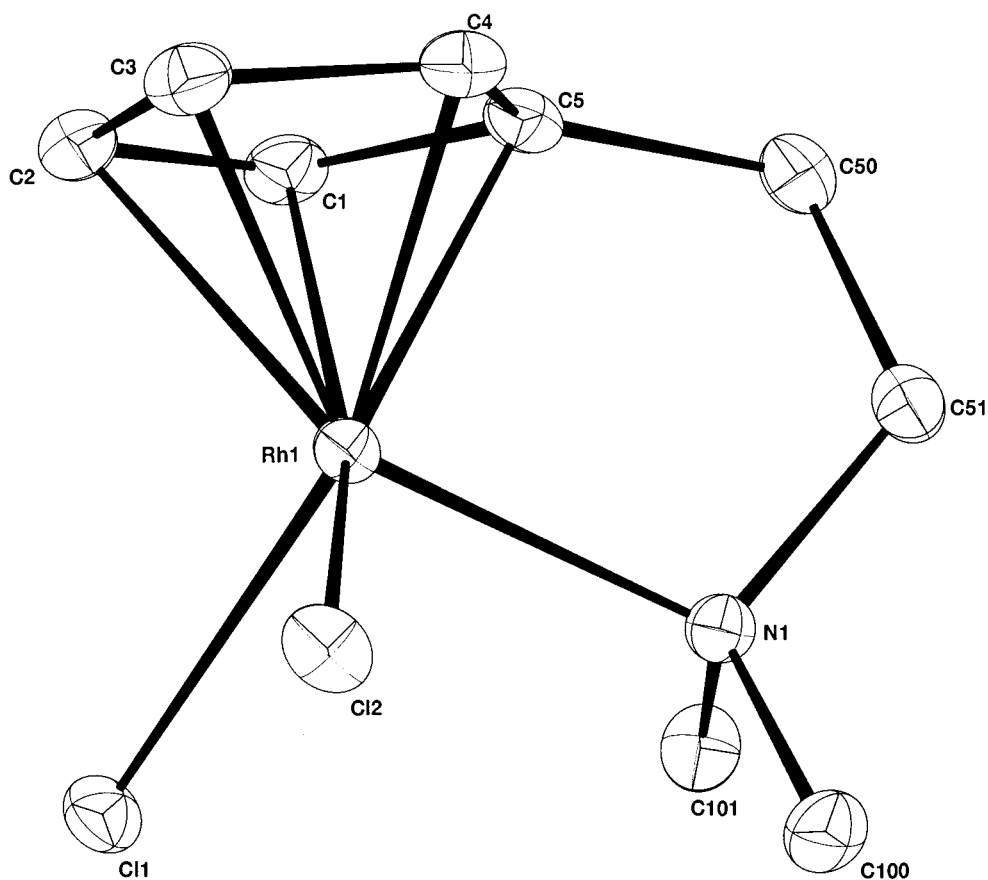

Fig. 2. An ORTEP diagram of complex **3**.

tertiary amino fragment coordinates to the rhodium in the remaining basal site of the overall 'piano-stool' conformation giving a five-membered ring. The metal nitrogen distance is 2.196(4) Å. This distance is only slightly shorter than that of 2.241(5) Å reported for the $[\{\eta^5\text{-}C_5Me_4(CH_2)_2NMe_2\}RhI_2]$ analogue [20]. The lengths of the Rh–Cl bonds are 2.404(1) Å within the normal limits. Known cyclopentadienyl dichloro–rhodium(III) complexes show values slightly longer (2.419(1) Å for $[\{\eta^5\text{-}C_5Me_4C_6H_4CH(Me)NMe_2\}RhCl_2]$) [21] but within the same range. The distance between the rhodium and the ring atoms vary in the range of 2.096(5)–2.160(5) Å, while the angles between the three basal ligands are close to 90°. The structure also reveals that the side chain is bent by 9.45° towards the rhodium. This value is very similar to that mentioned in the $[\{\eta^5\text{-}C_5Me_4(CH_2)_2NMe_2\}RhI_2]$ analogue. Finally an interesting detail is that the $-(CH_2)_2NMe_2$ side chain is coordinated to the rhodium in a zigzag fashion.

4. Supplementary material

For the structure of complex **3**, tables of (a) structure determination summary; (b) complete bond lengths; (c) complete bond angles; (d) atomic coordinates and equivalent isotropic thermal parameters for H atoms; (e) anisotropic thermal parameters and (f) structure factors are available on request from the authors.

Acknowledgements

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