Carbene Complexes. Part 18.[1] Synthetic Routes to Electron-rich Olefin-derived Monocarbenerhodium(I) Neutral and Cationic Complexes and their Chemical and Physical Properties

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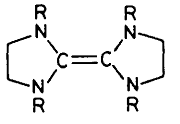
Electron-rich olefins of general type $[{=}\overline{\mathrm{C(NR)CH_2CH_2N}}\mathrm{R}]_2$ ($L^R{}_2$; R = Me, Et, Ph, 4-MeC_6H_4, 4-$MeOC_6H_4$, or 2-$MeOC_6H_4$) undergo reaction with a variety of rhodium(I) precursors *via* ligand displacement or chloride-bridge cleavage to afford monocarbenerhodium(I) complexes, such as $[RhCl(L^R)(PPh_3)_2]$, $[Rh(cod)Cl(L^R)]$, or $[Rh(CO)Cl(L^R)(PPh_3)]$ [$L^R = {=}\overline{\mathrm{C(NR)CH_2CH_2N}}\mathrm{R}$, cod = cyclo-octa-1,5-diene]; complexes $[RhCl(L'^{Me})(PPh_3)X]$ [$L'^{Me} = {=}\overline{\mathrm{CN(Me)CH_2CH_2CH_2N}}\mathrm{Me}$, X = CO or PPh_3] have similarly been obtained from the olefin $L'^{Me}{}_2$. From these, further complexes may be obtained by ligand (neutral or anionic) exchange processes: *trans*-$[RhBr(L^R)(PPh_3)_2]$, *trans*-$[Rh(CO)(L^R)(PPh_3)_2]X$ (X = Br, Cl, ClO_4, or I), $[Rh(CO)X(L^R)(PPh_3)]$ (X = BH_4 or ClO_4), *cis*-$[Rh(CO)_2X(L^R)]$ (X = Cl or NO_3), $[Rh(cod)X(L^R)]$ (X = CH_2SiMe_3, ClO_4, or NO_3), *cis*-$[Rh(cod)(L^R)(PPh_3)][ClO_4]$, and $[Rh(CO)_3(L^R)][ClO_4]$. In many of the reactions some of these ligand displacements at Rh^I proceed without retention of stereochemistry and it is likely that the observed product is the thermodynamically preferred isomer. Other chemical properties of the monocarbene-rhodium(I) complexes relate to (*i*) rare examples of the displacement of L^R from Rh by PPh_3 or $Ph_2PCH_2CH_2PPh_2$ under rather forcing conditions, and (*ii*) oxidative addition (not particularly facile) of HCl, $[NMe_2CHCl]Cl$, or $C_2(CN)_4$. The 45 new complexes have been characterised by analysis and spectroscopy (i.r. and ^1H and ^{31}P n.m.r.) and, where appropriate, relative molecular mass determination, and electrical conductivity. From $J(^{31}P-^{103}Rh)$ coupling constants it is concluded that L^R has a greater *trans* influence than PPh_3 [also indicated by $\nu(Rh-Cl)$] but a lower *cis* influence.

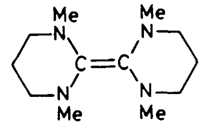
We have shown that electron-rich olefins, such as (A) and (B), are convenient precursors to a variety of transition-metal carbene complexes, the metal generally being in a low oxidation state.[2-7]

We have published several preliminary communications concerning electron-rich olefin-derived carbenerhodium(I) complexes. These have dealt with (*i*) Rh^I-catalysed electron-rich olefin metathesis,[8] (*ii*) the stereochemistry and mechanism of nucleophilic displacement reactions of certain carbene-rhodium(I) complexes,[9] (*iii*) restricted rotation about the $Rh-C_{carbene}$ bond,[10] (*iv*) a *cis*-chelating dicarbenerhodium(I) complex derived ultimately from 1,4,8,11-tetra-azacyclotetradecane,[11] (*v*) optically active carbenerhodium(I) complexes,[12,13] and (*vi*) carbenerhodium(I) complexes as catalysts for hydrogenation and hydrosilylation.[13] Another paper has also dealt with (*vi*).[14] The complex *trans*-$[Rh(L^{Me})\{N{=}C(CF_3)_2\}(PPh_3)_2]$ (L^{Me} = 1,3-dimethylimidazolidin-2-ylidene) has been described elsewhere:[15] its *X*-ray crystal structure revealed that, as in another carbenerhodium(I) complex,[12] the co-ordination plane of the carbene ligand is approximately orthogonal to the co-ordination plane about the metal; this is a general feature of electron-rich olefin-derived carbenemetal complexes.[1]

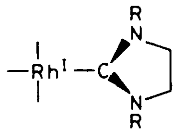
Carbenerhodium complexes have been prepared by pathways independent of electron rich-olefins, using a Rh^I substrate and a reagent (where *e.g.* R = R′ = Me or Ph) such as $[R_2NC(X)Cl]Cl$ (X = H, Cl, or NR_2),[16,17] $[Me\overline{\mathrm{NC(Me)=CHSC}}Cl][BF_4]$,[18] $RN{=}C(Cl)R'$,[19,20] NH_2R (with a Rh^I- or a Rh^{III}-$CNBu^t$ complex),[21,22] RNCS,[23] or MeI (with a Rh^I-CS complex).[24]



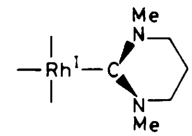
(A), $L^R{}_2$



(B), $L'^{Me}{}_2$



(C), $Rh(L^R)$

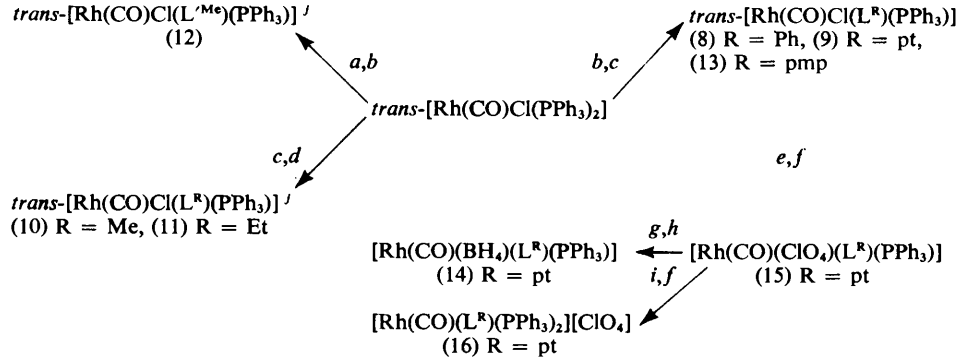


(D), $Rh(L'^{Me})$

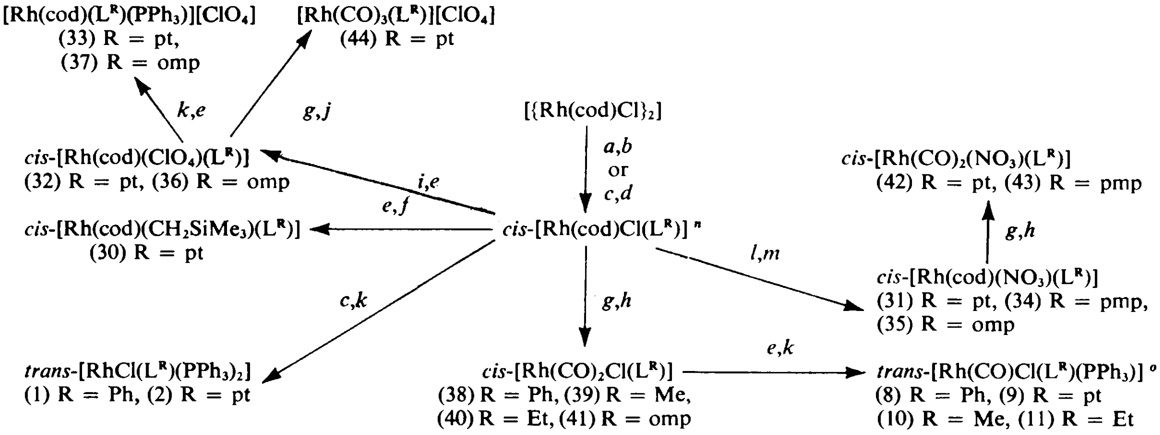
The present paper provides full details relating to the synthesis and spectroscopic characterisation of 44 monocarbenerhodium(I) complexes (and one Rh^{III} analogue) of structures (C) [R = Me, Et, Ph, *p*-tolyl (pt), *p*-methoxyphenyl (pmp), or *o*-methoxyphenyl (omp)] and (D), derived from the olefins (A) and (B), respectively, of seven distinct types: (*a*) $[RhX(L^R$ or $L'^{Me})(PPh_3)_2]$ (X = Br or Cl), (*b*) $[Rh(CO)X(L^R$ or $L'^{Me})(PPh_3)]$ (X = BH_4, Cl, or ClO_4), (*c*) $[Rh(CO)(L^R)(PPh_3)_2]X$ (X = Br, Cl, or I), (*d*) *cis*-$[Rh(CO)_2X(L^R)]$ (X = Cl or NO_3), (*e*) $[Rh(CO)_3(L^R)][ClO_4]$, (*f*) *cis*-$[Rh(cod)X(L^R)]$ (X = CH_2SiMe_3, Cl, ClO_4, or NO_3; cod = cyclo-octa-1,5-diene), and (*g*) *cis*-$[Rh(cod)(L^R)(PPh_3)][ClO_4]$. Subsequently we shall report on bis- and tris-(carbene)rhodium(I) complexes.

Results and Discussion

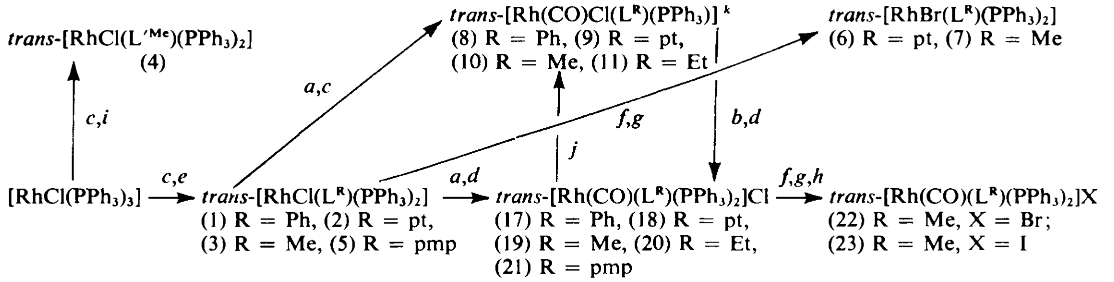
Synthetic Routes to Monocarbenerhodium(I) *Complexes.*—A large number of carbenerhodium(I) complexes have been prepared using three convenient starting materials: *trans*-$[Rh(CO)Cl(PPh_3)_2]$ (Scheme 1), $[\{Rh(cod)Cl\}_2]$ (Scheme 2), and $[RhCl(PPh_3)_3]$ (Scheme 3). As has been noted before, the carbene ligand L^R or L'^{Me} was readily introduced using the electron-rich olefin $L^R{}_2$ or $L'^{Me}{}_2$. The resultant carbene-rhodium(I) complexes, obtained by ligand (PPh_3) displacement or $(\mu\text{-}Cl)_2$-bridge splitting, have the carbene ligand firmly



Scheme 1. Routes to electron-rich olefin-derived monocarbenerhodium(I) complexes from *trans*-$[Rh(CO)Cl(PPh_3)_2]$: [a] ½ L'^{Me}_2; [b] xylene, 140 °C; [c] ½L^R_2; [d] benzene, 80 °C; [e] $Ag[ClO_4]$; [f] benzene, 25 °C; [g] $Na[BH_4]$; [h] ethanol; [i] PPh_3; [j] CO *trans* to Cl^-. Abbreviations: L^R = ½ (A), L'^{Me} = ½ (B), pmp = *p*-methoxyphenyl, omp = *o*-methoxyphenyl, pt = *p*-tolyl



Scheme 2. Routes to electron-rich olefin-derived monocarbenerhodium(I) complexes from $[\{Rh(cod)Cl\}_2]$: [a] ½L^R_2, (R = alkyl); [b] C_6H_6, 70 °C; [c] xylene, 140 °C; [d] ½L^R_2 (R = aryl); [e] C_6H_6, 25 °C; [f] $Li[CH_2SiMe_3]$; [g] CO; [h] $CHCl_3$, 25 °C; [i] $Ag[ClO_4]$; [j] CH_2Cl_2, 25 °C; [k] PPh_3; [l] $Ag[NO_3]$; [m] acetone, water, 25 °C; [n] (24) R = Ph, (25) R = pt, (26) R = Me, (27) R = Et, (28) R = pmp, (29) R = omp; [o] CO *trans* to Cl^-



Scheme 3. Reactions of monocarbenerhodium(I) complexes with CO or PPh_3, showing the role of the solvent, and syntheses from $[RhCl(PPh_3)_3]$: [a] CO; [b] PPh_3; [c] toluene, 110 °C; [d] $CHCl_3$, 25 °C; [e] ½L^R_2; [f] NaBr; [g] acetone, 25 °C; [h] NaI; [i] ½L'^{Me}_2; [j] xylene, 140 °C (the product was incompletely characterised); [k] CO *trans* to Cl^-

bound to the rhodium(I) centre. Consequently, further carbenerhodium(I) complexes were obtained by reactions involving substitution of one or more other ligands from the metal inner co-ordination sphere, as illustrated in Schemes 1—3. Forty-five new complexes, with yields, analytical and other descriptive data (Table 1), i.r. (Table 2) and ^1H n.m.r. (Table 3) spectroscopic characteristics, are presented herein.

Although it is well known[25] that one triphenylphosphine ligand of Wilkinson's compound, $[RhCl(PPh_3)_3]$, is particularly labile, it is perhaps a little surprising, in view of the ease of replaceability of the PPh_3 groups of the otherwise similar Ru analogue $[RuCl_2(PPh_3)_3]$,[2,4] that *only one* PPh_3 is displaced by L^R (irrespective of the nature of R). Thus, the complexes *trans*-$[RhCl(L^R)(PPh_3)_2]$ [R = Ph (1), pt (2), Me (3), or pmp (5)] or *trans*-$[RhCl(L'^{Me})(PPh_3)_2]$ (4) are obtained as summarised in Scheme 3.

This transformation of $[RhCl(PPh_3)_3]$ into *trans*-$[RhCl(L^R)(PPh_3)_2]$ provides one of the rare examples {for another, see the reactions[4] of $[Mo(\eta\text{-}C_5H_5)(CO)_2(NO)]$} of similar reactivity of the exocyclic electron-rich olefins L^R_2 for R =

Table 1. Characterisation [a] of electron-rich olefin-derived monocarbenerhodium(I) complexes and a Rh^{III} analogue

No.	Compound	Yield (%)	M.p. (θ_c/°C)	Colour	Analysis [b] C	H	N	Halogen
(1)	*trans*-$[RhCl(L^{Ph})(PPh_3)_2]$	79	194—195	Orange	69.6 (69.2)	5.2 (5.0)	3.0 (3.2)	
(2)	*trans*-$[RhCl(L^{pt})(PPh_3)_2]$	83	191—192	Orange	69.8 (69.7)	5.4 (5.3)	3.1 (3.1)	4.0 (3.9)
(3)	*trans*-$[RhCl(L^{Me})(PPh_3)_2]$	75	184	Orange	63.9 (64.7)	5.5 (5.3)	4.1 (3.7)	5.0 (4.7)
(4)	*trans*-$[RhCl(L'^{Me})(PPh_3)_2]$	80	287	Orange	65.1 (65.1)	5.4 (5.5)	3.7 (3.6)	
(5)	*trans*-$[RhCl(L^{pmp})(PPh_3)_2]$	80	185—190	Orange	68.7 (67.3)	5.6 (5.1)	3.2 (3.0)	
(6)	*trans*-$[RhBr(L^{pt})(PPh_3)_2]$	75	184—186	Orange	63.5 (66.5)	5.3 (5.0)	3.1 (2.9)	
(7)	*trans*-$[RhBr(L^{Me})(PPh_3)_2]$	76	*c*	Orange	*c*	*c*	*c*	9.5 (9.9)
(8)	*trans*-$[Rh(CO)Cl(L^{Ph})(PPh_3)]$ [d]	96	193—195	Yellow	62.7 (62.7)	4.7 (4.5)	4.3 (4.3)	5.9 (5.5)
(9)	*trans*-$[Rh(CO)Cl(L^{pt})(PPh_3)]$ [d]	93	207—212	Yellow	63.2 (63.7)	4.9 (4.9)	4.2 (4.1)	
(10)	*trans*-$[Rh(CO)Cl(L^{Me})(PPh_3)]$ [d]	90	148	Yellow	55.2 (54.7)	4.9 (4.8)	5.4 (5.3)	7.0 (6.9)
(11)	*trans*-$[Rh(CO)Cl(L^{Et})(PPh_3)]$ [d]	90	178—183	Yellow	56.2 (56.3)	5.5 (5.2)	5.4 (5.1)	
(12)	*trans*-$[Rh(CO)Cl(L'^{Me})(PPh_3)]$ [d]	20	233 (decomp.)	Pale yellow	55.5 (55.5)	5.3 (5.0)	5.4 (5.2)	
(13)	*trans*-$[Rh(CO)Cl(L^{pmp})(PPh_3)]$ [d]	93	201—208	Yellow	60.6 (60.8)	4.7 (4.6)	4.0 (3.9)	
(14)	$[Rh(CO)(BH_4)(L^{pt})(PPh_3)]$	86	105—108	Very pale yellow	65.3 (65.7)	5.9 (5.7)	4.2 (4.2)	
(15)	$[Rh(CO)(ClO_4)(L^{pt})(PPh_3)]$	80	*c*	Yellow	60.4 (59.2)	5.1 (4.5)	3.6 (3.8)	
(16)	$[Rh(CO)(L^{pt})(PPh_3)_2][ClO_4]$ [e]	80	*c*	Yellow	60.3 (60.6)	5.0 (4.6)	2.6 (2.6)	
(17)	*trans*-$[Rh(CO)(L^{Pb})(PPh_3)_2]Cl$	100	107—110	Yellow	66.0 (65.8)	5.3 (5.1)	2.6 (3.0)	
(18)	*trans*-$[Rh(CO)(L^{pt})(PPh_3)_2]Cl$	100	131—132	Yellow	66.0 (66.4)	5.4 (5.3)	2.9 (2.9)	
(19)	*trans*-$[Rh(CO)(L^{Me})(PPh_3)_2]Cl$	100	156	Yellow	63.2 (63.9)	5.2 (5.1)	3.6 (3.6)	
(20)	*trans*-$[Rh(CO)(L^{Et})(PPh_3)_2]Cl$	100	123—124	Yellow	*c*	*c*	*c*	
(21)	*trans*-$[Rh(CO)(L^{pmp})(PPh_3)_2]Cl$	100	135—140	Yellow	*c*	*c*	*c*	14.1 (14.1)
(22)	*trans*-$[Rh(CO)(L^{Me})(PPh_3)_2]Br$	100	152—154	Yellow	59.7 (60.5)	4.8 (4.8)	3.6 (3.4)	9.4 (9.6)
(23)	*trans*-$[Rh(CO)(L^{Me})(PPh_3)_2]I$	100	165—166	Yellow	55.4 (57.3)	4.4 (4.6)	3.4 (3.2)	
(24)	*cis*-$[Rh(cod)Cl(L^{Ph})]$	94	204—206	Yellow	58.9 (58.9)	5.7 (5.6)	5.9 (6.0)	7.8 (7.6)
(25)	*cis*-$[Rh(cod)Cl(L^{pt})]$	95	216—219	Yellow	61.4 (60.4)	5.4 (6.0)	5.7 (5.6)	7.2 (7.0)
(26)	*cis*-$[Rh(cod)Cl(L^{Me})]$	90	176—178	Yellow	45.6 (45.3)	6.7 (6.4)	8.3 (8.1)	10.5 (10.3)
(27)	*cis*-$[Rh(cod)Cl(L^{Et})]$	93	132—134	Yellow	48.3 (48.3)	7.0 (7.0)	7.5 (7.5)	
(28)	*cis*-$[Rh(cod)Cl(L^{pmp})]$	85	197—200	Yellow	56.6 (56.8)	5.7 (5.7)	5.3 (5.3)	
(29)	*cis*-$[Rh(cod)Cl(L^{omp})]$	80	190—193	Yellow	56.7 (56.8)	5.7 (5.7)	5.3 (5.3)	
(30)	*cis*-$[Rh(cod)(CH_2SiMe_3)(L^{pt})]$	90	*c*	Orange	63.5 (63.5)	7.8 (7.5)	5.3 (5.1)	
(31)	*cis*-$[Rh(cod)(NO_3)(L^{pt})]$	80	*c*	Yellow	56.9 (57.4)	5.9 (5.8)	8.1 (8.1)	
(32)	*cis*-$[Rh(cod)(ClO_4)(L^{pt})]$	80	*c*	Yellow	53.8 (53.5)	5.9 (5.4)	5.1 (5.0)	
(33)	*cis*-$[Rh(cod)(L^{pt})(PPh_3)][ClO_4]$	80	*c*	Orange	62.5 (62.7)	5.7 (5.5)	3.4 (3.4)	
(34)	*cis*-$[Rh(cod)(NO_3)(L^{pmp})]$	80	*c*	Yellow	54.5 (54.1)	5.7 (5.4)	7.7 (7.6)	
(35)	*cis*-$[Rh(cod)(NO_3)(L^{omp})]$	75	150 (decomp.)	Yellow	54.1 (54.1)	5.7 (5.5)	7.5 (7.6)	
(36)	*cis*-$[Rh(cod)(ClO_4)(L^{omp})]$	80	150 (decomp.)	Yellow	50.7 (50.7)	5.3 (5.1)	4.6 (4.7)	
(37)	*cis*-$[Rh(cod)(L^{omp})(PPh_3)][ClO_4]$	95	173—176 (decomp.)	Orange	60.6 (60.4)	5.8 (5.3)	3.3 (3.3)	
(38)	*cis*-$[Rh(CO)_2Cl(L^{Ph})]$	100	138	Yellow	48.7 (49.0)	3.5 (3.4)	6.5 (6.7)	
(39)	*cis*-$[Rh(CO)_2Cl(L^{Me})]$	100	108—112	Yellow	28.9 (28.7)	3.6 (3.5)	9.5 (9.6)	
(40)	*cis*-$[Rh(CO)_2Cl(L^{Et})]$	100	88—91	Yellow	33.9 (33.7)	4.5 (4.4)	8.8 (8.8)	
(41)	*cis*-$[Rh(CO)_2Cl(L^{omp})]$	98	165—168 (decomp.)	Pale yellow	47.8 (47.9)	3.9 (3.8)	5.9 (5.9)	
(42)	*cis*-$[Rh(CO)_2(NO_3)(L^{pt})]$	80	*c*	Yellow	48.4 (48.4)	3.7 (3.8)	8.7 (8.9)	
(43)	*cis*-$[Rh(CO)_2(NO_3)(L^{pmp})]$	95	*c*	Yellow	45.1 (45.3)	3.6 (3.6)	8.3 (8.3)	
(44)	$[Rh(CO)_3(L^{pt})][ClO_4]$	80	102—105 (decomp.)	Yellow	45.4 (45.7)	4.1 (3.4)	5.2 (5.2)	
(48)	*trans*-$[Rh\{CH(NMe_2)\}(CO)Cl_3(L^{Et})]$ [f]	75	185	Pale yellow	31.4 (31.0)	5.0 (5.0)	9.9 (10.0)	

[a] Abbreviations: pt = *p*-tolyl, pmp = *p*-methoxyphenyl, omp = *o*-methoxyphenyl, cod = cyclo-octa-1,5-diene, $L^R = \frac{1}{2}$ (A), $L'^{Me} = \frac{1}{2}$ (B). For compounds of the type $[Rh(CO)Cl(L^R)(PPh_3)]$, the designation '*trans*' refers to the relative disposition of the CO and Cl ligands. [b] Calculated values are in parentheses. [c] Not determined. [d] CO *trans* to Cl^-. [e] CH_2Cl_2 solvate. [f] Prepared by Dr. D. B. Shaw (see ref. 35).

alkyl or aryl, or $L'^{Me}{}_2$; however, the acyclic $C_2(NMe_2)_4$ proved to be unreactive. Generally the order of reactivity is[26] (A)(R = alkyl) > (A)(R = aryl) > (B); *e.g.* $[RuCl_2(PPh_3)_3]$ gave *trans*-$[RuCl_2(L^{Me})_4]$ with $L^{Me}{}_2$, but with $L^{Ph}{}_2$ only one carbene ligand was introduced in the form of the *ortho*-metallated complex $[RuCl(L^{Ph})(PPh_3)_2]$.[2]

A PPh_3 ligand may also be displaced from *trans*-$[Rh(CO)Cl(PPh_3)_2]$ (Scheme 1), although more than one phosphine may be replaced if using $L^R{}_2$ (R = alkyl) {to give *cis*- or *trans*-$[Rh(CO)(L^R)_2(PPh_3)]Cl$[9] or $[Rh(CO)(L^R)_3]Cl$ (R = Me or Et)}. With a stoicheiometric quantity of alkene, the complexes *trans*-$[Rh(CO)Cl(L^R)(PPh_3)]$ [R = Ph (8), pt (9), Me (10), Et (11), or pmp (13)], or using $L'^{Me}{}_2$, *trans*-$[Rh(CO)Cl(L'^{Me})(PPh_3)]$ (12), were obtained. These derivatives may be prepared by an alternative method. Thus, $[RhCl(L^R)(PPh_3)_2]$ proved to be a convenient source of the monocarbonyl derivatives. One PPh_3 ligand was substituted by CO, when using a warm non-polar solvent such as toluene (Scheme 3); this route has the advantage of not having to separate possible dicarbenerhodium(I) complexes that can result from direct reaction of *trans*-$[Rh(CO)Cl(PPh_3)_2]$ with the electron-rich olefin.[9,27] A variation of this procedure is PPh_3/CO exchange using PPh_3 and *cis*-$[Rh(CO)_2Cl(L^R)]$; the synthesis of the latter complexes is described later (see Scheme 2).

Complexes of the type $[Rh(CO)Cl(L^R)(PPh_3)]$ are also susceptible to exchange of anionic ligand (Scheme 1). Thus, neutral complexes containing co-ordinated BH_4^-, (14), or ClO_4^-, (15), were obtained. A further reaction type, involving PPh_3/Cl^- exchange, required treatment with an excess of PPh_3; this gave the cationic complexes $[Rh(CO)(L^R)(PPh_3)_2]X$

Table 2. Selected i.r. spectroscopic, molecular weight, and electrical conductance data for some monocarbenerhodium(I) complexes and a Rh^{III} analogue

Compound	ν(CO) [a]/cm^{-1}	ν(CN$_2$) [b]/cm^{-1}	ν(Rh–Y) [b]/cm^{-1}	M [c]
(1)		1 498s	285w,br	
(2)		1 513s	298w	
(3)		1 506s, 1 512 (sh)	282w,br	
(4)		1 520ms	289w	
(5)		1 507s, 1 513 (sh)	288w,br	1 023 (945.2)
(6)		1 513s		
(7)		1 512m,br		
(8)	1 957vs	1 495s	299w	
(9)	1 955vs	1 513s	294w	655.5 (679.0)
(10)	1 958vs	1 520s,br	296w	508.3 (526.5)
(11)	1 957vs	1 512s	295w	
(12)	1 949vs [b]	1 548s	293w	
(13)	1 948vs [b]	1 511s	296w	
(14)	1 928vs, 1 935vs [b]	1 510s		
(15) [d]	1 980vs [b]	1 510s		
(16)	1 990vs, 2 000vs [b]	1 508s		
(17)	2 009vs	1 493		
(18) [e]	2 007vs	1 512s		
(19) [e]	2 008vs	1 534s,br		
(20)	2 010vs	1 534s,br		
(21)	1 944vs [b]	1 508s		
(22) [e]	2 008vs	1 535s,br		
(23) [e]	2 006vs [b]	1 536s,br		
(24)		1 490s	287m,br	504.5 (468.5)
(25)		1 512ms	289m,br	540 (540) [f]
(26)		1 515s,br	287m,br	344 (344) [f]
(27)		1 500s,br	287m,br	372 (372) [f]
(28)		1 508s,br		
(29)		1 500vs		
(30)		1 512s		548 (548) [f]
(31)		1 508s		
(32)		1 508s		
(33)		1 508s		
(34)		1 510vs,br		
(35)		1 505vs, 1 510 (sh)		
(36)		1 505vs, 1 510 (sh)		
(37)		1 502s, 1 508 (sh)		
(38)	2 085vs, 2 004vs	1 500s,br	298m	
(39)	2 090vs, 2 005vs	1 529s,br	310m	
(40)	2 094vs, 2 003vs	1 520s	314m	
(41)	1 995vs, 2 080vs [b]	1 510vs		
(42)	1 988vs, 1 998vs [b], 2 015vs, 2 075vs	1 508vs		
(43)	2 020vs, 2 090vs [b]	1 510s		
(44) [g]	2 020s, 2 038s [b], 2 075vs, 2 100vs, 2 150s	1 508s		
(48) [h]	2 100s	1 621s,[i] 1 515m	325w	

[a] Recorded in $CHCl_3$ solution (unless otherwise stated); calibrated *via* polystyrene peak at 1 601 cm^{-1}. [b] Nujol mull, Y = halogen. [c] Molecular weight determinations were measured osmetrically in $CHCl_3$ solution, except where noted. Calculated values are in parentheses. [d] ν(ClO_4) = 1 130s, 1 010s, 885m, and 674m cm^{-1}. [e] Molar conductances (in CH_3NO_2): (18) 84.6; (19) 89.5; (22) 91.2; (23) 86.1 Ω^{-1}. [f] Mass spectrometrically; based on ^{35}Cl when present. [g] ν(ClO_4) = 1 090vs cm^{-1}. [h] By Dr. D. B. Shaw, [i] From CH(NMe_2).

[R = pt, X = ClO_4, (16); R = Ph, X = Cl, (17); R = pt, X = Cl, (18); R = Me, X = Cl, (19); R = Et, X = Cl, (20); R = pmp, X = Cl, (21); R = Me, X = Br, (22); or R = Me, X = I, (23)]. An alternative path to such complexes was based on [RhX(L^R)(PPh_3)$_2$]; reaction with CO in a *polar* solvent, *e.g.* $CHCl_3$, effected X^- displacement, rather than the PPh_3 substitution which took place under non-polar conditions (*cf.* steps *a,c* and *a,d* in Scheme 3).

A chloride bridge-splitting process provided the pathway to the first electron-rich olefin-derived carbenemetal complex [of platinum(II)] [28] and this method has also now found application in Rh^I chemistry. Thus, [{Rh(cod)Cl}$_2$] was a convenient source of monocarbene derivatives of type *cis*-[Rh(cod)Cl(L^R)] [R = Ph (24), pt (25), Me (26), Et (27), pmp (28), or omp (29)], *cis*-[RhL_2Cl(L^R)], by subsequent displacement of the chelating diene cod [*e.g.* L = CO and R = Ph (38), Me (39), Et (40), or omp (41)], and [Rh(cod)X(L^R)] by anion (Cl^-/X^-) exchange [X = ClO_4 and R = pt (32) or omp (36); X = NO_3 and R = pt (31), pmp (34), or omp (35); or X = CH_2SiMe_3 and R = pt (30)]. The above three basic reactions [(μ-Cl)$_2$-splitting, cod/L_2 exchange, or Cl^-/X^- exchange] may be combined to afford complexes such as *cis*-[Rh(cod)(L^R)(PPh_3)][ClO_4] [R = pt (33) or omp (37)] and the novel tricarbonyl [Rh(CO)$_3$(L^R)][ClO_4] [R = pt (44)]. {Complexes of the type [Rh(CO)$_3$L]$^+$ appear to be without precedent; however, the cations [Rh(CO)$_3$$L_2$]$^+$ [L = PPh_3 or P(OPh)$_3$] are known.[29a]} Complex (44) is conveniently soluble in ethanol, which may be of interest in the context of its possible use as a hydrogenation catalyst for acylaminoacrylates which are also soluble in the same solvent. It is likely that the reaction of L^R_2, (A), or L'^{Me}_2, (B), with [RhCl(PPh_3)$_3$] also proceeds *via* a (μ-Cl)$_2$-dirhodium(I)

Table 3. Selected ^{1}H n.m.r. spectroscopic data [a] for some monocarbenerhodium(I) complexes and a Rh^{III} analogue

Compound	Solvent	Ring CH$_2$	CH$_3$ [b]	N–CH$_2$–	Other resonances [c]
(1)	$CDCl_3$	6.98	—	—	
(2)	$CDCl_3$	6.98	7.64	—	
(3)					
(4)					
(5)					
(6)	$CDCl_3$	7.05 (s)	7.70 (s)	—	2.1—3.2 (m)
(7)					
(8)	$CDCl_3$	5.77	—	—	
(9)	$CDCl_3$	5.75	7.60	—	
(10)	$CDCl_3$	6.34	6.48	—	
(11)	$CDCl_3$	6.35	8.73 (t)	5.96 (m) [d]	
	$C_6D_5CD_3$	7.23 (m) [e]	8.91 (t)	6.06 (q)	
(12)	$CDCl_3$	—	6.10	6.7 (m)	
(13)	$CDCl_3$	5.77 (s)	6.15 (s)	—	2.48 (q)
(14)	C_6D_6	6.64 (m) [e]	7.85		
(15)	CD_2Cl_2	5.62 (s)	7.47 (s)		1.8—2.67 (m)
(16)	$CDCl_3$	6.77 (s)	7.62 (s)		2.22—3.22 (m)
(17)	$CDCl_3$	6.28	—	—	2.2—3.4 (m)
(18)	$CDCl_3$	6.38	7.65	—	2.97 (q), 2.3—3.0 (m)
(19)	$CDCl_3$	7.17	7.38	—	2.16—2.8 (m)
(20)	$CDCl_3$	6.85 (s)	9.58 (t)	7.00 (q)	2.1—2.6 (m)
(21)	$CDCl_3$	6.32 (s)	6.18 (s)	—	2.96 (q), 2.3—3.0 (m)
(22)	$CDCl_3$	7.17	7.38	—	2.1—2.8 (m)
(23)	$CDCl_3$	7.14 (s)	7.38 (s)	—	2.1—2.8 (m)
(24)	$CDCl_3$	5.82 (m) [e]	—		
(25)	$CDCl_3$	5.92 (m) [e]	7.62		
(26)	$C_6D_5CD_3$	7.49 (m) [e]	6.82		
(27)	$CDCl_3$	6.52	8.71	5.85 (m) [d]	
	$C_6D_5CD_3$	7.19 (m) [e]	8.90 (t)	6.02 (m)	
(28)	$CDCl_3$	5.8 (m) [e]	6.0 (s)	—	2.36 (q)
(29)	$CDCl_3$	5.65 (m)	6.1 (s)	—	2.5—3.2 (m)
(30)	$C_6D_5CD_3$	6.62br	7.72	—	9.65 (s),[f] 10.2 (d) [g]
(31)	$CDCl_3$	5.8 (m) [e]	7.44 (s)		2.2 (q)
(32)	$CDCl_3$	5.84 (s)	7.47 (s)		2.27 (q)
(33)	$CDCl_3$	6.0 (m)	7.4 (s)		2.2—3.0 (m)
(34)	$CDCl_3$	5.87 (m) [e]	6.07 (s)		2.34 (q)
(35)	$CDCl_3$	5.65 (m)	6.1 (s)	—	1.77—2.04(m), 2.5—3.2(m)
(36)					
(37)	$CDCl_3$	5.84 (m) [e]	6.23 (s)		2.3—3.5 (m)
(38)	$CDCl_3$	5.67	—		
(39)	$CDCl_3$	6.33	6.37		
	$C_6D_5CD_3$	7.51 (m) [e]	7.17 (s)		
(40)	$CDCl_3$	6.34	8.75 (t)	6.16 (m) [d]	
	$C_6D_5CD_3$	7.30 (m) [e]	9.90 (t)	6.49 (q)	
(41)	$CDCl_3$	5.8 (br)	6.1 (s)		2.1—3.17 (m)
(42)	$CDCl_3$	5.6 (s)	7.47 (s)		2.47 (q)
(43)	$CDCl_3$	5.75 (s)	6.12 (s)		2.7
(44)	$CDCl_3$	5.5 (s)	7.54 (s)		2.54 (q)
(48) [h]	$CDCl_3$	6.7 (m)	9.0	6.3 (m)	7.6 (m),[h] −0.7 [h]

[a] Values quoted in τ, relative to internal $SiMe_4$ = 10. Compounds (3) and (4) had inadequate solubility. [b] N–*Me*, N–C_6H_4*Me*, or N–C_6H_4O*Me*. [c] Aromatic resonances, except where noted. [d] Centre of overlapping ABX_3. [e] Centre of AA′BB′ pattern. [f] –Si(C*H*$_3$)$_3$ resonance. [g] –C*H*$_2$–Si resonance. [h] By Dr. D. B. Shaw; the signal at 7.6 (m) is due to C(H)N(C*H*$_3$)$_2$ and that at −0.7 to *C*(*H*)NMe$_2$.

complex, [{RhCl(PPh$_3$)$_2$}$_2$]. The reaction conditions (PhMe, 110 °C) are such that the latter would rapidly be formed if L$^R_2$ were absent and it would certainly react subsequently with the alkene (A) or (B) to yield the observed *trans* monocarbene derivatives (1)—(5) (Scheme 3).

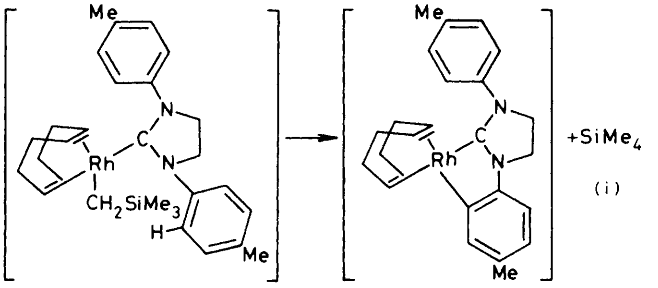
It is evident that use of the complex [{Rh(cod)Cl}$_2$] offers a valuable entry into carbenerhodium(I) complexes that would otherwise be inaccessible. Thus, the complexes *cis*-[Rh(CO)$_2$Cl(L^R)] (38)—(41), formed from [Rh(cod)Cl(L^R)] by treatment with CO (Scheme 2), are themselves versatile precursors for the introduction of various neutral ligands in a position *trans* to the carbene by loss of one carbon monoxide. (Such complexes have been of interest to us in our studies of activation parameters associated with rotation about the Rh–C$_{carbene}$ bond.[10]) An illustration is provided here by their conversion into the complexes *trans*-[Rh(CO)Cl(L^R)(PPh$_3$)] (8)—(11).

The Rh^I alkyl *cis*-[Rh(cod)(CH$_2$SiMe$_3$)(L^R)] [R = pt (30)] is noteworthy as it represents one of the more stable rhodium(I) alkyl derivatives; it shows a parent ion in its mass spectrum.[29b] Generally, with PPh$_3$ ligands present, loss of alkane occurs with concomitant *ortho*-metallation of a *P*-aryl ring.[30] It was expected that complex (30) might be induced to undergo a similar elimination, giving an *N*-aryl *ortho*-metallated carbene species (this occurs spontaneously in certain Ru^{II} [2] or Ir^{III} [31] complexes), according to equation (i). Heating up to 80 °C (C$_6$D$_6$) or irradiation (C$_6$D$_6$, 25 °C) in a sealed ^{1}H n.m.r. tube appeared to effect such a reaction. This is supported by ^{1}H

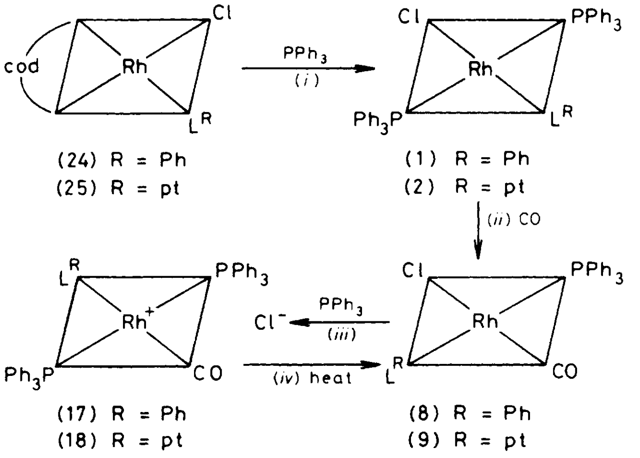
Table 4. Selected ^{31}P n.m.r. spectroscopic data [a] for some monocarbenerhodium(I) and related complexes

Compound	*trans* Ligands	*cis* Ligands	$\delta(^{31}P)$ [b]	$^1J(^{31}P-^{103}Rh)$/Hz
$[RhCl(PPh_3)_3]$ [c,d]	Cl	PPh_3,PPh_3	93.0 (t)	189
$[RhCl(PPh_3)_3]$ [c,d]	PPh_3	PPh_3,Cl	109.5 (d)	142
trans-$[RhCl(L^{pmp})(PPh_3)_2]$	PPh_3	L^{pmp},Cl	115.4 (d)	156
trans-$[Rh(L^{Me})\{N{=}C(CF_3)_2\}(PPh_3)_2]$ [e]	PPh_3	$L^{Me},NC(CF_3)_2$	107.6 (d)	163.6
trans-$[RhCl(L^{pt})\{N{=}C(CF_3)_2\}(PPh_3)_2]$ [e]	PPh_3	$L^{pt},NC(CF_3)_2$	114.3 (d)	168.5
trans-$[Rh(CO)Cl(PPh_3)_2]$ [c]	PPh_3	CO,Cl	117.3 (d)	129
trans-$[Rh(CO)Cl(L^{Ph})(PPh_3)]$ [f]	L^{Ph}	CO,Cl	107.0 (d)	117
trans-$[Rh(CO)Cl(L^{pt})(PPh_3)]$ [f]	L^{pt}	CO,Cl	107.0 (d)	115
trans-$[Rh(CO)Cl(L^{pmp})(PPh_3)]$ [f]	L^{pmp}	CO,Cl	107.1 (d)	115
trans-$[Rh(CO)Cl(L^{Et})(PPh_3)]$ [f]	L^{Et}	CO,Cl	109.6 (d)	112
trans-$[Rh(CO)(L^{Ph})(PPh_3)_2]Cl$	PPh_3	L^{Ph},CO	111.3 (d)	133
trans-$[Rh(CO)(L^{pt})(PPh_3)_2]Cl$	PPh_3	L^{pt},CO	111.3 (d)	135
trans-$[Rh(CO)(L^{pmp})(PPh_3)_2]Cl$	PPh_3	L^{pmp},CO	111.2 (d)	134
trans-$[Rh(CO)(L^{Et})(PPh_3)_2]Cl$	PPh_3	L^{Et},CO	110.3 (d)	132
cis-$[Rh(CO)(L^{Et})_2(PPh_3)]Cl$	L^{Et}	L^{Et}, CO		117.2

[a] Spectra recorded on solutions in $CDCl_3$ using a JEOL PFT 100 MHz spectrometer. [b] Chemical shifts in p.p.m. relative to $P(OMe)_3$. [c] T. H. Brown and P. J. Green, *J. Am. Chem. Soc.*, 1969, **91**, 3378. [d] S. P. Jesson, C. A. Tolman, and P. Meakin, *J. Am. Chem. Soc.*, 1972, **94**, 3242. [e] Ref. 15. [f] CO *trans* to Cl^-.



(30) (45)



Scheme 4. Some nucleophilic displacement reactions of monocarbenerhodium(I) complexes which proceed without retention of stereochemistry at the metal; for further details, see Schemes 2 and 3

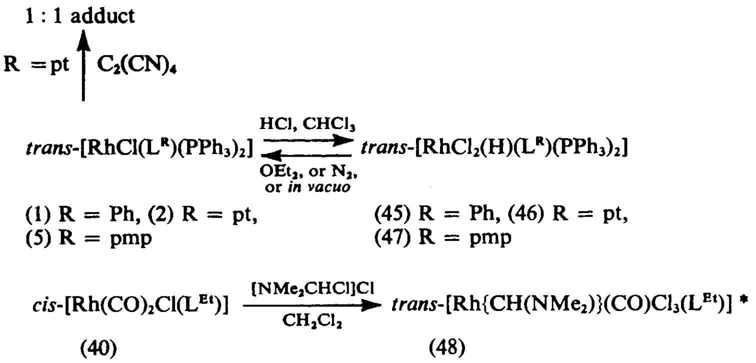
n.m.r. spectroscopic evidence, which showed the formation of $SiMe_4$, the cleavage of the $Rh-CH_2SiMe_3$ bond [loss of $^3J(Me_3SiC^1H_2{}^{103}Rh)$ of 3 Hz in (30)], and a change in the L^R proton resonances. However, a crystalline product (45) was not isolated, perhaps because of its rapid decomposition leading to free cyclo-octa-1,5-diene and rhodium metal.

One recently synthesised electron-rich olefin (A), investigated in the present studies, was bis[1,3-di(2-methoxyphenyl)-imidazolidin-2-ylidene].[2] Although the general reactivity of *N*-aryl derivatives is considerably lower compared to *N*-alkyl analogues of L^R_2, the *o*-anisyl compound,[2] L^{omp}_2, was found to be sluggish even when compared to its *para* analogue, L^{pmp}_2. Thus $[RhCl(PPh_3)_3]$ did not react with L^{omp}_2 to afford a product isomeric with *trans*-$[RhCl(L^R)(PPh_3)_2]$ [R = pmp (5)], and reaction with $[\{Rh(cod)Cl\}_2]$, although occurring, was again slow. As the *o*- and *p*-anisyl compounds are expected to be similar in electronic terms, we assume that the *ortho* substituents sterically reduce the nucleophilicity of L^{omp}_2 compared with L^{pmp}_2, as formation is believed to proceed by initial nucleophilic attack of L^R_2 at the metal *via* a nitrogen centre and subsequent 1,2-sigmatropic shift of the metal fragment from N to $C_{carbene}$.[26]

Assignment of Stereochemistry and Steric Course of Substitution Reactions at Rhodium.—Complexes of the type $[RhX(L^R)(PPh_3)_2]$ and $[Rh(CO)(L^R)(PPh_3)_2]X$ are assigned as having a *trans* orientation of the two PPh_3 ligands, largely on the basis of ^{31}P n.m.r. spectra, which reveals (Table 4) a single ^{31}P magnetic environment.

The evidence for a neutral *trans*-CO/Cl arrangement in $[Rh(CO)Cl(L^R)(PPh_3)]$ is not definitive. However, it is plausible because this configuration is found in *trans*-$[Rh(CO)Cl(PPh_3)_2]$ and in *trans*-$[Rh(CO)Cl(L^R)_2]$ (R = Me or Et), in which the two L^R ligands are magnetically equivalent (^1H or ^{13}C n.m.r.).[27] Moreover a *trans*-CO/Cl^- structure appears to be invariant in other complexes of the type [Rh(CO)ClLL′] (where L and L′ are the same or different and each is a tertiary phosphine, arsine, or stibine).[25b] It is further supported by the similarity in ν(CO) in the three types of complexes, and ν(CO) is expected to be primarily influenced in Rh^I complexes by the ligand *trans* to CO.

Each of the reactions shown in Schemes 1—3 may be regarded as a nucleophilic displacement at Rh^I. It will be evident that in some of these substitution occurs with loss of stereochemical integrity at the metal centre, as summarised in Scheme 4. We take the view that for each of these four reaction types [(*i*)—(*iv*) in Scheme 4], the rearranged product is the thermodynamically most stable isomer, and may be formed *via* the intermediary of the kinetic product of retention. The evidence for this rests with ^1H n.m.r. spectra of analogous reactions of dicarbenerhodium(I) complexes, *e.g.*[27] *trans*-



$$\textit{trans}\text{-}[RhCl(L^{R})(PPh_3)_2] \xrightarrow[R\,=\,pt]{C_2(CN)_4} 1:1\ \text{adduct}$$

$$\textit{trans}\text{-}[RhCl(L^{R})(PPh_3)_2] \underset{OEt_2,\ \text{or}\ N_2,\ \text{or}\ \textit{in vacuo}}{\overset{HCl,\ CHCl_3}{\rightleftharpoons}} \textit{trans}\text{-}[RhCl_2(H)(L^{R})(PPh_3)_2]$$

(1) R = Ph, (2) R = pt, (5) R = pmp; (45) R = Ph, (46) R = pt, (47) R = pmp

$$\underset{(40)}{\textit{cis}\text{-}[Rh(CO)_2Cl(L^{Et})]} \xrightarrow[CH_2Cl_2]{[NMe_2CHCl]Cl} \underset{(48)}{\textit{trans}\text{-}[Rh\{CH(NMe_2)\}(CO)Cl_3(L^{Et})]\,*}$$

Scheme 5. Oxidative addition reactions of some monocarbenerhodium(I) complexes. The transformation (40) → (48) was carried out by Dr. D. B. Shaw (see ref. 35). The complex indicated (*) is believed to have Cl^-/CO and Cl^-/Cl^- mutually *trans* from its spectroscopic data and analogy with the similarly formulated $[Rh\{CH(NMe_2)\}(CO)Cl_3(PPh_3)]$[16]

$[Rh(CO)Cl(L^{Et})_2] + PPh_3 \longrightarrow$ *trans*-$[Rh(CO)(L^{Et})_2(PPh_3)]Cl \longrightarrow$ *cis* isomer; the initial formation of the *trans* cation is observed followed by its progressive decay with concomitant growth of the eventual product, the *cis* isomer. Even in those reactions of monocarbenerhodium(I) complexes which are slow enough to follow by ^1H n.m.r., *e.g.* reactions *(iii)* of Scheme 4 (which take *ca.* 1 h in refluxing xylene; interestingly, the corresponding reaction involving the L^{Me} or L^{Et} complexes, rather than L^{Ph} or L^{pt}, is complete in seconds), such intermediates were not detected. We therefore conclude that either the isomerisations are significantly faster than the initial substitutions or alternatively the substitutions lead directly to the rearranged products.

Chemical Properties.—In the section dealing with synthetic routes, the interconversion of various monocarbenerhodium(I) was described (Schemes 1—3). Here we are concerned only with other reactions. These are of two types, carbene displacements and oxidative additions.

In general, a carbene ligand L^R or L'^{Me} is extremely firmly bound to a transition metal. In the past, displacement reactions have only been observed for the tetracarbene complexes $[RuCl_2(L^R)_4]$ (R = Me or Et), *e.g.* that for L^{Me} with $P(OMe)_3$ gives $[RuCl(L^R)_2\{P(OMe)_3\}_3]Cl$ (R = Me).[4] We now find that heating complexes (8), (9), or (13) with a three-fold excess of triphenylphosphine in refluxing xylene affords *trans*-$[Rh(CO)Cl(PPh_3)_2]$, equation (ii) {but under identical conditions there

$$\textit{trans}\text{-}[Rh(CO)Cl(L^{R})(PPh_3)] + PPh_3 \longrightarrow \textit{trans}\text{-}[Rh(CO)Cl(PPh_3)_2] \quad (ii)$$

R = Ph (8), pt (9), or pmp (13)

was no reaction between PPh_3 and *trans*-$[RhCl(L^R)(PPh_3)_2]$ (R = Ph or pt)}. Similarly, under the same conditions, 1,2-bis(diphenylphosphino)ethane (dppe) in four-fold excess, or $L^R{}_2$, caused the substitutions of equations (iii)—(v) to be effected.

$$\underset{(1)}{\textit{trans}\text{-}[RhCl(L^{Ph})(PPh_3)_2]} + 2dppe \longrightarrow [Rh(dppe)_2]Cl \quad (iii)$$

$$\underset{(8)}{\textit{trans}\text{-}[Rh(CO)Cl(L^{Ph})(PPh_3)]} + 2dppe \longrightarrow [Rh(dppe)_2]Cl \quad (iv)$$

$$\underset{(1)}{\textit{trans}\text{-}[RhCl(L^{Ph})(PPh_3)_2]} + \tfrac{1}{2}L^{pt}{}_2 \rightleftharpoons \underset{(2)}{\textit{trans}\text{-}[RhCl(L^{pt})(PPh_3)_2]} + \tfrac{1}{2}L^{Ph}{}_2 \quad (v)$$

The system of equation (v) (equilibrium constant = *ca.* 1 at 25 °C; equilibrium reached after heating for *ca.* 2 h in refluxing xylene) has a bearing on the Rh^I-catalysed metathesis of the olefins $L^{Ph}{}_2$ and $L^{pt}{}_2$ to give $2(L^{Ph}\text{–}L^{pt})$.[8] In none of the reactions of equations (ii)—(iv) was the fate of the displaced carbene ligand ascertained.

The oxidative addition reactions are summarised in Scheme 5. The evidence that the HCl adducts have the formulae (45)—(47) rests on (*a*) the colour change from the orange Rh^I substrate (1), (2), or (5) to the colourless adduct, (*b*) the reversion upon addition of diethyl ether [*i.e.*, we propose that OEt_2 is a stronger base towards HCl than the Rh^I complex (1)—(5)], and (*c*) the high-field ^1H n.m.r. spectrum, which showed a doublet of triplets for $Rh^{III}\text{–}H$ [with $^1J(^1H\text{–}^{103}Rh)$ = 38 and $^2J(^1H\text{–}^{31}P)$ = 11 Hz for (45)], indicating the mutual *trans* orientation of the two PPh_3 ligands. Although compounds (45)—(47) were precipitated from a chloroform solution by addition of n-hexane, they dissociated into their factors upon attempting to remove last traces of solvent *in vacuo*; consequently analytical data are not available. The three-fragment oxidative addition of $[NMe_2CHCl]Cl$ to the Rh^I complex (40) gave the adduct (48), the first stable electron-rich olefin-derived carbene-rhodium(III) complex to be characterised. In summary, we note that, in general, oxidative addition reactions of monocarbenerhodium(I) complexes are less facile than those of (tertiary phosphine)rhodium(I) analogues, and the 1 : 1 Rh^{III} adducts are less stable with respect to dissociation into their factors.

Spectroscopic and other Physical Properties.—The monocarbenerhodium(I) complexes (1)—(44) are crystalline and range in colour from pale yellow to orange. It is noteworthy that substitution of PPh_3 by L^R causes a shift from the red end of the spectrum, *cf.* the deep red or dark orange $[RhCl(PPh_3)_3]$, the dark orange *cis*-$[Rh(cod)Cl(PPh_3)]$, and the bright yellow *trans*-$[Rh(CO)Cl(PPh_3)_2]$. The cationic Rh^I halides are insoluble in aromatic hydrocarbons at ambient temperature and the neutral complexes are sparingly soluble; they are much more soluble in $CHCl_3$ or CH_2Cl_2. In general, carbene complexes are more soluble than PPh_3 analogues, and the *N,N'*-dialkyl L^R complexes (R = Me or Et) are more soluble than the diaryl compounds. The ionic complexes had conductances in CH_3NO_2 appropriate for 1 : 1 electrolytes.

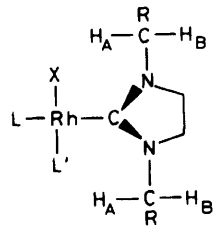
The complexes *cis*-$[Rh(cod)Cl(L^R)]$ (24)—(29) gave parent ions, P^+, in their mass spectra. The base peak was $[P - L^R]^+$, which when R = Me or Et (but not R = aryl) led to fragmentation by loss of C_2H_4. Other features were loss of chlorine as HCl (metastable peak) from P^+, and a high abundance of the aminyl ion $[L^R - H]^+$; there was no peak corresponding to the known olefin radical cation $[(A)]^+$. I.r., ^1H, and selected ^{31}P n.m.r. spectroscopic data are summarised in Tables 2—4. Carbon-13 n.m.r. spectra were not examined for all the complexes; however, some results are to be found in ref. 27, and others will be discussed in a later paper together with data on di- and tri-carbene-rhodium(I) complexes.

The main diagnostic information elicited by examination of i.r. spectra resides in the values for ν(CO), $\nu(CN_2)$, and ν(Rh–Cl) (indicative of a *trans* influence of $L^R > PPh_3$). The CN_2 asymmetric stretching mode in carbenerhodium(I) complexes is in the range 1 490—1 550 cm^{-1}, the majority being at 1 510—1 520 cm^{-1}. The highest values were found in (*a*) complexes containing the L'^{Me} ligand [*e.g.*, complex (12) has $\nu(CN_2)$ at 1 548 cm^{-1} which compares with 1 512 cm^{-1} found for the L^{Me} analogue (11)], and (*b*) cationic complexes derived from the L^{Me} or L^{Et} ligand, as in *trans*-$[Rh(CO)(L^{Me})(PPh_3)_2]Cl$ (19). In general $\nu(CN_2)$ for $Rh^I(L^{Alkyl})$ complexes is higher than for $Rh^I(L^{aryl})$ analogues, showing the greater C ⋯ N multiple bonding in the former. Likewise, none of these complexes has $\nu(CN_2)$ as high as found in Rh^{III} complexes derived from the ligand $=C(H)NMe_2$,[16] because in the latter C ⋯ N bond multiplicity is the greater.

The carbonyl stretching mode, ν(CO), is more sensitive to substituent effects than is $\nu(CN_2)$, as also observed in many other carbonyl-L^R-metal complexes, and for monocarbonyls it is found at highest wavenumber in the cationic complexes. Neutral monocarbenerhodium(I) complexes of type $[Rh(CO)(L^R)_n(PPh_3)_{2-n}X]$ ($n = 1$ or 2) give rise to a single band in the range 1 980—1 984 cm^{-1}. The high value (1 980 cm^{-1}) in the perchlorato-complex $[Rh(CO)(ClO_4)(L^{pt})(PPh_3)]$ (15) may well arise from some ionic character in this complex. Although ClO_4^- is a poor nucleophile, generally preferring an ionic environment, it is unquestionably covalent in (15), with $\nu(ClO_4)$ at 674m, 885m, 1 010s, and 1 130s cm^{-1}; in contrast the ionic complex $[Rh(CO)_3(L^{pt})][ClO_4]$ (44) has a very strong band at 1 090 cm^{-1}. I.r. spectroscopy is diagnostic for the mode of perchlorate bonding: ionic at *ca.* 1 180 cm^{-1} and covalent monodentate, $M–OClO_3$, with this split into a doublet.[32] However, in complex (15), the latter is evident from the i.r. characteristics. In $[Rh(CO)(L^R)_n(PPh_3)_{3-n}]Cl$ ($n = 1—3$), ν(CO) is at higher wavenumber (2 000—2 010 cm^{-1}) than in corresponding neutral complexes; this compares with 2 029 cm^{-1} in $[Rh(CO)(PPh_3)_3][ClO_4]$ [33] and 2 006 cm^{-1} in *trans*-$[Rh\{CSCH{=}C(Me)NMe\}(CO)(PPh_3)_2][BF_4]$.[18] In both the neutral and cationic complexes there is the expected trend in ν(CO) being lower for an L^R complex than a PR_3 analogue, attributable (as noted previously, *e.g.* ref. 5) to the higher σ-donor strength of L^R compared with PR_3. The lack of significant π contribution to the $M–C_{carbene}$ (L^R) bond has been commented on before (*e.g.* refs. 2, 4, and 15) and the *X*-ray structure [15] of *trans*-$[Rh(L^{Me})\{N{=}C(CF_3)_2\}(PPh_3)_2]$ showed the $Rh–C_{carbene}$ bond length [2.006(15) Å] to be that of a Rh–C single bond, *cf.* the Rh–C distance of 1.808(11) Å in $[\{Rh(CO)_2(\mu\text{-}Cl)\}_2]$.[34]

Hydrogen-1 n.m.r. spectroscopy has proved of value in our studies concerning barriers to $Rh–C_{carbene}$ bond rotation.[10] In $CDCl_3$, a temperature-dependent AB pattern is observed for the CH_2 protons in the $N–CH_2R$ substituent in complexes of general type (E) [L′ = CO, X = Cl, R = Ph, and L = L^{benzyl}, PMe_2Ph, $PMePh_2$, PEt_3, PPh_3, $P(C_6H_{11})_3$, CO, or pyridine; L′ = CS, X = Cl, R = Ph, and L = L^{benzyl}; L′ = CO, X = Cl, R = Me, and L = L^{Et}, PPh_3, or CO; X = Cl, R = Me, and LL′ = cod]; [27,35] this problem will be considered in more detail elsewhere.

From the $^{31}P–^{103}Rh$ coupling constant data of Table 4 it appears that L^R ligands have a greater *trans* influence than PPh_3, because as for Pt^{II},[36] a ligand of high *trans* influence is expected to lower the coupling. Thus, $^1J(^{31}P–^{103}Rh)$ falls in the



(E)

sequences: *trans*-$[Rh(CO)Cl(PPh_3)_2]$ (129) [37] > *trans*-$[Rh(CO)Cl(L^R)(PPh_3)]$ (112—117 Hz); *trans*-$[Rh(CO)(L^{Et})(PPh_3)_2]Cl$ (132) > *cis*-$[Rh(CO)(L^{Et})_2(PPh_3)]$ (117 Hz).[27] The $L^R > PPh_3$ *trans* influence order is supported by trends in ν(Rh–Cl) for appropriate complexes (see Table 2).

It also seems that the *cis* influence of L^R is smaller than that of PPh_3; thus we compare $^1J(^{31}P–^{103}Rh)$ of *trans*-$[RhCl(PPh_3)(\dot{P}Ph_3)_2]$ (142) [37] and *trans*-$[RhCl(L^{pmp})(\dot{P}Ph_3)_2]$ (156 Hz), where the asterisk indicates the *trans* ligand for which the coupling constant is given.

Experimental

General procedures were as described previously.[2-4] Complexes $[RhCl(PPh_3)_3]$,[29] $[\{Rh(cod)Cl\}_2]$,[30] and *trans*-$[Rh(CO)Cl(PPh_3)_2]$ [31] were made by published procedures from $RhCl_3·3H_2O$. Only typical syntheses or reactions are described.

Complexes of the Type trans-$[RhCl(L^R)(PPh_3)_2]$ *and trans*-$[RhCl(L'^{Me})(PPh_3)_2]$ (R = Ph, pt, *or* Me).—A suspension of chlorotris(triphenylphosphine)rhodium(I) (0.20 mmol) and bis(1,3-diphenylimidazolidin-2-ylidene) (0.11 mmol) was heated at 140 °C for 1 h in xylene (30 cm^3) under reflux. The suspension dissolved to give an orange solution which was filtered hot. Upon cooling orange crystals of trans-*chloro-(*1,3-*diphenylimidazolidin*-2-*ylidene)bis(triphenylphosphine)-rhodium*(I) were deposited.

Complexes of the Type trans-$[Rh(CO)Cl(L^R)(PPh_3)]$ (R = Me, Et, Ph, pt, *or* pmp).—*Method* 1, *from trans*-$[RhCl(L^R)(PPh_3)_2]$. Gaseous carbon monoxide was gently bubbled (10 min) through a hot (110 °C) solution of *trans*-$[RhCl(L^{Ph})(PPh_3)_2]$. The orange solution became paler and on cooling deposited yellow crystals of the product, trans-*carbonylchloro-(*1,3-*diphenylimidazolidin*-2-*ylidene)(triphenylphosphine)-rhodium*(I). For R = Me or Et, crystallisation was assisted by addition of n-hexane and cooling to −30 °C.

Method 2, *from trans*-$[Rh(CO)Cl(PPh_3)_2]$. To a suspension of *trans*-carbonylchlorobis(triphenylphosphine)rhodium(I) (0.20 mmol) in xylene (10 cm^3) was added bis(1,3-dimethylimidazolidin-2-ylidene) (0.10 mmol). The mixture was heated for 1 h at 130 °C, and the resulting yellow solution was allowed to cool. Crystals of the product, trans-*carbonylchloro-(*1,3-*dimethylimidazolidin*-2-*ylidene)(triphenylphosphine)-rhodium*(I), were obtained by adding n-hexane (10 cm^3) and cooling (−30 °C).

Method 3, *from cis*-$[Rh(CO)_2Cl(L^R)]$. To a solution of *cis*-dicarbonylchloro(1,3-dimethylimidazolidin-2-ylidene)-rhodium(I) (0.05 mmol) in benzene (10 cm^3) was added triphenylphosphine (0.05 mmol). Carbon monoxide evolution was observed as the mixture was stirred (25 °C, 30 min). Addition of n-hexane resulted in slow crystallisation of the product, trans-*carbonylchloro(*1,3-*dimethylimidazolidin*-2-*ylidene)(triphenylphosphine)rhodium*(I).

Complexes of the Type trans-$[Rh(CO)(L^R)(PPh_3)_2]X$ (X = Cl, Br, I, *or* ClO_4; R = Me, Et, Ph, pt, *or* pmp).—To a solution of *trans*-carbonylchloro(1,3-diphenylimidazolidin-2-ylidene)(triphenylphosphine)rhodium(I) (0.10 mmol) in $CHCl_3$ (5 cm^3) was added triphenylphosphine (0.11 mmol). The mixture was stirred at 25 °C for 2 h, whereafter the solvent was removed *in vacuo*. The residue was extracted with warm n-hexane and recrystallised ($CHCl_3$–C_6H_{14}, −30 °C) to afford trans-*carbonyl*(1,3-*diphenylimidazolidin*-2-*ylidene*)*bis*(*triphenylphosphine*)*rhodium*(I) *chloride*. (For R = Me or Et, the reaction time was shorter, of the order of minutes.)

Complexes of the Type cis-[Rh(cod)Cl(L^R)] (R = Me, Et, Ph, pt, pmp, *or* omp).—A mixture of di-μ-chloro-bis(cyclo-octa-1,5-diene)dirhodium(I) (0.10 mmol) and bis(1,3-diphenylimidazolidin-2-ylidene) (0.11 mmol) was heated under reflux (140 °C) in xylene (20 cm^3) for 1 h. The yellow suspension was filtered hot and the filtrate was allowed to cool. Crystals of cis-*chloro*(*cyclo-octa*-1,5-*diene*)(1,3-*diphenylimidazolidin*-2-*ylidene*)*rhodium*(I) were deposited, which were washed successively with toluene and n-hexane and dried *in vacuo*. (For R = Me or Et, a reaction temperature of 80 °C and a reaction time of 30 min was sufficient; crystallisation was assisted by careful addition of n-hexane and cooling to −30 °C.)

Complexes of the Type cis-[$Rh(CO)_2X(L^R)$] (X = Cl or NO_3; R = Me, Et, Ph, pt, pmp, *or* omp).—Carbon monoxide was bubbled (10—30 min) through a solution of *cis*-chloro-(cyclo-octa-1,5-diene)(1,3-diphenylimidazolidin-2-ylidene)-rhodium(I) (0.10 mmol) in $CHCl_3$ or CH_2Cl_2 (5 cm^3). The colour faded from orange to pale yellow. Slow addition of n-hexane resulted in the formation of the microcrystalline product, cis-*dicarbonylchloro*(1,3-*diphenylimidazolidin*-2-*ylidene*)*rhodium*(I).

cis-[$Rh(cod)(CH_2SiMe_3)(L^R)$] (R = Ph *or* pt).—To the complex *cis*-chloro(cyclo-octa-1,5-diene)(1,3-di-*p*-tolylimidazolidin-2-ylidene)rhodium(I) (1.00 mmol) in benzene (30 cm^3), was added a solution of trimethylsilylmethyl-lithium (1.26 mmol) in hexane (2.5 cm^3). The mixture was protected from the light and stirred at 25 °C for 1 h, and was then filtered. n-Hexane (*ca.* 20 cm^3) was layered onto the orange solution, which was left in the dark for 16 h. The yellow-orange crystals of cis-*cyclo-octa*-1,5-*diene*(1,3-*di*-p-*tolylimidazolidin*-2-*ylidene*)-(*trimethylsilylmethyl*)*rhodium*(I) were separated by filtration, washing with n-hexane (2 × 5 cm^3), and drying *in vacuo*.

Anionic Ligand Exchange Reactions.—Synthesis of [Rh(cod)-(ClO_4)(L^R)] (R = pt *or* omp).—A mixture of *cis*-chloro-(cyclo-octa-1,5-diene)[1,3-di(2-methoxyphenyl)imidazolidin-2-ylidene]rhodium(I) (0.20 mmol) and silver(I) perchlorate (0.25 mmol) in benzene (15 cm^3) was stirred at 25 °C for 1 h in the dark. The colour of the solution became paler, and the resulting precipitate was filtered off, and extracted with CH_2Cl_2. Slow addition of n-hexane to the extract afforded pale yellow crystals of cis-*cyclo-octa*-1,5-*diene*[1,3-*di*(2-*methoxyphenyl*)-*imidazolidin*-2-*ylidene*](*perchlorato*)*rhodium*(I).

Synthesis of cis-[Rh(cod)(NO_3)(L^R)] (R = pt, pmp, *or* omp).—To a solution of *cis*-chloro(cyclo-octa-1,5-diene)-[1,3-di(2-methoxyphenyl)imidazolidin-2-ylidene]rhodium(I) (0.1 mmol) in acetone (10 cm^3) was added silver(I) nitrate (0.13 mmol) in water (2 cm^3). The mixture was protected from the light and was stirred for 1 h at 25 °C, whereafter it was filtered. The filtrate was evaporated to dryness, dissolved in CH_2Cl_2, and dried ($MgSO_4$). Filtration and slow addition of n-hexane afforded yellow crystals of cis-*cyclo-octa*-1,5-*diene*[1,3-*di*(2-*methoxyphenyl*)*imidazolidin*-2-*ylidene*](*nitrato*)-*rhodium*(I).

Synthesis of [$Rh(CO)(BH_4)(L^{pt})(PPh_3)$].—Sodium tetrahydroborate (0.70 mmol) in ethanol (10 cm^3) was added to carbonyl(1,3-di-*p*-tolylimidazolidin-2-ylidene)(perchlorato)-(triphenylphosphine)rhodium(I) (0.71 mmol) in ethanol (40 cm^3) and the mixture was stirred at *ca.* 25 °C for *ca.* 0.5 h. A very pale yellow precipitate of (*carbonyl*)(1,3-*di*-p-*tolyimidazolidin*-2-*ylidene*)(*tetrahydroborato*)(*triphenylphosphine*)-*rhodium*(I) was deposited, filtered off, washed with ethanol, and dried *in vacuo*.

Synthesis of cis-[$Rh(cod)(L^{omp})(PPh_3)$][ClO_4].—To a solution of *cis*-cyclo-octa-1,5-diene[1,3-di(2-methoxyphenyl)-imidazolidin-2-ylidene](perchlorato)rhodium(I) (0.1 mmol) in CH_2Cl_2 (10 cm^3) was added triphenylphosphine (0.2 mmol). The colour slowly changed from yellow to orange. The solution was evaporated to dryness and the crude product was recrystallised (CH_2Cl_2–OEt_2) to afford crystals of cis-*cyclo-octa*-1,5-*diene*[1,3-*di*(2-*methoxyphenyl*)*imidazolidin*-2-*ylidene*]-(*triphenylphosphine*)*rhodium*(I) *perchlorate*.

Synthesis of [$Rh(CO)_3(L^{pt})$][ClO_4].—Carbon monoxide was bubbled into a solution of *cis*-cyclo-octa-1,5-diene(1,3-di-*p*-tolylimidazolidin-2-ylidene)(perchlorato)rhodium(I) (0.15 mmol) in CH_2Cl_2 (10 cm^3) for *ca.* 0.5 h at *ca.* 25 °C. The mixture was stirred for a further 0.5 h. Addition of n-hexane, filtration, and recrystallisation of the precipitate afforded yellow crystals of *tricarbonyl*(1,3-*di*-p-*tolylimidazolidin*-2-*ylidene*]*rhodium*(I) *perchlorate*.

Carbene Displacement Reactions from Monocarbene-rhodium(I) *Complexes*.—(*a*) *From trans*-[$Rh(CO)Cl(L^R)$-(PPh_3)] *by* PPh_3. Complex (8) (R = Ph) (0.05 mmol) suspended in xylene (10 cm^3) was heated with PPh_3 (0.30 mmol) under reflux for *ca.* 3 h. Upon cooling, large yellow crystals of *trans*-[$Rh(CO)Cl(PPh_3)_2$] were deposited, filtered off, and recrystallised (PhMe). A similar procedure gave the same product from the title compound in which L^R = L^{pt}, (9), or L^{pmp}, (13).

(*b*) *From trans*-[$Rh(CO)Cl(L^{Ph})(PPh_3)$] (8) *by* 1,2-*bis*-(*diphenylphosphino*)*ethane*. Complex (8) (0.05 mmol) and dppe (0.20 mmol) in xylene (25 cm^3) were heated under reflux for 2 h. Using the procedure of (*a*), yellow crystalline [$Rh(dppe)_2$]Cl was isolated.

(*c*) *From trans*-[$RhCl(L^{Ph})(PPh_3)_2$] (1) *by dppe* (*but not* PPh_3). Complex (1) (0.05 mmol) and dppe (0.20 mmol) were heated in refluxing toluene for *ca.* 5 h. Cooling afforded yellow crystals of [$Rh(dppe)_2$]Cl. Under similar conditions, there was no reaction between (1) and a ten-fold excess of PPh_3.

(*d*) *From trans*-[$RhCl(L^{Ph})(PPh_3)_2$] (1) *and* $L^{pt}{}_2$.—A mixture of complex (1) (0.05 mmol) and olefin (A) (R = pt) (0.025 mmol) in xylene (10 cm^3) was heated under reflux for *ca.* 2 h. Upon cooling, the orange crystals were shown to be (by comparison of ^1H n.m.r. spectra) an approximately 1 : 1 mixture of complex (1) and *trans*-[$RhCl(L^{pt})(PPh_3)_2$] (2). The same product was obtained under identical conditions from (2) (0.05 mol) and $L^{Ph}{}_2$ (0.025 mmol).

Oxidative Addition Reactions.—(*a*) *trans*-[$RhCl(L^{Ph})$-($PPh_3)_2$] (1) + HCl. Hydrogen chloride was bubbled through a suspension of complex (1) (0.05 mmol) in chloroform (3 cm^3). The solid rapidly dissolved to give a colourless solution. Addition of n-hexane precipitated a white solid, which upon exposure to air, or drying under vacuum, yielded the orange starting material (1). The latter was also obtained when diethyl ether (*ca.* 20 cm^3) was added to the colourless solution in n-C_6H_{14}. Similar observations were made for HCl and complex (2) or (5).

(*b*) *Reaction of trans*-[RhCl(L^{Pr})(PPh_3)$_2$]. A benzene (5 cm^3) solution of tetracyanoethylene (0.10 mmol) was added to a stirred suspension of the orange complex (2) (0.10 mmol) in C_6H_6 (25 cm^3) under ambient conditions. The solid gradually dissolved to give a dark solution from which the orange solid 1 : 1 adduct (73%) (Found: C, 67.1; H, 4.5; N, 8.6. $C_{59}H_{48}ClN_6P_2Rh$ requires C, 68.0; H, 4.6; N, 8.1%) was obtained by filtration, washing with successively benzene and n-hexane, and drying *in vacuo*.

(*c*) *Reaction of cis*-[Rh(CO)$_2$Cl(L^{Et})] *and* [NMe_2CHCl]Cl. A solution of [NMe_2CHCl]Cl (2 mmol) in dichloromethane (10 cm^3) was slowly (*ca.* 0.5 h) added to complex (40) in CH_2Cl_2 (15 cm^3) at ambient temperature. After *ca.* 12 h at 25 °C, concentration *in vacuo* to *ca.* 15 cm^3, and cooling to −30 °C, pale yellow crystals of *trans*-[Rh{CH(NMe$_2$)}(CO)Cl$_3$(L^{Et})] (48) (75%) were obtained.

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