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The synthesis and characterisation of an ortho-metallated carbeneruthenium(II) complex, containing a metallated *N*-benzyl substituent with a 6-membered metallate nucleus, crystal structure of $[RuCl(CN(CH_2C_6H_5)CH_2CH_2NCH_2C_6H_4)(PPh_3)_2]$

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Abstract

The complex $[RuCl(H)(PPh_3)_3]$ reacts with the tetra-benzyl substituted electron-rich alkene $[=CN(CH_2Ph)CH_2CH_2NCH_2Ph]_2$ with elimination of H_2 and PPh_3 to form the five coordinate carbeneruthenium(II) complex, abbreviated as $[RuCl(L^{Bz})(PPh_3)_2]$ (**1**), containing a 6 membered metallate nucleus, *via* *ortho*-metallation of one of the *N*-benzyl substituents. Reaction with PEt_3 gives the unusual bisphosphine complex $[RuCl(L^{Bz})(PEt_3)(PPh_3)]$ which contains a chiral metal atom. Small π-acceptor ligands (*e.g.* CO, $P(OMe)_3$) add to form stable 6-coordinate complexes. ^{13}C NMR spectroscopic data provides information on the stereochemistry of the molecules as $^2J(^{13}C-^{31}P)_{trans} \gg {}^2J(^{13}C-^{31}P)_{cis}$. The complexes appear stereochemically rigid in solution at 25°. The crystal structure of the title compound has been determined. The two Ru–C(sp^2) distances are 1.968 (6) Å [$Ru-C_{carb}$] and 2.014 (7) Å [$Ru-C^2_{aryl}$].

Introduction

Many examples of carbene metal species formed by the reaction between a cyclic electron-rich alkene, ERA, and a suitable transition metal substrate have been reported [1]. Our first aim in studying this system was to synthesise novel, 5-coordinate, 16e molecules containing an *ortho*-metallated carbene fragment and to evaluate their activity as potential homogeneous catalysts. Initial studies have shown $[RuCl(L^{p\text{-tol}})(PPh_3)_2]$ to be an active catalyst for the hydrogenation of

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1-alkenes [2]. Our second aim was to prepare chiral carbeneruthenium complexes possessing five different ligands around the ruthenium atom [3], to give diasteriomeric complexes by the incorporation of a second chiral centre and to evaluate their role as asymmetric homogeneous catalysts.

Cyclic *N*-alkyl electron-rich alkenes are more reactive towards carbene metal formation than their cyclic *N*-aryl analogues; thus treatment of $[\mathrm{RuCl_2(PPh_3)_3}]$ with $\mathrm{L_2^R}$ (R = Me, Et) yields 6-coordinate, 18e tetracarbene ruthenium(II) complexes [4], *i.e.* *trans*-$[\mathrm{RuCl_2(L^R)_4}]$. The reaction between $[\mathrm{RuCl_2(PPh_3)_3}]$ with tetra-aryl substituted electron-rich alkenes results in the incorporation of one carbene fragment, with spontaneous *ortho*-metallation of one of the *N*-aryl rings, to form a 5-membered ruthenated nucleus [5]. The reactivity of the benzyl electron-rich alkene, $\mathrm{L_2^{Bz}}$, has been shown to be generally more typical of simple *N*-alkyl derivatives, but in this reaction appears to resemble that of *N*-aryl ERA's, the spontaneous metallation inhibiting further phosphine substitution.

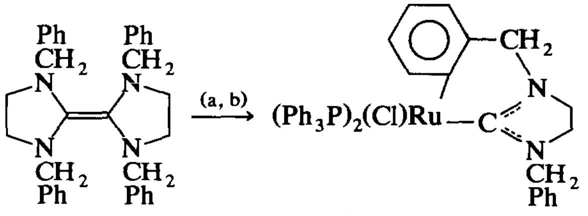
Results and discussion

Initial investigations of the reaction between the benzyl ERA with $[\mathrm{RuCl_2(PPh_3)_3}]$ resulted in a report of the formation of the 18e tetracarbene species *trans*-$[\mathrm{RuCl_2(L^{Bz})_4}]$ as the sole characterised product [4]. We now report the isolation of a 5-coordinate, 16e monocarbene *ortho*-metallated ruthenium(II) complex $[\mathrm{R}\overline{\mathrm{uCl(L}}^{\mathrm{Bz}})(\mathrm{PPh_3})_2]$ (1), exhibiting a 6-membered metallate nucleus. This material, complex **1**, is prepared by heating $[\mathrm{RuCl_2(PPh_3)_3}]$, or preferably, the hydride $[\mathrm{RuCl(H)(PPh_3)_3}]$ with $\mathrm{L_2^{Bz}}$ in xylene at 140°C with the loss of $\mathrm{PPh_3}$ and the elimination of HCl or $\mathrm{H_2}$ respectively (Scheme 1). In the former case the HCl is removed as the insoluble salt $[\mathrm{HL^{Bz}}]^+\mathrm{Cl}^-$ by use of an excess of the alkene. The latter reaction is the method of choice, since it consistently gives the desired product. The former process appears less reliable, a variety of products being obtained under apparently essentially constant reaction conditions. This may be due, in part, to the fact that formation of the salt $[\mathrm{HL^{Bz}}]^+\mathrm{Cl}^-$ is unfavourable [6].

The reaction between $[\mathrm{R}\overline{\mathrm{uCl(L}}^{\mathrm{Bz}})(\mathrm{PPh_3})_2]$ and the more basic trialkylphosphine, $\mathrm{PEt_3}$, was expected to afford the disubstituted product $[\mathrm{R}\overline{\mathrm{uCl(L}}^{\mathrm{Bz}})(\mathrm{PEt_3})_2]$ *via* tertiary phosphine exchange, as observed in previous work [5]. In the event, phosphine ligand exchange did occur, but only one triphenylphosphine ligand was replaced, to give an interesting 5-coordinate, 16e, mixed-phosphine complex $[\mathrm{R}\overline{\mathrm{uCl(L}}^{\mathrm{Bz}})(\mathrm{PPh_3})(\mathrm{PEt_3})]$ (3). This molecule has five different ligands surrounding the central ruthenium(II) atom, creating a potential chiral environment around the metal. The possible resolution of this complex is being investigated [6]. Subsequent reaction with carbon monoxide in dichloromethane/hexane at 25°C afforded a mixture of the expected product $[\mathrm{R}\overline{\mathrm{uCl(L}}^{\mathrm{Bz}})(\mathrm{CO})(\mathrm{PPh_3})(\mathrm{PEt_3})]$ (4) but also the phosphine symbiosis product $[\mathrm{R}\overline{\mathrm{uCl(L}}^{\mathrm{Bz}})(\mathrm{CO})(\mathrm{PEt_3})_2]$ (6) (identified by IR and NMR spectroscopy) in an approximately 1:2 ratio.

$$\begin{tikzcd} & {[\mathrm{R}\overline{\mathrm{uCl(L}}^{\mathrm{Bz}})(\mathrm{CO})(\mathrm{PEt_3})_2]\ (6)} \\ {[\mathrm{R}\overline{\mathrm{uCl(L}}^{\mathrm{Bz}})(\mathrm{PEt_3})(\mathrm{PPh_3})]} \arrow[ur, "\mathrm{CO}"] \arrow[dr, "(a)"'] & \\ & {[\mathrm{R}\overline{\mathrm{uCl(L}}^{\mathrm{Bz}})(\mathrm{CO})(\mathrm{PEt_3})(\mathrm{PPh_3})]\ (4)} \end{tikzcd}$$

(a) Dichloromethane/hexane, 25°C



L_2^{Bz}

$[\overline{\mathrm{RuCl(L}}^{\mathrm{Bz}})(\mathrm{PPh_3})_2]$

Scheme 1. (a) $[RuCl_2(PPh_3)_3]$ or $[RuCl(H)(PPh_3)_3]$, (b) Xylene, 140°C.

Surprisingly, there was no evidence, from either ^1H NMR or IR spectroscopy, for the formation of the bistriphenylphosphine symbiosis product (complex **2**). Recrystallisation of the crude mixture *via* dichloromethane/pentane gave complex **6** as white needles; but attempts to isolate an analytically pure sample of complex **4** have so far proved unsuccessful. When heated complex **6** loses carbon monoxide to give a red solid, judged to be the 5-coordinate precursor $[\overline{\mathrm{RuCl(L}}^{\mathrm{Bz}})(\mathrm{PEt_3})_2]$, and this may provide a useful route to the latter complex. Complex **1** will react readily with small π-acceptor molecules such as CO and $P(OMe)_3$ to obtain coordinatively saturated species. This phenomenon has been observed in related systems [5].

The ^1H and ^{13}C spectroscopic data are listed in Tables 2 and 3. In the ^1H NMR spectra (Table 2) three distinct regions can be identified,
(i) The orthometallated ring protons; (ii) The ring methylene protons; and (iii) The benzyl methylene protons. The signals from the metallated ring protons are shifted upfield from those from the non-metallated aryl ring protons, and appear as a

Table 1

Carbeneruthenium(II) *ortho*-metallated complexes and their characterisation by microanalysis and IR spectroscopy

Compound	Colour	Yield (%)	M.p. (θ/°C)	Analysis (%) [a] C	H	N	IR [b] $\nu(CN_2)$	$\nu(CO)$
$[\overline{\mathrm{RuCl(L}}^{\mathrm{Bz}})(\mathrm{PPh_3})_2]$	Crimson	80	265–270	69.56	5.44	2.92	1515	
(1)				(69.92)	(5.17)	(3.07) [c]		
$[\overline{\mathrm{RuCl(L}}^{\mathrm{Bz}})(\mathrm{CO})(\mathrm{PPh_3})_2]$	White	90	170–172	66.80	4.96	3.01	1503	1931
(2)				(66.70)	(4.90)	(2.86) [d]		
$[\overline{\mathrm{RuCl(L}}^{\mathrm{Bz}})(\mathrm{PEt_3})(\mathrm{PPh_3})]$	Red	65	75–77	64.20	6.33	3.40	1486	
(3)				(64.23)	(6.14)	(3.65)		
$[\overline{\mathrm{RuCl(L}}^{\mathrm{Bz}})(\mathrm{CO})(\mathrm{PEt_3})(\mathrm{PPh_3})]$ [e]	White	25						
(4)								
$[\overline{\mathrm{RuCl(L}}^{\mathrm{Bz}})\{\mathrm{P(OMe)_3}\}_3]$ [e]	White	45						
(5)								
$[\overline{\mathrm{RuCl(L}}^{\mathrm{Bz}})(\mathrm{CO})(\mathrm{PEt_3})_2]$ [e]	White	50	149–150				1485	1915
(6)								

[a] Calculated values in parenthesis. [b] KBr disc, values quoted in cm^{-1} calibrated against polystyrene. [c] Chlorine 3.30 (3.90). [d] Calculated for 0.5 CH_2Cl_2. [e] Satisfactory microanalysis not obtained.

Table 2

^{1}H NMR spectroscopic data [a] for carbeneruthenium(II) complexes

Complex	Carbene ring CH_2	Benzyl CH_2	Aryl-H	Others
1	2.35(t), 2.55(t)	2.95, 4.20	6.00–6.50(m) [c] 6.90–7.75(m) [b]	
2	2.50(t), 2.90(t)	3 60, 4.40	6.10(t), 6.50–6.75(m) [c] 6.90–7.50(m) [b], 7.95 [f]	
3	2.80–3.30(m)	3 95(q), 4.35(q)	6.20–7.00(m) [c] 7.00–7.80(m) [b]	0.98(m) [d] 1.58(m) [e]
4	3.09(m), 3.37(m)	4.06(q), 4.67(q)	6.61–7.00(m) [c], 8.08(d) 7 12–7.50(m) [b]	0.86(m) [d] 1.68(m) [e]
5 [g]	2.90–4.00(m)	3.00–3.90(m) 4.80–5.20(m)	6.60–6.90(m) [c] 7.16–7.70(m) [b]	3.10–3.90(m) [h]
6	3.57(t), 3.25(t)	4.50, 4.99	6.77–6.99 [c] 7.32–7.39 [b] 8.61(d)	0.86(m) [d] 1.68(m) [e]

[a] values quoted relative to $SiMe_4$ ($\delta = 0$ ppm), spectra recorded at 25°: all resonances are singlets unless stated as d = doublet, t = triplet, m = multiplet, spectra obtained in $CDCl_3$. [b] non-metallated ring protons. [c] *ortho*-metallated aryl protons. [d] PEt_3, CH_3. [e] PEt_3, CH_2. [f] *ortho*-metallated aryl C^3 proton. [g] one $P(OMe)_3$ ligand labile in solution, complex spectra. [h] $P(OMe)_3$, OCH_3

complex multiplet. The carbene ring methylene protons give a AA′BB′ pattern in complexes **1** and **2**, and a complex multiplet in complexes **3** to **6**. The benzyl CH_2 protons appear as two (A_2) singlets in complexes **1**, **2** and **6**, as would be expected for an AB system in which the two nuclei are isochronous [7]. The benzyl CH_2 protons in complexes **3** and **4** appear as two distinct AB quartets, the asymmetry of the molecule creating differing chemical environments for each pair of benzylic CH_2 moieties. ^{13}C NMR spectroscopic data (Table 3) allow determination of the stereochemistry around the central metal atom be determined, by use of the $^2J(C_{carb}–P)$, $^2J(C_{CO}–P)$ and $^2J(C^2_{aryl}–P)$ values. The chemical shifts are $\delta(C_{carb})$ at 210–217 ppm, δ(CO) at *ca.* 204 ppm and $\delta(C^2_{aryl})$ at 140–163 ppm. The 5-coordinate complexes appear to be stereochemically rigid in solution at 25° due, at least in part, to the constraint of *ortho*-metallation and the resulting fused tricyclic ring system. The non-fluxional behaviour of these compounds is indicated by similar values for $^2J(^{13}C–^{31}P)$ for C_{carb}/P and C^2_{aryl}/P. $^2J(C–P)_{trans}$ is much greater than $^2J(C–P)_{cis}$ hence values of 11.8 Hz and 11.7 Hz, for $^2J(C_{carb}–P)$ and $^2J(C^2_{aryl}–P)$, respectively, in complex **1**, indicate a *trans* arrangement of the two phosphine ligands and a mutually *cis* orientation of C_{carb}/C^2_{aryl}, C_{carb}/PPh_3 and C^2_{aryl}/PPh_3 (**6**), as supported by the observed ^{31}P magnetic equivalence of the two PPh_3 ligands, and confirmed for the solid state system by X-ray crystallography. A *trans* arrangement of C_{carb}–P has been noted, with ^2J *ca.* 88 Hz [5].

Molecular structure of $[Ru\overline{Cl(L}^{Bz})(PPh_3)_2]$ *(1)*

The molecular configuration and atom numbering scheme is shown in Fig. 1. In each phenyl ring carbon atoms are numbered sequentially (C_1 to C_6, only C_1 and C_2 being labelled below); the rings are labelled (a) to (h) and these letters are incorporated into the atomic numbering [C(*nm*), *n* = 1–6, *m* = a–h].

The PPh_3 groups are *trans* and eclipsed. Interestingly, the pendant benzyl ring (h) is twisted away from the imidazolidine ring which negates any *ortho*-Ru---H

Table 3

$^{13}C\{H\}$ NMR chemical shifts [a] and ^{2}J coupling constants (Hz) of carbeneruthenium(II) complexes

Complex	C_{carb}	$^{2}J(C_{carb}/P)$	CO	$^{2}J(C_{CO}/P)$	C^{2}_{aryl}	$^{2}J(C^{2}/P)$	Carbene ring CH_2	Benzyl CH_2	Others
1 [b]	215.8(t)	11.8			146.9(t)	11.7	46.6, 50.3	53.4, 56.5	
2	213.4(t)	10.7	204.2(t)	10.8	161.9(t)	14.2	47.5, 51.2	55.0, 56.2	
3	210.7(t)				142.0(t)		48.8, 51.2	54.8, 55.6	
4 [c]			204.3	11.2	162.7		48.4, 51.9	55.3, 57.9	7.3 [d], 17.6 [e]
5	214.5				148.8		49.1–54.3 [f]	56.1, 57.9	49.1–54.3 [f]
6	216.3		204.1		162.4		48.8, 52.2	55.6, 58.7	7.3 [d], 17.5 [e]

[a] values quoted relative to $SiMe_4$ ($\delta = 0$ ppm). All peaks singlets unless stated d = doublet, t = triplet, m = multiplet, spectra obtained in $CDCl_3$. [b] -104.3 ppm ^{31}P NMR PPh_3 singlet relative to $P(OMe)_3$ ($\delta = 0$ ppm). [c] C_{carb} not observed. [d] PEt_3, CH_3. [e] PEt_3, CH_2. [f] Unable to distinguish between ring CH_2 and $-OMe$ signals.

Table 4

Fractional coordinates (Ru, Cl, P: $\times 10^5$; C, N: $\times 10^4$) and equivalent isotropic thermal parameters (Ru, Cl, P: $\text{Å}^2 \times 10^4$; C, N: $\times \text{Å}^2 \times 10^3$)

Atom	*x*	*y*	*z*	U_{eq} [a]
Ru	21199(3)	18874(3)	28178(4)	318(3)
Cl	25075(9)	7327(10)	21819(17)	606(12)
P(1)	10651(8)	16212(9)	21542(13)	349(9)
P(2)	31808(9)	20873(9)	34495(15)	406(10)
N(1)	1750(3)	3355(3)	3535(5)	45(3)
N(2)	1953(3)	3338(3)	1922(5)	52(3)
C(1)	1924(3)	2919(3)	2797(5)	35(3)
C(2)	1655(4)	4101(4)	3202(7)	65(4)
C(3)	1643(5)	4023(4)	2056(8)	87(4)
C(4)	1753(4)	3211(4)	4609(6)	53(4)
C(5)	1927(5)	3013(5)	920(7)	73(4)
C(1a)	661(3)	875(4)	2772(6)	40(3)
C(2a)	77(4)	942(5)	3247(6)	56(4)
C(3a)	−190(5)	333(6)	3676(7)	76(4)
C(4a)	107(5)	−321(5)	3637(7)	67(4)
C(5a)	669(4)	−389(5)	3169(7)	64(4)
C(6a)	936(4)	208(4)	2743(6)	49(3)
C(1b)	942(3)	1315(3)	809(5)	37(3)
C(2b)	1444(4)	1285(4)	170(6)	48(3)
C(3b)	1340(4)	1045(5)	−840(7)	64(4)
C(4b)	748(4)	851(5)	−1228(6)	63(4)
C(5b)	249(4)	868(4)	−596(7)	65(4)
C(6b)	344(4)	1105(4)	424(6)	55(4)
C(1c)	508(3)	2382(4)	2210(6)	39(3)
C(2c)	388(4)	2671(4)	3156(6)	51(4)
C(3c)	5(4)	3273(4)	3241(8)	66(4)
C(4c)	−255(4)	3594(5)	2363(9)	79(4)
C(5c)	−129(4)	3322(4)	1419(8)	63(4)
C(6c)	238(4)	2716(4)	1325(7)	53(4)
C(1d)	3550(4)	1297(4)	4099(7)	53(4)
C(2d)	3284(4)	1046(5)	4978(8)	73(4)
C(3d)	3529(5)	401(5)	5449(9)	89(4)
C(4d)	4022(6)	65(5)	5039(10)	97(4)
C(5d)	4302(5)	322(5)	4188(10)	99(4)
C(6d)	4060(4)	931(4)	3712(8)	71(4)
C(1e)	3754(4)	2297(4)	2493(7)	55(4)
C(2e)	3598(5)	2173(5)	1460(8)	76(4)
C(3e)	4038(7)	2328(8)	707(9)	125(5)
C(4e)	4644(6)	2583(6)	1053(11)	105(4)
C(5e)	4794(5)	2713(6)	2059(10)	89(4)
C(6e)	4354(4)	2573(5)	2785(8)	72(4)
C(1f)	3337(3)	2852(4)	4351(6)	43(3)
C(2f)	3517(4)	2759(5)	5386(6)	56(4)
C(3f)	3616(5)	3361(6)	6014(7)	77(4)
C(4f)	3529(4)	4032(5)	5610(9)	78(4)
C(5f)	3366(5)	4124(5)	4583(8)	73(4)
C(6f)	3274(4)	3538(4)	3962(7)	51(4)
C(1g)	1707(4)	2447(4)	4915(6)	46(3)
C(2g)	1825(3)	1857(4)	4262(5)	39(3)
C(3g)	1745(4)	1176(4)	4678(6)	52(4)
C(4g)	1573(4)	1060(5)	5689(7)	66(4)
C(5g)	1472(5)	1651(6)	6303(8)	81(4)

Table 4 (continued)

Atom	x	y	z	U_{eq} ^{a}
C(6g)	1534(4)	2321(6)	5919(6)	67(4)
C(1h)	2303(4)	3356(5)	154(7)	63(4)
C(2h)	2810(5)	3821(6)	425(8)	88(4)
C(3h)	3182(6)	4131(7)	−281(9)	108(4)
C(4h)	3074(8)	3922(9)	−1311(10)	168(5)
C(5h)	2570(8)	3507(10)	−1615(9)	186(5)
C(6h)	2207(7)	3200(8)	−861(9)	136(5)
C(1s)	1303(8)	5014(9)	5982(13)	130(4) ^{b}
C(2s)	849(8)	5211(9)	5197(13)	130(4) ^{b}
C(3s)	224(8)	4953(9)	5199(13)	130(4) ^{b}
C(4s)	53(8)	4496(9)	5986(13)	130(4) ^{b}
C(5s)	506(8)	4298(9)	6770(13)	130(4) ^{b}
C(6s)	1131(8)	4557(9)	6768(13)	130(4) ^{b}
C(7s)	1878(16)	5477(19)	5775(24)	130(4) ^{b}
C(1t)	1797(20)	5039(22)	6338(29)	124(5) ^{b}
C(2t)	1328(20)	5261(22)	5593(29)	124(5) ^{b}
C(3t)	715(20)	4966(22)	5574(29)	124(5) ^{b}
C(4t)	571(20)	4451(22)	6302(29)	124(5) ^{b}
C(5t)	1040(20)	4230(22)	7047(29)	124(5) ^{b}
C(6t)	1653(20)	4524(22)	7066(29)	124(5) ^{b}

^{a} $U_{eq} = \frac{1}{3}\Sigma_i \Sigma_j U_{ij} a^*_i a^*_j (\mathbf{a}_i \cdot \mathbf{a}_j)$.

interaction in direct contrast to the 5-coordinate systems containing a 5-membered metallate nucleus [5] where the pendant aryl ring is coplanar with the imidazolidine ring allowing significant Ru---H_{aryl} interaction. In the 6-coordinate carbonyl

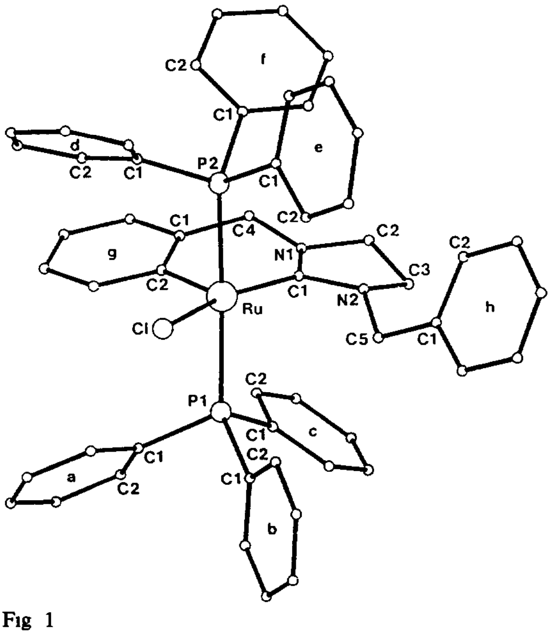


Fig 1

Table 5

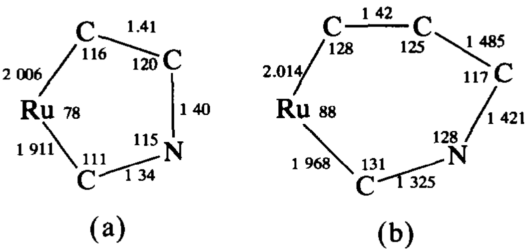
Bond lengths (Å) and bond angles (°)

Cl–Ru	2.464(2)	C(1f)–P(2)	1.861(8)
P(1)–Ru	2.370(2)	C(1)–N(1)	1.325(9)
P(2)–Ru	2.346(2)	C(2)–N(1)	1.468(9)
C(1)–Ru	1.968(6)	C(4)–N(1)	1.421(10)
C(2g)–Ru	2.014(7)	C(1)–N(2)	1.384(9)
C(1a)–P(1)	1.841(8)	C(3)–N(2)	1.450(11)
C(1b)–P(1)	1.839(7)	C(5)–N(2)	1.432(11)
C(1c)–P(1)	1.841(7)	C(3)–C(2)	1.494(15)
C(1d)–P(2)	1.843(8)	C(1g)–C(4)	1.485(11)
C(1e)–P(2)	1.826(9)	C(1h)–C(5)	1.457(13)
P(1)–Ru–Cl	90.9(1)	C(5)–N(2)–C(3)	119.4(7)
P(2)–Ru–Cl	86.0(1)	N(1)–C(1)–Ru	131.1(5)
P(2)–Ru–P(1)	176.9(1)	N(2)–C(1)–Ru	122.9(5)
C(1)–Ru–Cl	157.5(2)	N(2)–C(1)–N(1)	106.1(6)
C(1)–Ru–P(1)	90.7(2)	C(3)–C(2)–N(1)	101.2(6)
C(1)–Ru–P(2)	92.3(2)	C(2)–C(3)–N(2)	103.2(7)
C(2g)–Ru–Cl	114.6(2)	C(1g)–C(4)–N(1)	116.6(6)
C(2g)–Ru–P(1)	89.8(2)	C(1h)–C(5)–N(2)	116.4(8)
C(2g)–Ru–P(2)	91.2(2)	C(2a)–C(1a)–P(1)	124.0(6)
C(2g)–Ru–C(1)	87.9(3)	C(6a)–C(1a)–P(1)	118.0(6)
C(1a)–P(1)–Ru	116.4(2)	C(2b)–C(1b)–P(1)	121.2(5)
C(1b)–P(1)–Ru	118.6(2)	C(6b)–C(1b)–P(1)	120.1(6)
C(1b)–P(1)–C(1a)	98.0(3)	C(2c)–C(1c)–P(1)	119.4(6)
C(1c)–P(1)–Ru	113.7(2)	C(6c)–C(1c)–P(1)	122.4(6)
C(1c)–P(1)–C(1a)	104.8(3)	C(2d)–C(1d)–P(2)	117.9(6)
C(1c)–P(1)–C(1b)	103.2(3)	C(6d)–C(1d)–P(2)	122.5(7)
C(1d)–P(2)–Ru	113.0(2)	C(2e)–C(1e)–P(2)	120.2(7)
C(1e)–P(2)–Ru	116.5(3)	C(6e)–C(1e)–P(2)	121.2(7)
C(1e)–P(2)–C(1d)	102.0(4)	C(2f)–C(1f)–P(2)	122.7(6)
C(1f)–P(2)–Ru	117.7(2)	C(6f)–C(1f)–P(2)	118.2(6)
C(1f)–P(2)–C(1d)	106.0(4)	C(2g)–C(1g)–C(4)	124.6(7)
C(1f)–P(2)–C(1e)	99.6(4)	C(6g)–C(1g)–C(4)	115.9(8)
C(2)–N(1)–C(1)	114.1(7)	C(1g)–C(2g)–Ru	127.6(6)
C(4)–N(1)–C(1)	127.7(6)	C(3g)–C(2g)–Ru	116.0(6)
C(4)–N(1)–C(2)	117.3(6)	C(2h)–C(1h)–C(5)	122.4(8)
C(3)–N(2)–C(1)	110.8(7)	C(6h)–C(1h)–C(5)	121.3(10)
C(5)–N(2)–C(1)	120.4(6)		
Phenyl rings a to h [a]			
C–C:	mean = 1.38(2) Å	range = 1.35(2)–1.43(1) Å	for 48 bonds
C–C–C	mean = 120(2)°	range = 116(1)–123(1)°	for 48 angles

[a] A complete list of bond lengths and bond angles within these rings is given as supplementary material.

complex [5] the pendant aryl ring is 85° out of plane, allowing an approximately octahedral coordination at Ru. The vacant site seems to be blocked by a solvent molecule (toluene), which appears to confer significant solid state air-stability to the molecule and perhaps accounts for the observed orientation of the pendant benzyl phenyl group.

The imidazolidine ring has dimensions similar to those in related carbene derivatives [8]; the C(2)–C(3) bond of 1.494 Å shows some shortening from the



Scheme 2. Molecules (a) $[\overline{\mathrm{RuCl(L}}^{p\text{-tol}})(\mathrm{PEt}_3)_2]$ and (b) $[\overline{\mathrm{RuCl(L}}^{\mathrm{Bz}})(\mathrm{PPh}_3)_2]$. Bond lengths (Å) and angles (°) are shown for comparison.

ideal single bond distance between two sp^3- hybridised C-atoms [1.52 Å], but the value of 1.494 Å is 0.031 Å longer than the corresponding bond [4] in $[\mathrm{RuCl}_2(\mathrm{L}^{\mathrm{Et}})_4]$ whilst it is 0.026 Å shorter than in $[\overline{\mathrm{RuCl(L}}^{p\text{-tol}})(\mathrm{PEt}_3)_2]$ [5]. The $\mathrm{M{-}C_{carb}}$ bond length of 1.968 Å is intermediate between other $\mathrm{M{-}C_{carb}}$ lengths in related d^6 ruthenium complexes $[\overline{\mathrm{RuCl(L}}^{p\text{-tol}})(\mathrm{PEt}_3)_2]$, 1.911 Å, and $[\overline{\mathrm{RuCl(L}}^{p\text{-tol}})(\mathrm{CO})(\mathrm{PEt}_3)_2]$, 1.989 Å [5]. The carbene-metal bond length of 2.105 Å in $[\mathrm{RuCl}_2(\mathrm{L}^{\mathrm{R}})_4]$ complexes [4] suggests that the shortening of the $\mathrm{M{-}C_{carb}}$ bond is an inherent characteristic of the constraint of the fused tricyclic chelating system, rather than any $\mathrm{Ru{-}C_{carb}}$ d_π–p_π interaction. This is supported by the continued observation of $\mathrm{C_{carb}{-}N}$ distances entirely compatible with essentially 100% double bond character, a view reinforced by spectroscopic data.

The C(2g)–Ru–C(1) bond angle is 87.9°; this is approximately 10° larger than that in the analogous 5-membered metallocycles [5] as a result of the increase in ring size from 5 to 6 (Scheme 2).

The Ru–C(2) bond length of 2.014 Å is similar to that observed in an *ortho*-metallated perfluoroazobenzene complex [9] [M–C(sp^2) 2.013 Å] and to the estimated Ru–C(sp^2) bond distance of 2.00 Å [10]. The difference in the two M–C(sp^2) bond lengths $\mathrm{M{-}C_{carb}/M{-}C^2_{aryl}}$ of 0.046 Å is unlikely to imply any $\mathrm{Ru{-}C_{carb}}$ double bond character, but to be a consequence of the nature of carbon substitution and the constraints of the fused ring system.

Experimental

All reactions were carried out under argon *via* standard Schlenk techniques. Solvents were dried prior to use over sodium wire, sodium benzophenone, or $\mathrm{CaH_2}$. ^{1}H, ^{13}C and ^{31}P NMR spectra were obtained at 250 MHz with a Bruker AC-250 spectrometer under argon in $\mathrm{CDCl_3}$ at 25°C with tetramethylsilane as internal standard. Microanalyses were carried out by Medac Ltd., Brunel University. The benzyl ERA was prepared by the published method [11]. The starting materials $[\mathrm{RuCl_2(PPh_3)_3}]$ and $[\mathrm{RuCl(H)(PPh_3)_3}]$ were prepared from $\mathrm{RuCl_3 \cdot 3H_2O}$ by published procedures [12,13].

$[\overline{\mathrm{RuCl(L}}^{\mathrm{Bz}})(\mathrm{PPh}_3)_2]$ *(1)*

A mixture of chlorohydridotris(triphenylphosphine)ruthenium(II) (1.0 g, 0.985 mmol) and bi(1,3-dibenzylimidazolidin-2-ylidene] (0.52 g, 1.04 mmol) in xylene (15 cm^3) was heated (140°C, 1 h). The purple suspension gradually dissolved with evolution of gas, giving a purple solution, and when this was cooled to room temperature crimson crystals were formed. The solvent was decanted and the product washed with hexane (5 × 5 cm^3) and dried *in vacuo* to give [1,3-dibenzylimidazolidin-2-ylidene-C^2,$C^{2'}$]chlorobis(triphenylphosphine)ruthenium(II) (0.67 g, 75%), which was recrystallised from hot toluene.

$[\overline{RuCl(L}^{Bz})(CO)(PPh_3)_2]$ *(2)*

Carbon monoxide was slowly bubbled through a solution of complex **1** (0.50 g, 0.550 mmol) in dichloromethane (10 cm^3) (25°C, 2 min), the initially intense clear purple solution becoming colourless. Hexane (5 cm^3) was added and the mixture cooled (−30°C, 2 days) to afford an off-white solid. This was recrystallised from dichloromethane/hexane at −30°C to give [1,3-dibenzylimidazolidin-2-ylidene-C^2,$C^{2'}$]carbonylchlorobis(triphenylphosphine)ruthenium(II) as a white solid (0.45 g, 87%).

$[\overline{RuCl(L}^{Bz})(PEt_3)(PPh_3)]$ *(3)*

To a solution of complex **1** (0.38 g, 0.418 mmol) in tetrahydrofuran (20 cm^3) was added triethylphosphine (0.05 g, 0.424 mmol). The deep-purple solution was refluxed (2 h) then allowed to cool to room temperature, and the solvent removed *in vacuo* to yield a red oil. This was extracted with warm hexane (6 × 5 cm^3) and the extracts were combined and cooled (−30°C, 12 h) to deposit [1,3-dibenzylimidazolidin-2-ylidene-C^2,$C^{2'}$]chlorotriphenylphosphinetriethylphosphineruthenium(II) as a light red solid (0.20 g, 63%).

$[\overline{RuCl(L}^{Bz})(CO)(PPh_3)(PEt_3)]$ *(4)* / $[RuCl(L^{Bz})(CO)(PEt_3)_2]$ *(6)*

Carbon monoxide was slowly bubbled through a solution of complex **3** (0.20 g, 0.261 mmol) in dichloromethane (5 cm^3)/hexane (25 cm^3) (25°C, 1 min), the initially intense red solution becoming light green or colourless. The solution was cooled (−30°C, 2 days) to afford a mixture of [1,3-dibenzylimidazolidin-2-ylidene-C^2,$C^{2'}$]chlorocarbonyltriphenylphosphinetriethylphosphineruthenium(II) (**4**) and [1,3-dibenzylimidazolidin-ylidine-C^2,$C^{2'}$]chlorocarbonylbis(triethylphosphine)ruthenium(II) (**6**) as an off-white solid (0.17 g, 82%), which was recrystallised from dichloromethane/pentane at 25°C to give [1,3-dibenzylimidazolidin-ylidine-C^2,$C^{2'}$]chlorocarbonylbis(triethylphosphine)ruthenium(II) (**6**) as white needles.

$[\overline{RuCl(L}^{Bz})\{P(OMe)_3\}_3]$ *(5)*

To a solution of complex **1** (0.45 g, 0.495 mmol) in toluene (15 cm^3) was added trimethylphosphite (0.19 cm^3, 1.59 mmol). The purple suspension was heated under reflux to give a clear red solution, which on continued stirring became yellow. The mixture was cooled (40°C), filtered and hexane (8 cm^3) was added. The solution was kept at −30°C for 7 days to afford [1,3-dibenzylimidazolidin-2-ylidene-C^2,$C^{2'}$]chlorotris(trimethylphosphite)ruthenium(II) (0.18 g, 48%) as a white solid.

Structural determinations

The title compound crystallized from toluene as crimson cubic crystals. A specimen of 0.4 × 0.2 × 0.2 mm was used for unit cell and intensity measurements, which were carried out on a Philips PW 1100 diffractometer using graphitemonochromated Mo-K_α radiation ($\lambda = 0.71069$ Å). *Crystal data*: Formula: $C_{53}H_{47}N_2ClP_2Ru \cdot \frac{1}{2}C_6H_5CH_3$, $M = 954.49$, monoclinic, $a = 20.943(4)$, $b = 18.659(3)$, $c = 12.986(2)$ Å, $\beta = 93.83(2)°$, $V = 5063(2)$ Å^3, space group $P2_1/n$ (non-standard No. 14), $Z = 4$, $D_c = 1.252$ g cm^{-3}, $F(000) = 1972$, μ(Mo-K_α) = 4.5 cm^{-1}.

Unit cell parameters were obtained from least-squares fit of the setting angles of 25 reflections with 2θ values *ca.* 20°. The space group was uniquely determined by the systematic absences ($h0l$: $h + l = 2n + 1$; $0k0$: $k = 2n + 1$).

Intensity data were measured using a $\theta:2\theta$ scan mode with a constant scan speed of 0.5°/sec and scan width of 0.8°. All reflections up to $\theta = 25°$ in one quadrant ($-24 \le h \le 24$, $0 \le k \le 22$, $0 \le l \le 15$) were recorded. Three standard reflections (-3 -3 0, 5 0 1 and 1 -4 -2), which were monitored every 5 h during data collection, showed no significant variation in their intensities. A total of 4514 unique reflections ($R_{int} = 0.0389$) was collected, of which 4095 with $I > 3\sigma(I)$ were used in the structure analysis. The data were scaled using the check reflections and corrected by Lorentz and polarization effects; no absorption correction was applied.

Solution and refinement

The structure was solved by Patterson and Fourier methods and refined by blocked-matrix least-squares. Hydrogen atoms were placed at calculated positions using a riding atom model (C–H = 0.96 Å; $U_{iso} = 1.2$ U_{eq} of the parent atom). At this stage ($R = 0.059$) the Fourier difference map showed a cloud of peaks (0.8–1.0 e Å^{-3}) located out of the range of bonding distances from the complex molecule. This feature was described as a disordered solvent molecule (toluene) occupying two sites (labelled *s* and *t*). It was refined with some constraints [regular hexagons, C–C = 1.395 Å; no constraints for methyl (C(7s); no satisfactory position for C(7t) could be found], a common isotropic temperature factor for all atoms in each site, and complementary occupancy factor, which refined to a final value of $x = 0.363(3)$ for *s* and $0.5 - x$ for *t* (both sites are close to an inversion centre and, therefore, the centrosymmetrically-related positions are mutually excluded).

During the last cycles of refinement a weighting scheme was applied such that $w = 0.7385/[\sigma^2(F) + 0.001972\ F^2]$. For the last cycle $R = 0.0485$, $R_w = 0.0631$ and $S = 0.96$ for 550 variables; the largest Δ/σ for any parameter was 0.027 and the average value was 0.003. In the final Fourier difference map the residual electron density was within the range -0.30 to 0.49 eÅ^{-3}.

Calculations were made using SHELX-76 [14] and XANADU [15] programs while for the drawings the PLUTO [16] program was used. Complex neutral-atom scattering factors [17] were employed.

Supplementary material available. Tables of anisotropic temperature factors for the non-hydrogen atoms, positional and isotropic thermal parameters for the hydrogen atoms, bond lengths and angles within the phenyl rings and observed and calculated structure factors are available from the authors.

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