Carbene Complexes. Part 14.[1] The Synthesis and Steric and Electronic Effects in Electron-rich Olefin-derived Bis-, Tris-, and Tetrakis-(carbene)-ruthenium(II) and a Tetrakis(carbene)osmium(II) Complex; the Crystal and Molecular Structure of *trans*-Dichlorotetrakis(1,3-diethylimidazolidin-2-ylidene)ruthenium(II) †

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The reaction of $[\mathrm{RuCl_2(PPh_3)_3}]$ with $[\overline{\mathrm{CN(R)CH_2CH_2N}}\mathrm{R}]_2(\mathrm{L^R}_2$; R = Me, Et, or $\mathrm{CH_2Ph}$) affords *trans*-$[\mathrm{RuCl_2(L^R)_4}]$ [R = Me (1), Et (2), or $\mathrm{CH_2Ph}$ (3)]. The instability and reactivity of these complexes increases in the order (3) < (1) < (2). Thus in $\mathrm{CH_2Cl_2}$ complex (2) readily loses $\mathrm{L^{Et}}$ to give $[\mathrm{RuCl_2(L^{Et})_3}]$ (13), but (1) requires prolonged heating for similar $\mathrm{L^{Me}}$ loss, affording $[\mathrm{RuCl_2(L^{Me})_3}]$ (12), and (3) does not react. Complex (1) (*i*) loses $\mathrm{L^{Me}}$ on reaction with NaI to form $[\mathrm{RuI_2(L^{Me})_3}]$ (4), (*ii*) reacts with excess of $\mathrm{P(OMe)_3}$ to give $[\mathrm{RuCl(L^{Me})_2\{P(OMe)_3\}_3]Cl}$ (14), and (*iii*) reacts with $\mathrm{C_5H_5N}$ in the presence of CO to give *trans*-$[\mathrm{Ru(CO)Cl(L^{Me})_2(NC_5H_5)_2]Cl}$ (16). Carbon monoxide displaces $\mathrm{Cl^-}$ from complex (1) to give *trans*-$[\mathrm{Ru(CO)Cl(L^{Me})_4]Cl}$ (9), but (2) preferentially eliminates $\mathrm{L^{Et}}$, forming *trans*-$[\mathrm{Ru(CO)Cl_2(L^{Et})_3}]$ (7) which isomerises in $\mathrm{CHCl_3}$ or $\mathrm{CH_2Cl_2}$ to the *cis* isomer (8), and the benzyl derivative (3) does not react. With $\mathrm{PF_3}$, complex (1) forms *trans*-$[\mathrm{RuCl(L^{Me})_4(PF_3)]Cl}$ (10) which exhibits severe steric crowding and restricted rotation of the carbene ligands, as is also shown for the tris- or tetrakis-(carbene)ruthenium(II) complexes derived from $\mathrm{L^{Et}}$ or $\mathrm{L^{CH_2Ph}}$ ligands, by analysis of their ^{1}H and ^{13}C n.m.r. spectra. The complex *mer*-$[\mathrm{OsCl_3(PBu^n{}_2Ph)_3}]$ and the olefin $\mathrm{L^{Me}{}_2}$ give *trans*-$[\mathrm{OsCl_2(L^{Me})_4}]$. An *X*-ray crystal structure determination of the title complex (as its $0.5\mathrm{OBu^n{}_2}$ solvate) has been refined to *R* 0.055 (*R'* 0.087) for 2 641 independent reflections measured with Mo-K_α radiation: the molecule has nearly D_4 symmetry, with regular octahedral co-ordination about the metal, *trans*-chlorine atoms, and the four carbene ligands in a propeller arrangement in the equatorial plane; each almost planar imidazolidine ring is arranged at an angle of *ca.* 45° to the $\mathrm{RuC_4}$ equatorial plane. The Ru–C$_{\mathrm{carb.}}$ distance is 2.105(5) Å and Ru–Cl is 2.459(4) Å. Crystals are monoclinic with a = 19.076(2), b = 13.409(1), c = 14.952(2) Å, β = 102.85(6)°, Z = 4, and space group $P2_1/c$ (No. 14).

SEVERAL examples of carbeneruthenium(II) species have been reported (*e.g.* refs. 2—6). They were synthesised by oxidative addition [equations (1)[3] or (2)[2]], alkylation [equation (3)],[4] or modification of a co-ordinated isocyanide [equation (4)].[5] However, little attention has been given to their chemistry.

Because of the observed similarity of the electron-rich olefin $[:\overline{\mathrm{CN(R)CH_2CH_2N}}\mathrm{R}]_2$ ($\mathrm{L^R}_2$; R = Me, Et, or

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† No reprints available.

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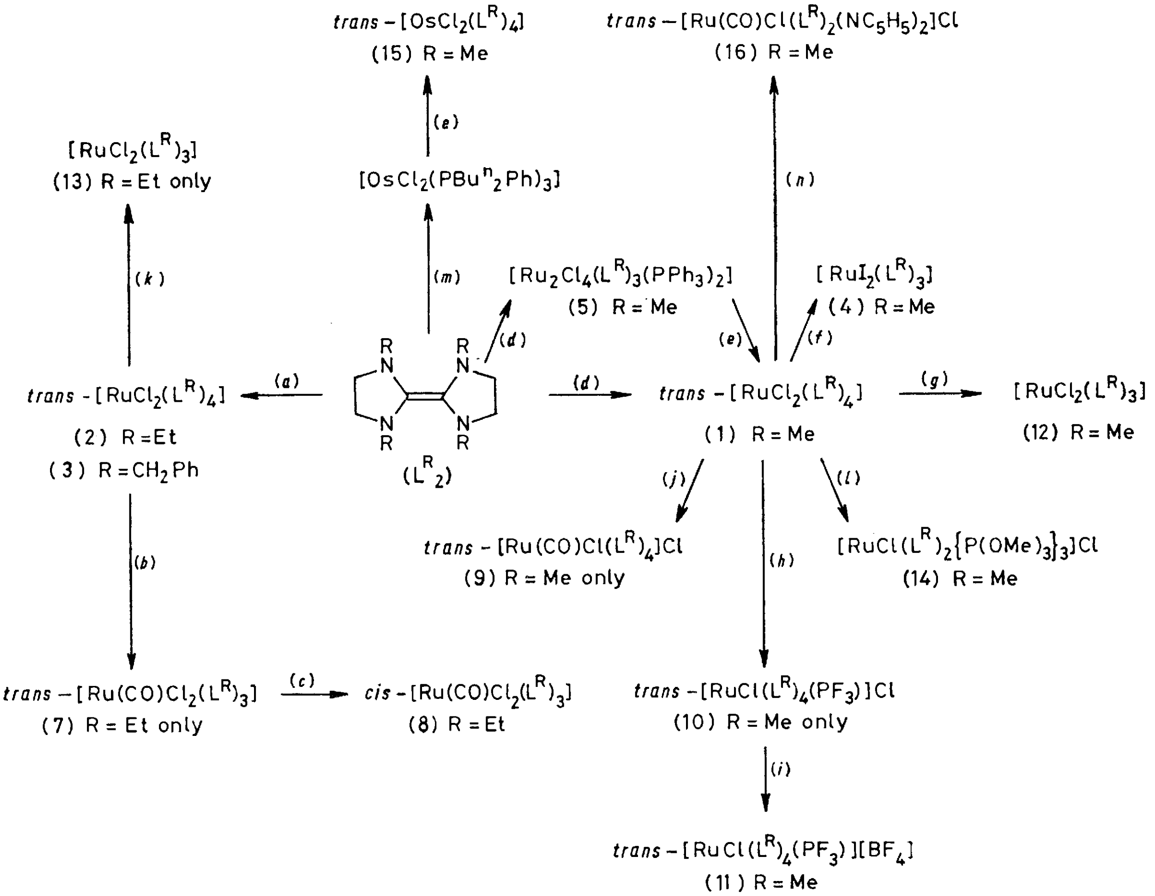
CH_2Ph) to PPh_3 in its complex-forming ability,[7,8] usually affording complexes containing one or more carbene ligands $\dot{\overline{\text{C}}}\overline{\text{N(R)CH}_2\text{CH}_2\text{N}}\text{R}$ (L^R), and its ability to displace PPh_3 from the metal co-ordination sphere, we now report on the interaction of L^R_2 and $[RuCl_2(PPh_3)_3]$.



SCHEME Synthesis and reactions of oligocarbeneruthenium(II) complexes and an osmium(II) complex. (*a*) $[RuCl_2(PPh_3)_3]$, $C_6H_{11}Me$, 100 °C; (*b*) CO, $C_6H_{11}Me$, or toluene, 100 °C; (*c*) $CHCl_3$, 25 °C; (*d*) $[RuCl_2(PPh_3)_3]$, xylene, 130—140 °C; (*e*) L^{Me}_2, xylene, 130—140 °C; (*f*) NaI, acetone, 25 °C; (*g*) CH_2Cl_2, sealed tube, 60—80 °C; (*h*) PF_3, $CHCl_3$, 50—55 °C; (*i*) $Na[BF_4]$, acetone, 25 °C; (*j*) CO, $CHCl_3$, 50—55 °C, or toluene, 110 °C; (*k*) CH_2Cl_2, 25 °C; (*l*) $P(OMe)_3$, $CHCl_3$, 50—55 °C; (*m*) $[OsCl_3(PBu^n_2Ph)_3]$, xylene, 25 °C; (*n*) C_5H_5N, CO, 60 °C, 6 h

$$[Ru(\eta\text{-}C_5H_5)(CO)_2]^- + ClCH_2CH_2CH_2COCl \longrightarrow [Ru(\eta\text{-}C_5H_5)(CO)_2\{\overline{C(O)CH_2CH_2CH_2}\}]Cl \quad (1)$$

$$[Ru(CO)_3(PPh_3)_2] + [NMe_2(CHCl)]Cl \longrightarrow [Ru\{CH(NMe_2)\}(CO)Cl_2(PPh_3)_2] \quad (2)$$

The synthesis and chemistry of the resulting oligocarbeneruthenium(II) complexes is summarised in the Scheme. Data for the characterised new complexes are given in Table 1. A preliminary publication has appeared.[9]

RESULTS AND DISCUSSION

The lability of the phosphine ligands in $[RuCl_2(PPh_3)_3]$ is well known.[10,11] The versatility and reactivity of L^R_2 is now clearly demonstrated by the ease with which the neutral tetrakis(carbene)ruthenium(II) complexes *trans*-$[RuCl_2(L^R)_4]$ [R = Me (1), Et (2), or CH_2Ph (3)] were formed. Generally, stable complexes containing three or more carbenoid ligands are mono- or di-cationic (*e.g.* refs. 5 and 12—14), and often contain

$$[Ru(\eta\text{-}C_5H_5)(CO)\{C(O)Me\}\{P(C_6H_{11})_3\}] + [OEt_3][BF_4] \longrightarrow [Ru(\eta\text{-}C_5H_5)(CO)\text{-}\{C(OEt)Me\}\{P(C_6H_{11})_3\}][BF_4] \quad (3)$$

$$[Ru(CNMe)_6]^{2+} + 2NH_2Me \longrightarrow [Ru\{C(NHMe)_2\}_2(CNMe)_4]^{2+} \quad (4)$$

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good π-acceptor ligands [2,15] in order to relieve build-up of excessive electron density at the metal. Presumably for complexes (1)—(3) the strongly electronegative chloride ligands assist stabilisation. Additional evidence for this is provided by reaction of (1) with NaI; displacement of Cl^- by the less electronegative iodide was accompanied by elimination of one carbene ligand, forming $[RuI_2(L^{Me})_3]$ (4).

TABLE 1

Oligocarbene-ruthenium(II) and -osmium(II) complexes and their characterisation [a]

	Complex	Yield (%)	M.p. (θ_c/°C)	Colour	Analysis (%) [b] C	H	N
(1)	*trans*-$[RuCl_2(L^{Me})_4]$ [c]	90	236 (decomp.)	Yellow	43.1 (42.5)	7.1 (7.1)	19.4 (19.8)
(2)	*trans*-$[RuCl_2(L^{Et})_4]$	50	149 (decomp.)	Orange-yellow	49.8 (49.7)	8.4 (8.3)	16.3 (16.5)
(3)	*trans*-$[RuCl_2(L^{CH_2Ph})_4]$	60	168	Yellow	69.6 (69.6)	6.4 (6.2)	9.3 (9.5)
(4)	$[RuI_2(L^{Me})_3]$	85	202	Red-brown	28.1 (27.7)	4.7 (4.6)	12.9 (12.9)
(5)	$[Ru_2Cl_4(L^{Me})_3(PPh_3)_2]$ [d]	60	235—237	Orange-brown	52.6 (52.6)	5.2 (5.2)	7.2 (7.2)
(6)	*cis*-$[Ru(CO)_2Cl_2(L^{Me})_2]$	20	279	White	33.9 (34.0)	4.9 (4.8)	12.9 (13.2)
(7)	*trans*-$[Ru(CO)Cl_2(L^{Et})_3]$	95	175	Pale yellow	45.8 (45.7)	7.3 (7.3)	14.6 (14.5)
(8)	*cis*-$[Ru(CO)Cl_2(L^{Et})_3]$	75	*e*	White	42.4 (42.3)	6.7 (6.7)	13.2 (13.2)
(9)	*trans*-$[Ru(CO)Cl(L^{Me})_4]Cl$	80	278 (decomp.)	White	42.0 (42.5)	6.7 (6.8)	18.7 (18.9)
(10)	*trans*-$[RuCl(L^{Me})_4(PF_3)]Cl$	60	130	Pink	33.1 (32.7)	5.4 (5.7)	14.5 (14.5) [g]
(11)	*trans*-$[RuCl(L^{Me})_4(PF_3)][BF_4]$	90	214	Pink	34.1 (34.1)	5.8 (5.7)	15.7 (15.9)
(12)	$[RuCl_2(L^{Me})_3]$	100 [h]	*e*	Red-brown		*i*	
(13)	$[RuCl_2(L^{Et})_3]$	100 [h]	*e*	Red-brown		*i*	
(14)	$[RuCl(L^{Me})_2\{P(OMe)_3\}]Cl$	60	*e*	White	30.7 (30.8)	6.5 (6.4)	7.7 (7.6)
(15)	*trans*-$[OsCl_2(L^{Me})_4]$	95	256 (decomp.)	Orange	37.2 (36.8)	6.3 (6.2)	17.1 (17.1)
(16)	*trans*-$[Ru(CO)Cl(L^{Me})_2(NC_5H_5)_2]Cl$	40	318	White	45.0 (45.5)	5.6 (5.4)	15.2 (15.2)

[a] $L^R = \dot{\overline{C}N(R)CH_2CH_2\overline{N}}R$ (R = Me, Et, or CH_2Ph). [b] Calculated values are given in parentheses. [c] Cl, 12.5 (12.6%). [d] Cl, 12.3 (12.2%). [e] Not obtained. [f] Calculated for $0.5CHCl_3$ adduct. [g] Calculated for $CHCl_3$ adduct. [h] Yield based on ^1H n.m.r. spectrum. [i] Characterised by ^1H and ^{13}C n.m.r. spectroscopy only.

The reactions of (1)—(3) with the small good π-acceptor ligands CO or PF_3 are of interest. Unexpected differences were found in reactivity, dependent on the carbene *N*-alkyl substituent (Me, Et, or CH_2Ph). Unlike $[RuCl_2(PPh_3)_n]$ ($n = 3$ or 4) which on reaction with CO only afforded bis(phosphine) derivatives [16] {*i.e.* various isomers of $[Ru(CO)_2Cl_2(PPh_3)_2]$, probably because of the well known ease of dissociation of PPh_3 [10,11,16-18]}, complex (2) lost only one L^{Et} ligand forming pale yellow *trans*-$[Ru(CO)Cl_2(L^{Et})_3]$ (7). This was resistant to further substitution. However, in halogenated solvents (*e.g.* $CHCl_3$) conversion into the *cis* isomer (8) occurred, as noted for tertiary alkylphosphine analogous; [19] furthermore, (2) resembles $[RuCl_2(PEtPh_2)_4]$ [10] in much of its chemistry. Complex (1) behaved quite differently, Cl^- surprisingly being displaced rather than L^{Me}, in forming *trans*-$[Ru(CO)Cl(L^{Me})_4]Cl$ (9). A small quantity of *cis*-$[Ru(CO)_2Cl_2(L^{Me})_2]$ (8) was also isolated, but no tris(carbene) complex. Similarly with PF_3, *trans*-$[RuCl(L^{Me})_4(PF_3)]Cl$ (10) was formed, a species without analogues in tertiary phosphineruthenium(II) chemistry.[20] On heating (1) with a large excess of $P(OMe)_3$, $[RuCl(L^{Me})_2\{P(OMe)_3\}_3]Cl$ was formed; heating in pyridine in the presence of CO also resulted in displacement of two L^{Me} fragments forming the salt *trans*-$[Ru(CO)Cl(L^{Me})_2(NC_5H_5)_2]Cl$ (16). These observations suggest the possibility that, under pressure, reactions of (1), (2), or (3) with CO or PF_3 might provide further L^R displacement. The *N*-benzyl-substituted electron-rich olefin, $L^{CH_2Ph}{}_2$, has a reactivity comparable to $L^{Me}{}_2$ or $L^{Et}{}_2$; [7,15] but when L^{CH_2Ph} is attached to a metal this carbene fragment serves to reduce reactivity at the metal in solution; thus, (3) did not react with CO, even in boiling $CHCl_3$, nor was a carbene fragment displaced. These quite different modes of behaviour of complexes (1)—(3) are attributed to steric rather than electronic effects. Previously published comparative data on L^R ligands concerning

$$[M(CO)_2I_2(L^R)_2] \underset{-CO}{\overset{+CO}{\rightleftharpoons}} [M(CO)_3I_2(L^R)_2] \qquad (5)$$

$$\begin{aligned}&\textit{trans}\text{-}[Rh(CO)Cl(L^R)_2] \xrightarrow{PPh_3} \\ &\qquad \textit{trans}\text{-}[Rh(CO)(L^R)_2(PPh_3)]Cl \longrightarrow \\ &\qquad\qquad \textit{cis}\text{-}[Rh(CO)(L^R)_2(PPh_3)]Cl \qquad (6)\end{aligned}$$

their σ-donor–π-acceptor ratio, ^{13}C n.m.r. and i.r. spectroscopic data, and reactivity in sterically demanding situations show them to be electronically similar.[2,7,15,21] Differences in reactivity and reaction rate [Me > Et in the forward reactions (5) or (6); Et ≫ Me in the reverse reaction (5)] between complexes

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containing L^{Me} and L^{Et} ligands have been noted before, as in equations (5) (M = Mo or W) [8] or (6).[22,23]

TABLE 2

Hydrogen-1 n.m.r. spectra of oligocarbeneruthenium complexes [a]

Complex	Solvent	NCH_2CH_2N	NCH_3	NCH_2–( ) (H_A and H_B)	N–( )–CH_3
(1) [b]	CD_2Cl_2	6.52	7.0		
(2) [c,d]	C_6D_6	6.78 (m) [e,f]		[4.91 (d), 7.3 (d)] [c]	8.6 (t)
(3)	C_6D_6	6.78 (m) [f,g]		[2.8 (d), 6.23 (d)] [h]	
(4)	CH_2Cl_2	6.58	7.05		
(5)	*i*				
(6)	$CDCl_3$	6.55	6.70		
(7)	C_6D_6	6.70 (m),[f,j] 6.97 (m) [f,k]		{[4.91 (d), 5.62 (d)] [j] [5.21 (d), 7.03 (d)] [k] [5.52 (d), 6.96 (d)] [k]} [l]	8.82 (t),[j] 8.90 (t) [k]
(8)	$CDCl_3$	6.5 (br)		6.0—7.0 (m)	8.80 (t)
(9) [m]	$CDCl_3$	6.4 (br, s)	7.02, 6.85		
(10) [m]	$CDCl_3$	6.32 (br, s)	7.01 (q),[n] 6.78		
(11)	$CDCl_3$	6.32 (br, s)	7.04 (q),[n] 6.80		
(12) [o]	CD_2Cl_2	6.50	6.95		
(13) [p]	CD_2Cl_2	6.50		6.52 (m)	8.82 (t)
(14)	$CDCl_3$	6.25 (br, s), 6.83 (br, s)	{6.5, 6.6 7.1, 7.2}		
(15) [q]					
(16)	$CDCl_3$	6.30 (br, s)	7.50, 7.35		

[a] All the values quoted are in τ relative to $SiMe_4$ at τ 10, or to the corrected solvent resonance: solutions of all the air-sensitive complexes were prepared in n.m.r. tubes sealed *in vacuo*; all the resonances were singlets unless stated in parentheses. d = doublet, t = triplet, m = multiplet, q = quartet, and br = broad. [b] Spectrum obtained after heating in sealed n.m.r. tube (40 °C), 20 h. [c] N–CH_2–( ) resonances observed as a 16-peak multiplet (ABX_3): identified and assigned by ^1H irradiation procedures. Data quoted for irradiation at the X_3 protons. [d] Spectrum obtained *via* Fourier-transform technique. [e] Observed as a singlet in $(CD_3)_2CO$ or CD_2Cl_2 solution: rapid decomposition occurs in the latter solvent. [f] AA′BB′ multiplet. [g] Observed as a singlet in $(CD_3)_2CO$ (τ 6.3). [h] AB quartet. [i] Spectrum not recorded. [j] One *cis*-L^{Et}. [k] Two mutually *trans* L^{Et}. [l] NCH_2–( ) resonances observed as three sets of 16-peak (ABX_3) multiplets: identified and assigned as in footnote *c*. [m] Spectrum invariant to *ca.* 60 °C: decomposition then occurs [in $CDCl_3$ or $(CD_3)_2SO$]. [n] Through-space $^1H\cdots{}^{19}F$ coupling; $^6J \approx 1.5$ Hz. Quartet collapses to a singlet on ^{19}F irradiation. [o] After heating (1) in a sealed n.m.r. tube (80 °C, 72 h). [p] After heating (2) in a sealed n.m.r. tube (25 °C, 2 h). [q] Too insoluble for spectrum to be obtained.

Hydrogen-1 n.m.r. spectroscopy (see below) indicates considerable steric interaction in both the neutral tetrakis(carbene) complexes (1)—(3) and their reaction products with CO (or PF_3), (7)—(11). It is therefore not surprising that one carbene fragment L^{Et} is readily eliminated to relieve, at least partially, such steric interactions. Presumably, from (1), the smaller methyl groups allow the retention of the four equatorially disposed L^{Me} ligands whilst Cl^- is displaced. Nevertheless, displacement of L^{Me} from complex (1) can be achieved *via* iodide ion to give (4), or by prolonged heating in CH_2Cl_2 to give $[RuCl_2(L^{Me})_3]$ (12). It seems, therefore, that thermal loss of Cl^- or L^R are competing processes and are dependent to varying extents on (*i*) the size and electronegativity (or π-acceptor capacity) of the incoming ligand, (*ii*) the bulk effect of ' R ' in destabilising the square-planar MC_4 arrangement of four carbene ligands L^R, and (*iii*) the additional stabilisation afforded by formation of cationic carbene complexes.[9,12]

The reason for the much increased stability of (3) to L^R or Cl^- loss compared with L^{Me} or L^{Et} analogues is attributed to the ability of the planar Ph rings to orientate themselves so as to (*i*) decrease non-bonding steric interactions and (*ii*) shield the metal centre from attack even by a small ligand such as CO or PF_3. The probable consequence of decreased steric interaction is to provide an increased carbene-ligand planarity, allowing more substantial p_π–p_π ($\overset{..}{N}\overset{\downarrow}{-}C_{carb.}$) overlap with an increase in $\nu(CN_2)$ and less distortion from local MC_4 D_{4h} symmetry. In practice, an increase in $\nu(CN_2)$ of *ca.* 15 and 30 cm^{-1} was observed for (3) compared with the methyl or ethyl analogues (1) or (2). Furthermore, only the ν_{asym} $(RuCl_2)$ mode was observed in (3), whereas both sym and asym modes were seen in (1) and (2). In complexes such as *trans*-$[PtCl_2(L^R)(PEt_3)]$ [24] and *cis*-$[Mo(CO)_4(L^R)_2]$,[15] $\nu(CN_2)$ is similar whether R = CH_2Ph or Et. It is also noteworthy that $\Delta G^\ddagger$ values for the barrier to Mo–$C_{carb.}$ rotation in *cis*-$[Mo(CO)_4(L^R)_2]$ are at a minimum for R = CH_2Ph in the series R = CH_2Ph < Me < Et.[15] Participation of an electronic effect cannot, of course, be ruled out. If the σ-donor strength of L^{CH_2Ph} were only slightly less than that of L^{Me} or L^{Et} this would result in the metal atom being less electron-rich for L^{CH_2Ph} complexes, and displacement therefrom of Cl^- or L^{CH_2Ph} would be less obligatory; however, the $^{13}C_{carb.}$ chemical shifts do not support this. Nevertheless, there is increasing evidence that cationic metal complexes are often ' stabilised ' by L^{Me} or L^{Et} but not by L^{CH_2Ph} ligands.

The synthetic route to the neutral tetrakis(carbene)-osmium(II) complex *trans*-$[OsCl_2(L^{Me})_4]$ (15) illustrates an additional facet of the chemistry of electron-rich olefins, *viz.* as reducing agents; thus *mer*-$[OsCl_3(PBu^n{}_2Ph)_3]$ is initially reduced by $L^{Me}{}_2$, giving a green solution

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containing Os^{II}. Reaction with an excess of olefin then effects PBu^n_2Ph substitution affording (15). The chemistry of this species has not yet been further examined. It is possible, however, that tris(carbene)-osmium(III) complexes (*i.e.* paramagnetic oligocarbene complexes) may be obtainable by dihalogen oxidation of (15).

TABLE 3

Infrared spectroscopic data of oligocarbene-ruthenium(II) and -osmium(II) complexes

Complex	$\nu(CO)$	$\nu(CN_2)$ [a]	$\nu(Ru-Cl)$ [a]
(1)		1 485m	318ms, 260m
(2)		1 470m	316ms, 262m
(3)		1 500m	314ms
(4)		1 500m	*b*
(5)		1 495m	*b*
(6)	2 039s, 1 969vs [c]	1 525ms	315m, 280w
(7)	1 938s [d]	1 490m	322ms
(8)	1 920s [d]	1 492m	*b*
(9)	1 923s [c]	1 510ms	292w
(10)		1 504ms	*b*
(11)		1 506ms	*b*
(14)		1 503m	310w
(15)		1 485m	295ms, 240m
(16)	1 917s [a]	1 505ms	292w

[a] Dilute Nujol mull. [b] $\nu(Ru-Cl)$ not assigned. [c] In CH_2Cl_2 solution. [d] In toluene solution.

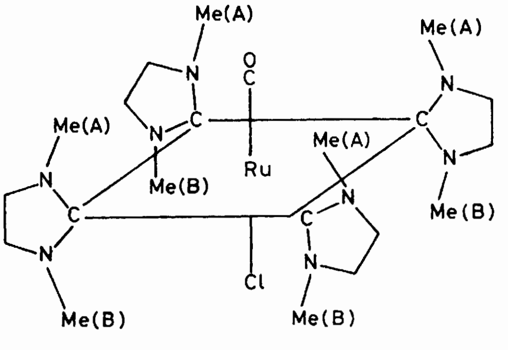
TABLE 4

Carbon-13 n.m.r. spectroscopic data of oligocarbene-ruthenium complexes [a]

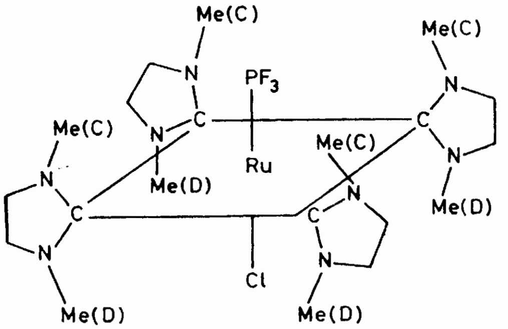
Complex	Solvent	$C_{carb.}$	CO	NCH_2CH_2N	NCH_3	$N-CH_2-()$
(2)	C_6D_6	227.8 [b]		47.7		45.5
(3)	CD_2Cl_2	228.1		48.9		56.2
(4) [c]	CD_2Cl_2	216.3		52.2	38.6	
(7)	C_6D_6	218.5,[d] 212.7 [e]	207.6	47.2 [d,e]		46.3,[d] 45.5 [e]
(9)	$CDCl_3$	208.1	203.9	51.8, 51.0	38.4, 37.8	
(10)	$CDCl_3$	208.1 [f]		52.7, 51.7	39.4	
(12) [g]	CD_2Cl_2	216.3		51.5	37.2	
(13) [h]	CD_2Cl_2	216.5		47.4		44.7

[a] All the complexes were run as saturated solutions in 8 or 10-mm tubes at 25 °C, using a 1-s repetition rate and 6 250-Hz sweep width. The resonances are quoted in p.p.m. relative to $SiMe_4$ (0 p.p m.). [b] In CD_2Cl_2, $\delta(C_{carb.})$ 226.3 p.p.m.: rapid decomposition occurs (*ca.* 1 h) in this solvent. [c] On cooling (−95 °C) there was no change in the $C_{carb.}$ resonance: ring CH_2 and $N-CH_3$ signals broadened slightly. [d] Signals due to one *cis*-L^{Et} group. [e] Signals due to two mutually *trans*-L^{Et} groups. [f] $C_{carb.}$ doublet [$^2J(^{13}C-^{31}P)$ 16.8 Hz]. [g] *trans*-$[RuCl_2(L^{Me})_4]$ after 72 h at 80 °C in a sealed ^{13}C n.m.r. tube; signals assignable to $[X-L^{Me}]^+$ species were also present. [h] *trans*-$[RuCl_2(L^{Et})_4]$ after 48 h at 25 °C in a sealed ^{13}C n.m.r. tube: signals assignable to $[X-L^{Et}]^+$ species were also present.

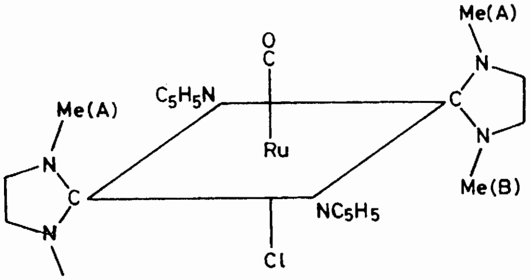
Spectroscopic Properties.—Hydrogen-1 n.m.r., i.r., and ^{13}C n.m.r. spectroscopic data are shown in Tables 2, 3, and 4, respectively. Of considerable interest are the complicated ^1H n.m.r. spectra shown by many of the oligocarbeneruthenium(II) complexes, from which their stereochemistry may be deduced. The $N-CH_2-X$ (X = Me or Ph) signals of (2) or (3) are seen as an AB quartet pattern [in (2), after irradiation of the CH_3 protons] with very different chemical shifts for the A and B protons. This is because of restricted rotation not only about $M-C_{carb.}$[25] but also N–R.



(17)



(18)



(19)

For complex (2), chemical shift values of τ 4.91 and 7.30 (Δ τ 2.39), and for (3) of τ 2.8 and 6.23 (Δ τ 3.43) indicate a considerable difference in the shielding of the two protons, reflecting also differing H · · · Cl contacts; this is borne out by the cystallographic study. Although steric congestion, resulting in van der Waals deshielding, may be a factor, this does not account for the observed shielding of one proton and the effect must be predominantly anisotropic in nature. Whereas the complex $N-CH_2R$ resonances were unchanged in a variety of solvents [CD_2Cl_2, C_6D_6, or $(CD_3)_2CO$], the ring methylene (NCH_2CH_2N) signals were solvent dependent; thus, in C_6D_6 a multiplet (AA′BB′) was observed, whilst in CD_2Cl_2 or $(CD_3)_2CO$ only a sharp singlet was seen. Similar observations have been made on some rhodium(I)

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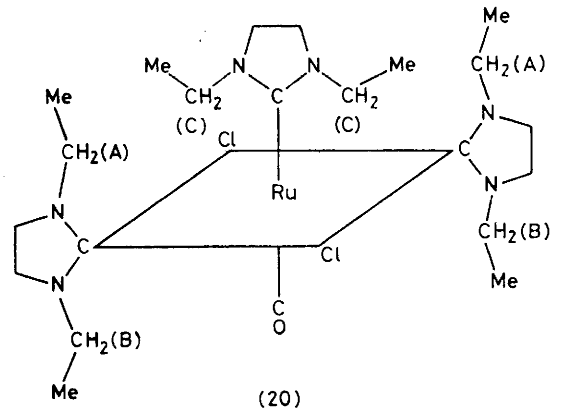
[25] M. J. Doyle and M. F. Lappert, *J.C.S. Chem. Comm.*, 1974, 679.

complexes containing the L^{Et} ligand.[23,25] The cations *trans*-$[Ru(CO)Cl(L^{Me})_4]^+$ (17), *trans*-$[RuCl(L^{Me})_4(PF_3)]^+$ (18), and *trans*-$[Ru(CO)Cl(L^{Me})_2(NC_5H_5)_2]^+$ (19) exhibited interesting room-temperature spectra, indicating considerable steric constraints within the complexes. The importance of steric effects in hindering rotation around $M-C_{carb.}$ bonds has also been shown for some platinum(II) complexes, such as *trans*-$[Pt\{C(NHR)(NR_2)\}Cl(PMe_2Ph)_2][ClO_4]$.[26] Observation of the $P-CH_3$ resonances was used as the spectroscopic probe.[26-28] Thus (9) and (16) each showed two sharp singlets corresponding to the Me groups A and B, differing because of restricted rotation around the $Ru-C_{carb.}$ bond; *i.e.* the carbene ligands are ' fixed ' with respect to the equatorial plane, one Me group ' up ' (A) and one ' down ' (B), but in (10) or (11) one sharp singlet and one quartet ($J \approx 1.5$ Hz) are seen for the methyl groups C and D in (18). The observation of a quartet is attributed to a ' through-space ' interaction (*e.g.* see refs. 29 and 30) of the three equivalent fluorine atoms of the PF_3 ligand with the protons of four equivalent methyl groups (C); this was confirmed by ^{19}F decoupling when the quartet collapsed to a sharp singlet. Heating complexes (9), (10), or (11) to *ca.* 60 °C caused no change in the spectra; at higher temperatures decomposition occurred.

A detailed analysis of the complicated spectrum of (7) (48 resonances for the $N-CH_2-CH_3$ protons) is consistent with the stereochemistry shown in (20). Because of the high barrier to $Ru-C_{carb.}$ rotation, the Et groups of the mutually *trans* L^{Et} ligands are magnetically inequivalent (one is *syn* to L^{Et}, the other to CO) and this is most clearly reflected in the observation of two different sets of ABX_3 signals for the methylene protons [A and B in (20)]. The ethyl CH_2 groups of L^{Et} *trans* to CO (marked C) are magnetically equivalent (both are *syn* and *anti* to L^{Et} and Cl groups) and give rise to only one set (the third in total) of ABX_3 Et signals. This equivalence of the two ethyl groups of the unique L^{Et} ligand confirms the stereochemistry of (20); for either of the two isomeric structures, magnetic inequivalence would result. Irradiation of the Me proton signals caused collapse of the triplet of sixteen-peak ABX_3 multiplets to three overlapping sets of AB quartets, parts of which were partially obscured by the ring methylene-proton resonances. Assignment was made by selective irradiations at various frequencies of the original AB part of the ABX_3 multiplets and by INDOR for the obscured signals.



(20)

That the barrier to rotation is primarily associated with intramolecular non-bonding *cis* interactions of the carbene *N*–R substituents and not because of any significant double-bond character in the $Ru-C_{carb.}$ bond is indicated by *X*-ray crystallography [9,31] and i.r. spectra. We have previously found no evidence for particularly short $M-C_{carb.}$ bonds in complexes containing L^R ligands,[9,15,32,33,*] including *trans*-$[RuCl_2(L^{Et})_4]$.[9] Infrared data on ν(CO) stretching frequencies (Table 3) also indicate L^R to have negligible π-acceptor behaviour because of the low [compared with ER_3 (E = P or As) analogues] values of ν(CO) observed. For example, (7) has ν(CO) at 1 910 cm^{-1}, which may be compared with *trans*-$[Ru(AsPh_3)_3(CO)Cl_2]$ [16] at 1 961 cm^{-1}, or *cis*-$[Rh\{CH[NH(C_6H_4Me\text{-}p)]\}(CO)Cl_2(PPh_3)_2]$ [6] at 1 960 cm^{-1}; likewise *cis*-$[Ru(CO)_2Cl_2(L^{Me})_2]$ has ν(CO) at 2 039 and 1 969 cm^{-1}, to be compared with 2 064 and 2 001 cm^{-1} for *cis*-$[Ru(CO)_2Cl_2(PPh_3)_2]$.[35]

Various complexes have been examined by ^{13}C n.m.r. spectroscopy but the sparingly soluble nature of (1) prevented its spectrum being obtained. However, heating this complex in a sealed n.m.r. tube gave a deep red-brown solution, with a spectrum almost identical to that of (4); it is therefore likely that the species observed was (12). Cooling complex (4) to −96 °C caused no significant change in the ^{13}C n.m.r. spectrum with $C_{carb.}$ remaining as a sharp singlet, and the $N-CH_3$ and ring methylene-carbon atom signals broadening slightly. In contrast, square-pyramidal $[RuCl_2(PPh_3)_3]$ showed [10] two ^{31}P signals of relative intensity 2 : 1. These observations suggest that the apparently five-co-ordinate complexes $[Ru(L^R)_3X_2]$, (4), (12), or (13) may be formulated as (21): R = Me, X = I (4); R = Me (12) or Et (13), X = Cl. This type of structure is well established

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[*] Some evidence has been found for a Ru^{II} *ortho*-metallated ruthenium(II) complex containing a *p*-tolyl group, in which the plane of the carbene ligand is fixed in the equatorial plane of the complex because of the constraint applied *via* the *ortho*-metallation of the *N*-aryl substituent.[34]

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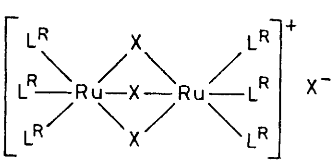
[33] Lj. Manojlović-Muir and K. W. Muir, *J.C.S. Dalton*, 1974, 2427.

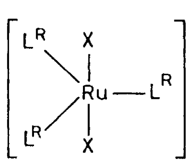
[34] P. B. Hitchcock, M. F. Lappert, and P. L. Pye, *J.C.S. Chem. Comm.*, 1977, 196.

[35] J. J. Levison and S. D. Robinson, *J. Chem. Soc. (A)*, 1970, 2947.

in ruthenium(II) tertiary phosphine complexes[10,36-38] whose formation is promoted by use of polar solvents, such as CH_2Cl_2 (see, for example, refs. 10, 39, and 40). However, six-co-ordinate Ru^{II}, as in (21), does not clearly account for the extremely air-sensitive nature of the complexes or the red-brown colour of the solutions which support a five-co-ordinate metal environment. By analogy, these complexes might have been expected to be of square-pyramidal rather than trigonal-bipyramidal (t.b.p.) geometry.[18,41,42] However, the latter structure accounts for the observed $C_{carb.}$ equivalence (three equatorial L^R ligands), and is also the observed geometry of $[RuCl(H)(PPh_3)_3]$.[43] The balance of evidence thus favours the t.b.p. stereochemistry (22).



(21)



(22)

There is little difference in the shieldings of $C_{carb.}$ in the neutral *trans*-$[RuCl_2(L^R)_4]$ when R = Et (2) or CH_2Ph (3), and the greatly increased stability of the benzyl complex (3) is not reflected in a $C_{carb.}$ chemical-shift change. The most noticeable trends for the ruthenium(II) carbene complexes (Scheme) is a high-field shift of $C_{carb.}$ on either L^R loss [*e.g.* in complexes (4), (7), (12), or (13)], or cationic complex formation [*e.g.* in (9) or (10)]. The latter observation confirms the view (see, for example, ref. 44) that charge may be significantly delocalised on to the carbene ligands. For *trans*-$[RuCl(L^{Me})_4X]Cl$ [X = CO (9) or PF_3 (10)] the stereochemically rigid environment is further demonstrated by the observation of ^{13}C doublet signals for the inequivalent CH_3 groups and the ring CH_2 carbon atoms; in complex (10) the small value * of $^2J(^{13}C-^{31}P)$, 16.8 Hz, is consistent[2,34,46] with the designated stereochemistry of complex (18) (established by the equivalence of all the four carbene-carbon atoms).

In (7) two distinct $C_{carb.}$ atoms were observed. Surprisingly, the mutually *trans* $C_{carb.}$ atoms are more shielded than those *trans* to CO, in contrast to the cases of $[Rh(CO)(L^{Me})_3]Cl$[23,24] or the *cis–trans* isomer pairs $[M(CO)_4(L^R)_2]$ (M = Mo, R = Me or Et;[15,47] M = W, R = Me[7]).

As expected, values of $\delta(C_{CO})$ are at higher field than $\delta(C_{carb.})$ in the same complex, but lower than for *cis*-$[Ru(CO)_2Cl_2(PR_3)_2]$ ($R_3 = Et_3$, Et_2Bu^t, or Et_2Ph)[46] and for *trans*-$[\mathrm{Ru\{\overline{CN(H)CR{:}CRNH}\}(CO)(NH_3)_4}]^{2+}$; for the latter, the signals at 180 and 200 p.p.m. were not unequivocally assigned to *C*O or *C*$_{carb.}$[31]

TABLE 5

Intramolecular distances (Å) and angles (°)

(*a*) Distances

Ru–Cl(1)	2.455(3)	C(6)–N(1)	1.422(13)
Ru–Cl(2)	2.463(3)	C(9)–N(2)	1.446(13)
Ru–C(1)	2.109(10)	C(12)–N(3)	1.479(13)
Ru–C(2)	2.111(9)	C(15)–N(4)	1.441(13)
Ru–C(3)	2.098(9)	C(18)–N(5)	1.422(12)
Ru–C(4)	2.103(9)	C(21)–N(6)	1.436(13)
C(1)–N(1)	1.349(12)	C(24)–N(7)	1.435(13)
C(1)–N(2)	1.348(12)	C(27)–N(8)	1.476(12)
C(2)–N(3)	1.355(12)	C(7)–C(8)	1.451(16)
C(2)–N(4)	1.337(12)	C(13)–C(14)	1.435(15)
C(3)–N(5)	1.373(12)	C(19)–C(20)	1.483(17)
C(3)–N(6)	1.334(12)	C(25)–C(26)	1.479(18)
C(4)–N(7)	1.351(12)	C(5)–C(6)	1.505(16)
C(4)–N(8)	1.344(12)	C(9)–C(10)	1.530(16)
C(7)–N(1)	1.456(14)	C(11)–C(12)	1.481(16)
C(8)–N(2)	1.476(14)	C(15)–C(16)	1.533(16)
C(13)–N(3)	1.465(14)	C(17)–C(18)	1.501(15)
C(14)–N(4)	1.486(14)	C(21)–C(22)	1.495(17)
C(19)–N(5)	1.432(14)	C(23)–C(24)	1.492(16)
C(20)–N(6)	1.466(14)	C(27)–C(28)	1.548(16)
C(25)–N(7)	1.459(15)	O(1)–C(29)	1.24(4)
C(26)–N(8)	1.492(15)	C(29)–C(30)	1.14(5)

(*b*) Angles

Cl(1)–Ru–Cl(2)	178.6(1)	N(1)–C(7)–C(8)	104.3(10)
C(1)–Ru–C(4)	178.7(4)	N(2)–C(8)–C(7)	102.4(10)
C(2)–Ru–C(3)	179.3(4)	N(3)–C(13)–C(14)	103.5(9)
Cl(1)–Ru–C(1)	91.0(3)	N(4)–C(14)–C(13)	103.9(9)
Cl(1)–Ru–C(2)	91.0(3)	N(5)–C(19)–C(20)	104.0(10)
Cl(1)–Ru–C(3)	89.1(3)	N(6)–C(20)–C(19)	102.9(10)
Cl(1)–Ru–C(4)	89.7(3)	N(7)–C(25)–C(26)	104.4(11)
Cl(2)–Ru–C(1)	89.8(3)	N(8)–C(26)–C(25)	100.6(10)
Cl(2)–Ru–C(2)	90.3(3)	C(1)–N(1)–C(6)	127.5(8)
Cl(2)–Ru–C(3)	89.7(3)	C(1)–N(2)–C(9)	129.5(9)
Cl(2)–Ru–C(4)	89.6(3)	C(2)–N(3)–C(12)	127.0(9)
C(1)–Ru–C(2)	88.6(4)	C(2)–N(4)–C(15)	129.0(9)
C(1)–Ru–C(3)	90.7(4)	C(3)–N(5)–C(18)	128.7(8)
C(4)–Ru–C(2)	90.2(4)	C(3)–N(6)–C(21)	129.4(9)
C(4)–Ru–C(3)	90.5(4)	C(4)–N(7)–C(24)	127.2(9)
Ru–C(1)–N(1)	127.5(7)	C(4)–N(8)–C(27)	127.9(8)
Ru–C(1)–N(2)	126.4(7)	C(6)–N(1)–C(7)	118.2(9)
Ru–C(2)–N(3)	127.2(7)	C(8)–N(2)–C(9)	116.2(9)
Ru–C(2)–N(4)	127.2(7)	C(12)–N(3)–C(13)	118.1(8)
Ru–C(3)–N(5)	126.2(7)	C(14)–N(4)–C(15)	117.6(8)
Ru–C(3)–N(6)	127.2(7)	C(18)–N(5)–C(19)	117.6(9)
Ru–C(4)–N(7)	127.2(7)	C(20)–N(6)–C(21)	116.6(9)
Ru–C(4)–N(8)	126.5(7)	C(24)–N(7)–C(25)	117.8(9)
N(1)–C(1)–N(2)	106.0(8)	C(26)–N(8)–C(27)	116.6(9)
N(3)–C(2)–N(4)	105.6(8)	C(5)–C(6)–N(1)	114.6(10)
N(5)–C(3)–N(6)	106.5(8)	C(10)–C(9)–N(2)	113.2(9)
N(7)–C(4)–N(8)	106.3(8)	C(11)–C(12)–N(3)	112.0(10)
C(1)–N(1)–C(7)	112.5(8)	C(16)–C(15)–N(4)	111.5(9)
C(1)–N(2)–C(8)	112.8(9)	C(17)–C(18)–N(5)	112.7(9)
C(2)–N(3)–C(13)	113.6(9)	C(22)–C(21)–N(6)	112.7(10)
C(2)–N(4)–C(14)	112.8(8)	C(23)–C(24)–N(7)	113.1(10)
C(3)–N(5)–C(19)	112.7(8)	C(28)–C(27)–N(8)	113.4(9)
C(3)–N(6)–C(20)	112.9(8)	C(29)–O(1)–C(29′)	180.0
C(4)–N(7)–C(25)	112.4(9)	O(1)–C(29)–C(30)	166(5)
C(4)–N(8)–C(26)	113.4(9)		

Molecular Structure of Crystalline trans-$[RuCl_2(L^{Et})_4]$ (1).—The molecular conformation and atom-numbering

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* Carbeneruthenium(II) complexes containing L^R *trans* to a tertiary phosphine ligand show $^2J(^{13}C-^{31}P)$ *ca.* 88 Hz.[34,45]

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[45] P. B. Hitchcock, M. F. Lappert, and P. L. Pye, unpublished work.

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[47] M. F. Lappert and P. L. Pye, *Proc. 2nd Internat. Conf. Chem. and Uses of Molybdenum*, Climax, London, 1976, p. 101; *J. Less-Common Metals*, 1977, **54**, 191.

scheme of the ruthenium complex are shown in the ORTEP[48] drawing (Figure 1). The labelling of the hydrogen atoms follows that of the carbon atoms to which they are attached. Bond lengths and angles are listed in Table 5. Calculation of intermolecular distances shows that none are significantly shorter than the sum of the relevant van der Waals radii so that there are discrete molecules of both the complex and solvent. The molecule of the complex is seen to have regular octahedral co-ordination with *trans* chlorine atoms and the four carbene ligands in a propeller arrangement in the equatorial plane. The molecule has nearly D_4 point-group symmetry, not imposed by the space group.

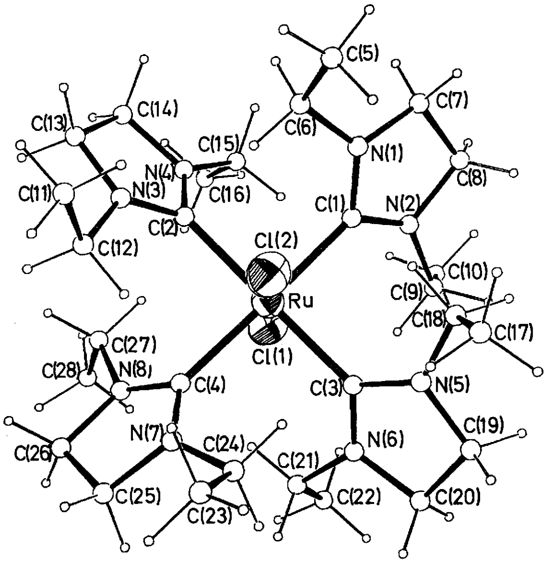

FIGURE 1 ORTEP drawing of *trans*-$[RuCl_2(L^{Et})_4]$

In each of the carbene ligands the imidazolidine ring and the substituent methylene-carbon atoms are essentially coplanar (Table 6), the small amounts of ring puckering being presumably due to steric effects of adjacent ligands, and bond lengths and angles within the carbene ligands show excellent internal consistency. Figure 2 shows these values averaged over both halves of all the four carbene ligands together with the root-mean-square (r.m.s.) deviations in parentheses, and these values are used throughout the discussion. The r.m.s. deviations are of approximately the same magnitude as the individual estimated standard deviations derived from the least-squares refinement. The averaged dimensions are in good agreement with those of similar carbene ligands in the complexes *cis*-$[Mo(CO)_4(L^{Me})_2]$,[15] both *cis*- and *trans*-$[PtCl_2(L^{Ph})(PEt_3)]$,[33] and *trans*-$[RhL^{Me}\{NC(CF_3)_2\}(PPh_3)_2]$.[32] The N–C(carbenoid) distance [1.349(11) Å] indicates a slightly lower multiple bond order for each C–N bond where the carbene carbon is attached to two nitrogens, compared to a carbenoid carbon attached to only one nitrogen where the C–N distance from several structures[14] averages 1.31(1) Å and the estimated bond order is 1.7. The C–C distance [1.463(21) Å] in the imidazolidine ring is significantly shorter than expected for a single bond between two *sp*^{3}-hybridised carbon atoms. The explanation put forward in the case of the platinum complexes[33] was that it is due to the effects of librational shrinkage, but it seems unlikely that in all the five structures containing this ligand only the one bond is observed to be consistently shortened, with no obvious effect on the other bonds. Another possible cause might be that the observed bond length is calculated as between the positions of the two CH_2 carbon atoms averaged over two possible non-planar ring conformations which are not resolved in the structures. However, this again seems highly unlikely, since in the structure of the molybdenum complex[15] these atoms were refined anisotropically and show no signs of this type of disorder. Equally, in the ruthenium complex the difference-Fourier synthesis provides no evidence for disorder between equivalent

TABLE 6

Deviations (Å) of atoms from mean planes. Atoms not used in defining the plane are indicated by an asterisk

Plane (a): C(1) −0.006, C(2) 0.006, C(3) 0.005, C(4) −0.005, Ru* 0.007
Plane (b): C(1) 0.000, N(1) −0.055, C(7) 0.081, C(8) −0.080, N(2) 0.053, C(6)* 0.098, C(9)* −0.071, Ru* −0.002
Plane (c): C(2) −0.003, N(3) −0.028, C(13) 0.044, C(14) −0.045, N(4) 0.032, C(12)* 0.166, C(15)* −0.044, Ru* −0.083
Plane (d): C(3) −0.003, N(5) −0.034, C(19) 0.052, C(20) −0.053, N(6) 0.038, C(18)* 0.095, C(21)* −0.086, Ru* −0.033
Plane (e): C(4) −0.006, N(7) −0.062, C(25) 0.096, C(26) −0.097, N(8) 0.069, C(24)* 0.127, C(27)* −0.064, Ru* −0.085

Angles (°) between planes: (a)–(b) 45, (a)–(c) 49, (a)–(d) 45, (a)–(e) 44, (b)–(c) 60, (b)–(d) 61, (b)–(e) 90, (c)–(d) 94, (c)–(e) 62, and (d)–(e) 61

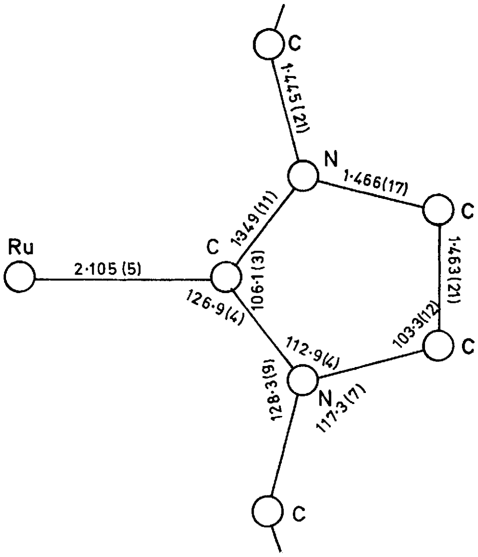

FIGURE 2 Average bond lengths and angles for each of the ruthenium-carbene units

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[48] C. K. Johnson, Oak Ridge National Laboratory, Report ORNL-3794.

non-planar ring structures. We can find no convincing explanation for this phenomenon at present.

The highly crowded nature of the ruthenium complex is obvious from the drawing of the molecule (Figure 1). All the four carbene ligands are arranged at an angle of *ca.* 45° to the co-ordination plane defined by C(1), C(2), C(3), and C(4), as is also seen in the molybdenum complex. Although an all-*trans* arrangement of four carbene ligands is, by analogy with phosphine complexes, presumably disfavoured on the basis of metal–carbene bonding, it is forced on the molecule by steric considerations. Indeed, it seems intuitively unlikely that it would be possible to have a stable octahedral complex with three L^{R} carbene ligands arranged in a *fac* manner, although the unstable *fac*-$[W(CO)_3(L^{Me})_3]$ has been obtained.[7]

The M–C bond length [2.105(5) Å] is similar to that observed in a complex of ruthenium with a 2-(4,5-dimethylimidazolium) ligand[31] *trans* to a carbonyl group [Ru–C(carbene) 2.128 Å]. Both these distances are in the middle of the range of Ru–C bond lengths observed in a variety of complexes with σ-bonded carbon ligands,[31,49] and by comparison, with for instance, the Ru–C bond [2.16(1) Å] to a σ-bonded naphthyl group[50] show no evidence of multiple bonding between the metal and the carbene. Shorter Ru–C bond lengths have been observed in other complexes of carbene and formimidoyl ligands, *e.g.* 2.045 Å in $[Ru\{CH[NMe(C_6H_4Me\text{-}p)]\}(CNC_6H_4Me\text{-}p)(CO)I_2(PPh_3)]$,[51] 1.96 Å in $[Ru\{CH(NC_6H_4Me\text{-}p)\}(CO)(O_2CMe)(PPh_3)]$,[52] and 1.901 Å in an *ortho*-metallated $L^{p\text{-tolyl}}$ complex of ruthenium.[34] The Ru–Cl distances do not differ significantly from their average value [2.459(4) Å], which is slightly longer than that usually found for Ru–Cl (*trans* to Cl), *e.g.* 2.39 Å in $[RuCl_2(PPh_3)_3]$,[41] 2.398(7) Å in $[RuCl_3(NO)(PMePh_2)_2]$,[53] and 2.37 Å in $[Ru_2Cl_5(PBu^n_3)_4]$.[54]

EXPERIMENTAL

General reaction procedures were as previously described.[1,7,15] Analysis were carried out in our microanalytical laboratory by Mr. and Mrs. A. G. Olney, and for air-sensitive compounds by the Butterworth Microanalytical Consultancy Ltd. or A. Bernhardt Microanalytical Laboratory, West Germany. Carbon-13 and ^{19}F n.m.r. spectra were obtained by Mr. T. M. Siverns on a Jeol PFT-100 Fourier-transform spectrometer. Infrared spectra (250—4 000 cm^{-1}) were examined as dilute Nujol mulls between CsI plates or dilute solutions in NaCl cells using a Perkin-Elmer 457 grating spectrophotometer and calibrated *via* a polystyrene film. Hydrogen-1 n.m.r. spectra were routinely recorded in tubes sealed *in vacuo* on Varian Associates HA100 or T60 spectrometers or (for decoupling studies) a Perkin-Elmer R32 90-MHz spectrometer.

The electron-rich olefins were prepared by literature methods,[55] and $[RuCl_2(PPh_3)_3]$ was prepared according to the literature procedure.[16]

trans-$[RuCl_2(L^{Me})_4]$.—To a suspension of dichlorotris(triphenylphosphine)ruthenium(II) (0.96 g, 1.0 mmol) in xylene (40 cm^3) was added bi(1,3-dimethylimidazolidin-2-ylidene) (L^{Me}_2) (0.49 g, 2.5 mmol). The mixture was heated (130 °C, 20 min) to deposit a yellow microcrystalline precipitate which was removed by filtration after cooling (30 °C) the reaction mixture. The solid was washed with OEt_2 (4 × 5 cm^3), acetone (2 × 5 cm^3), and OEt_2 (5 × 5 cm^3), and dried *in vacuo* to afford trans-*dichlorotetrakis*(1,3-*dimethylimidazolidin*-2-*ylidene*)*ruthenium*(II) (0.53 g, 94%).

trans-$[RuCl_2(L^{Et})_4]$.—To a suspension of $[RuCl_2(PPh_3)_3]$ (0.96 g, 1.0 mmol) in $C_6H_{11}Me$ (20 cm^3) was added bi(1,3-diethylimidazolidin-2-ylidene) (0.63 g, 2.5 mmol) and the mixture heated (100 °C, 30 min). The suspension dissolved to give a red-orange solution and a red oil. The mixture was allowed to cool (10 °C) and filtered. Further cooling (−25 °C, 7 d) gave orange crystals. The solvent was removed, the solid washed with OEt_2 (3 × 5 cm^3), and twice recrystallised from $C_6H_{11}Me$ by allowing the hot solution to cool slowly to afford yellow-orange crystals of trans-*dichlorotetrakis*(1,3-*diethylimidazolidin*-2-*ylidene*)*ruthenium*(II) (0.34 g, 50%).

trans-$[RuCl_2(L^{CH_2Ph})_4]$.—To a suspension of $[RuCl_2(PPh_3)_3]$ (0.96 g, 1.0 mmol) in $C_6H_{11}Me$ (20 cm^3) was added bi(1,3-dibenzylimidazolidin-2-ylidene) (1.5 g, 3.0 mmol) and the mixture heated (100 °C, 1 h). The brown-red suspension was slowly replaced by a yellow precipitate which was removed by filtration and recrystallised from a small volume of acetone (−25 °C, 7 d) to afford yellow crystals of trans-*dichlorotetrakis*(1,3-*dibenzylimidazolidin*-2-*ylidene*)-*ruthenium*(II) (0.70 g, 60%).

$[Ru_2Cl_4(L^{Me})_3(PPh_3)_2]$.—To a suspension of $[RuCl_2(PPh_3)_3]$ (1.40 g, 1.46 mmol) in toluene (15 cm^3) was added L^{Me}_2 (0.41 g, 2.1 mmol) and the mixture slowly warmed (80 °C, 20 min). A brown-orange precipitate formed, which was removed by filtration and washed with OEt_2 (5 × 5 cm^3). The solid was recrystallised from CH_2Cl_2–OEt_2 (−20 °C, 5 d) to afford brown-orange microcrystals of *tri*-μ-*chloro-chlorotris*(1,3-*dimethylimidazolidin*-2-*ylidene*)*bis*(*triphenylphosphine*)*diruthenium*(II) (0.51 g, 60%).

$[RuI_2(L^{Me})_3]$.—A suspension of *trans*-$[RuCl_2(L^{Me})_4]$ (0.56 g, 1.0 mmol) and sodium iodide (0.35 g, 2.3 mmol) was stirred (25 °C, 72 h) in acetone (20 cm^3). The pale yellow suspension slowly disappeared and was replaced by an orange solution above an orange-brown solid. The solvent was removed *in vacuo*, the residue dissolved in CH_2Cl_2 (10 cm^3), and filtered. Addition of OEt_2 (5 cm^3) and cooling (−30 °C, 24 h) afforded brown-orange crystals of *tris*-(1,3-*dimethylimidazolidin*-2-*ylidene*)*di-iodoruthenium*(II) (0.54 g, 83%).

trans-$[Ru(CO)Cl(L^{Me})_4]Cl$.—A suspension of *trans*-$[RuCl_2(L^{Me})_4]$ (0.56 g, 1.0 mmol) in $CHCl_3$ (10 cm^3) was slowly warmed (50—60 °C) whilst CO was gently bubbled through the mixture. The suspension disappeared and was replaced by a brownish solution (5 min). Addition of OEt_2 (4 cm^3) and cooling (−25 °C, 48 h) gave a pale pink powder which was twice recrystallised from CH_2Cl_2–OEt_2 (−30 °C, 24 h) to

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afford trans-*carbonylchlorotetrakis*(1,3-*dimethylimidazolidin*-2-*ylidene*)*ruthenium*(II) *chloride* (0.47 g, 80%).

cis-$[Ru(CO)_2Cl_2(L^{Me})_2]$.—A suspension of *trans*-$[RuCl_2(L^{Me})_4]$ (0.25 g, 0.44 mmol) in $CHCl_3$ (10 cm^3) was heated (60 °C, 1 h) whilst CO was bubbled through the solution. On cooling OEt_2 (10 cm^3) was added to precipitate *trans*-$[Ru(CO)Cl(L^{Me})_4]Cl$ and the mixture filtered. Cooling (−25 °C, 7 d) gave an off-white solid which was recrystallised from CH_2Cl_2–C_6H_{14} to afford cis-*dicarbonyldichlorobis*(1,3-*dimethylimidazolidin*-2-*ylidene*)*ruthenium*(II) (0.028 g, 20%).

trans- and *cis*-$[Ru(CO)Cl_2(L^{Et})_3]$.—A solution of *trans*-$[RuCl_2(L^{Et})_4]$ (0.20 g, 0.3 mmol) in $C_6H_{11}Me$ (10 cm^3) was heated (80 °C, 5 min) whilst CO was gently bubbled through the solution. A pale yellow solid precipitated, the mixture was cooled (20 °C), filtered, and the solid recrystallised from C_6H_5Me–C_6H_{14} (−30 °C, 2 d) to afford pale yellow crystals of trans-*carbonyldichlorotris*(1,3-*diethylimidazolidin*-2-*ylidene*)*ruthenium*(II) (0.17 g, 95%). Dissolution of this complex (0.12 g) in $CHCl_3$ (25 °C, 72 h) resulted in a colour change from yellow to colourless. Layering hexane on to the surface and allowing the mixture to stand (25 °C, 48 h) afforded white crystals of the *cis-complex* (0.09 g, 75%).

trans-$[RuCl(L^{Me})_4(PF_3)]X$ ($X = Cl^-$ *or* $[BF_4]^-$).—(*i*) $X = Cl^-$. The complex *trans*-$[RuCl_2(L^{Me})_4]$ (0.30 g, 0.54 mmol) was suspended in $CHCl_3$ (5 cm^3) and gently heated (50 °C) whilst PF_3 was bubbled through the solution (*ca.* 5 min). The solution became clear and pale brown. Addition of OEt_2 (5 cm^3) and cooling gave a pale-pink solid. The solvent was removed and the residue recrystallised from CH_2Cl_2–OEt_2 (−30 °C, 24 h) to afford trans-*chlorotetrakis*-(1,3-*dimethylimidazolidin*-2-*ylidene*)(*trifluorophosphine*)-*ruthenium*(II) *chloride* (0.21 g, 60%).

(*ii*) $X = [BF_4]^-$. To a suspension of the above complex (0.10 g, 0.15 mmol) in acetone (5 cm^3) was added $Na[BF_4]$ (0.01 g, 0.16 mmol) and the mixture stirred (25 °C, 15 min) to form a pale pink solution and a pale suspension. The mixture was filtered, OEt_2 (2 cm^3) added, and cooling (−20 °C, 24 h) afforded the *tetrafluoroborate salt* (0.086 g, 80%).

$[RuCl_2(L^R)_3]$ (R = Me *or* Et).—(*i*) R = Me. A suspension of *trans*-$[RuCl_2(L^{Me})_4]$ in CD_2Cl_2 (*ca.* 0.5—1.0 cm^3) was heated (60—80 °C) in a ^{13}C or ^1H n.m.r. tube sealed *in vacuo* (72 h) forming a deep red-brown solution, identified by ^{13}C and ^1H n.m.r. spectroscopy only as containing *dichlorotris*(1,3-*dimethylimidazolidin*-2-*ylidene*)*ruthenium*(II) (*ca.* 100%).

(*ii*) R = Et. A solution of *trans*-$[RuCl_2(L^{Et})_4]$ in CD_2Cl_2 (*ca.* 0.5—1.0 cm^3) in a ^{13}C or ^1H n.m.r. tube sealed *in vacuo* was allowed to stand (25 °C, 2 h). The initial golden-yellow solution quickly became red-brown and was identified by ^1H and ^{13}C n.m.r. spectroscopy as containing *dichlorotris*(1,3-*diethylimidazolidin*-2-*ylidene*)*ruthenium*(II) (*ca.* 100%).

$[RuCl(L^{Me})_2\{P(OMe)_3\}_3]Cl$.—To a suspension of *trans*-$[RuCl_2(L^{Me})_4]$ (0.15 g, 0.27 mmol) in $CHCl_3$ (5 cm^3) was added an excess of trimethyl phosphite (2 cm^3) and the mixture warmed to 50 °C. The solution became clear and pale brown. Diethyl ether was carefully added until a slight cloudiness persisted in the solution and cooling (−30 °C, 72 h) afforded *chlorobis*(1,3-*dimethylimidazolidin*-2-*ylidene*)*tris*(*trimethyl phosphite*)*ruthenium*(II) *chloride* (0.12 g, 60%) as an off-white solid which was recrystallised from $CHCl_3$–OEt_2 (10 cm^3, *ca.* 1 : 1, −30 °C) as a white solid.

trans-$[Ru(CO)Cl(L^{Me})_2(NC_5H_5)_2]Cl$.—A suspension of *trans*-$[RuCl_2(L^{Me})_4]$ (0.56 g, 1.0 mmol) in pyridine (10 cm^3) was heated at 60 °C (6 h) whilst carbon monoxide was gently bubbled through the hot solution. A white precipitate formed which was removed by filtration, washed with OEt_2, and dried to afford trans-*carbonylchlorobis*(1,3-*dimethylimidazolidin*-2-*ylidene*)*dipyridineruthenium*(II) *chloride* (0.22 g, 40%). The filtrate, on addition of OEt_2, afforded a second crop of the same material (0.03 g, 5%).

trans-$[OsCl_2(L^{Me})_4]$.—To a suspension of *mer*-trichlorotris-(di-n-butylphenylphosphine)osmium(III) (0.19 g, 0.2 mmol) in xylene (25 cm^3, 25 °C) was added L^{Me}_2 (0.04 g, 0.2 mmol). Immediate reduction occurred to give a dark green solution. The mixture was filtered and to the filtrate a further quantity of olefin (0.12 g, 0.6 mmol) added and the mixture heated (120 °C, 10 min) to give an orange precipitate, which was removed by filtration, washed with OEt_2 (5 × 10 cm^3), and dried to afford trans-*dichlorotetrakis*(1,3-*dimethylimidazolidin*-2-*ylidene*)*osmium*(II) (0.12 g, 95%).

TABLE 7

Final atomic co-ordinates (× 10^4) with estimated standard deviations in parentheses

	x	*y*	*z*
Ru	2 324(1)	0 005(1)	2 933(1)
Cl(1)	2 179(1)	1 266(2)	1 715(2)
Cl(2)	2 468(1)	−1 293(2)	4 125(2)
N(1)	3 555(4)	0 777(6)	4 519(6)
N(2)	3 827(5)	0 997(6)	3 210(6)
N(3)	1 329(4)	0 655(6)	4 229(6)
N(4)	1 885(4)	1 918(6)	3 845(5)
N(5)	3 462(4)	−1 469(6)	2 494(6)
N(6)	2 674(4)	−1 080(6)	1 260(6)
N(7)	1 171(5)	−1 605(5)	2 166(6)
N(8)	0 720(5)	−0 129(6)	1 933(6)
C(1)	3 310(5)	0 642(7)	3 608(7)
C(2)	1 800(5)	0 935(7)	3 719(6)
C(3)	2 856(5)	−0 913(7)	2 161(6)
C(4)	1 331(5)	−0 626(7)	2 286(7)
C(5)	3 536(8)	0 080(10)	6 038(10)
C(6)	3 162(6)	0 677(8)	5 218(7)
C(7)	4 233(6)	1 318(10)	4 735(9)
C(8)	4 478(7)	1 314(10)	3 883(8)
C(9)	3 896(6)	0 911(8)	2 270(7)
C(10)	3 994(8)	1 916(10)	1 829(10)
C(11)	1 035(8)	−0 750(11)	5 131(10)
C(12)	0 959(6)	−0 318(8)	4 203(8)
C(13)	1 062(7)	1 488(9)	4 693(9)
C(14)	1 483(6)	2 320(9)	4 511(8)
C(15)	2 371(6)	2 583(8)	3 527(8)
C(16)	1 965(7)	3 386(10)	2 885(9)
C(17)	4 035(7)	−2 469(9)	3 812(10)
C(18)	3 921(6)	−1 453(8)	3 384(7)
C(19)	3 711(7)	−1 987(10)	1 786(8)
C(20)	3 134(7)	−1 822(10)	0 954(9)
C(21)	2 037(6)	−0 786(9)	0 604(8)
C(22)	2 200(8)	−0 215(10)	−0 184(10)
C(23)	1 439(8)	−3 307(11)	2 720(10)
C(24)	1 669(6)	−2 421(8)	2 252(8)
C(25)	0 439(7)	−1 771(10)	1 641(9)
C(26)	0 082(7)	−0 793(10)	1 648(9)
C(27)	0 572(6)	0 943(8)	2 020(7)
C(28)	0 237(7)	1 449(10)	1 094(9)
O(1)	5 000	0 000	0 000
C(29)	4 559(24)	0 382(33)	−0 639(30)
C(30)	4 078(18)	0 565(26)	−1 221(24)

Crystal Data.—$C_{28}H_{56}Cl_2N_8Ru{\cdot}0.5C_8H_{18}O$, $M = 629.92$, Monoclinic, $a = 19.076(2)$, $b = 13.409(1)$, $c = 14.952(2)$ Å, $\beta = 102.85(6)°$, $U = 3\,728.9$ Å^3, $D_c = 1.12$, $Z = 4$, $F(000) = 1\,356$. Mo-K_α radiation, $\mu = 5.73$ cm^{-1}. Space group $P2_1/c$ (no. 14) from systematic absences of $0k0$ for k odd and $h0l$ for l odd.

A crystal of dimensions *ca.* 0.3 × 0.2 × 0.2 mm sealed in a capillary tube was used for data collection on a Hilger and Watts Y290 four-circle diffractometer. Initially, cell dimensions were thought to be the same as those of the previous batch,[9] but accurate cell dimensions derived by least-squares treatment of the setting angles of 12 reflections [λ(Mo-K_{α_1}) 0.709 26 Å] showed small but significant differences, particularly in β. This was subsequently found to be due to inclusion of solvent (di-n-butyl ether) molecules in the lattice. It is to be noted that in the initial study $C_6H_{11}Me$ was used as the recrystallisation solvent but OBu^n_2 was superior in providing crystals suitable for the *X*-ray structure determination, and the inclusion of 0.5 OBu^n_2 of crystallisation also increased the aerial stability of the complex. Intensity data with $\theta < 22°$ were collected by an ω—2θ step scan with Mo-K_α radiation (graphite-crystal monochromator). Three standard reflections re-measured after every 100 reflections showed an overall decrease of *ca.* 5% during the data collection, but not equally for the three standards and no correction was applied. The 5 448 reflections measured were corrected for Lorentz and polarisation effects but not for absorption, and standard deviations were calculated in the usual manner[56] with $p = 0.04$. After averaging of equivalent reflections, 2 641 unique reflections with $I > 3\sigma(I)$ were used in the structure analysis.

Structure Solution and Refinement.—The positions of all the non-hydrogen atoms of the ruthenium complex were derived by the usual heavy-atom technique and refined by full-matrix least squares (Ru and Cl anisotropic) to a residual R 0.081. A difference-Fourier map revealed three peaks, one of which lay on a centre of symmetry, which were taken to be two carbon atoms and one oxygen atom of a disordered solvent di-n-butyl ether molecule with the oxygen atom at the centre of symmetry. Further small peaks appeared to be consistent with extensive disorder of the remaining atoms of the molecule. The two carbon atoms and one oxygen atom of the solvent were included in further refinement with isotropic temperature factors. At this point hydrogen atoms for the carbene ligands were included at idealised positions (C–H 1.08 Å). The three hydrogen atoms and one carbon atom of each methyl group were refined as a rigid group with refinement of a common isotropic temperature factor for all the methyl hydrogens. A common temperature factor was also refined for the methylene hydrogen atoms which were constrained to ride on their corresponding carbon atom. Continued refinement finally converged at R 0.055 (R' 0.087) * with a maximum shift-to-error of 0.1. A final difference-Fourier synthesis had peaks of up to 0.6 e Å^{-3} in the region of the disordered solvent, but was elsewhere featureless. The weighting scheme used in the least-squares refinement was $\omega = 1/[\sigma^2(F) + 0.005\,7|F|^2]$. Scattering factors for neutral atoms and dispersion corrections for Ru and Cl were taken from ref. 57. The structure solution and refinement was carried out with the SHELX program system of G. M. Sheldrick. Final non-hydrogen atom positions are listed in Table 7. Lists of temperature factors (Table 8), hydrogen-atom positions (Table 9), and structure factors (Table 10) are available as a Supplementary Publication No. SUP 22223 (20 pp.).†

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* $R = \Sigma\Delta/\Sigma|F_o|, R' = [\Sigma\omega\Delta^2/\Sigma\omega|F_o|^2]^{\frac{1}{2}}$, where $\Delta = ||F_o| - |F_c||$.

† For details see Notices to Authors No. 7, *J.C.S. Dalton*, 1977, Index issue.

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