Preparation, Crystal Structure and Spectroscopic Studies of Mixed valence Compound $[(Cp^{4i}Rh)_2(\mu\text{-}Cl)_3][Rh(CO)_2Cl_2]$

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$[(Cp^{4i}Rh)_2(\mu\text{-}Cl)_3][Rh(CO)_2Cl_2]$ (Cp^{4i} = tetraisopropylcyclopenta-dienyl) has been prepared and its crystal is in the space group of *Pbar* with $a = 0.9417(8)$, $b = 1.4806(3)$, $c = 1.5062(2)$ nm, $\alpha = 92.980(10)$, $\beta = 97.42(3)$, $\gamma = 93.98(3)°$, $V = 2.0735(18)$ nm^3 and $Z = 2$. The crystal structure consists of a cation of $[(\eta^5\text{-}Cp^{4i})Rh(III)(\mu\text{-}Cl)_3Rh(III)(\eta^5\text{-}Cp^{4i})]^+$ and an anion of $[Rh(I)(CO)_2Cl_2]^-$. The two bulky tetraisopropylcyclopentadienyl ligands are in the ecliptic conformation with angle of 10.19° between two cyclopentadienyl ring planes.

Keywords Rhodium(I)-rhodium(III) compound, chloro bridged compound, crystal structure, tetraisopropylcyclopentadienyl

Introduction

Pentamethylcyclopentadiene has been widely used in organometallic compounds. Its sterically bulky structure, strong electron donating ability, increased solubility in nonpolar media and improved volatility make these compounds extend application in many fields. The structure and reactivity of the organometallic compound should be significantly altered by introducing more steric bulk into peralkylated cyclopentadienyl ring. Encapsulation effect of the extreme steric bulky ligand, such as tetraisopropylcyclopentadienyl, showed good stabilizing ability for the compounds towards air. Examples of such compounds have been reported for the main-group metals.[1] Iron complex with such ligand can form stable radicals in solution.[2] A series of new compounds of electron rich cobalt atom having such ligand were synthesized and they did show some interesting properties.[3] Rhodium is in the same family of cobalt and is a metal of more catalytic reactivity. Rhodium complexes with such an extreme steric bulk and strong electron donor ligand should show some interesting properties.

In our research of half-sandwich compounds with functionalized substituent on the cyclopentadienyl ring, tetraisopropylcyclopentadienyl is a good choice. It has good ability to stabilize the compound in which one open space still leaves in the cyclopentadienyl ring where another substituent with desired functional group can be introduced to form an interesting bidentate new ligand. We report here a novel rhodium compound of tetraisopropylcyclopentadienyl ligand containing mixed valences of rhodium metal atoms.

Experimental

All of the operations of the synthesis were carried out using standard Schlenk techniques under dinitrogen. Neutral alumina used in column chromatography had been dried in an oven under 100℃ for several days, and then was heated under reduced pressure on a rotary evaporator to remove residual water and oxygen. The alumina was subsequently deactivated with 5% (by

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weight) of degassed water. All solvents were predried over sodium wire and then distilled under a nitrogen atmosphere from sodium/benzophenone. $RhCl_3 \cdot 3H_2O$ was analytically pure chemical reagent from Shanghai Chemical Incorporation without further treatment. Potassium tetraisopropylcyclopentadienide (KCp^{4i}) was prepared according to the literature method.[4]

The elemental analyses were performed on a Rapid CHN-O 240C Analyzer (Heraeus, ermany) at the Shanghai Institute of Organic Chemistry, Chinese Academy of Science. ^1H NMR spectra were recorded on a Bruker MSL-300 NMR spectrometer and chemical shifts are reported in ppm referenced to TMS. Electronic spectra were recorded on a Shimadzu UV 240 spectrometer in CH_2Cl_2. IR spectra were recorded on a Nicolet AVATAR-360IR spectrophotometer. Mass spectra were measured on an HP 5989A instrument by EI techniques (70 eV).

Synthesis

$RhCl_3 \cdot 3H_2O$ (0.5244 g, 1.99 mmol) was dissolved in 35 mL of ethanol in a 250 mL volume of Schlenk bottle. KCp^{4i} (0.5426 g, 1.99 mmol) was dissolved in 10 mL of mixed solvent of ethanol and THF in 1∶1 ratio and was added dropwise into $RhCl_3$ solution under stirring. After the addition of KCp^{4i}, the dinitrogen atmosphere was changed to 1 atm CO and the stirring was continued at 40℃ for 36 h. The color of the solution was changed from deep red to pink and the clear reaction mixture became turbid. The reaction mixture was filtered through Celite and the volume of the red filtrate was reduced to about 10 mL under vacuum. After 20 mL of hexane was added slowly into the vigorously stirred filtration orange-red precipitate was formed and collected on a glass frit, washed with hexane, dried under vacuum to give 0.22 g of red powder, yield 31.8%. λ_{max} (CH_2Cl_2): 243(log ε 4.45), 256(4.89), 335(3.91), 410(3.92) nm. ν_{max}(KBr palette): 2062(CO), 1977(CO), 1474(Cp), 1419(Cp), 1390(Cp), 1367(Cp), 1177(Cp), 1068(Cp). $\delta_H(CDCl_3)$: 1.19 (d, J = 6.8 Hz, 12H, CH_3); 1.33(d, J = 7.1 Hz, 12H, CH_3), 1.38(d, J = 6.8 Hz, 12H, CH_3), 1.47(d, J = 7.1 Hz, 12H, CH_3), 2.69—2.84(m, 4H, Me_2CH), 2.86 (br. s, 4H, Me_2CH), 5.41(s, 2H, $Cp^{4i}H$). Anal. $C_{36}H_{58}Cl_5O_2Rh_3$. Calcd: C, 42.86; H, 5.79. Found: C, 42.40; H, 5.66.

The red powder (0.05 g) was dissolved in 10 mL of THF. Hexane was added until the solution became saturation. Crystals were grown from the saturated solution via ether diffusion technique. Red prismatic crystals suitable for X-ray structural determination were obtained and the structure of the compound was determined as $[(C_5H(CHMe_2)_4Rh)_2(\mu\text{-}Cl)_3][RhCl_2(CO)_2]$ (**1**).

From the filtration of the red precipitate, another product was separated by chromatography. Eluted with hexane, the first yellow band was collected from alumina column. The eluent was evaporated under vacuum and gave about 0.2 g of orange-red oil. The orange-red oil was determined by the spectroscopic methods as $C_5H(CHMe_2)_4Rh(CO)_2$ (**2**). λ_{max}(neat): 2025(CO), 1960(CO), 1463(Cp), 1380(Cp), 1365(Cp), 1312, 1260(Cp), 1182, 1099(Cp), 1078(Cp) cm^{-1}. *m/z* (%): 392.1 (M^+, 14.82), 364.0 (M^+ − CO, 20.41), 336.2 (M^+ − 2CO, 100). $\delta_H(CDCl_3)$: 0.99 (d, J = 6.8 Hz, 12H, CH_3); 1.12 (d, J = 7.3 Hz, 12H, CH_3); 2.80—2.90(m, 2H, Me_2CH); 2.93—2.97(m, 2H, Me_2CH); 5.75(br. s, 1H, $Cp^{4i}H$). Some tetraisopropyl-cyclopentadiene formed during the reaction as by-product and they are very difficult to be separated from the product either by chromatography or by sublimation, trace of it remains in the target product. Analytically pure **2** has not been obtained.

X-Ray crystallography and structural solution of complex **1**

Crystal data and full details of the data collection and data processing are listed in Table 1. A single crystal of suitable size was mounted on a four-circle ENRAF-NONIUS CAD4 diffractometer with graphite monochromated Mo-K_α radiation using the ω-2θ scan technique to a maximum 2θ value of 50℃ at the room temperature of 20 ± 1 ℃. 7863 reflections were collected. From these data, 3975 reflections with $I > 2\sigma(I)$ were considered observed and used for refinements. The structure was solved by direct methods and expanded using Fourier techniques. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were located by difference Fourier map and refined isotropically. The maximum and minimum peaks (with rmd = 117 e/nm^3) on the final difference Fourier map corresponding to 577 and − 716 e/nm^3, respectively. The final agreement factors are R_1 = 0.0312 and wR_2 = 0.0691 for observed

reflections. All calculations were performed on a PC computer using SHELX97 (sheldrick, 1997). Atomic coordinates are listed in Table 2. Selected bond lengths and bond angles are given in Table 3.

Table 1 Crystal data and structure refinement for $[(C_5H(CHMe_2)_4Rh)_2(\mu\text{-}Cl)_3][RhCl_2(CO)_2]$

Empirical formula	$C_{36}H_{58}Cl_5O_2Rh_3$
Formula weight	1008.80
Temperature	293(2) K
Wavelength	0.071073 nm
Crystal system, space group	triclinic, *Pbar*
Lattice Parameters	$a = 0.9417(8)$ nm $\alpha = 92.980(10)°$
	$b = 1.4806(3)$ nm $\beta = 97.42(3)°$
	$c = 1.5062(2)$ nm $\gamma = 93.98(3)°$
Volume	2.0735(18) nm^3
Z, Calculated density	2, 1.616 Mg/m^3
Absorption coefficient	1.531 mm^{-1}
$F(000)$	1020
Crystal size	0.20 × 0.15 × 0.10 mm
θ range for data collection	1.37 to 25.07°.
Index ranges	$0 \le h \le 11$, $-17 \le k \le 17$, $-17 \le l \le 17$
Reflections collected/unique	7863/7372 [R(int) = 0.0436]
Completeness to $2\theta = 25.07$	100.0%
Max. and min. transmission	0.8619 and 0.7492
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	7372/0/648
Goodness-of-fit on F^2	1.009
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0312$, $wR_2 = 0.0691$
R indices (all data)	$R_1 = 0.1241$, $wR_2 = 0.0887$
Extinction coefficient	0.00068(12)
Largest diff. peak and hole	577 and −716 e/nm^3

Table 2 Atomic coordinates (× 10^4) and equivalent isotropic displacement parameters (nm^2 × 10) for $[(C_5H(CHMe_2)_4Rh)_2(\mu\text{-}Cl)_3]$-$[RhCl_2(CO)_2]$. U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Atom	x	y	z	U(eq)	Atom	x	y	z	U(eq)
Rh(1)	1664(1)	2201(1)	7414(1)	28(1)	C(14)	1545(12)	4731(6)	9257(7)	73(3)
Rh(2)	42(1)	157(1)	7268(1)	27(1)	C(15)	291(7)	4185(4)	6886(4)	39(2)
Rh(3)	6307(1)	045(1)	6864(1)	57(1)	C(16)	-466(8)	3812(6)	5982(5)	52(2)
Cl(1)	1984(2)	820(1)	6509(1)	46(1)	C(17)	945(11)	5145(6)	6817(8)	71(3)
Cl(2)	-870(2)	1640(1)	6988(1)	42(1)	C(21)	-997(6)	-964(3)	6435(4)	28(1)
Cl(3)	1372(2)	1090(1)	8548(1)	49(1)	C(22)	51(6)	-1226(3)	6878(4)	27(1)
Cl(4)	8186(3)	6163(2)	8058(2)	109(1)	C(23)	291(6)	-1117(3)	7823(4)	30(1)
Cl(5)	7813(2)	6515(2)	5820(2)	93(1)	C(24)	-1123(6)	-807(4)	7954(4)	31(1)
O(1)	3913(7)	5839(6)	5371(5)	112(2)	C(25)	-1925(6)	-746(3)	7078(4)	29(1)
O(2)	4414(9)	5513(7)	8172(5)	160(4)	C(26)	1525(7)	-1560(4)	6389(4)	41(2)

Continued

Atom	x	y	z	U(eq)	Atom	x	y	z	U(eq)
C(1)	2487(6)	3291(4)	6722(4)	31(1)	C(27)	1292(9)	-1384(6)	5401(5)	56(2)
C(2)	3659(6)	2943(3)	7276(4)	30(1)	C(28)	1635(10)	-2571(5)	6510(7)	64(2)
C(3)	3351(6)	3039(4)	8189(4)	33(1)	C(29)	1427(7)	-1258(5)	8603(4)	41(2)
C(4)	1984(6)	3462(3)	8180(4)	31(1)	C(30)	2973(8)	-1078(6)	8436(6)	54(2)
C(5)	1510(6)	3649(3)	7267(4)	29(1)	C(31)	1146(10)	-2176(6)	8987(7)	67(2)
C(6)	4961(7)	2607(4)	6922(4)	40(2)	C(32)	-1680(7)	-665(5)	8843(4)	44(2)
C(7)	4738(9)	2360(6)	5933(5)	54(2)	C(33)	-2288(11)	251(7)	8977(6)	61(2)
C(8)	6202(9)	3346(7)	7154(8)	75(3)	C(34)	-2764(10)	-1457(7)	8974(7)	64(2)
C(9)	4230(8)	2781(5)	9037(4)	45(2)	C(35)	-3477(6)	-582(4)	6831(4)	37(1)
C(10)	5061(10)	1952(6)	8952(6)	62(2)	C(36)	-4294(8)	-1496(6)	6549(7)	59(2)
C(11)	5112(11)	3610(7)	9520(7)	78(3)	C(37)	-3732(10)	19(7)	6047(8)	75(3)
C(12)	1319(7)	3712(4)	9018(4)	42(2)	C(38)	4833(10)	5916(6)	5945(6)	78(2)
C(13)	-Q255(9)	3400(7)	8970(6)	60(2)	C(39)	5145(11)	5714(7)	7673(6)	94(3)

Table 3 Selected interatomic distances (nm) and interbond angles (°) for $[(C_5H(CHMe_2)_4Rh)_2(\mu\text{-}Cl)_3][RhCl_2(CO)_2]$

Rh(1)—C(1)	0.2121(6)	Rh(3)—Cl(4)	0.2345(3)
Rh(1)—C(4)	0.2125(5)	Rh(3)—Cl(5)	0.2349(2)
Rh(1)—C(3)	0.2127(5)	O(1)—C(38)	0.1137(10)
Rh(1)—C(2)	0.2149(5)	O(2)—C(39)	0.1121(10)
Rh(1)—C(5)	0.2180(5)	C(1)—C(5)	0.1421(7)
Rh(1)—Cl(1)	0.24557(15)	C(1)—C(2)	0.1438(8)
Rh(1)—Cl(3)	0.24596(16)	C(2)—C(3)	0.1443(8)
Rh(1)—Cl(2)	0.2464(2)	C(2)—C(6)	0.1503(8)
Rh(2)—C(23)	0.2118(5)	C(3)—C(4)	0.1469(8)
Rh(2)—C(21)	0.2127(5)	C(3)—C(9)	0.1511(8)
Rh(2)—C(24)	0.2130(5)	(4)—C(5)	0.1437(7)
Rh(2)—C(22)	0.2150(5)	C(4)—C(12)	0.1519(8)
Rh(2)—C(25)	0.2186(5)	C(5)—C(15)	0.1510(8)
Rh(2)—Cl(2)	0.24500(16)	C(6)—C(7)	0.1500(10)
Rh(2)—Cl(1)	0.2454(2)	C(6)—C(8)	0.1537(11)
Rh(2)—Cl(3)	0.24607(17)	C(9)—C(10)	0.1510(10)
Rh(3)—C(39)	0.1804(10)	C(9)—C(11)	0.1528(10)
Rh(3)—C(38)	*0.1822(10)*	*C(12)—C(13)*	*0.1513(10)*
Cl(1)-Rh(1)-Cl(3)	81.45(6)	Cl(4)-Rh(3)-Cl(5)	93.33(11)
Cl(1)-Rh(1)-Cl(2)	80.41(6)	Rh(2)-Cl(1)-Rh(1)	83.77(5)
Cl(3)-Rh(1)-Cl(2)	78.94(6)	Rh(2)-Cl(2)-Rh(1)	83.69(6)
Cl(2)-Rh(2)-Cl(1)	80.70(6)	Rh(1)-Cl(3)-Rh(2)	83.55(5)
Cl(2)-Rh(2)-Cl(3)	79.18(6)	O(1)-C(38)-Rh(3)	179.8(7)
Cl(1)-Rh(2)-Cl(3)	81.45(7)	O(2)-C(39)-Rh(3)	179.4(10)

Results and discussion

The reaction of potassium cyclopentadienide with metal chloride is expected to be fast and efficient for removing KCl. But in our case, the bulky Cp^{4i} ligand slowed down the reaction due to steric demand of the ligand. The solubility of CO in the solvent is low under 1 atm pressure. So the reduction of $RhCl_3 \cdot 3H_2O$ by CO was incomplete. In the reaction mixture, $Cp^{4i}RhCl_2 \cdot$ (solvent) and $[RhCl_2(CO)_2]^-$ as reaction intermediates co-existed in considerable amount. $Cp^{4i}RhCl_2 \cdot$ (solvent) has a strong tendency of dimerization and the anion $[RhCl_2(CO)_2]^-$ serves as a good counter anion. Then **1** became a major product at this condition. $C_5H(CHMe_2)_4Rh(CO)_2$ (**2**) was also formed but in lower yield.

In the ^1H NMR spectrum of compound **2**, the methyl protons of the isopropyl group give two resonance peaks, indicating a free rotation of cyclopentadienyl ring around the central axis of the ring in **2**. There are two typical CO absorption bands between 1900 and 2100 cm^{-1} for **1** and **2**. Both of them are stretching frequencies of CO which bonds to a Rh(I) atom.

Compound **1** dissolves easily in polar solvent, but undissolves in non-polar solvents such as diethyl ether and hexane. The rhodium atoms in the compound are in different valence charges. Rh(III) exists in the cation $[(C_5H(CHMe_2)_4)Rh)_2(\mu\text{-}Cl)_3]^+$ while Rh(I) exists in the anion $[RhCl_2(CO)_2]^-$, and the latter shows its CO stretching frequencies at 1977 and 2061 cm^{-1}, respectively. The CO stretching frequencies in **1** are much higher (about several tens wavenumbers higher) than those observed in **2**. In ^1H NMR spectrum, the methyl protons of the isopropyl group give four resonance peaks, different from that found in **2**, indicating a rigid skeleton of the compound. Perhaps it is the bridged chloro atoms that block the free rotation of cyclopentadienyl ring. If the cyclopentadienyl ring can rotate freely, then the resonance peaks of the methyl groups will be two as we see in **2**. This explanation is supported by the crystal structure of **1**.

The crystal structure of $[(C_5H(CHMe_2)_4Rh)_2(\mu\text{-}Cl)_3][RhCl_2(CO)_2]$ (**1**) is shown in Fig. 1. It has the symmetry of triclinic and is in the space group of *Pbar*. Three bridged chloro atoms form a mirror plane in its cation. The remarkable feature of the crystal structure is that the two bulky tetraisopropylcyclopentadienyl ligands are in the ecliptic conformation. The two ring planes deviate from parallel position, inclined by 10.19° towards each other against Cl(2) atom between two isopropyl groups from each cyclopentadienyl ring, showing steric hindrance from the bridged chloro atom. Its cobalt analogue $[(C_5H(CHMe_2)_4Co)_2(\mu\text{-}Cl)_3]^+$ has only 2.7° between the two bulky rings.[3] It is helpful to make comparison between the structures of **1** and its analogue $[(C_5(CH_3)_5Rh)_2(\mu\text{-}Cl)_3]_2[PtCl_6]$. Different from **1**, the two cyclopentadienyl ring planes in $[(C_5(CH_3)_5Rh)_2(\mu\text{-}Cl)_3]^+$ are perfectly parallel.[5] The average angles of Rh-Cl-Rh in **1** is 83.66°, larger than 81.57° found in its pentamethylcyclopentadienyl analogue. However, the average angles of Cl-Rh-Cl is 80.36°, smaller than the corresponding value of 82.33° found in $[(C_5(CH_3)_5Rh)_2(\mu\text{-}Cl)_3]^+$. As a result, the Rh···Rh distance in **1** is 0.32785 nm, a little longer than 0.3216 nm found in $[(C_5(CH_3)_5Rh)_2(\mu\text{-}Cl)_3]^+$, which is another evidence of repulsive interaction due to the steric hindrance of bridged chloro atoms to the Cp^{4i} ligand. Such metal-metal distance also indicates a non-bonding state between two rhodium atoms, which agrees to the formal electron count of 18 valence electrons. The average distances of Rh-C(ring) and Rh-Cl(bridge) are 0.2141 and 0.2457 nm respectively, almost the same as 0.2135 and 0.2462 nm found in $[(C_5(CH_3)_5Rh)_2(\mu\text{-}Cl)_3]^+$.

In anion of **1**, the bond length of Rh and terminal chloride is 0.2347 nm, in the normal range. The average angles of O-C-Rh and C-Rh-Cl are 179.6° and 178.4°, respectively. It indicates that all the seven atoms in the anion of **1** are in the same plane. A large π bonding system forms with two chloro atoms of strong electron negativity located at the *trans* position to the CO ligand, which weakens the back bonding from Rh(I) atom to CO ligand. So higher ν(CO) values of **1** than those of **2** are understandable. The angle between anion plane and C1-C5 ring plane is found 39.50°. It is not common that the same metal element shows different formal charges in one molecule of compound. Such compound should show unique behaviors during redox reaction and catalytic process. The study of the chemistry of **1** and its derivatives is underway.

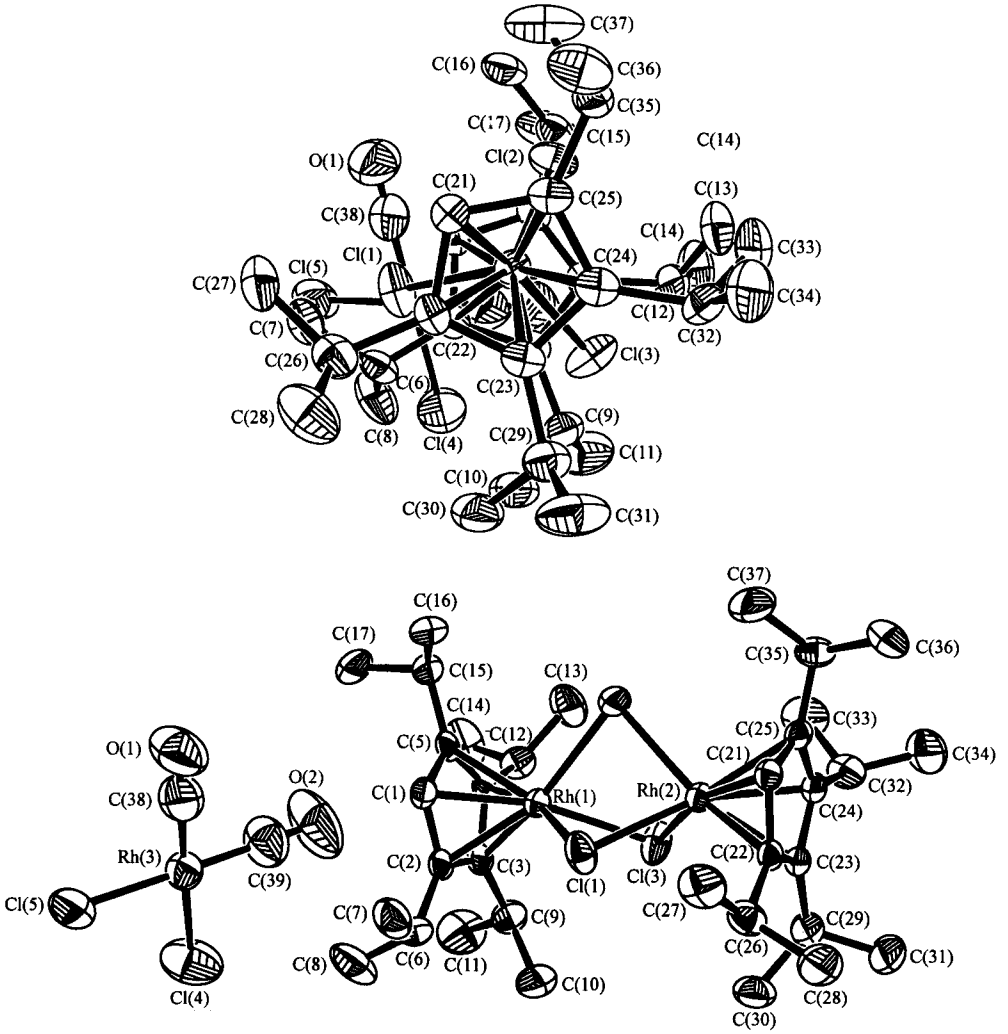

Fig 1. An ORTEP diagram of the molecule of $[(C_5H(CHMe_2)_4Rh)_2(\mu\text{-}Cl)_3][RhCl_2(CO)_2]$ (**1**) in 50 % clearity. (a) Ecliptic conformation is observed along the Rh-Rh axis. Cl(2) is located in the center of two isopropyl groups from two cyclopentadienyl rings. (b) A side view of $[(C_5H(CHMe_2)_4Rh)_2(\mu\text{-}Cl)_3][RhCl_2(CO)_2]$.

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