Carbene Complexes. Part 16.[1] Synthesis and Properties of *NN′N″N‴*-Tetra-aryl-substituted Electron-rich Olefin-derived Carbeneruthenium(II) Complexes containing a Spontaneously formed *ortho*-Metallated-*N*-Arylcarbene Ligand; the Crystal and Molecular Structures of $[RuCl\{CN(C_6H_4Me\text{-}4)CH_2CH_2NC_6H_3Me\text{-}4\}(PEt_3)_2]$ (6) and $[Ru(CO)Cl\{CN(C_6H_4Me\text{-}4)CH_2CH_2NC_6H_3Me\text{-}4\}(PEt_3)_2]$ (16) †‡

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The complex $[RuCl_2(PPh_3)_3]$ reacts thermally with the electron-rich olefin $[{=}CN(R')CH_2CH_2NR']_2$ (R′ = Ph, C_6H_4Me-4, C_6H_4OMe-4, or C_6H_4OMe-2), $L^{R'}_2$, with elimination of PPh_3 and HCl, forming the five-co-ordinate carbeneruthenium(II) complex containing an *ortho*-metallated *N*-arylcarbene ligand $[RuCl\{CN(R')CH_2CH_2NR''\}(PPh_3)_2]$, abbreviated as $[RuCl(L^{R'})(PPh_3)_2]$. One of these complexes (R′ = C_6H_4Me-4) is also formed from $[RuCl(NO)(PPh_3)_2]$ and $L^{R'}_2$. The five-co-ordinate ruthenium(II) complexes readily undergo PR_3 exchange [R_3 = Et_3, $Bu^n{}_3$, $Bu^n{}_2Ph$, Et_2Ph, Me_2Ph, but not $(C_6H_{11})_3$]; with $[{=}CN(Et)CH_2CH_2NEt]_2$ ($L^{Et}{}_2$), the unusual bis(carbene) complex $[RuCl(L^{R'})(L^{Et})(PPh_3)]$ (R′ = C_6H_4Me-4) is formed. Small ligands [*e.g.* CO, PF_3, $P(OMe)_3$, or NCMe] generally add to form six-co-ordinate complexes of variable thermal stability. The complex $[RuCl_3(NO)(PPh_3)_2]$ with $L^{R'}_2$ also affords an *ortho*-metallated complex $[RuCl_2(L^{R'})(NO)(PPh_3)]$; this, like the other six-co-ordinate ruthenium(II) derivatives, does not undergo PR_3 exchange, but with $L^{Et}{}_2$ NOCl is lost and $[RuCl(L^{R'})(L^{Et})(PPh_3)]$ (R′ = C_6H_4Me-4) is formed. Spectroscopic data provide information on the nature and stereochemistry of the complexes, the magnitude of $^2J(^{13}C-^{31}P)$ being especially useful, with $^2J_{trans} \gg {}^2J_{cis}$. The five- and six-co-ordinate complexes are stereochemically rigid in solution. *X*-Ray analyses of the two title compounds have been refined to *R* and *R′* of 0.054 and 0.093 for $[RuCl(L^{R'})(PEt_3)_2]$ (R′ = C_6H_4Me-4) (6), and 0.045 and 0.053 for $[Ru(CO)Cl(L^{R'})(PEt_3)_2]$ (R′ = C_6H_4Me-4) (16), respectively. In overall pseudo-octahedral geometry about ruthenium, complexes (6) and (16) differ only in the replacement of a weak Ru · · · HC contact (2.23 Å) in the former for a CO ligand in the latter. The bond lengths within the co-ordination sphere of (6) are slightly greater in (16), the smallest increase (0.011 Å) being for the Ru–P bonds and the largest (0.119 Å) for the Ru–C(6) bond [C(6) is the C of the metallated phenyl ring]. In complex (6) the two Ru–C(sp^2) distances are 2.006(8) [Ru–C(6)] and 1.911(6) Å (Ru–$C_{carb.}$).

GENERALLY, tetra-aryl-substituted electron-rich olefins, $[{=}CN(R')CH_2CH_2NR']_2$, $L^{R'}_2$ (R′ = Ph, C_6H_4Me-4, or C_6H_4OMe-4), have proved to be less reactive towards carbenemetal complex formation than their alkyl counterparts $L^R{}_2$.[2-4] Only a substrate for which $L^R{}_2$ in the limit yields at least a *tri*carbene complex is active to $L^{R'}_2$ and then only one aryl ligand is incorporated. Treatment of $[RuCl_2(PPh_3)_3]$ with $L^R{}_2$ (R = Me, Et, or CH_2Ph) yielded[5] tetracarbeneruthenium(II) complexes, *trans*-$[RuCl_2(L^R)_4]$, and reaction with aryl derivatives was thus expected to afford $[RuCl_2(L^{R'})(PPh_3)_n]$ (n = 2 or 3). In the event, the reactions proved to be much more complicated, and involved spontaneous *ortho*-metallation of the $L^{R'}$ ligand. Details on the new compounds (1)—(26) are in Table 1 and synthetic routes are outlined in Schemes 1 and 2.

Heating $[RuCl_2(PPh_3)_3]$ with $L^{R'}_2$ in xylene (ratio *ca.* 1 : 0.67) at 140 °C gave a deep red solution and a green precipitate (Scheme 3); using a ratio of *ca.* 1 : 1.2 also gave the red solution, but a pale yellow precipitate (Scheme 4). These observations are compatible with (*i*) incorporation of the $-CN(R')CH_2CH_2NR'$ (abbreviated as $L^{R'}$) fragment into the metal co-ordination sphere, and (*ii*) spontaneous *ortho*-metallation of one carbene NR′ substituent,[6] the eliminated HCl being removed by excess of $L^{R'}_2$. A preliminary communication[6] described Scheme 4 for $L^{R'}$ = $L^{C_6H_4Me\text{-}4}$ and details of the crystal structure of the complex $[RuCl(L^{R'})(PEt_3)_2]$ derived therefrom.

Several other ruthenium(II) *ortho*-metallated complexes have been described:[7-9] these arise as a result of H_2 elimination *via* reaction of $[RuCl(H)(PPh_3)_3]$ with various ligands, *e.g.* $P(OPh)_3$[7] or RCH=CHR;[10] in the former, one phosphite phenyl ring is metallated producing a ring system (27) related to ours (28), giving credence to the idea of an ionic mechanism for the metallation. Both *O*-aryl and *N*-aryl are activated to electrophilic attack at the aryl 2 position, but this does not negate the involvement of a transient ruthenium(IV) species *via*

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† Names for these complexes are [1,3-bis(4-tolyl)imidazolidin-2-ylidene-$C^2C^{2'}$]chlorobis(triethylphosphine)ruthenium(II) and [1,3-bis(4-tolyl)imidazolidin-2-ylidene-$C^2C^{2'}$]carbonylchlorobis(triethylphosphine)ruthenium(II).

‡ No reprints available.

TABLE 1

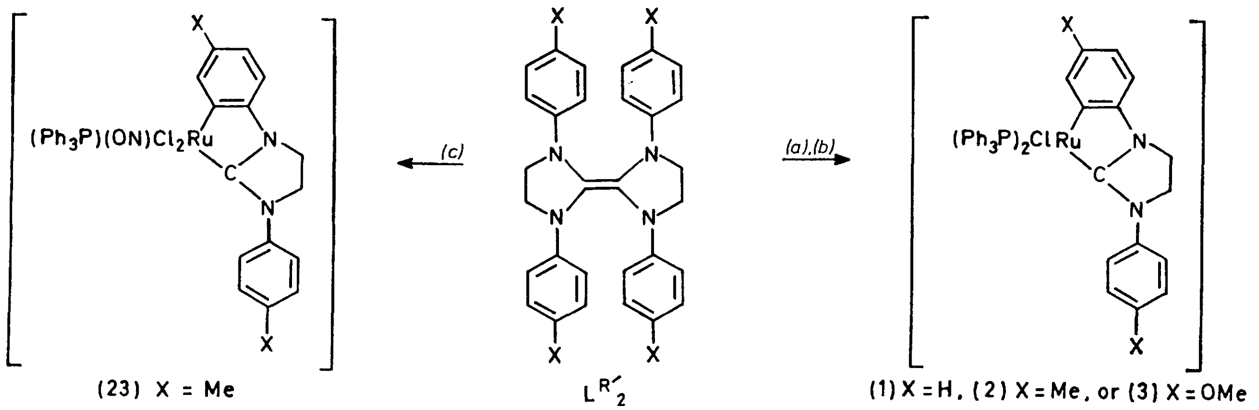
Carbeneruthenium(II) complexes containing the 3-ruthena-1-aza-4,5-benzocyclopentane nucleus, the olefin $L^{C_6H_4OMe-2}{}_2$, and the salt (26)

	Compound	Yield (%)	M.p. (θc/°C)	Colour	Analysis (%) [a]			
					C	H	N	Cl
(1)	$[RuCl(L^{Ph})(PPh_3)_2]$	90	>340	Dark red	69.7 (69.4)	5.3 (4.9)	3.1 (3.2)	4.1 (4.0)
(2)	$[RuCl(L^{C_6H_4Me-4})(PPh_3)_2]$	85	>335	Dark red	69.3 (69.9)	5.4 (5.2)	3.2 (3.1)	4.1 (3.9)
(3)	$[RuCl(L^{C_6H_4OMe-4})(PPh_3)_2]$	85	318 (decomp.)	Dark red	67.5 (67.5)	5.2 (5.0)	3.2 (3.0)	
(4)	$[RuCl(L^{Ph})(PEt_3)_2]$	90	205	Red-orange	54.2 (54.5)	7.1 (7.3)	4.7 (4.7)	
(5)	$[RuCl(L^{Ph})(PBu^n{}_2Ph)_2]$	90	159 (decomp)	Brown-orange	64.0 (64.3)	7.1 (7.4)	3.6 (3.5)	
(6)	$[RuCl(L^{C_6H_4Me-4})(PEt_3)_2]$	95	200—202	Red-orange	55.9 (56.0)	7.8 (7.6)	4.6 (4.5)	
(7)	$[RuCl(L^{C_6H_4Me-4})(L^{Et})(PPh_3)]$	80	242	Brown-orange	65.5 (65.2)	6.1 (6.0)	7.4 (7.3)	
(10)	$[Ru(CO)Cl(L^{Ph})(PPh_3)_2]$	80	293 (decomp.) [b]	White	68.0 (68.6)	4.8 (4.8)	3.1 (3.0)	
(11)	$[Ru(CO)Cl(L^{Ph})(PEt_3)_2]$	85	206	White	54.7 (54.9)	7.0 (6.8)	4.5 (4.4)	
(12)	$[Ru(CO)Cl(L^{Ph})(PBu^n{}_3)_2]$	60	158	White	60.4 (60.8)	8.3 (8.5)	3.6 (3.5)	
(13)	$[RuCl(L^{Ph})\{P(OMe)_3\}_3]$	90	130 (decomp.)	White	39.6 (39.5)	5.7 (5.5)	3.9 (3.8)	
(14)	$[Ru(CO)Cl(L^{Ph})(L^{Et})(PPh_3)]$	60	282—284 [c]	White	61.1 (61.1)	5.4 (5.3)	7.0 (6.9) [d]	
(15)	$[Ru(CO)Cl(L^{C_6H_4Me-4})(PPh_3)_2]$	80	264 (decomp.) [e]	White	68.5 (69.1)	5.3 (5.1)	3.0 (3.0)	
(16)	$[Ru(CO)Cl(L^{C_6H_4Me-4})(PEt_3)_2]$	90	198	White	55.4 (55.4)	7.3 (7.3)	4.3 (4.3)	
(8)	$[RuCl(L^{C_6H_4Me-4})(PMe_2Ph)_2]$	90		Orange				
(9)	$[RuCl(L^{C_6H_4Me-4})(PEt_2Ph)_2]$	85		Red-orange				
(17)	$[RuCl(L^{C_6H_4Me-4})(PEt_3)_2\{P(OMe)_3\}]$	80	122 (decomp.)	White	50.6 (51.5)	7.8 (7.6)	3.8 (3.8)	
(18)	$[RuCl(L^{C_6H_4Me-4})(PF_3)(PPh_3)_2]$	90	140–150 (decomp.) [e]	White	63.1 (63.8)	4.9 (4.8)	2.7 (2.8)	
(19)	$[RuCl(L^{C_6H_4Me-4})(PEt_3)_2(PF_3)]$	80	180—190 (decomp.) [f]	White	49.7 (49.7)	6.7 (6.7)	3.8 (3.9)	
(20)	$[RuCl(L^{C_6H_4Me-4})(NCMe)(PPh_3)_2]$	85	>25 (decomp.) [g]	White	*g*			
(21)	$[Ru(L^{C_6H_4Me-4})I(PPh_3)_2]$	90		Dark crimson	63.6 (63.5)	4.9 (4.7)	2.8 (2.8)	
(22)	$[RuCl(L^{C_6H_4Me-4})(dppe)(PPh_3)]$	60		Pale yellow	69.8 (70.0)	5.7 (5.4)	2.8 (2.7)	
(23)	$[RuCl_2(L^{C_6H_4Me-4})(NO)(PPh_3)]$	90		Dark orange	58.3 (58.9)	4.9 (4.5)	6.0 (5.9)	
(24)	$[Ru(CO)Cl(L^{C_6H_4OMe-2})(PPh_3)_2]$	50		White	66.9 (66.7)	5.0 (5.0)	2.9 (2.9)	
(25)	$[{=}CN(R')CH_2CH_2NR']_2$ $(R' = C_6H_4OMe\text{-}2)$	30		Yellow	72.2 (72.3)	6.7 (6.4)	9.7 (9.9)	
(26)	$[HL^{C_6H_4OMe-4}]_2[RuCl_4(PPh_3)_2]$	85		Green	63.1 (63.0)	5.3 (5.1)	7.0 (6.8)	10.3 (10.6)

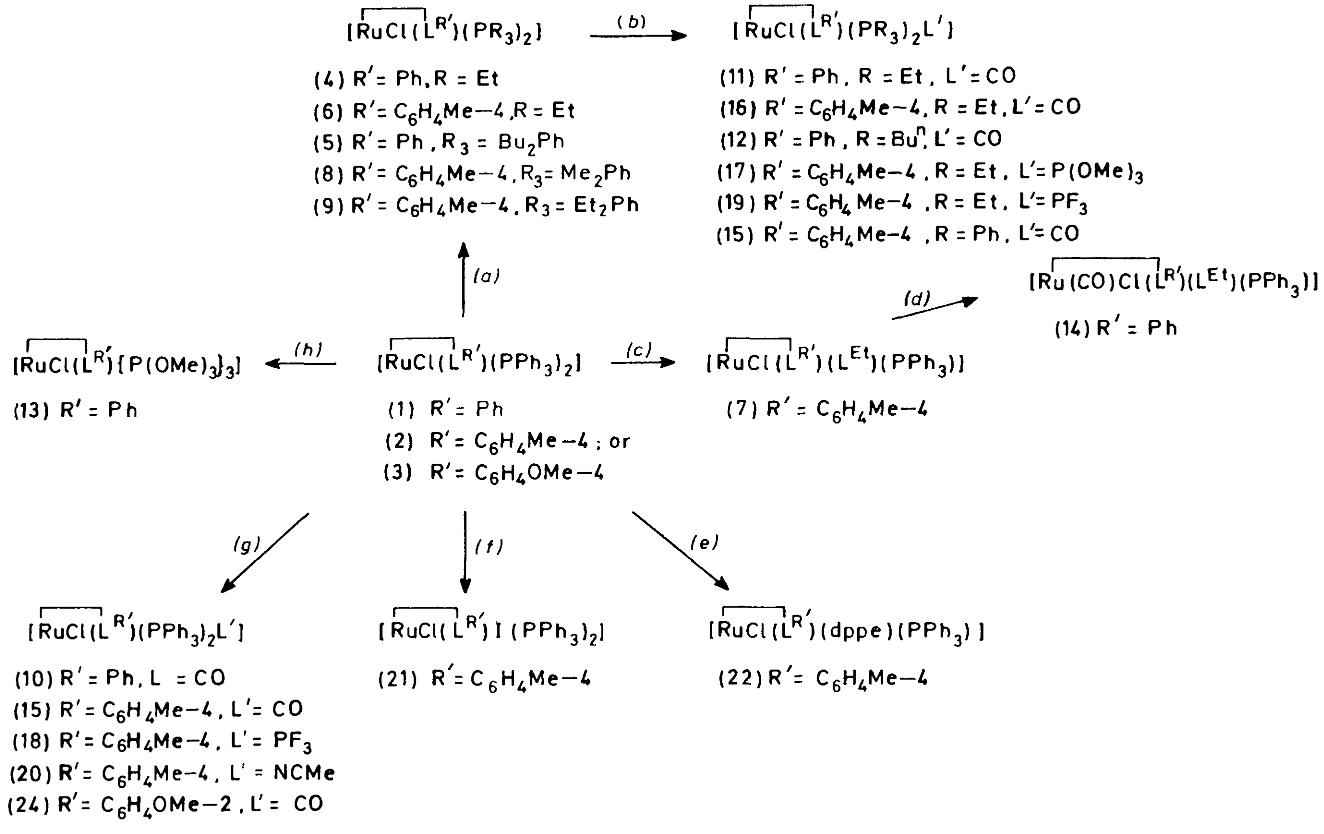
[a] Calculated values are given in parentheses. [b] Decomposes to (1). [c] Slow loss of CO at >230 °C. [d] Calculated for $0.5CH_2Cl_2$. [e] Decomposes to (2). [f] Decomposes to (6). [g] MeCN loss occurs slowly at 25 °C.

an oxidative addition of aryl H with subsequent reduction (in our case by $L^{R'}{}_2$) and elimination of H_2 or HCl.[11,12]

One other authenticated *ortho*-metallation (although not spontaneous) of a carbene *N*-aryl appendage has been described,[13] induced by Cl_2 oxidation of a platinum(II) to a platinum(IV) complex. In an earlier attempt (Scheme 5) to effect a thermal or photochemical transformation of an electron-rich olefin-derived carbenerhodium(I) complex into an *ortho*-metallated complex (29; cod = cyclo-octa-1,5-diene), a characterisable species was not isolated,[3,14] although there was ^1H n.m.r. evidence; thus decay of the $Rh{-}CH_2{-}Si$ protons was noted and simultaneous build-up of an $SiMe_4$ signal as well as a change in the carbene ring-methylene proton resonances, but rapid further decomposition also occurred, unlike in the $[RhCl(PPh_3)_3]{-}Li(CH_2SiMe_3)$ system which leads to $SiMe_4$ and complex (30).[15] In rhodium and iridium systems *ortho*-metallation appears to be favoured by formation of four- rather than five-membered ring systems. This is in contrast to ruthenium(II) complexes; thus, for example, $[RuCl_2(PPh_3)_3]$ does not eliminate HCl with ring closure, although an *ortho*-H of one aryl ring is close to the metal[16] (as was also found in some of our complexes, after *ortho*-metallation) and effectively occupies the otherwise vacant sixth site around Ru^{II}. Hence initial hydrogen transfer to the metal in an *ortho*-metallation oxidative-addition process, although sterically viable,[17] appears to be unfavourable. In the present case (Scheme 3) initial loss of PPh_3 from $[RuCl_2(PPh_3)_3]$ in solution (known to occur readily)[18] seems to be followed by (*i*) complexation of the $L^{R'}$ ligand to Ru and (*ii*) an internal electrophilic substitution at the 2 position of the activated aryl ring with elimination of HCl (removed by excess of $L^{R'}_2$ as the insoluble hydrochloride $[HL^{R'}]Cl$. A transient seven-co-ordinate 18-electron ruthenium(IV) species may be involved[19] as an intermediate in step (*ii*), excess of $L^{R'}_2$ then functioning as a reducing agent; we note that $Ir^{I} \rightleftharpoons Ir^{III}$ tautomers have both been isolated in a Vaska system.[20,21]

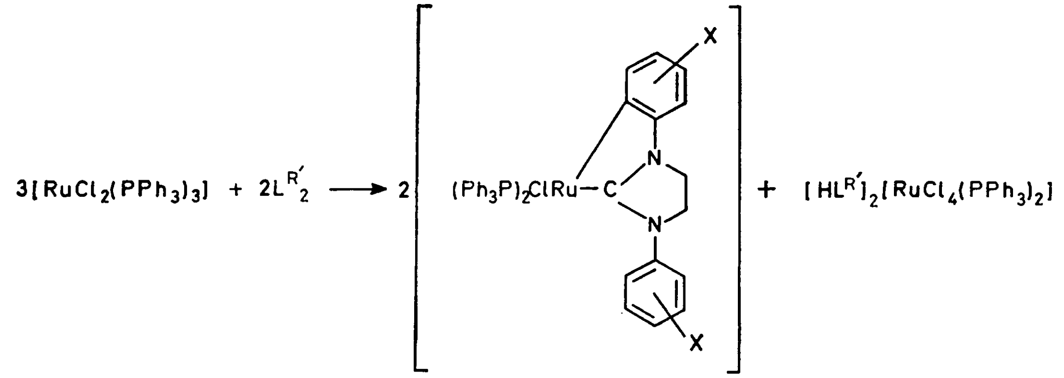


SCHEME 1 Synthetic routes to complexes of the type $[RuCl(L^{R'})(PPh_3)_2]$ [(1), (2), or (3)] and $[RuCl_2(L^{R'})(NO)(PPh_3)]$ (23). (*a*) $[RuCl_2(PPh_3)_3]$, xylene, 140 °C; (*b*) $[RuCl(NO)(PPh_3)_2]$, xylene, 140 °C; (*c*) $[RuCl_3(NO)(PPh_3)_2]$ and (*i*) xylene, 140 °C, (*ii*) water, 100 °C



SCHEME 2 Some reactions of $[RuCl(L^{R'})(PPh_3)_2]$ and related complexes. (*a*) PR_3, MeC_6H_{11}, 100 °C; (*b*) L', toluene, 25 °C; (*c*) L^{Et}_2, toluene, 110 °C; (*d*) CO, toluene, 25 °C; (*e*) $Ph_2PCH_2CH_2PPh_2$, MeC_6H_{11}, 100 °C; (*f*) NaI, acetone, 40 °C; (*g*) L', toluene or CH_2Cl_2, 25 °C; (*h*) $P(OMe)_3$, MeC_6H_{11}, 100 °C

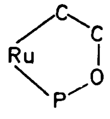
Two apparently general types of reaction are demon-



{abbreviated as $[\overline{\mathrm{RuCl(L}}^{\mathrm{R}'})(\mathrm{PPh}_3)_2]$, where R′ = Ph (1), C_6H_4Me-4 (2), or C_6H_4OMe-4 (3)}

SCHEME 3

strated (Schemes 1 and 2): those in which the Ru atom remains five-co-ordinate, and others in which co-ordinatively saturated complexes are obtained; in both cases the 3-ruthena-1-aza-4,5-benzocyclopentane nucleus (28) remains intact.



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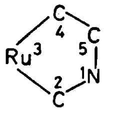
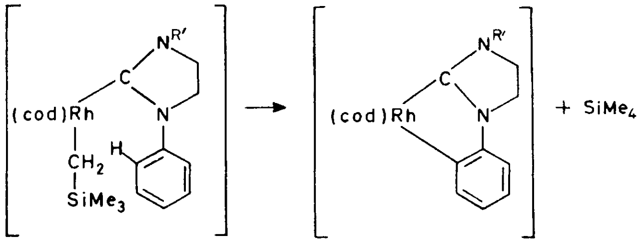


(28)

$[\mathrm{RuCl_2(PPh_3)_3}] + \mathrm{L}^{\mathrm{R}'}{}_2 \longrightarrow [\overline{\mathrm{RuCl(L}}^{\mathrm{R}'})(\mathrm{PPh_3})_2] + [\mathrm{HL}^{\mathrm{R}'}]\mathrm{Cl}$

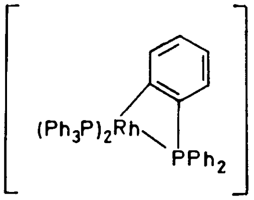
SCHEME 4



(29)

SCHEME 5

Simple P-ligand-displacement or ligand-addition reactions may occur. Thus, many tertiary phosphines (*e.g.* PEt_3, PEt_2Ph, PMe_2Ph, $PBu^n{}_2Ph$, or $PBu^n{}_3$) readily (MeC_6H_{11}, 100 °C) displace both PPh_3 groups, but the bulky tricyclohexylphosphine does not react even with a large excess of phosphine in xylene at 140 °C. Although $[=\overline{\mathrm{CN(Et)CH_2CH_2N}}\mathrm{Et}]_2$ (abbreviated as $L^{Et}{}_2$) affords a tetracarbeneruthenium complex upon reaction with $[RuCl_2(PPh_3)_3]$,[5] it has proved possible to displace only *one* PPh_3 ligand in $[\overline{\mathrm{RuCl(L}}^{\mathrm{R}'})(\mathrm{PPh}_3)_2]$ (2; R′ = C_6H_4Me-4) forming the unusual mixed dicarbene five-co-ordinate complex $[\overline{\mathrm{RuCl(L}}^{\mathrm{R}'})(\mathrm{L}^{\mathrm{Et}})(\mathrm{PPh}_3)]$ (7; R′ = C_6H_4Me-4); for many Rh^I–$L^{R'}$ complexes, the aliphatic olefin $L^R{}_2$ (R = Me or Et) caused displacement of co-ordinated $L^{R'}$ by L^R fragments.[3] This cannot occur here because the *ortho*-metallated ring system deactivates the complex towards oligocarbene complex formation *via* $L^{Et}{}_2$. Steric effects, both in the olefin $L^{Et}{}_2$ and the ruthenium(II) complex, may be important. In that context we draw attention to: (*i*) the failure of $P(C_6H_{11})_3$ to displace PPh_3 from complex (1); (*ii*) the substitution inertness, *e.g.*, to phosphine exchange, of related six-co-ordinate d^6 ruthenium(II) complexes; and (*iii*) the stability of *trans*-$[RuCl_2(L^{Et})_4]$,[5,6] which indicates that electronic factors with regard to formation of oligocarbeneruthenium(II) complexes are favourable.



(30)

It is interesting that the rate of reaction of $L^{R'}{}_2$ with the complex $[RuCl_2(PPh_3)_3]$ increases in the sequence R′ = Ph < C_6H_4Me-4 < C_6H_4OMe-4, which parallels not only the increasing olefin solubility in xylene (at 140 °C), but also the basic character at N. The 2-methoxyphenyl olefin does not fit into this pattern; it has comparable basicity and xylene-solubility to its *para*-isomer, but the reactivity is much reduced. By using this new olefin (25; R′ = C_6H_4OMe-2) we expected to prevent *ortho*-metallation. However, although the presence of the substituent dramatically reduced the rate of carbenemetal complex formation, presumably *via* initial attack at N[22] {(25) does not react with $[RhCl(PPh_3)_3]$ unlike other $L^{R'}{}_2$ species},[14] the *ortho*-metallation process itself appeared rapid. These further observations also suggest that reactivity in our ruthenium(II) system is governed by steric factors: ligand lability accompanied by the accessibility of a suitable vacant site at the metal centre are therefore essential requirements.

Formation of six-co-ordinate complexes (31) occurs only with small ligands such as CO, PF_3, $P(OMe)_3$, or NCMe; the position of equilibrium (Scheme 6) with respect to the five-co-ordinate precursor is dependent upon both the size and the π-acceptor : σ-donor ratio of the incoming ligand. Stability to thermal dissociation

$$[RuCl(L^{R'})(PR_3)_2] + L' \rightleftharpoons \underset{(31)}{[RuCl(L^{R'})L'(PR_3)_2]}$$

SCHEME 6

of our complexes (31) decreases in the order CO > PF_3 > $P(OMe)_3$ $\gg$ NCMe, but is greater for alkyl- rather than aryl-phosphine complexes. In $[RuCl(L^{R'})\{P(OMe)_3\}_3]$ (13; R' = Ph) one $P(OMe)_3$ ligand is labile in solution, to yield the red-orange five-co-ordinate precursor (not isolated), but on cooling complex (13) reforms. More pronounced is the ready loss of MeCN from $[RuCl(L^{R'})(NCMe)(PPh_3)_2]$ (20; R' = C_6H_4Me-4), which occurs rapidly in solution at 25 °C and slowly even in the solid state. Complexes containing CO or PF_3 are relatively inert, PF_3 being lost more easily than CO from $[RuCl(L^{R'})(PR_3)_2L']$ (R = Et or Ph, L' = PF_3 or CO). For example, for R = Et, PF_3 is eliminated at *ca.* 180 °C to give $[RuCl(L^{R'})(PEt_3)_2]$, whereas the CO complex melts unchanged at *ca.* 200 °C. We have been unable to isolate a thermally stable dinitrogen complex by reaction of N_2 with any of the new five-co-ordinate complexes, although for $[RuCl(L^{R'})(PMe_2Ph)_2]$ (8; R' = C_6H_4Me-4) passage of a rapid stream of N_2 through a MeC_6H_{11} solution cooled to −50 °C precipitated a white solid. Infrared spectroscopy showed a weak band attributable to $\nu(N_2)$ at 1 930 cm^{-1}; decomposition of the solid was rapid at room temperature, but the presence of $[RuCl(L^{R'})(N_2)(PMe_2Ph)_2]$ is inferred.

The tendency for the $L^{R'}$ ligand to undergo *N*-aryl 2-metallation in ruthenium systems is very pronounced. Thus, although reaction of $[RuCl(NO)(PPh_3)_2]$ with $L^{Me}{}_2$ produces $[Ru(L^{Me})_4(NO)]Cl$, and $L^{CH_2Ph}{}_2$ yields $[RuCl(L^{CH_2Ph})_2(NO)]$,[5] $L^{R'}{}_2$ affords $[RuCl(L^{R'})(PPh_3)_2]$ (2; R' = C_6H_4Me-4). The displacement of NO is itself a rare event [23,24] and the accompanying *ortho*-metallation is even more surprising. Effectively, an oxidation process has occurred, $Ru^0 \longrightarrow Ru^{II}$, but we have been unable so far to trace the fate of the eliminated fragments NO and the aryl H; H_2O and N_2O (or NO and H_2) may be formed.

A nitrosylruthenium complex $[RuCl_2(L^{R'})(NO)(PPh_3)]$ (23; R' = C_6H_4Me-4), containing an *ortho*-metallated carbeneruthenium(II) ring (28) has been obtained from $[RuCl_3(NO)(PPh_3)_2]$, by treatment with $L^{R'}{}_2$. The reaction again differs from that with an aliphatic olefin $L^R{}_2$ in which initial reduction to $[RuCl(NO)(PPh_3)_2]$ occurs.[23] Complex (23), like the other six-co-ordinate compounds, does not undergo phosphine exchange. An attempted reduction of complex (23), utilising $L^{Et}{}_2$, did not give $[Ru(L^{R'})(NO)L']$ (L' = PPh_3 or L^{Et}), but instead afforded $[RuCl(L^{R'})(L^{Et})(PPh_3)]$ (7; R' = C_6H_4Me-4); formally this arises by loss of NOCl, although $[CN(Et)CH_2CH_2NEt]_2Cl_2$ was isolated from the reaction mixture. The formation of complex (7) is rather surprising and may involve the sequence in Scheme 7.

TABLE 2

Selected i.r. spectroscopic data (cm^{-1}) for carbene-ruthenium(II) complexes

Complex	$\nu(CN_2)$ [a]	$\nu(CO)$ (NO)	$\nu(Ru-Cl)$ [a]
(1)	1 502mw		*b*
(2)	1 519m		*b*
(3)	1 512m		*b*
(4)	1 502m		*b*
(5)	1 500w		*b*
(6)	1 519mw		*b*
(7)	1 520mw, [c] 1 502mw [d]		*b*
(8)	1 515m		*b*
(9)	1 512m		*b*
(10)	1 507w	1 969s, [a] 1 954s [e]	*b*
(11)	1 498w	1 935s [f]	248mw
(12)	1 501mw	1 942s [f]	*b*
(13)	1 503w		*b*
(14)	1 501w, [c] 1 488w [d]	1 922s [e]	*b*
(15)	1 523m	1 951s [e]	*b*
(16)	1 518mw	1 932s [f]	*b*
(17)			228w
(18)	1 514w		242w
(19)	1 521mw		230m
(20) [g]	1 518mw		234m
(21)	1 517mw		
(22)	1 520w		*b*
(23)	1 521	(1 808s [a])	301w, 291m
(24)	1 511m	1 961s [a]	*b*
(26)	1 620vs, 1 518s		340m, 310w

[a] Dilute Nujol mull. [b] Bands due to $\nu(Ru-Cl)$ in the region 210—250 cm^{-1}, vw and not assigned. [c] $\nu(CN_2)(L^{R'})$. [d] $\nu(CN_2)(L^{Et})$. [e] In CH_2Cl_2 solution. [f] In MeC_6H_{11} solution. [g] Slow loss of MeCN; $\nu(C{\equiv}N)$ at 2 268w cm^{-1}.

Spectroscopic Properties.—The data obtained by i.r. and ^1H, ^{13}C, and ^{31}P n.m.r. spectroscopy are listed in Tables 2—5.

Both five- and six-co-ordinate complexes exhibit a characteristic $\nu(CN_2)$ band (Table 2), typically at 1 490—1 525 cm^{-1}, and those containing a carbonyl ligand give rise to $\nu(CO)$ at 1 920—1 960 cm^{-1}, comparable to $\nu(CO)$ (*trans* to Cl) at 1 960 cm^{-1} in $[Ru(CO)Cl_2\{C(H)NH(C_6H_4Me\text{-}4)\}(PPh_3)_2]$.[25] The lowest value of $\nu(CO)$, at 1 922 cm^{-1}, was in the bis(carbene) complex (14), $[Ru(CO)Cl(L^{Ph})(L^{Et})(PPh_3)]$, consistent with the higher σ-donor : π-acceptor ratio of the ligand L^{Et} com-

$$\underset{(23;\ R' = C_6H_4Me\text{-}4)}{[RuCl_2(L^{R'})(NO)(PPh_3)]} \xrightarrow{-Cl^-} [RuCl(L^{R'})(NO)(PPh_3)] + \tfrac{1}{2}[CN(Et)CH_2CH_2NEt]_2Cl_2 \xrightarrow{-NO} \underset{(7;\ R' = C_6H_4Me\text{-}4)}{[RuCl(L^{R'})(L^{Et})(PPh_3)]}$$

SCHEME 7

TABLE 3

Hydrogen-1 n.m.r. spectroscopic data [a] for carbeneruthenium(II) complexes

Complex	Solvent	Carbene ring CH_2	Aryl-( )-CH_3	Aryl H	Others
(1)	$CDCl_3$	7.1 (m)		(2.2—4.0) (m)	
(2)	$CDCl_3$	7.1 (m)	7.87, 7.58	2.9 (s) [b] (3.5, 3.2, 4.2) (m) [c]	
(3)	$CDCl_3$	7.15 (m)	6.4, 6.1	3.0 (q), [b] (4.2, 3.8, 3.2) (m) [c]	
(4)	C_6D_6	6.41 (m)		3.2, 2.7, 2.2	9.1 (m), 8.4 (m) [d]
(5)	$CDCl_3$	6.9 (m)		(2.4—3.0) (m), (3.1—3.9) (m)	
(6)	C_6D_6	6.3 (m)	7.73, 7.41	1.8, [e] 3.0, [b] 3.5 (q) [f]	
(7)	CD_2Cl_2	6.8 (m), 6.6 (m)	7.65, 7.58	(2.0—4.2) (m)	7.5 (m), [g] 9.3 (t) [h]
(8)	C_6D_6	7.4 (m,br)	7.6, 7.75	(2.0—4.2) (m)	
(9)	C_6D_6	7.30 (m,br)	7.50, 7.80	(2.0—4.2) (m)	
(10)	$CDCl_3$	6.6 (m,br)		(2.0—4.0) (m)	
(11)	$CDCl_3$	5.8 (br)		(2.0—3.4) (m)	9.0 (m), 8.4 (m) [d]
(12)	$CDCl_3$	5.95 (br)		(2.1—3.5) (m)	(7.8—9.1) [d]
(13) [i]	$CDCl_3$	6.08 (m)		(2.6—3.6) (m)	{(6.1—7.0) (m), [g] 9.1 (t) [h]
(14)	$CDCl_3$	6.0 (br)		(2.0—4.7) (m)	
(15)	$CDCl_3$	6.57 (m)	7.9, 7.5	2.8, (3.3—4.2) (m)	
(16)	$CDCl_3$	5.98 (br)	7.65, 7.58	2.0, [e] 2.7, [b] 3.6 (q) [f]	
(17)	$CDCl_3$	6.0 (m)	7.70, 7.60	(2.2—3.6) (m)	9.0 (m), 8.4 (m) [d]
(18)	$CDCl_3$	6.52 (br)	7.80, 7.67	(2.2—3.6) (m)	
(19)	$CDCl_3$	6.0 (br)	7.63, 7.58	(2.2—3.5) (m)	9.0 (m), 8.4 (m) [d]
(20) [j]	$CDCl_3$				
(21)	$CDCl_3$				
(22)	$CDCl_3$				
(23)	$CDCl_3$	6.3 (m)	8.03, 7.60	(2.3—2.8) (m), (3.3q) [f]	
(24)	$CDCl_3$	6.4 (m)	6.52, 6.48	(2.2—4.0) (m)	
(38) [k]	$CDCl_3$	6.70 (m)	6.5, 6.15	2.7 (q), [b] (3.4—4.2) [c]	
(39) [l]	C_6D_6	7.0 (br)	7.5, 7.8	(1.7—3.8) (m)	
(40) [m]	C_6D_6	7.4 (m,br)	7.4, 7.8	(2.6—4.0) (m)	

[a] Values quoted relative to $SiMe_4$ ($\tau = 10$), spectra recorded at 35 °C; all resonances singlets unless stated as d = doublet, t = triplet, m = multiplet or complex, br = broad. [b] Non-*ortho*-metallated aryl-ring protons. [c] *ortho*-Metallated aryl-ring protons. [d] PR_3 proton resonances. [e] *ortho*-Metallated aryl-C^3 proton. [f] *ortho*-Metallated aryl-C^5 and -C^6 protons, AB quartet. [g] N–CH_2CH_3 from L^{Et} ligand. [h] N–CH_2CH_3 from L^{Et} ligand. [i] One $P(OMe)_3$ labile in solution. [j] MeCN labile in solution. [k] $[Ru(CO)Cl(L^{R'})(PPh_3)_2]$ (36; R′ = C_6H_4OMe-4) not characterised by analysis. [l] $[Ru(CO)Cl(L^{R'})(PMe_2Ph)_2]$ (37; R′ = C_6H_4Me-4). [m] $[Ru(CO)Cl(L^{R'})(PEt_2Ph)_2]$ (38; R′ = C_6H_4Me-4); (38) and (40) were not analysed.

TABLE 4

Selected ^{13}C n.m.r. chemical shifts [a] and coupling constants [b] (Hz) of carbeneruthenium(II) complexes

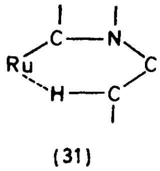
Complex	Solvent	$C_{carb.}$	$^2J(C_{carb.}–P)$	CO	$^2J(C_{CO}–P)$	Ru–C^2	$^2J(C^2–P)$	NCH_2CH_2N	Aryl-( )-CH_3
(2)	$CDCl_3$	220.5 (t)	9.9			149.1 (t)		42.2, 47.8	20.9
(6)	C_6D_6	223.3 (t)	9.7			157.3 (t)	12.2	44.1, 48.5	21.7, 20.7
(7)	CD_2Cl_2	220.6 (d)	9.1			158.2 (d)	14.4	43.7, 50.5	21.0, 20.6
		213.4 (d) [c]	88.5 [c]					47.9	
(11)	$CDCl_3$	219.9 (t)	9.9	201.1 (t)	11.4	161.1 (t)	14.5	44.4, 54.8	
(15)	$CDCl_3$	216.9 (t)	9.9	202.4 (t)	9.9	158.9 (t)	15.2	43.6, 53.5	21.3, 21.0
(16)	$CDCl_3$	219.3 (t)	9.7	201.2 (t)	10.7	161.2 (t)	15.2	44.4, 54.9	21.3
(19)	$CDCl_3$	217.4 (q)	9.2 [d]			159.2 (m)	*ca.* 82 [e]	44.0, 55.9	
(23)	$CDCl_3$	205.9 (d)	7.6			164.1 (d)	16.8	44.2, 54.6	20.1, 20.5
(24)	$CDCl_3$	219.3 (t)	9.9	202.0 (t)	9.9	160.2 (t)	15.3	47.4, 53.3	54.5, 56.2

[a] Values quoted relative to $SiMe_4$ ($\delta = 0$ p.p.m.); all peaks singlets unless stated d = doublet, t = triplet, q = quartet, m = multiplet. [b] ±1.5 Hz. [c] Values for L^{Et} ligand. [d] $^2J(AX) \approx {}^2J(BX)$. [e] $^2J(C^2–PF_3)$.

pared with PPh_3 (*cf.* refs. 26 and 27). The observation generally of only one ν(CO) absorption confirms ^{13}C, ^1H, and ^{31}P n.m.r. spectroscopic results which indicate the presence of only one stereochemical isomer in each of the carbonylruthenium(II) complexes.

Hydrogen-1 n.m.r. spectroscopy (Table 3) clearly differentiates (*i*) the aryl ring-CH_3 substituent, (*ii*) the ring CH_2 protons, and (*iii*) the *ortho*-metallated ring protons. For the complexes derived from the methoxyphenyl or tolyl olefin $L^{R'}{}_2$ [R′ = C_6H_4OMe-4(or -2) or C_6H_4Me-4] two sharp singlets are observed for the different Me groups, and the ring-methylene protons form a distinct AA′BB′ pattern; in complexes other than (1)—(3) the latter feature is less clear.

For $[RuCl(L^{R'})(PEt_3)_2]$ (6; R′ = C_6H_4Me-4) crystallographic data (see below and ref. 6) demonstrate that the formally vacant sixth co-ordination site about an octahedral Ru^{II} atom is occupied by an *ortho*-hydrogen atom. Evidence was sought for the same phenomenon in solution by low-temperature n.m.r. studies, as had previously been observed in a few other systems (*e.g.*



(31)

TABLE 5

Phosphorus-31 n.m.r. chemical shifts * for carbene-ruthenium(II) complexes

Complex	PPh_3	PEt_3	PF_3
(2)	−109.4 (s)		
(15)	−111.7		
(16)		−127.5 (s)	
(18)	−113.1 (d) $^2J(P_{F_3} - P_{Ph_3})$ 34.8		−12.3 (q of t) $^1J(F - P)$ 1 303.7 $^2J(P_{Ph_3} - P_{F_3})$ 35
(19)		−131.0 (d) $^2J(P_{F_3} - P_{Et_3})$ 36.4	−14.7 (q of t) $^1J(F - P)$ 1 301.2 $^2J(P_{Et_3} - P_{F_3})$ 36.6

* In $CHCl_3$, relative to $P(OMe)_3$; C_6D_6 capillary internal lock. Negative sign to high field of $P(OMe)_3$. All peaks singlets unless stated, d = doublet, t = triplet, q = quartet. *J* values in Hz.

ref. 28). However, even at −95 °C, there was no evidence for a locked Ru · · · H interaction as in (31). Presumably the *N*-aryl rotation $NC_6H_4CH_3$ is too rapid even at −95 °C in solution and the *p*-tolyl ring protons are seen as a singlet (not the more normal AA′BB′ ' quartet ') which merely broadens upon cooling.

The greatest amount of new data (Table 4) derives from ^{13}C n.m.r. spectroscopic studies. The values of $^2J(C_{carb.}-P)$, $^2J(C_{CO}-P)$, and $^2J(C_{o-Me}-P)$ [$^2J(C^2-P)$] are essential for stereochemical assignments. The chemical shift $\delta(C_{carb.})$ is at 225—215 p.p.m. (relative to $SiMe_4$), similar to that in related compounds such as *trans*-$[Ru(CO)Cl_2(L^{Et})_3]$ or $[RuX_2(L^R)_3]$ (R = Me, X = Cl or I; R = Et, X = Cl).[5] The carbonyl chemical shift, $\delta(C_{CO})$, is at slightly higher field (*ca.* 200 p.p.m.); and $\delta(C^2)$ at *ca.* 160 p.p.m. is shifted (33—44 p.p.m.) to lower field from its free-ligand ($C^{2',6'}$) value of ~116 p.p.m. in the five-co-ordinate and ~127 p.p.m. in the six-co-ordinate complexes (Table 5). The latter difference of 10—13 p.p.m. may be a consequence of the non-bonded Ru · · · H interaction being possible only in the five-co-ordinate complexes. Similarly low values of $\delta(C^2)$(aryl) have previously been observed; *e.g.* for $[Pt(L^{Et})_2(C_6H_4F-3)_2]$,[29a,b] $\delta(C_{aryl})$ is at 165 p.p.m.[29b]

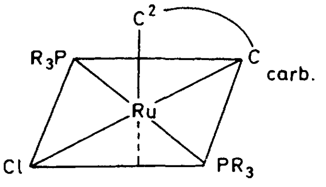
Both of the complexes $[RuCl_2(PPh_3)_3]$[16] and $[RuCl(L^{R'})(PEt_3)_2]$ (see below and ref. 6), (6), are square pyramidal, as predicted from second-order Jahn–Teller effects for low spin d^6 complexes,[30,31] an *ortho*-H from an aryl ring (31) completing a pseudo-octahedral environment around Ru. However, the tris(phosphine) complex, as shown by ^{31}P n.m.r. studies, is fluxional,[18] and loses PPh_3 in solution to form a binuclear species. By contrast, the new five-co-ordinate compounds are stereochemically rigid because of the constraint of *ortho*-metallation which requires $C_{carb.}$ and C^2 (C_{o-Ru}) to be mutually *cis* and the closer proximity of an *N*-aryl H to the metal.

For $[RuCl(L^{R'})(PR_3)_2]$ complexes generally [see (32)], ^{31}P n.m.r. spectroscopy shows (Table 5) (*i*) magnetic equivalence of the two PR_3 ligands in the temperature range −90 to +25 °C and (*ii*) similar values of $^2J(CP)$ for both $C_{carb.}$ and C_2 (as found from ^{13}C n.m.r.), indicating non-fluxional behaviour for this class of complex (This has also been noted for the unusual purple cation $[Ru(PR_3)_3\{S_2C(PR_3)H\}]^+$ ($R_3 = Me_2Ph$), in which a phenyl ring occupies the vacant site;[32] this has the added effect of preventing co-ordination of an amine or MeCN, although no mention was made of reaction with CO.[32]) Typical values of 9—10 or 12—14 Hz for $^2J(C_{carb.}-P)$ or $^2J(C^2-P)$, respectively, are comparable to those observed in various complexes *cis*-$[Ru(CO)_2Cl_2(PR_3)_2]$,[33] and are indicative of (*i*) *trans* arrangements of the PR_3 ligands and (*ii*) *cis* disposition of each of $C_{carb.}/C^2$, $C_{carb.}/PR_3$, and C^2/PR_3, as confirmed for complex (6) by *X*-ray crystallography (see below).

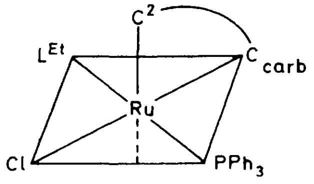
The ^{13}C n.m.r. spectrum of $[RuCl(L^{R'})(L^{Et})(PPh_3)]$ (7; R′ = C_6H_4Me-4) shows low ^2J values for both $C_{carb.}$ ($L^{R'}$) and C^2, at 9.1 and 14.4 Hz, respectively. However, $^2J(C-P)$ [$C_{carb.}(L^{Et})-PPh_3$] is very large, 88.5 Hz, thus indicating that (*i*) L^{Et} is *trans* to PPh_3 as in (33) and (*ii*) the complex is sterically rigid at 25 °C.

Six-co-ordinate low-spin d^6 metal complexes are expected to be octahedral and stereochemically rigid. For the appropriate bis(phosphine) complexes, a single ^{31}P signal indicates *trans* arrangements of these ligands, but ^{13}C n.m.r. spectroscopy, from $^2J(C-P)$ provides more information on stereochemistry.[34] In the spectra of the complexes $[Ru(CO)Cl(L^{R'})(PR_3)_2]$ the three Ru–*C* signals are each a triplet, with $^2J(C-P)$ values of *ca.* 10, 10—11, and 14—15 Hz for P–$C_{carb.}$, P–C_{CO}, and P–C^2, respectively. This shows that these three ligating C atoms are each *cis* with respect to a phosphine. Hence $C_{carb.}$ and C^2 must be mutually *cis*, but CO or Cl may be *trans* to either, corresponding to structure (34) or (35). Substitution of CO by PF_3 provides an additional spectroscopic probe because of the large variation in $^2J(C-P)$ depending on whether the coupling across the metal is *cis* or *trans*. Thus in the ^{13}C n.m.r. spectrum of $[RuCl(L^{R'})(PEt_3)_2(PF_3)]$, $C_{carb.}$ is observed as a quartet, with $^2J(C-P)$ 9.2 Hz, and the couplings $C_{carb.}-PEt_3$ and $C_{carb.}-PF_3$ are essentially identical, indicating $C_{carb.}$ to be in an environment *cis* to the three phosphine ligands. The C^2 signal, observed as a doublet [each peak being broad with poorly resolved fine structure due to additional couplings *via* the ^{19}F and the two ^{31}P (from PEt_3) nuclei] with $^2J(C^2-PF_3)$ *ca.* 82 Hz, indicated PF_3 to be *trans* to C^2 and the overall stereochemistry to be as shown in (36). By analogy,[35] we conclude that the PF_3 and CO complexes have the same configuration, with CO *trans* to C^2 as in (34), and this is confirmed for $[Ru(CO)Cl(L^{R'})(PEt_3)_2]$ (16; R′ = C_6H_4Me-4) by *X*-ray crystallography (see below). Such a stereochemistry is probably thermodynamically the most favoured in complexes of the general type $[RuL(L')(PR_3)_2X(X')]$ (L = CO or PF_3, L′ = neutral ligand, R = aryl or alkyl, X,X′ = anionic ligands),[25,33,36-38] and is often referred to as that of the *cis* isomer.

Values of ${}^2J$(C–P) are similarly used to assign the stereochemical arrangement of ligands in $[\mathrm{RuCl_2(L^{R'})(NO)(PPh_3)}]$ (23; R′ = $\mathrm{C_6H_4Me}$-4) as being that shown in (37), the *cis* isomer. One rather surprising consequence is the mutual *cis* configuration of the neutral phosphorus- and carbon-ligating donors; they are generally *trans*, *e.g.* in complexes $[\mathrm{RuCl_3L_2(NO)}]$ (L = phosphine [36] or carbene [23]). However, it is advantageous that the good π-acceptor ligand NO is *trans* to C², as is the case in (34) and (36) for the π acceptors CO or $\mathrm{PF_3}$.



(32)



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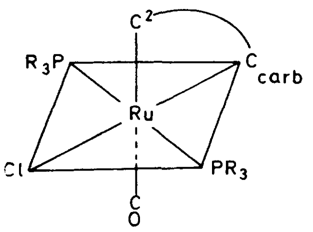
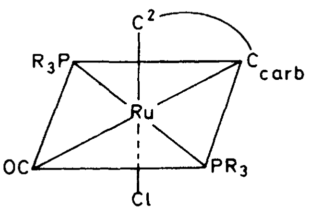
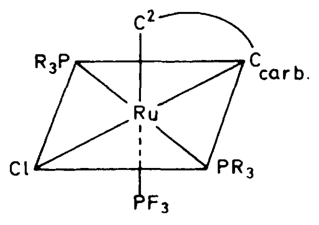


(34)
cis



(35)
trans



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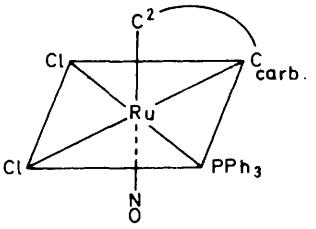

(37)

Molecular Structure of Crystalline (6) *and* (16).—The molecular configuration of the two molecules $[\mathrm{RuCl(L^{R'})(PEt_3)_2}]$ (6) and $[\mathrm{Ru(CO)Cl(L^{R'})(PEt_3)_2}]$ (16) (R′ = $\mathrm{C_6H_4Me}$-4) and the atom-numbering schemes are shown in Figure 1. No attempt has been made to show the alternative sites for disordered carbon atoms of the ethyl groups. Figure 2 contains views of the mean co-ordination planes of the carbene ligands with the $\mathrm{PEt_3}$ groups removed, together with selected bond lengths and angles. In both molecules the $\mathrm{PEt_3}$ groups are *trans* and eclipsed, the torsion angles Cl–Ru–P(1)–C(19) and Cl–Ru–P(2)–C(17) being both nearly equal in magnitude and opposite in sign, as are the other two pairs of Cl–Ru–P–C torsion angles in both molecules. In both cases the Ru–P bonds are bent slightly towards the Cl atom with a mean Cl–Ru–P angle of 87.4°.

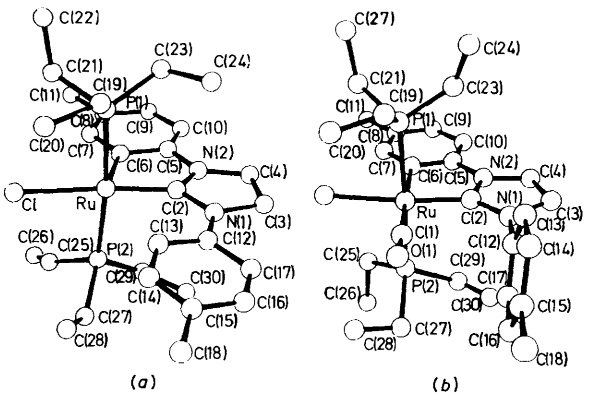

FIGURE 1 Equivalent views of the two molecules (*a*) (6) and (*b*) (16), showing the molecular conformation and atom-numbering schemes. Only the major sites for the disordered ethyl-carbon atoms are shown

The imidazoline rings have dimensions similar to those observed in related carbene ligands except that the C(3)–C(4) bonds [average 1.52(1) Å] are as expected for a single bond between two sp^3-hybridised C atoms and do not show the shortening seen in related molecules.[5] In complex (6) the ring is strictly planar (±0.008 Å), whilst in (16) there is slight puckering (±0.052 Å), perhaps reflecting slightly higher steric strain. The *ortho*-metallated phenyl ring is in both cases coplanar with the carbene ring, whilst the pendant phenyl ring is very different in the two molecules.

The major change in conformation on adding the carbonyl ligand to complex (6) to form (16) can be seen to involve an anticlockwise rotation of the Ru–Cl bond around the normal to the plane (as viewed in Figure 2) to bring it nearer to C(7), together with a rotation of the pendant phenyl ring about the bond N(1)–C(12) to bring it from coplanar with the imidazoline ring to 85° out of plane, thus allowing the CO ligand to occupy a site

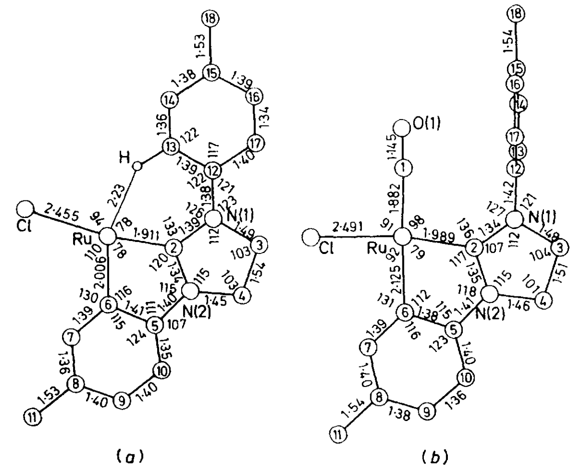

FIGURE 2 Molecules (*a*) (6) and (*b*) (16), viewed perpendicular to the mean plane of the carbene, chlorine, and carbonyl ligands, with the $\mathrm{PEt_3}$ groups omitted. Bond lengths (Å) and angles (°) are shown for comparison

giving overall closely octahedral co-ordination at Ru. Less obvious is a further slight change in the geometry of the carbene ligand involving a clockwise rotation about its normal of the imidazoline ring and its pendant phenyl group to move it slightly further away from the CO ligand, together with a concomitant anticlockwise rotation of the *ortho*-metallated phenyl ring about its normal. This can best be seen from the increase in the angles C(6)–C(5)–N(1), C(2)–N(2)–C(5), and the decrease in Ru–C(1)–N(2) and Ru–C(6)–C(5) on comparing (6) with (16).

In complex (6) the calculated position of H(13) assuming normal phenyl-ring geometry with C–H 1.08 Å puts it in the formally vacant sixth co-ordination site of the Ru with a contact distance Ru ··· H(13) of 2.23 Å. Such a close contact would normally be regarded as strongly repulsive, and since we know that the phenyl ring can rotate so as to move the H atom away from the metal without getting too close to the PEt_3 groups it seems highly probable that the Ru ··· H(13) interaction is in fact weakly bonding. The contact distance of 2.23 Å is smaller than most other ' non-primary valence ' interactions [39] of metals with phenyl-ring hydrogens such as 2.45 Å in $[RuCl_2(PPh_3)_3]$ [16] and 2.73 Å in $[Pd(PBu^t{}_2Ph)_2]$.[40] Similarly short M ··· H interactions have only been seen in a palladium(II) complex of tetrakis(methoxycarbonyl)buta-1,3-diene (Pd ··· H 2.3 Å) [41] and in dialkylpyrazol-1-ylborate complexes of molybdenum (Mo ··· H ~2.2 Å).[42] In the latter case Cotton *et al.*[28] have suggested that the molybdenum complex, formally a 16-electron system, attains the inert-gas (18-electron) configuration by forming a three-centre two-electron bond with a hydrogen atom of the B–C–H ligand moiety. It seems that the favourable geometry in our *ortho*-metallated carbene complex enables a similar M ··· H–C interaction to give a formal 18-electron configuration. This close contact to the metal of a phenyl ring separated from the metal by two atoms (as in phosphite complexes [7]) is presumably the reason for the ready metallation of the other phenyl ring in the formation of complex (6).

In complex (6) the two Ru–C(sp^2) distances are significantly different. That to the metallated phenyl ring [Ru–C(6) 2.006(8) Å] is similar to that seen in an *ortho*-metallated perfluoroazobenzene complex of Ru^{II} [2.013(6) Å],[42] both being at the short end of the range of Ru–C bond lengths discussed in ref. 42. The Ru–C(2) bond to the carbene C atom of length 1.911(9) Å is one of the shortest such bonds so far reported, *cf.* $[RuCl_2(L^{Et})_4]$ [average Ru–C 2.105(5) Å],[5] and as such might be indicative of some multiple-bond character in the Ru–C bond. However, the carbene is now part of a chelating ligand forming a tricyclic fused three-ring system with the metal. In another metallocycle of this type, $[PtCl_2(PEt_3)_2\{C(NHC_6H_3Cl\text{-}4)(NHMe)\}]^+$,[13] the Pt–C(carbene) bond of 1.985(16) Å is 0.04 Å shorter than the Pt–C(phenyl) bond of 2.033(13) Å, and once again the Pt–C(carbene) distance is shorter than that in non-chelating systems, *e.g.* *trans*-$[PtCl_2\{C(CH_2NPh)_2\}(PEt_3)]$ [2.020(16) Å] and *cis*-$[PtCl_2\{C(CH_2NPh)_2\}(PEt_3)]$ [2.009(13) Å].[43] It may simply be that in a chelating system with a relatively small ' bite ' angle the metal–ligand bonds are inherently shorter.

Since complexes (6) and (16) differ only in the replacement of a weak Ru ··· H–C contact for a carbonyl ligand, it is interesting to compare corresponding bond lengths in the two structures. The only significant differences in bond length are from the Ru atom to the first co-ordination sphere and in every case the bond increases in length on changing from (6) to (16). The smallest increase is 0.011 Å for the Ru–P bonds, the largest 0.119 Å for the Ru–C(6) bond, and the other two Ru–C(2) 0.078 Å and Ru–Cl 0.036 Å are intermediate. It is difficult to apportion this result between σ- and π-bond effects. If it were purely a π-bonding effect, then the π-acceptor qualities of the CO ligand might be regarded as leaving less metal π-electron density to participate in π bonding to the delocalised π system of the carbene and phenyl rings. This would suggest that the major effect would be to increase the M–C bond lengths and would not explain the effect on the M–Cl and to a lesser extent the M–P bonds. If, on the other hand, it were purely a σ-bond effect, then it might be expected that the σ-donor properties of CO are greater than those for the C–H ··· Ru bond and that this would increase the bond length to the *trans* ligand, Ru–C(2), with much less effect on the *cis* ligand. Alternatively, the addition of the CO ligand might simply decrease the effective nuclear charge of the Ru atom and thus increase all the ruthenium–ligand bond lengths. Probably it is a combination of possible causes giving the observed bond-length differences.

EXPERIMENTAL

General procedures have been described previously.[1] The electron-rich olefins were prepared by the literature method [44] from the relevant diamine, and $[RuCl_2(PPh_3)_3]$ and $[RuCl_3(NO)((PPh_3)_2]$ were prepared from $RuCl_3{\cdot}3H_2O$ by the published procedures; [45] only typical experiments are described.

Complexes of the Type $[RuCl(L^{R'})(PPh_3)_2]$.—A mixture of dichlorotris(triphenylphosphine)ruthenium(II) (0.96 g, 1.0 mmol) and bi[1,3-bis(4-methoxyphenyl)imidazolidin-2-ylidene] (0.59 g, 1.05 mmol) in xylene (25 cm³) was heated to a vigorous reflux. The brown suspension slowly disappeared and was replaced by a deep red solution and a brown-green precipitate, which slowly became pale yellow (20 min). The mixture was rapidly filtered (*ca.* 130 °C) and on cooling deposited red crystals. These were filtered off, washed copiously with diethyl ether (10 × 5 cm³) and pentane (5 × 5 cm³), and dried under high vacuum to afford [*1,3-bis(4-methoxyphenyl)imidazolidin-2-ylidene-*$C^2C^{2'}$]*chlorobis(triphenylphosphine)ruthenium*(II), (3) (0.80 g, 85%).

Notes. (*a*) On performing syntheses of this type a deficiency of the electron-rich olefin and a shorter reaction period results in incomplete conversion, green $[HL^{R'}]_2[RuCl_4(PPh_3)_2]$ being formed. Refluxing the green ruthenium(II) complex in xylene with more olefin results in formation of the red *ortho*-metallated species and the pale yellow hydrochloride salt [HL$^{R'}$]Cl.

(*b*) For R′ = Ph, an increased volume of solvent and rapid filtration through a sinter preheated to *ca.* 140 °C is necessary to prevent crystallisation occurring during the filtration process.

Complexes of the Type [RuCl(L$^{R'}$)(PR$_3$)$_2$] (R = *alkyl*).—To a suspension of complex (2) (0.51 g, 0.58 mmol) in methylcyclohexane (10 cm^3) was added triethylphosphine (0.14 g, 1.2 mmol) and the mixture slowly heated to 100 °C. The suspension dissolved and the solution became a deep red-orange. Cooling slowly to 20 °C and then to 0 °C afforded [1,3-*bis*(4-*tolyl*)*imidazolidin*-2-*ylidene*-C^{2}C$^{2'}$]*chlorobis*(*triethylphosphine*)*ruthenium*(II), (6) (0.32 g, 95%), as dark red-orange, rather air-sensitive crystals.

[RuCl(L$^{R'}$)(L^{Et})(PPh$_3$)] (R′ = C$_6$H$_4$Me-4).—To a suspension of complex (2) (0.64 g, 0.70 mmol) in toluene (10 cm^3) was added bi(1,3-diethylimidazolidin-2-ylidene) (0.38 g, 1.5 mmol) and the mixture refluxed (5 h), cooled (0 °C), and filtered. Further cooling (−25 °C, 72 h) afforded an orange-brown microcrystalline precipitate, removed by filtration. Addition of hexane (5 cm^3) to the filtrate and further cooling (−25 °C, 48 h) gave a second crop of product. The portions were combined, washed with cold (0 °C) diethyl ether (2 × 5 cm^3), hexane (3 × 5 cm^3), and dried under vacuum to give [1,3-*bis*(4-*tolyl*)*imidazolidin*-2-*ylidene*-C^{2}C$^{2'}$]*chloro*(1,3-*diethylimidazolidin*-2-*ylidene*)(*triphenylphosphine*)*ruthenium*(II), (7) (0.44 g, 80%).

Complexes of the Type [Ru(CO)Cl(L$^{R'}$)(PPh$_3$)$_2$].—Into a solution of complex (2) (0.96 g, 1.0 mmol) in toluene (10 cm^3) was slowly bubbled carbon monoxide until the solution became colourless (2 min). Hexane (5 cm^3) was added, and the mixture cooled (−20 °C, 12 h) to give an off-white solid, recrystallised by layering hexane onto a CH$_2$Cl$_2$ solution of the complex (20 °C, 72 h) to afford [1,3-*bis*(4-*tolyl*)*imidazolidin*-2-*ylidene*-C^{2}C$^{2'}$]*carbonylchlorobis*(*triphenylphosphine*)*ruthenium*(II), (15) (0.80 g, 80%).

Complexes of the Type [Ru(CO)Cl(L$^{R'}$)(PEt$_3$)$_2$].—Carbon monoxide was slowly bubbled through a suspension of complex (6) (0.62 g, 1.00 mmol) in MeC$_6$H$_{11}$ (10 cm^3) at 20 °C and the deep red-orange suspension became colourless (*ca.* 1 min). Toluene was added dropwise until the solid just dissolved, and the mixture was filtered then cooled (−25 °C, 7 d) to afford white crystals of [1,3-*bis*(4-*tolyl*)-*imidazolidin*-2-*ylidene*-C^{2}C$^{2'}$]*carbonylchlorobis*(*triethylphosphine*)*ruthenium*(II), (16) (0.59 g, 90%).

Complexes of the Type [RuCl(L$^{R'}$)(PF$_3$)(PR$_3$)$_2$] (R = Ph *or* Et).—Trifluorophosphine was gently bubbled through a solution of complex (6) (0.37 g, 0.60 mmol) in toluene (5 cm^3) for *ca.* 2 min and the solution became colourless. Diethyl ether (10 cm^3) was added and the reaction mixture filtered; cooling (−25 °C, 72 h) gave an off-white powder, recrystallised from toluene–pentane (1 : 1; −25 °C, 72 h) to afford white crystals of [1,3-*bis*(4-*tolyl*)*imidazolidin*-2-*ylidene*-C^{2}C$^{2'}$]*chlorobis*(*triethylphosphine*)(*trifluorophosphine*)*ruthenium*(II), (19) (0.35 g, 80%).

[RuCl(L$^{R'}$)(PEt$_3$)$_2${P(OMe)$_3$}].—To a solution of complex (6) (0.30 g, 0.48 mmol) in benzene (5 cm^3) was added trimethyl phosphite (0.18 g, 1.5 mmol) and the solution became colourless. Addition of hexane (10 cm^3) and cooling (−25 °C, 24 h) gave off-white oily crystals. These were twice recrystallised from hot methylcyclohexane (10 cm^3) containing trimethyl phosphite (0.01 g) by allowing the hot solution, after filtration, to cool slowly to −20 °C to afford white crystals of [1,3-*bis*(4-*tolyl*)*imidazolidin*-2-*ylidene*-C^{2}C$^{2'}$]*chlorobis*(*triethylphosphine*)*trimethyl phosphite*-*ruthenium*(II), (17) (0.28 g, 80%).

[RuCl(L$^{R'}$){P(OMe)$_3$}$_3$].—To a suspension of complex (1) (0.88 g, 1.0 mmol) in MeC$_6$H$_{11}$ (15 cm^3) was added trimethyl phosphite (0.37 g, 3.5 mmol) and the mixture heated (100 °C, 10 min) to give a deep red solution which then became colourless. The solution was cooled (40 °C), filtered, and allowed to stand (20 °C, 48 h) to deposit white crystals. These were recrystallised from hot MeC$_6$H$_{11}$ containing 0.01 g trimethyl phosphite, affording white crystals of *chloro*(1,3-*diphenylimidazolidin*-2-*ylidene*-C^{2}C$^{2'}$]-*tris*(*trimethyl phosphite*)*ruthenium*(II), (13) (0.28 g, 80%).

[RuCl$_2$(L$^{R'}$)(NO)(PPh$_3$)].—Trichloronitrosylbis(triphenylphosphine)ruthenium (0.76 g, 1.0 mmol) and bi[1,3-bis(4-tolyl)imidazolidin-2-ylidene] (0.50 g, 1.0 mmol) in xylene (30 cm^3) were vigorously refluxed to give a brown-orange suspension. The solid was filtered off, washed with OEt$_2$ (5 × 5 cm^3), and dried. It was then washed with water (100 °C, 3 × 10 cm^3) (to remove the hydrochloride salt), ethanol (2 × 5 cm^3), OEt$_2$ (3 × 5 cm^3), and dried to afford [1,3-*bis*(4-*tolyl*)*imidazolidin*-2-*ylidene*-C^{2}C$^{2'}$]*dichloronitrosyl*(*triphenylphosphine*)*ruthenium*(II), (23) (0.63 g, 90%).

Reaction of [RuCl(NO)(PPh$_3$)$_2$] *with* L$^{R'}_2$ (R′ = C$_6$H$_4$Me-4).—A mixture of chloronitrosylbis(triphenylphosphine)ruthenium (0.69 g, 1.0 mmol) and bi[1,3-bis(tolyl)-imidazolidin-2-ylidene] (0.50 g, 1.0 mmol) in xylene (20 cm^3) was heated (140 °C, 30 min) to give a deep red solution, which was filtered and cooled (−25 °C, 7 d) to afford complex (2), identified by ^{1}H n.m.r. and i.r. spectroscopy.

Reaction of [RuCl$_2$(L$^{R'}$)(NO)(PPh$_3$)] *with* L$^{Et}_2$.—A suspension of complex (21) (0.35 g, 0.5 mmol) in xylene (10 cm^3) was heated (100 °C) with bi(1,3-diethylimidazolidin-2-ylidene) (0.25 g, 1.0 mmol) to give a brown-red solution and off-white solid, removed by filtration. Diethyl ether (15 cm^3) was added to the filtrate which was then cooled (−30 °C, 7 d) to afford small brownish crystals of complex (7), identified by ^{1}H n.m.r. and i.r. spectroscopy.

Reaction of [RuCl(L$^{R'}$)(PPh$_3$)$_2$] *with* NaI.—To complex (2) (0.45 g, 0.5 mmol) in acetone (15 cm^3) was added NaI (0.15 g, 1.0 mmol) and the mixture stirred (50 °C, 12 h). The solvent was removed, extracted with hot (70 °C) toluene (3 × 5 cm^3), and the extract filtered. Addition of OEt$_2$ (15 cm^3) and cooling (−25 °C, 72 h) afforded small deep crimson crystals of [1,3-*bis*(4-*tolyl*)*imidazolidin*-2-*ylidene*-C^{2}C$^{2'}$]*iodobis*(*triphenylphosphine*)*ruthenium*(II), (21) (0.45 g, 90%).

Reaction of [RuCl(L$^{R'}$)(PPh$_3$)$_2$] *with* Ph$_2$PCH$_2$CH$_2$PPh$_2$ (dppe).—A mixture of complex (2) (0.22 g, 0.25 mmol) and dppe (0.10 g, 0.25 mmol) in MeC$_6$H$_{11}$ (10 cm^3) was heated to reflux (1 h) to give a pale yellow precipitate which was filtered off, washed with OEt$_2$ (5 × 5 cm^3), then pentane (5 × 5 cm^3), and dried under vacuum to afford [1,2-*bis*(*diphenylphosphino*)*ethane*][1,3-*bis*(4-*tolyl*)*imidazolidin*-2-*ylidene*-C^{2}C$^{2'}$]*chloro*(*triphenylphosphine*)*ruthenium*(II), (22).

[Ru(CO)Cl(L$^{R'}$)(PPh$_3$)$_2$] (R′ = C$_6$H$_4$OMe-2).—To a suspension of dichlorotris(triphenylphosphine)ruthenium(II) (0.48 g, 0.5 mmol) in xylene (20 cm^3) was added bi[1,3-bis-

(2-methoxyphenyl)imidazolidin-2-ylidene] (0.30 g, 0.5 mmol) and the mixture was vigorously refluxed (12 h) and filtered (50 °C). Carbon monoxide was bubbled through the filtrate (2 min) to give a colourless solution. The slow addition of hexane caused precipitation of a white solid, recrystallised by flotation of hexane onto a CH_2Cl_2 solution to afford white crystals of [1,3-*bis*(2-*methoxyphenyl*)*imidazolidin*-2-*ylidene*-$C^2C^{6'}$]*carbonylchlorobis*(*triphenylphosphine*)-*ruthenium*(II), (24) (0.24 g, 50%).

$[\overline{=CN(R)CH_2CH_2NR}]_2$ ($R = C_6H_4OMe$-2).—A mixture of *NN'*-bis(2-methoxyphenyl)ethylenediamine (10.9 g, 0.04 mol) in triethyl orthoformate (75 cm³) was refluxed (120 h) using a hot-water condenser fitted with a T piece to allow the removal of EtOH, and an oil-bath temperature of *ca.* 200 °C. Cooling (40 °C) afforded *bi*[1,3-*bis*(2-*methoxyphenyl*)*imidazolidin*-2-*ylidene*] (3.4 g, 30%) as a yellow microcrystalline precipitate. This was filtered off, washed with OEt_2 (5 × 10 cm³), and dried *in vacuo*.

Structural Investigations.—Originally it was intended to determine the crystal structure of $[\overline{RuCl(L^{Ph}})(PPh_3)_2]$ (4), but crystals obtained from methylcyclohexane solution on cooling were needle shaped, each having a hole through the centre, like beads, and they only diffracted to low angle. This phenomenon has been seen elsewhere.[46] Changing to the C_6H_4Me-4 analogue gave normal crystals suitable for structure determination.

(*a*) $[\overline{RuCl(L^{R'}})(PEt_3)_2]$ (6; $R' = C_6H_4Me$-4). *Crystal data.* $C_{29}H_{47}ClN_2P_2Ru$, $M = 622.3$, Triclinic, $a = 12.342(4)$, $b = 16.387(6)$, $c = 9.683(3)$ Å, $\alpha = 65.41(2)$, $\beta = 117.97(2)$, $\gamma = 103.79(2)°$, $U = 1\ 570.5$ Å³, $Z = 2$, $D_c = 1.32$ g cm⁻³, $F(000) = 652$, Mo-K_α radiation, $\mu = 7.0$ cm⁻¹, space group $P\bar{1}$.

TABLE 6

Final atom co-ordinates (× 10^4) for complex (6) with estimated standard deviations (e.s.d.s) in parentheses in units of the last significant figure

Atom	*X*	*Y*	*Z*
Ru	2 290.8(5)	2 644.9(4)	3 603.2(7)
P(1)	4 319(2)	3 112(1)	3 901(2)
P(2)	234(2)	2 125(2)	3 043(3)
Cl	1 641(2)	3 194(2)	567(3)
N(1)	2 719(7)	2 886(4)	6 758(8)
N(2)	3 142(7)	1 579(5)	7 050(8)
C(2)	2 750(7)	2 391(5)	5 915(9)
C(3)	3 135(9)	2 363(7)	8 586(10)
C(4)	3 436(12)	1 460(7)	8 754(11)
C(5)	3 205(8)	981(5)	6 398(10)
C(6)	2 808(7)	1 377(5)	4 644(9)
C(7)	2 860(8)	828(5)	3 904(11)
C(8)	3 240(8)	−29(6)	4 743(14)
C(9)	3 628(9)	−375(4)	6 481(14)
C(10)	3 605(9)	143(6)	7 311(12)
C(11)	3 303(11)	−596(8)	3 866(16)
C(12)	2 359(7)	3 757(5)	6 037(9)
C(13)	2 087(9)	4 265(6)	4 363(10)
C(14)	1 664(9)	5 107(6)	3 637(11)
C(15)	1 507(7)	5 498(6)	4 538(11)
C(16)	1 815(8)	4 995(6)	6 221(11)
C(17)	2 220(7)	4 162(6)	6 962(10)
C(18)	1 020(8)	6 437(6)	3 698(13)
C(19)	4 759(9)	4 307(6)	3 403(12)
C(20)	4 036(11)	4 900(7)	1 544(14)
C(21)	4 672(8)	2 784(6)	2 558(11)
C(22)	5 965(9)	3 100(8)	2 518(15)
C(23)	5 558(8)	2 628(7)	5 978(12)
C(24)	5 764(10)	3 086(9)	7 221(12)
C(25) *	−546(37)	1 588(38)	1 509(39)
C(26) *	−780(40)	1 069(17)	1 122(37)
C(27) *	−917(18)	2 921(16)	2 093(53)
C(28) *	−884(13)	3 793(12)	1 280(20)
C(29) *	−119(13)	1 224(9)	4 717(19)
C(30) *	−128(17)	1 495(14)	5 992(25)

* Occupancy 0.5.

TABLE 7

Final atom co-ordinates (× 10^4) for complex (16) with e.s.d.s in parentheses in units of the last significant figure

Atom *	*X*	*Y*	*Z*
Ru	1 960.7(4)	3 368.1(2)	2 998.6(2)
P(1)	1 993(2)	2 230(1)	2 732(1)
P(2)	2 136(2)	4 469(1)	3 452(1)
Cl	1 049(1)	3 094(1)	4 215(1)
O	−1 083(5)	3 487(3)	2 037(3)
N(1)	2 644(5)	3 734(3)	1 371(3)
N(2)	4 446(5)	3 526(3)	2 342(3)
C(1)	77(7)	3 450(3)	2 391(4)
C(2)	3 005(5)	3 570(3)	2 142(3)
C(3)	3 907(8)	3 757(4)	1 005(4)
C(4)	5 171(8)	3 683(4)	1 700(4)
C(5)	5 083(6)	3 369(2)	3 138(4)
C(6)	4 125(6)	3 257(2)	3 622(3)
C(7)	4 713(5)	3 094(2)	4 412(3)
C(8)	6 200(6)	3 054(3)	4 704(4)
C(9)	7 109(7)	3 168(3)	4 191(4)
C(10)	6 563(6)	3 319(3)	3 414(5)
C(11)	6 786(7)	2 878(4)	5 584(4)
C(12)	1 238(6)	3 812(3)	896(3)
C(13)	620(8)	3 311(3)	393(4)
C(14)	−751(9)	3 377(4)	−40(4)
C(15)	−1 539(8)	3 931(5)	−3(4)
C(16)	−894(10)	4 441(4)	496(4)
C(17)	475(8)	4 376(3)	918(4)
C(18)	−3 094(9)	4 006(6)	−473(5)
C(19)	287(9)	1 880(4)	2 233(5)
C(20)	−846(9)	1 886(4)	2 727(5)
C(21)	2 644(11)	1 730(3)	3 612(5)
C(22)	2 607(14)	983(4)	3 535(7)
C(23)	3 142(15)	1 974(6)	1 986(10)
C(24)	3 082(38)	1 406(12)	1 472(23)
C(24′)	4 780(72)	1 872(24)	2 216(28)
C(24″)	2 942(36)	1 830(23)	1 374(15)
C(25)	2 723(8)	4 549(3)	4 528(4)
C(26)	2 801(10)	5 273(4)	4 873(6)
C(27)	584(11)	4 982(4)	3 145(7)
C(28)	−579(11)	4 756(5)	3 567(8)
C(29)	3 633(27)	4 985(6)	3 131(10)
C(30)	3 421(21)	5 200(13)	2 484(16)
C(30′)	4 431(55)	5 143(14)	3 028(33)

* Alternative sites for disordered atoms are indicated by primes and double primes.

A crystal of size 0.4 × 0.3 × 0.3 mm was used for data collection on a Hilger and Watts Y290 four-circle diffractometer. Accurate cell parameters were derived by least-squares treatment of setting angles for 12 reflections. Intensities for $h \pm k \pm l$ data with $2 < \theta < 22°$ were collected by an ω—2θ step scan using Mo-K_α radiation with a graphite crystal monochromator. Each reflection was measured over 100 steps of 0.01° and 0.5 s with background counts of 25 s at each end of the scan. The intensities of three standard reflections monitored every 100 reflections showed no significant variation. The 4 201 data measured were corrected for Lorentz and polarisation effects, but not for absorption, and after averaging of any equivalent data the 3 035 unique reflections with $I > 3\sigma(I)$ based on counting statistics were used in the structure analysis.

The positions of the non-hydrogen atoms were derived by routine heavy-atom methods. It was found that the ethyl groups on P(2) were significantly disordered. The main positions were accounted for with partial occupancy, but all attempts to include further alternative sites resulted

TABLE 8

Bond lengths and bond angles with e.s.d.s in parentheses and selected torsion angles for the two structures (6) and (16)

(*a*) Bonds (Å)

	(6)	(16)
Ru–P(1)	2.351(2)	2.360(1)
Ru–P(2)	2.351(3)	2.363(2)
Ru–Cl	2.455(2)	2.491(2)
Ru–C(1)		1.882(6)
Ru · · · H(13)	2.23	
Ru–C(2)	1.911(9)	1.989(6)
Ru–C(6)	2.006(8)	2.125(5)
C(2)–N(1)	1.386(15)	1.335(7)
C(2)–N(2)	1.342(9)	1.348(7)
C(3)–N(1)	1.492(10)	1.477(9)
C(4)–N(2)	1.447(14)	1.456(9)
C(3)–C(4)	1.535(19)	1.511(9)
N(2)–C(5)	1.402(15)	1.408(7)
C(5)–C(6)	1.414(11)	1.380(9)
C(6)–C(7)	1.391(17)	1.391(7)
C(7)–C(8)	1.363(13)	1.402(7)
C(8)–C(9)	1.402(17)	1.383(10)
C(9)–C(10)	1.402(21)	1.358(10)
C(10)–C(5)	1.348(12)	1.395(8)
C(8)–C(11)	1.531(23)	1.535(9)
N(1)–C(12)	1.381(11)	1.422(7)
C(12)–C(13)	1.390(11)	1.381(8)
C(13)–C(14)	1.364(14)	1.366(10)
C(14)–C(15)	1.375(19)	1.364(12)
C(15)–C(16)	1.389(12)	1.400(11)
C(16)–C(17)	1.342(13)	1.358(11)
C(17)–C(12)	1.403(17)	1.363(9)
C(15)–C(18)	1.528(13)	1.537(11)
C(1)–O		1.145(7)
P(1)–C(19)	1.822(9)	1.815(8)
P(1)–C(21)	1.843(14)	1.815(8)
P(1)–C(23)	1.838(8)	1.928(17)
P(2)–C(25)	1.802(53)	1.817(7)
P(2)–C(27)	1.796(26)	1.796(10)
P(2)–C(29)	1.834(16)	1.947(23)
C(19)–C(20)	1.559(12)	1.512(13)
C(21)–C(22)	1.569(15)	1.522(10)
C(23)–C(24)	1.566(21)	1.447(35)
C(23)–C(24′)		1.544(68)
C(23)–C(24″)		1.067(32)
C(25)–C(26)	0.997(72)	1.582(11)
C(27)–C(28)	1.315(28)	1.523(17)
C(29)–C(30)	1.481(36)	1.169(32)
C(29)–C(30′)		0.880(59)

(*b*) Angles (°)

	(6)	(16)
Cl–Ru–P(1)	88.3(1)	88.0(1)
Cl–Ru–P(2)	86.2(1)	87.1(1)
Cl–Ru–C(2)	171.5(3)	170.6(1)
Cl–Ru–C(1)		91.0(2)
Cl–Ru–C(6)	110.2(3)	91.9(2)
P(1)–Ru–C(2)	91.9(3)	91.7(2)
P(1)–Ru–C(1)		91.8(2)
P(1)–Ru–C(6)	87.3(2)	86.6(1)
P(2)–Ru–C(2)	94.2(3)	92.1(2)
P(2)–Ru–C(1)		95.1(2)
P(2)–Ru–C(6)	90.6(2)	86.7(1)
C(1)–Ru–C(2)		98.4(2)
C(6)–Ru–C(2)	78.3(4)	78.7(2)
N(1)–C(3)–C(4)	102.8(9)	104.4(5)
C(3)–C(4)–N(2)	103.2(7)	100.9(6)
N(2)–C(5)–C(6)	111.0(7)	114.7(5)
N(2)–C(5)–C(10)	125.0(9)	122.7(6)
C(6)–C(5)–C(10)	124.0(11)	122.7(6)
Ru–C(6)–C(5)	115.8(8)	112.3(4)
Ru–C(6)–C(7)	129.7(6)	131.3(5)
C(5)–C(6)–C(7)	114.5(7)	116.4(5)
C(6)–C(7)–C(8)	124.8(10)	121.7(6)
C(7)–C(8)–C(9)	117.5(13)	119.4(5)
C(7)–C(8)–C(11)	122.5(10)	119.4(6)
C(9)–C(8)–C(11)	119.9(9)	121.3(5)
Ru–P(1)–C(19)	118.2(4)	115.3(3)
Ru–P(1)–C(21)	110.8(3)	113.8(2)
Ru–P(1)–C(23)	117.2(4)	115.2(4)
C(19)–P(1)–C(21)	104.6(5)	106.5(4)
C(19)–P(1)–C(23)	101.6(4)	99.4(5)
C(21)–P(1)–C(23)	102.7(5)	105.0(5)
P(1)–C(19)–C(20)	114.4(7)	114.3(6)
P(1)–C(21)–C(22)	117.3(8)	119.2(6)
P(1)–C(23)–C(24)	112.8(8)	131.8(18)
P(1)–C(23)–C(24′)		123.9(21)
P(1)–C(23)–C(24″)		136.1(22)
H(13)–Ru–P(1)	85.4	
H(13)–Ru–P(2)	99.3	
H(13)–Ru–C(2)	77.8	
H(13)–Ru–Cl	93.7	
C(2)–N(1)–C(3)	111.7(7)	111.7(5)
C(2)–N(1)–C(12)	125.5(7)	127.3(5)
C(3)–N(1)–C(12)	122.8(9)	120.7(5)
C(2)–N(2)–C(4)	115.1(10)	114.9(5)
C(2)–N(2)–C(5)	114.8(8)	117.7(5)
C(4)–N(2)–C(5)	130.1(7)	127.4(5)
Ru–C(2)–N(1)	132.6(5)	136.0(8)
Ru–C(2)–N(2)	120.1(8)	116.6(4)
N(1)–C(2)–N(2)	107.2(8)	107.4(5)
C(8)–C(9)–C(10)	120.7(9)	120.1(6)
C(9)–C(10)–C(5)	118.4(9)	119.7(7)
N(1)–C(12)–C(13)	122.1(10)	120.0(5)
N(1)–C(12)–C(17)	121.0(7)	121.5(5)
C(13)–C(12)–C(17)	116.9(8)	118.5(6)
C(12)–C(13)–C(14)	121.7(12)	119.9(6)
C(13)–C(14)–C(15)	121.4(9)	121.9(7)
C(14)–C(15)–C(18)	120.6(8)	122.6(8)
C(16)–C(15)–C(18)	122.8(11)	119.6(8)
C(14)–C(15)–C(16)	116.6(9)	117.8(7)
C(15)–C(16)–C(17)	123.3(12)	120.0(8)
C(16)–C(17)–C(12)	120.2(8)	121.8(6)
Ru–P(2)–C(25)	117.9(16)	113.8(2)
Ru–P(2)–C(27)	119.4(7)	117.2(3)
Ru–P(2)–C(29)	118.9(4)	114.9(5)
C(25)–P(2)–C(27)	95.1(22)	107.5(4)
C(25)–P(2)–C(29)	96.5(15)	98.9(5)
C(27)–P(2)–C(29)	104.5(14)	102.4(6)
P(2)–C(25)–C(26)	154.3(35)	116.3(5)
P(2)–C(27)–C(28)	130.0(21)	109.0(7)
P(2)–C(29)–C(30)	116.1(12)	118.9(18)
P(2)–C(29)–C(30′)		167.3(28)

(*c*) Torsion angles (°)

	(6)	(16)
Cl–Ru–P(1)–C(19)	76.3	82.4
Cl–Ru–P(1)–C(21)	−44.3	−41.1
Cl–Ru–P(1)–C(23)	−161.6	−162.5
C(2)–N(2)–C(5)–C(6)	−1.1	1.9
C(2)–N(2)–C(5)–C(10)	178.0	−179.1
N(1)–C(3)–C(4)–N(2)	−0.9	8.5
C(3)–C(4)–N(2)–C(2)	1.4	−6.8
C(4)–N(2)–C(2)–N(1)	−1.4	1.8
Cl–Ru–P(2)–C(27)	−72.0	−88.9
Cl–Ru–P(2)–C(25)	42.4	37.7
Cl–Ru–P(2)–C(29)	158.3	150.7
C(2)–N(1)–C(12)–C(13)	−6.0	−99.7
C(2)–N(1)–C(12)–C(17)	172.8	80.8
N(2)–C(2)–N(1)–C(3)	0.7	4.4
C(2)–N(1)–C(3)–C(4)	0.2	−8.5

in physically unreasonable temperature factors and bond lengths for the disordered atoms. However, since whatever model for the disordered atoms was tried the effect on the geometry of the remainder of the molecule was not significant, it was decided simply to omit the alternative sites from the refinement. Hydrogen atoms whose positions were fixed by the geometry of the molecule were included at calculated positions with C–H 1.08 Å and constrained to ride on the corresponding C atom and with a common isotropic temperature factor that refined to $U = 0.107$ Å^2. Continued large-block least-squares refinement with anisotropic temperature factors for non-H atoms converged at

TABLE 9

Distances (Å) of atoms from various mean planes. Atoms not defining the plane are marked with a dagger

(*i*) Complex (6)

Plane (a): Ru 0.004, Cl −0.002, C(2) −0.002, C(6) 0.000, H(13)† −0.314

Plane (b): C(2) −0.006, C(3) 0.003, C(4) −0.007, N(1) 0.001, N(2) 0.008, Ru† 0.051, C(5)† 0.030, C(12)† −0.002

Plane (c); C(5) 0.003, C(6) 0.001, C(7) −0.006, C(8) 0.006, C(9) −0.002, C(10) −0.002, C(11)† −0.031

Plane (d): C(12) 0.012, C(13) −0.010, C(14) 0.000, C(15) 0.009, C(16) −0.008, C(17) −0.003, Ru† 0.518, N(1)† 0.080, C(18)† 0.035

Angles (°) between planes: (a)–(b) 1.7, (a)–(c) 1.2, (a)–(d) 9.3, (b)–(c) 1.3, (b)–(d) 7.6, (c)–(d) 8.5

(*ii*) Complex (16)

Plane (a): Ru −0.011, Cl −0.011, C(1) 0.019, C(2) −0.015, C(6) 0.019

Plane (b): C(5) −0.006, C(6) −0.002, C(7) 0.007, C(8) −0.005, C(9) −0.002, C(10) 0.008, C(11)† −0.008, Ru† −0.007, N(2) −0.001

Plane (c): C(2) 0.008, C(3) 0.052, C(4) −0.048, N(1) −0.040, N(2) 0.029, Ru† 0.094, C(5)† 0.055, C(12)† −0.029

Plane (d): C(12) −0.018, C(13) 0.008, C(14) 0.004, C(15) −0.006, C(16) −0.004, C(17) 0.016, Ru† −3.078, N(1)† −0.067, C(18)† −0.041

Angles (°) between planes: (a)–(b) 0.9, (a)–(c) 2.4, (a)–(d) 100.3, (b)–(c) 1.7, (b)–(d) 100.8, (c)–(d) 102.6.

$R = 0.054$, $R' = 0.093$ where $w = 1/[\sigma^2(F) + 0.0077F^2]$ with a maximum shift-to-error of 0.1, except for two of the atoms involved in the disorder. A final difference map had peaks of up to 1 e Å^{-3} in the region of the disordered ethyl groups, but was elsewhere featureless.

(*b*) $[\mathrm{Ru(CO)Cl(L^{R'})(PEt_3)_2}]$ (16; R′ = C_6H_4Me-4). *Crystal data.* $C_{20}H_{47}ClN_2OP_2Ru$, $M = 650.3$, Monoclinic, $a = 9.556(1)$, $b = 20.324(3)$, $c = 17.154(2)$ Å, $\beta = 102.48(2)°$, $U = 3\,252.9$ Å^3, $Z = 4$, $D_c = 133$, $F(000) = 1\,360$, Mo-K_α radiation, $\mu = 6.8$ cm^{-1}, space group $P2_1/c$ from systematic absences of $h0l$ for l odd and $0k0$ for k odd.

The crystal used had dimensions 0.75 × 0.3 × 0.25 mm and data were collected and processed as for (*a*). Intensities of $hk \pm l$ reflections with $2 < \theta < 25°$ were estimated over 70 steps of 0.01° and 0.5 s with background counts of 17.5 s. Three standard reflections showed no significant variation during the data collection. Of 4 213 reflections measured, 3 142 with $I > 3\sigma(I)$ were used in the structure analysis.

The structure was solved by routine heavy-atom methods. The triethylphosphine carbon atoms of both phosphines showed evidence of disorder. This was accounted for by allowing three possible sites (occupancy 0.33) for C(24) and two sites (occupancy 0.5) for C(30). There was still evidence of further disorder, but all possible sites tried refined to give physically unreasonable parameters. Those hydrogen atoms whose positions were fixed by the geometry of the molecule were introduced at calculated positions (C–H 1.08 Å) and constrained to ride on the corresponding C atom with a common isotropic temperature factor, refined to $U = 0.149$ Å^2. Continued large-block least-squares refinement with anisotropic temperature factors for non-H atoms converged at $R = 0.045$, $R' = 0.053$, where $w = 1/[\sigma^2(F) + 0.0105F^2]$ when the maximum shift-to-error was 0.1, except for the disordered atoms. A final difference map was everywhere <0.5 e Å^{-3}.

For both structures, scattering factors for neutral atoms were taken from ref. 47 and dispersion corrections from ref. 48. The structure solution and refinement were done with the SHELX program system of G. M. Sheldrick. Final atom co-ordinates are listed in Tables 6 and 7, bond lengths and angles in Table 8, and distances of atoms from various mean planes in Table 9. Thermal parameters, hydrogen-atom co-ordinates, and structure-factor listings have been deposited as Supplementary Publication No. SUP 22562 (43 pp.).*

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