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Carbene complexes

XXIII *. Preparation, characterisation, and structures of the enetetramine-derived carbenerhodium(I) chloride complexes $[\mathrm{RhCl(L^R)_3}]$, *trans*-$[\mathrm{RhCl(CO)(L_2^{R'})}]$, and $[\{\mathrm{RhCl(COD)}\}_2\{\mu\text{-}\mathrm{L_2^{(323)R}}\}]$ $[\mathrm{L_2^{R\ or\ R'}} = \overline{\mathrm{CN(R\ or\ R')(CH_2)_2N}}\mathrm{R(or\ R')}$ $(\mathrm{R = CH_2Ph\ or\ Et,\ R' = Me})$ and $\mathrm{L^{(323)R}} = \overline{\mathrm{CN(R)(CH_2)_3N}}\mathrm{(CH_2)_2}\overline{\mathrm{N(CH_2)_3N(R)C}}$ $(\mathrm{R = CH_2Ph})]$ **

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Abstract

From $[\{\mathrm{Rh}(\mu\text{-Cl})(\mathrm{COD})\}_2]$ and the enetetramine $\mathrm{L_2^{Me}}$, $\mathrm{L_2^{Et}}$, $\mathrm{L_2^{CH_2Ph}}$, or $\mathrm{L_2^{(323)CH_2Ph}}$ the crystalline complexes $[\mathrm{RhCl(L^R)_3}]$ [R = $\mathrm{CH_2Ph}$ (**1**) or Et (**3**)], $[\{\mathrm{RCl(COD)}\}_2\{\mu\text{-}\mathrm{L_2^{(323)CH_2Ph}}\}]$ (**2**), or *trans*-$[\mathrm{RhCl(CO)(L^R)_2}]$ [R = $\mathrm{CH_2Ph}$ (**4**) or Me (**5**)] have been obtained in high yield [$\mathrm{L^R} = \overline{\mathrm{CN(R)(CH_2)_2N}}\mathrm{R}$ and $\mathrm{L^{(323)R}} = \overline{\mathrm{CN(R)(CH_2)_3N}}\mathrm{(CH_2)_2}\overline{\mathrm{N(CH_2)_3N(R)C}}$]. Complex **2** provides a rare example of a bridging bis(carbene)dimetal complex and the first for one derived from an enetetramine. The X-ray structures of **1**-**5** show that (i) the mutually *trans*-Rh-$\mathrm{C_{carb}}$ bonds for **1** and **3** are longer than the *cis*-; (ii) the Rh-Cl bond lengths range from 2.268(4) (**5**) to 2.464(6) (**3**) Å; (iii) in the bis(carbene) complexes **4** and **5**, as well as in **2**, the five-membered almost planar $\overline{\mathrm{C_{carb}NC_2N}}$ ring (or fragment for **2**) is approximately orthogonal to the plane containing Rh, Cl, and $\mathrm{C_{carb}}$, while in the tris(carbene) complexes **1** and **3** the mutually *trans*-carbene ligands are twisted from a parallel arrangement by 49°; and (iv) the sum of the bond angles at each $\mathrm{C_{carb}}$ or N is close to 360°.

1. Introduction

This series, reviewed in 1988 [1], deals with the chemistry of electron-rich carbenemetal complexes $[\mathrm{M(CXY)L}_n]$, L_n representing the sum of all other ligands apart from one carbene CXY within the inner coordination sphere of the metal. In general, at least one of the groups X or Y attached to the carbene-carbon atom $\mathrm{C_{carb}}$, has been nitrogen-centred. In many instances the ligand CXY was derived from an electron-rich bicyclic enetetramine such as $\mathrm{L_2^R}$ [R = $\mathrm{CH_2Ph}$ (**I**), Et (**III**), or Me (**IV**)]. The previous paper dealt with some *N,N*-functionalised carbenemetal complexes, *e.g.*, *cis*-$[\overline{\mathrm{Mo(CO)_4(L^{All}}})]$ (All = $\mathrm{CH_2CH{:}CH_2}$) [2].

A preliminary communication described some chlororhodium(I) complexes containing one or more $\mathrm{L^{CH_2Ph}}$ carbene ligands, including $[\mathrm{RhCl(L^{CH_2Ph})_3}]$ (**1**) and *trans*-$[\mathrm{RhCl(CO)(L^{CH_2Ph})_2}]$ (**4**) [3]. The present paper provides more details for **1** and **4** and additionally for $[\{\mathrm{RhCl(COD)}\}_2\{\mu\text{-}\mathrm{L_2^{(323)CH_2Ph}}\}]$ (**2**) (derived from the tricyclic enetetramine **II** [4]), $[\mathrm{RhCl(L^{Et})_3}]$ (**3**), and *trans*-$[\mathrm{RhCl(CO)(L^{Me})_2}]$ (**5**), the preparation of which, from $[\{\mathrm{Rh}(\mu\text{-Cl})(\mathrm{CO})_2\}_2]$ and $\mathrm{L_2^{Me}}$, has already been described [5]. The synthesis and spectroscopic characterisation of forty-five monocarbenerhodium(I) complexes has been described [6].

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* For Part XXII, see ref. 2. No reprints available.

** Dedicated to Professor E.O. Fischer, the father of carbenemetal chemistry, on the occasion of his 75th birthday.

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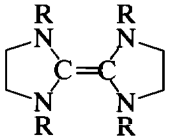
TABLE 1. Yields, colours, melting points and analytical data for complexes 1–4

Complex	Yield (%)	Colour	M.p (°C)	Analysis (Found (calcd.) (%)) C	H	N
$[RhCl(L^{CH_2Ph})_3]$ (1)	87	Orange-yellow	205–210 [a]	69.0 (68.8)	6.0 (6.1)	9.3 (9.4)
$[\{RhCl(COD)\}_2\{\mu\text{-}L_2^{(323)CH_2Ph}\}]$ (2)	65	Yellow	190 [a]	54.7 (55.4)	6.2 (6.2)	6.7 (6.5)
$[RhCl(L^{Et})_3]$ (3)	85	Yellow	[b]	[b]	[b]	[b]
trans-$[RhCl(CO)(L^{CH_2Ph})_2]$ (4)	57	Pale yellow	238–240 [a]	62.9 (63.0)	5.5 (5.5)	8.2 (8.4)

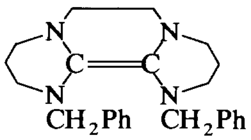
[a] With decomposition. [b] Not determined.



R = CH_2Ph **I** (abbreviated as $L_2^{CH_2Ph}$)

R = Et **III** (abbreviated as L_2^{Et})

R = Me **IV** (abbreviated as L_2^{Me})



II [abbreviated as $L_2^{(323)CH_2Ph}$]

2. Experimental details

2.1. General procedures

These have been described previously [2], as has the preparation of complex **5** [5]. Yields, colours, melting points, and microanalytical data for compounds **1–4** are shown in Table 1; while Tables 2 and 3 provide for **1–5** selected (a) IR and ^{13}C NMR spectroscopic data and (b) bond lengths, respectively.

2.2. Preparation of $[RhCl(L^{CH_2Ph})_3]$ (1)

Di(μ-chloro)bis(cyclo-octa-1,5-diene)dirhodium(I) (2.2 mmol) was heated under reflux with the enetetramine **I** [7] (6.6 mmol) in toluene (25 cm^3) for 1 h. The resulting orange solution was concentrated *in vacuo* and cooled (−30°C) yielding orange-yellow crystals of **1** (87%). X-Ray quality single crystals were grown by recrystallisation from toluene.

2.3. Preparation of $[\{RhCl(COD)\}_2(\mu\text{-}L_2^{(323)CH_2Ph})]$ (2)

Similarly, di(μ-chloro)bis(cyclo-octa-1,5-diene)dirhodium(I) (2.21 mmol) and the enetetramine **II** [4] (1.10 mmol) were heated under reflux in toluene (20 cm^3) for 1 h. The reaction mixture was filtered hot, and the filtrate was concentrated (to *ca.* 5 cm^3) *in vacuo* and n-hexane (20 cm^3) was added. Upon cooling to −30°C for *ca.* 1 d yellow crystals gradually formed. Recrystallisation from chloroform/pentane gave yellow crystals of **2** (0.62 g, 65%).

2.4. Preparation of $[RhCl(L^{Et})_3]$(3)

The enetetramine **III** [8] (0.44 mmol) and $[\{Rh(\mu\text{-}Cl)(COD)\}_2]$ (1.48 mmol) were heated in toluene (5 cm^3) at 60°C for 3 h. The yellow solution was concentrated (to *ca.* 2 cm^3) yielding yellow crystals of **3** (85%). Recrystallisation from toluene afforded X-ray quality crystals.

2.5. Preparation of trans-$[RhCl(CO)(L^{CH_2Ph})_2]$(4)

Carbon monoxide was passed through a solution of $[RhCl(L^{CH_2Ph})_3]$ (**1**) (0.50 mmol) in dichloromethane (5 cm^3) at 25°C for 5 min. Solvent was removed *in vacuo*; the residue was dissolved in toluene (5 cm^3) and heated under reflux for 1 h. Concentration *in vacuo* and

TABLE 2. Selected IR and ^{13}C NMR spectroscopic data at ambient temperature for complexes 1–5

Complex	IR (ν_{max}), cm^{-1} [a]		^{13}C NMR		
	$\nu(CN_2)$	$\nu(Rh-Cl)$	$\delta(C_{carb})$ (doublet)	$^1J(^{13}C-^{103}Rh)$ (Hz)	Solvent
1	1505brm	275w	223.4 [b], 221.9 [c]	42.5 [b], 64.7 [c]	C_6D_6
2	1518s	285w, 275w	207.0	46.4	$CDCl_3$
3	[d]	[d]	222.4 [b], 218.7 [c]	41.4 [b], 64.4 [c]	$CDCl_3$
4	1505ms	310m	212.9	37.7	$CDCl_3$
5	1529brs [e]	310m [e]	212.6	36.6	$CDCl_3$

[a] Nujol mull. [b] *cis* to Cl^-. [c] *trans* to Cl^-. [d] Not determined. [e] Reported previously [5].

TABLE 3. Selected bond lengths (Å) with estimated standard deviations in parentheses for the carbene(chloro)rhodium(I) complexes **1–5**

	1	**2**	**3**	**4**	**5**
Rh–C_{carb} *trans* to Cl^-	1.950(3)	–	1.91(2)	–	–
Rh–C_{carb} *cis* to Cl^-	2.046(3)	2.056(4)	1.98(2)	2.061(2)	2.053(3)
Rh–Cl	2.422(1)	2.385(1)	2.464(6)	2.386(3) [a]	2.268(4) [a]
⟨C_{carb}–N⟩, C_{carb} *trans* to Cl^-	1.359(5)	–	1.3892)	–	–
⟨C_{carb}–N⟩, C_{carb} *cis* to Cl^-	1.346(5)	1.337(5)	1.39(3)	1.332(3)	1.320(4)

[a] CO and Cl^- disordered.

cooling to −30°C yielded pale yellow crystals of **4** (57%).

Alternatively, complex **4** was prepared by heating under reflux *trans*-$[RhCl(CO)(PPh_3)_2]$ (0.70 g, 1 mmol) and the enetetramine **I** (0.50 g, 1 mmol) in toluene (20 cm^3) for 1 h. Filtration yielded a yellow filtrate, to which hexane (20 cm^3) was added. The solution was cooled to −30°C and gradually deposited yellow crystals of **4** (0.65 g, 95%).

2.6. *X-Ray structure determination of complexes 1–5*

Single crystals of each complex were mounted inside a Lindemann capillary and sealed under argon. Cell dimensions were calculated from the setting angles for 25 reflections with $8 < \theta < 15°$. Unique data sets were recorded at ambient temperature on an Enraf-Nonius CAD 4 diffractometer. Reflections were corrected for Lorentz and polarisation (Lp) effects and also for absorption [9]. Intensities were measured by an ω–θ scan and reflections regarded as observed if $I > \sigma(I)$, except for **3** where $I > 3\sigma(I)$. The weighting scheme was $w = 1/\sigma^2(F)$ where $\sigma(F^2) = \{\sigma^2(I) + (0.04I)^2\}^{1/2}/\mathrm{Lp}$. Structure solution was by routine heavy atom methods. Refinement was by full matrix least squares with non-H atoms anisotropic unless otherwise stated. Hydrogen atoms were fixed either at positions from a difference map or at calculated positions. In **4** and **5** the Cl and carbonyl groups are disordered across an inversion centre and the C and O atoms were fixed at idealised positions with Rh–C 1.91 Å and C–O 1.20 Å and with thermal parameters isotropic for **5** and anisotropic for **4**. Further details are given in Table 4. Tables of bond distances and angles, atomic coordinates, torsion angles, and anisotropic thermal parameters have been deposited at the Cambridge Crystallographic Data Centre.

TABLE 4. Crystal data and refinement parameters for complexes **1–5**

	1	**2**	**3**	**4**	**5**
Formula	$C_{51}H_{54}ClN_6Rh$	$C_{40}H_{54}Cl_2N_4Rh_2.3CHCl_3$	$C_{21}H_{42}ClN_6Rh$	$C_{35}H_{36}ClN_4ORh$	$C_{11}H_{20}ClN_4ORh$
M	889.4	1225.8	517.0	667.1	362.7
Crystal system	Triclinic	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	$P1$	$P2_1/c$	$C2/c$	$P2_1/n$	$P2_1/n$
a/Å	10.520(1)	10.976(1)	21.389(17)	11.427(4)	8.441(1)
b/Å	11.649(1)	19.789(2)	10.250(5)	11.823(3)	7.258(3)
c/Å	20.933(2)	12.561(1)	14.398(14)	11.948(3)	12.538(2)
α/°	96.59(9)				
β/°	100.60(7)	105.15(1)	123.55(8)	107.71(2)	97.50(1)
γ/°	114.54(9)				
U/Å^3	2240.7	2633.5	2612.3	1537.7	761
Z	2	2	4	2	2
D_c/g cm^{-3}	1.32	1.55	1.12	1.44	1.58
F(000)	928	1240	912	688	368
μ(Mo-Kα)/cm^{-1}	4.7	11.9	8.4	6.6	12.6
Size/mm^3	0.25 × 0.27 × 0.35	0.3 × 0.25 × 0.25	0.4 × 0.4 × 0.1	0.25 × 0.25 × 0.15	0.2 × 0.3 × 0.3
No	6547	2650	1378	2110	1086
R	0.070	0.046	0.10	0.033	0.040
R_w	0.086	0.053	0.15	0.042	0.053
Max. shift/error	0.04	0.2	0.1	0.4	0.01
$2\theta_{max}$	50	44	44	50	50

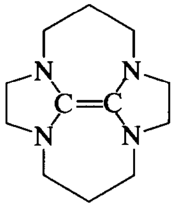
3. Results and discussion

3.1. Synthesis of the carbenerhodium(I) chlorides 1–5

The synthesis of the complexes **1–4** is summarised in Scheme 1. Yields, colours, melting points, and analytical data are summarised in Table 1.

The complexes $[RhCl(L^R)_3]$ [R = CH_2Ph (**1**) or Et (**3**)] are of interest as carbene analogues of Wilkinson's hydrogenation catalyst $[RhCl(PPh_3)_3]$. It is noteworthy that although the enetetramine-derived carbene ligands L^R are normally extremely firmly bound to a noble metal, in one case, the conversion of **1** with carbon monoxide into *trans*-$[RhCl(CO)(L^{CH_2Ph})_2]$ (**4**), an L^R displacement was achieved. We have shown elsewhere [3] that this proceeds by an associative mechanism, the eighteen-electron complex $[RhCl(CO)(L^{CH_2Ph})_3]$ being an isolable intermediate. The ready displacement of the carbene ligand from **1** parallels the similar facile loss of one PPh_3 molecule from $[RhCl(PPh_3)_3]$. In both instances the driving force is probably the relief of steric strain by having three such bulky L^R or PPh_3 ligands within the metal coordination sphere. The only precedent in L^R-metal chemistry, is the displacement of one L^{Et} ligand from *trans*-$[RuCl_2(L^{Et})_4]$ upon treatment with carbon monoxide [10].

Examples of bridging bis(carbene)dimetal complexes are extremely rare, an exception being $[\overline{W(CO)_5\{C(OEt)CH_2C_6H_4CH_2C(OEt)\text{-}o\}W(CO)_5}]$ [11]. However, an enetetramine has not hitherto been found to give rise to such a complex, the formation of **2** from the tricyclic enetetramine **II** being unprecedented. Although we have not previously reported on the transition metal complexes of such a tricyclic enetetramine, we have shown that the reaction between a tetracyclic analogue **IV** and $[\{Rh(\mu\text{-}Cl)COD\}_2]$ gave a chelating *cis*-discarbenerhodium(I) salt $[Rh(IV)(COD)][Rh(COD)Cl_2]$ [12].



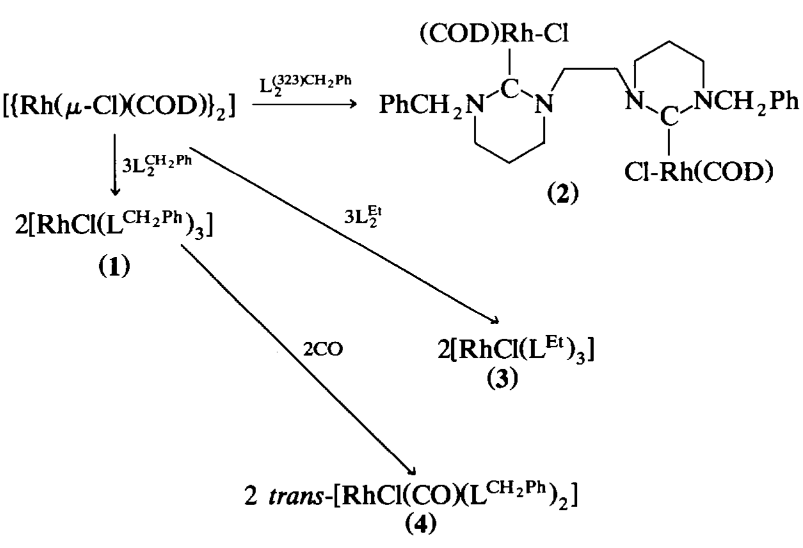
(IV)

3.2. Spectroscopic data on the carbenerhodium(I) chlorides 1–5

Selected IR [$\nu(CN_2)$ and $\nu(Rh–Cl)$] and ambient temperature solution ^{13}C NMR [chemical shifts and coupling constants for C_{carb}] spectroscopic data for compounds **1–5** are shown in Table 2.

From the latter it is evident that (i) $^1J(^{13}C–^{103}Rh)$ for C_{carb} *cis* to Cl^- ranges from 36.6 in **5** to 46.4 Hz in **2**, whereas for C_{carb} *trans* to Cl^- (in **1** and **3**) the value is significantly higher at 64.5 ± 0.2 Hz; and (ii) the $\delta(^{13}C)$ value for C_{carb} in the triscarbenerhodium(I) complexes **1** and **3** is exceptionally shielded. The observation (i) is consistent with C_{carb} having a greater *trans*-influence than Cl^-, a feature confirmed by some of the bond length data in Table 3, Section 3.3.

The ^1H NMR spectra details for complexes **1–4** (and indeed for **5** [5]) were unexceptional, except for variable temperature studies on *trans*-$[RhCl(CO)(L^{CH_2Ph})_2]$ (**4**). At ambient temperature **4** in $CDCl_3$ showed an AB pattern for the CH_2Ph protons, these being a quartet centred at δ 5.35. This is attributed to a restriction to rotation about the $Rh–C_{carb}$ bond on



Scheme 1.

the NMR spectroscopic time scale, as had previously been discussed for related L^{CH_2Et} complexes [13]. Observation of ^1H NMR spectra of **4** in $CDCl_3$ in a sealed tube at increasingly higher temperature showed a progressive line-broadening, until at 343 K coalescence was noted. This corresponds to $\Delta G^{\ddagger}_{T_c}$ of 74 ± 1 kJ mol^{-1}. Similar experiments were performed for a series of complexes *trans*-$[RhCl(CO)(L^{CH_2Ph})L]$ in which $L = L^{CH_2Ph}$ (343, 74), PMe_2Ph (343, 74), $PMePh_2$ (373, 78), PEt_3 (368, 79), CO (378, 80), NC_5H_5 (373, 81), PPh_3 (393, 83), or $P(C_6H_{11}\text{-}c)_3$ (393, 84); the numbers in parenteses represent successively the coalescence temperature T_c (K) and $\Delta G^{\ddagger}_{T}$. The data for **4** may be compared with $T_c = 314$ K and $\Delta G^{\ddagger}_{384\ K} = 67 \pm 1$ kJ mol^{-1} for *trans*-$[RhCl(CO)(L^{Et})_2]$ [13].

The $^{13}C\{^1H\}$ NMR spectrum of $[\{RhCl(CO)\}_2\{\mu\text{-}L^{(323)CH_2Ph}\}]$ (**2**) in CD_2Cl_2 showed the $CH{=}CH$ *trans* to Cl^- signals to be a pair of doublets centred at δ 196.0 and 96.3, $^1J(^{13}C-^{103}Rh)$ 7 Hz, while the $CH{=}CH$ *cis* to Cl^- signals were also found as a pair of doublets centred at δ 69.8 and 70.3 with $^1J(^{13}C-^{103}Rh)$ 15 Hz, Their inequivalence is attributed to a steric effect, see Section 3.3. A similar feature had been noted before in the complexes $[RhCl(COD)(L^{\star R})]$ $[L^{\star R} = CN(R')CH_2CH(^iBu)NEt\text{-}(+)$ (R′ = Me or Et)] [14].

3.3. *The molecular structures of the crystalline complexes 1–5*

The X-ray structures of several enetetramine-derived carbenemetal complexes $L_nM{=}L^R$ have been reported previously [1], including the following monocarbenerhodium(I) complexes: $[RhCl(COD)(L^{\star R})]$ $[L^{\star R} = CN(Me)CH_2CH(^iBu)NMe\text{-}(+)$, $CN(Me)CH_2CH(CH_2)_3N\text{-}(+)$, or $CN(Me)\{(CH_2)_6\text{-}c\}NMe\text{-}(+)$-*trans* [14]], and $[Rh(COD)(IV)][RhCl_2(CO)_2\text{-}cis]$ [12]. Hence, only selected bond lengths relating to the Rh and C_{carb} environments are provided in Table 3 for the complexes **1–5**. More details of geometric parameters are shown in Tables 5 and 6 for $[RhCl(L^{CH_2Ph})_3]$ (**1**) and $[\{RhCl(COD)\}_2\{\mu\text{-}L_2^{(323)R}\}]$ (**2**), respectively, because of the particularly unusual nature of these compounds, but similar data for the other compounds are available (see Section 2.6).

From the data of Table 3 it is evident that (i) the mutually *trans*-$Rh-C_{carb}$ bonds for **1** and the L^{Et} analogue **3** are longer than that *trans* to Cl^-, consistent with C_{carb} having a greater *trans*-influence than Cl^-; and (ii) the Rh–Cl bond lengths in **1–5** are unexceptional, but are longest in the sterically encumbered complexes **1** and **3**. As had been found previously for other related carbenemetal complexes [1], the five-membered $C_{carb}NC_2N$ imidazolidin-2-ylidene ring is almost planar with rather short C_{carb}–N bond lengths of 1.320(4) (**5**) to 1.39(3) Å (**3**). This is appropriate for there being sp^2 hybridisation at C_{carb} and the adjacent nitrogen atoms, as also evident from the trigonal planar geometry at each of these atoms. The same five-membered ring is approximately orthogonal to the plane containing Rh, Cl, and C_{carb} in complexes **2**, **4**, and **5**. Four planes (*a*)–(*d*) in *trans*-$[RhCl(CO)(L^{CH_2Ph})_2]$ (**3**) may be described as follows: (*a*) containing Rh, Cl, and C_{carb}; (*b*) the imidazolidin-2-ylidene ring of one L^{CH_2Ph} ligand; and (*c*) and (*d*) the phenyl planes of the two pendant CH_2Ph groups of the same L^{CH_2Ph} ligand. The angles between these planes are: *ab* 81°, *ac* 34°, *ad* 114°, *bc* 103°, *bd* 76° and *cd* 93°.

The molecular structure and atom labelling for $[RhCl(L^{CH_2Ph})_3]$ (**1**) are shown in Fig. 1. Each *N,N′*-benzyl group on each planar five-membered L^{CH_2Ph}

TABLE 5. Selected bond lengths (Å) and angles (°) with estimated standard deviations in parentheses for $[RhCl(L^{CH_2Ph})_3]$ (**1**)

(a) Bonds			
Rh–Cl	2.422(1)	Rh–C(1)	2.045(3)
Rh–C(18)	2.047(3)	Rh–C(35)	1.950(3)
C(1)–N(1)	1.342(4)	C(1)–N(2)	1.335(4)
C(2)–C(3)	1.488(5)	C(2)–N(1)	1.465(4)
C(3)–N(2)	1.480(4)	C(4)–C(5)	1.508(5)
C(4)–N(2)	1.452(4)	C(5)–C(6)	1.386(5)
C(11)–N(1)	1.466(4)	C(12)–C(13)	1.392(5)
C(16)–C(17)	1.427(6)	C(18)–N(3)	1.348(4)
C(18)–N(4)	1.359(4)	C(19)–C(20)	1.508(5)
C(19)–N(3)	1.475(4)	C(20)–N(4)	1.461(4)
C(21)–C(22)	1.526(5)	C(21)–N(3)	1.458(4)
C(28)–C(29)	1.506(4)	C(28)–N(4)	1.448(4)
C(35)–N(5)	1.361(4)	C(35)–N(6)	1.356(4)
C(36)–C(37)	1.513(5)	C(36)–N(5)	1.459(5)
C(37)–N(6)	1.472(4)	C(38)–C(39)	1.518(4)
C(38)–N(6)	1.442(4)	C(39)–C(40)	1.406(5)
C(45)–N(5)	1.441(4)	C(46)–C(47)	1.390(5)
(b) Angles			
Cl–Rh–C(1)	87.53(8)	Cl–Rh–C(18)	87.12(9)
Cl–Rh–C(35)	177.32(9)	C(1)–Rh–C(18)	173.2(1)
C(1)–Rh–C(35)	92.1(1)	C(18)–Rh–C(35)	93.4(1)
Rh–C(1)–N(1)	125.6(2)	Rh–C(1)–N(2)	128.1(2)
N(1)–C(1)–N(2)	106.3(3)	C(3)–C(2)–N(1)	102.5(3)
C(2)–C(3)–N(2)	101.8(3)	Rh–C(18)–N(3)	128.7(2)
Rh–C(18)–N(4)	125.2(2)	N(3)–C(18)–N(4)	105.9(3)
C(20)–C(19)–N(3)	102.4(3)	C(19)–C(20)–N(4)	102.6(3)
Rh–C(35)–N(5)	127.0(2)	Rh–C(35)–N(6)	128.5(2)
N(5)–C(35)–N(6)	104.5(3)	C(37)–C(36)–N(5)	102.2(3)
C(36)–C(37)–N(6)	101.4(3)	C(1)–N(1)–C(2)	113.3(3)
C(1)–N(1)–C(11)	124.3(3)	C(2)–N(1)–C(11)	119.8(3)
C(1)–N(2)–C(3)	113.4(3)	C(1)–N(2)–C(4)	126.0(3)
C(3)–N(2)–C(4)	120.0(3)	C(18)–N(3)–C(19)	113.7(3)
C(18)–N(3)–C(21)	124.8(3)	C(19)–N(3)–C(21)	120.3(3)
C(18)–N(4)–C(20)	114.0(3)	C(18)–N(4)–C(28)	123.9(3)
C(20)–N(4)–C(28)	119.8(3)	C(35)–N(5)–C(36)	114.5(3)
C(35)–N(5)–C(45)	125.0(3)	C(36)–N(5)–C(45)	118.6(3)
C(35)–N(6)–C(37)	114.6(3)	C(35)–N(6)–C(38)	124.0(3)
C(37)–N(6)–C(38)	120.1(3)		

TABLE 6. Selected bond lengths (Å) and angles (°) with estimated standard deviations in parentheses for [{RhCl(COD)}$_2${μ-L$_2^{(323)CH_2Ph}$}] (2)

(a) Bonds			
Rh–Cl(1)	2.385(1)	Rh-Cen1	2.005
Rh–Cen2	2.104	Rh–C(2)	2.056(4)
N(1)–C(1)	1.468(6)	N(1)–C(2)	1.340(5)
N(1)–C(5)	1.472(6)	N(2)–C(2)	1.334(5)
N(2)–C(3)	1.465(6)	N(2)–C(6)	1.472(6)
C(1)–C(1)′	1.527(9)	C(3)–C(4)	1.407(8)
C(4)–C(5)	1.367(9)	C(6)–C(7)	1.497(6)
(b) Angles			
Cl(1)–Rh–Cen1	173.6	Cl(1)–Rh–Cen2	90.3
Cl(1)–Rh–C(2)	89.8(1)	Cen1–Rh–Cen2	86.6
Cen1–Rh–C(2)	93.8	Cen2–Rh–C(2)	173.7
C(1)–N(1)–C(2)	121.3(4)	C(1)–N(1)–C(5)	114.8(4)
C(2)–N(1)–C(5)	123.7(4)	C(2)–N(2)–C(3)	125.2(4)
C(2)–N(2)–C(6)	121.6(4)	C(3)–N(2)–C(6)	113.2(4)
N(1)–C(1)–C(1)′	110.6(5)	N(1)–C(2)–N(2)	117.4(4)
N(2)–C(3)–C(4)	112.5(5)	C(3)–C(4)–C(5)	123.9(6)
N(1)–C(5)–C(4)	114.4(5)	N(2)–C(6)–C(7)	113.5(4)

Cen1 and Cen2 are the centres of the C(13)–C(14) and C(17)–C(18) bonds respectively.

Atoms marked ′ are related by symmetry $1-x$, $\bar{y}$, $\bar{z}$.

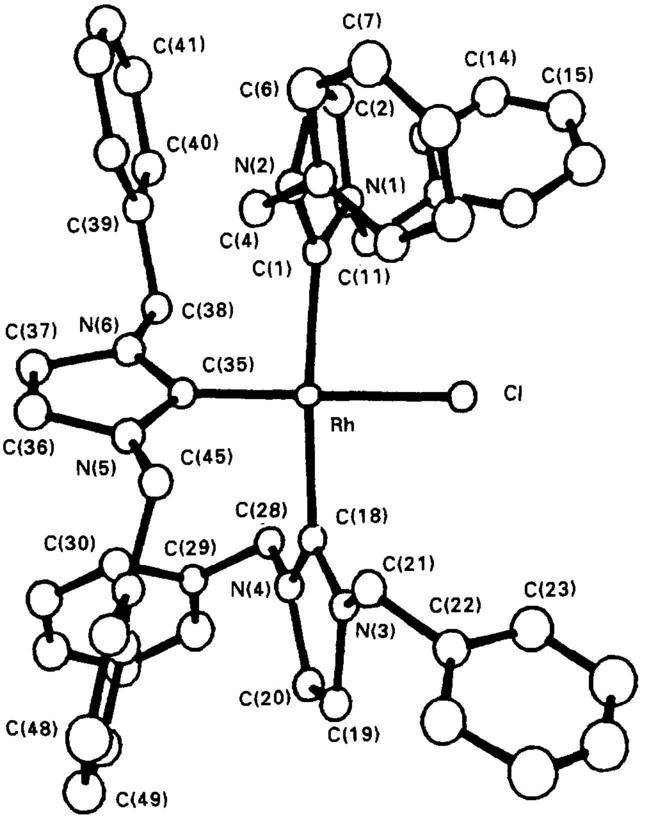


Fig. 1. X-Ray structure and atom labelling for [RhCl(L^{CH_2Ph})$_3$] (1).

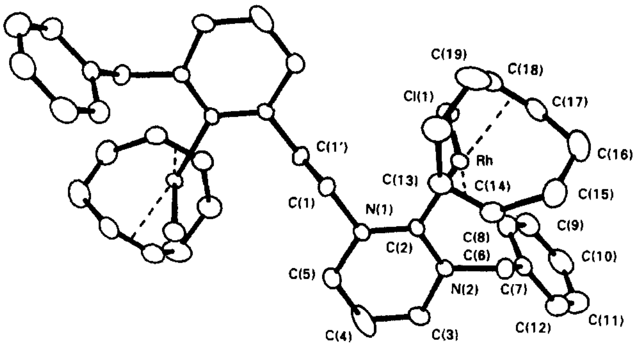


Fig. 2. X-Ray structure and atom labelling for [{RhCl(COD)}$_2${μ-L$_2^{(323)CH_2Ph}$}] (2).

ring has the benzylic carbon atom coplanar, the Ph group being out of the plane. For the ring containing N(1) and N(2), the phenyl groups are on the same side of the ring, but for each of the other two carbene ligands, the phenyl groups are on opposite sides of their rings. The mutually *trans*-L^{CH_2Ph} five-membered rings are twisted from a parallel arrangement (*cf.* **4** and **5**) by 49°.

The molecular structure and atom labelling for [{RhCl(COD)}$_2${μ-L$_2^{(323)CH_2Ph}$}] (**2**) are shown in Fig. 2. The molecule has an inversion centre, the mid-point of the C(1)–C(1)′ bond. The conformation of the molecule is such that there is close proximity of the *N*-benzyl group and the cyclo-octa-1,5-diene. The observation in the ^{13}C{^{1}H} NMR spectrum of 2 in CD$_2$Cl$_2$ that the olefinic carbons of the COD ligand are found as four doublets (see Section 3.2) would be consistent with this conformation being retained in solution.

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