

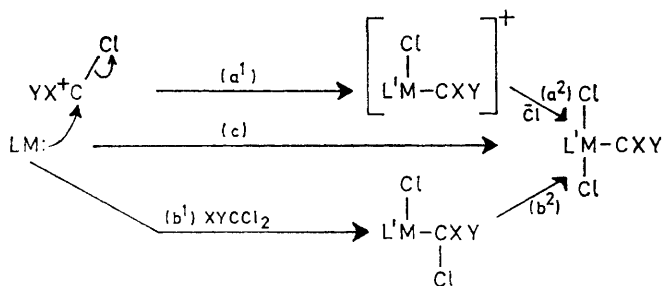
Carbene Complexes. Part VII.¹ Chloromethyleneammonium Chlorides. Electron-rich Carbenoids, as Precursors to Secondary Carbene Metal Complexes; Crystal and Molecular Structure of Trichloro(dimethylaminomethylene)bis(triethylphosphine)rhodium(III)

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The reaction of dialkyl(chloromethylene)ammonium chlorides $(R_2NCHCl)^+Cl^-$, ($R = Me, Et, Pr^i, \text{ or } Bu^a$), with Rh^I substrates $[RhCl(PPh_3)_3]$, $[RhCl(CO)PPh_3]_2$, or $[RhCl(CO)_2]_2$ affords Rh^{III} secondary carbene complexes, $[L'RhCl_3CHNR_2]_n$ [$L' = CO, n = 2$; $L' = (PPh_3)CO, n = 1$; $L' = (PEt_3)_2$ or $(PPh_3)_2, n = 1$], via a three-fragment oxidative-addition reaction. The secondary carbene Rh^{III} complexes are characterised by a high degree of CN double-bonding, greater than in tertiary carbene complexes or carboxylic acid dialkylamides. The $C_{carb}-H$ 1H n.m.r. resonance is at low field (τ ca. -1), $\nu(C_{carb}-H)$ at ca. 3050 cm^{-1} , and $\nu(C_{carb}=N)$ at ca. 1600 cm^{-1} ; coupling of $C_{carb}-H$ resonances are identified: $^2J(^{103}Rh-^1H)$, $^3J(^{31}P-^1H)$, and $trans-^4J(C^1H_3N-^1H)$. A single-crystal X-ray analysis of $[RhCl_3(PEt_3)_2CHNMe_2]$ has been carried out to $R = 0.050$; the complex has an approximately octahedral Rh environment with mutually *trans*-phosphine ligands. Bond distances (\AA) are $Rh-C_{carb} = 1.961(11)$, $C_{carb}-N = 1.289(14)$, $C_{carb}-H = 1.14(4)$, $Rh-P = 2.368(3)$ and $2.372(3)$, $Rh-Cl$ (mutually *trans*) = $2.357(4)$ and $2.364(3)$, $Rh-Cl$ (*trans*-carbene) = $2.445(4)$. The high *trans*-influence of the secondary carbene ligand is discussed in terms of X-ray, i.r., and n.m.r. data, and it appears to have the highest *trans*-influence of a neutral ligand of Rh^{III} .

As stated in Part I,² a major objective of our work is to seek organic precursors—carbenoids—for the synthesis of transition-metal carbene complexes. Because stable examples of such complexes are at present found only for nucleophilic carbene ligands,³ we have concentrated attention on electron-rich carbenoids, e.g. tetra-amino-olefins.^{2,4}

We now show that chloromethyleneammonium chlorides $(R_2NCHCl)^+Cl^-$ provide a convenient source for secondary carbene complexes, stoichiometrically by three-fragment oxidative addition.^{1,5} We regard these carbenoids as merely one suitable example of electron-rich *gem*-dichlorides (instead of chlorides, other good leaving groups which are also capable of forming strong bonds with metals should be equally useful); similar compounds are probably intermediates in the formation of carbene complexes from imidoyl chlorides.^{1,5} The general synthesis is shown in Scheme 1, in which LM



SCHEME 1

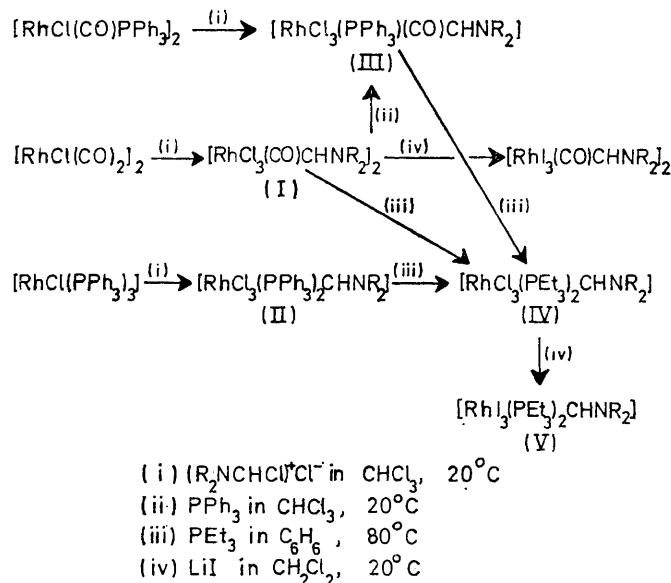
represents a co-ordinatively unsaturated low oxidation state metal substrate (e.g. a d^8 complex), and X and/or Y

¹ Part VI, P. B. Hitchcock, M. F. Lappert, G. M. McLaughlin, and A. J. Oliver, *J.C.S. Dalton*, 1974, 68.

² Part I, D. J. Cardin, B. Çetinkaya, E. Çetinkaya, and M. F. Lappert, *J.C.S. Dalton*, 1973, 514.

³ D. J. Cardin, B. Çetinkaya, and M. F. Lappert, *Chem. Rev.*, 1972, **72**, 545; F. A. Cotton and C. M. Lukehart, *Progr. Inorg. Chem.*, 1972, **16**, 487; D. J. Cardin, B. Çetinkaya, M. J. Doyle, and M. F. Lappert, *Chem. Soc. Rev.*, 1973, **2**, 99.

are electron-rich groups such as R_2N , RNH , or RO . A preliminary communication has been published.⁶ This paper deals with secondary carbene (X or $Y = H$) derivatives of Rh^{III} ; their preparation is illustrated by



SCHEME 2

Scheme 2. Suitable substrates LM, e.g., the Rh^I complexes of Scheme 2, are good nucleophiles. The mechanism of carbene complex formation may therefore initially (a^1) involve nucleophilic attack of LM at the electrophilic C of the *gem*-dichloride [pathway (a)]. A plausible alternative [initial two-fragment oxidative addition

⁴ Part II, B. Çetinkaya, E. Çetinkaya, and M. F. Lappert, *J.C.S. Dalton*, 1973, 906; B. Çetinkaya, P. Dixneuf, and M. F. Lappert, *J.C.S. Chem. Comm.*, 1973, 206.

⁵ Part V, M. F. Lappert and A. J. Oliver, *J.C.S. Dalton*, 1974, 65.

⁶ B. Çetinkaya, M. F. Lappert, and K. Turner, *J.C.S. Chem. Comm.*, 1972, 851.

(b¹) is shown in route (b), whereas a concerted three-fragment oxidation [route (c)] is much less probable. It may be a necessary requirement that the *gem*-dichloride has considerable ionic character; a complicating reaction may well be the oxidative dichloro-addition without concomitant carbene formation {e.g. $[\text{Pt}(\text{Ph}_3\text{P})_3] \rightarrow [\text{PtCl}_2(\text{Ph}_3\text{P})_2]$ }, a process which may be free radical.

A further aim of the present work is to attempt the detailed characterisation of secondary carbene complexes. We shall show that these compounds have (a) $C_{\text{carb}}\text{-H}$ at low field in the ^1H n.m.r. ($\tau -1.5$ to $+1$), (b) $\nu(C_{\text{carb}}\text{-H})$ at ca. 3050 cm^{-1} , (c) for amino-carbenes, $\nu(C\text{:}\ddot{\text{N}}$) at ca. 1600 cm^{-1} , (d) $l(\text{C-H})$, ca. 1.1 \AA , (e) for amino-carbenes $l(\text{C}\text{:}\ddot{\text{N}})$, ca. 1.3 \AA , (f) $l(\text{M-C}_{\text{carb}})$, appropriate for a MC single bond, (g) for amino-carbenes, a high degree of CN double-bond order (greater than in tertiary carbene complexes); furthermore, (h) a detailed $C_{\text{carb}}\text{-H}$ n.m.r. coupling pattern may be identified [e.g. see Figure (1)], and (i) the *trans*-influence of the

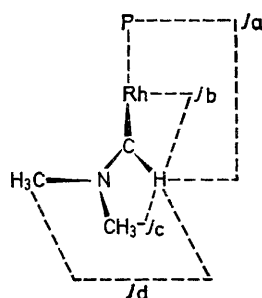


FIGURE 1 Diagrammatic representation of $C_{\text{carb}}\text{-H}$ coupling constants in $[\text{RhCl}_3(\text{PEt}_3)_2\text{CHNMe}_2]$ ($J_a = 2.0\text{ Hz}$, $J_b = 3.5\text{ Hz}$, $J_c = 0.7\text{ Hz}$, $J_d = 0.9\text{ Hz}$)

secondary carbene ligand in Rh^{III} complexes is higher than that of other neutral ligands such as CO or PEt_3 . It is evident, therefore, that there are several structural features in common with carboxylic acid amides, i.e. $[\text{LM-CHNMe}_2]$ may be compared with O=CHNMe_2 .

Previous reports of secondary carbene complexes relate to chelates of Mo^{II} , Mn^{I} , and Fe^{II} , containing the system

$[\text{LM-CHNMe-BH}_2\text{-NMeCH}]$ in which the $C_{\text{carb}}\text{-H}$ n.m.r. chemical shift lies in the range $\tau -0.9$ to -2.0 ,⁷ a Ru^{II} complex,⁸ some phosphido-bridged Fe/Ni species,⁹ and compounds tentatively formulated as (VII)^{10a} and (VIII).^{10b} The last two species were identified by ^1H n.m.r. spectroscopy as intermediates in transition metal-catalysed rearrangements of bicyclobutanes^{10a} or tricyclo[4.1.0.0]heptane,^{10b} and correct assignment of their structures has important implications with regard to

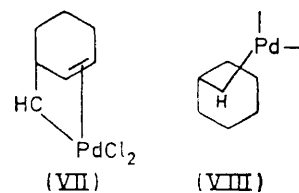
* The complex $[\text{RhCl}(\text{CO})_2\text{PPh}_3]$ now seems to be best regarded as the dimer $[\text{RhCl}(\text{CO})\text{PPh}_3]_2$.¹²

⁷ P. M. Treichel, J. P. Stenson, and J. J. Benedict, *Inorg. Chem.*, 1971, **10**, 1183; W. M. Butler and J. H. Enemark, *J. Organometallic Chem.*, 1973, **49**, 233.

⁸ D. F. Christian, G. R. Clark, W. R. Roper, J. H. Waters, and K. R. Whittle, *J.C.S. Chem. Comm.*, 1972, 458.

⁹ K. Yasufuku and H. Yamazaki, *J. Organometallic Chem.*, 1972, **35**, 365.

proposed mechanisms;¹¹ the $C_{\text{carb}}\text{-H}$ resonance in (VII) and (VIII) was assigned to signals at $\tau 6.21$ and



6.10 , respectively. In the light of our conclusion (a) above, we find these assignments surprising; as nucleophilic amino-carbene metal complexes have the $C_{\text{carb}}\text{-H}$ resonance similar in position to carboxylic acid amides, we should have expected electrophilic carbene complexes to absorb at a position comparable to that found in aldehydes, i.e. τ ca. 0 to 1. The phosphido-bridged Fe/Ni species were formulated as secondary carbene complexes on the basis of their n.m.r. spectra;⁹ we find this plausible in some cases ($\tau = 1.75\text{--}1.95$) but not in others ($\tau = \text{ca. } 5.5$).

The carbene complexes (I)–(VI) were identified on the basis of their elemental analyses, i.r. spectra, and where solubility permitted n.m.r. spectra and molecular weights (see Tables 1 and 2).

The complexes (III) shown in Scheme 2 can be prepared either from (I) by halogen-bridge splitting with PPh_3 , or by direct reaction between $(\text{R}_2\text{NCHCl})^+\text{Cl}^-$ and the dimer $[\text{RhCl}(\text{PPh}_3)(\text{CO})]_2$. That the latter complex is a dimer * is also inferred here by the fact that there is no evolution of CO when (III) is formed. This reaction is, therefore, a rare example of 'simultaneous' oxidative addition and halogen-bridge splitting within the same molecule (see also ref. 5).

The complex (Id) was shown to be dimeric by molecular-weight determination in chloroform, and complexes (Ia–c) are also presumed to be dimeric by comparison of their i.r. spectra with (Id), particularly of $\nu(\text{Rh-Cl})$. The identification of $\nu(\text{Rh-Cl})$ in (I) was achieved by comparison of the i.r. spectrum of (Ia) with that of its iodo-analogue, prepared from (Ia) by using LiI in dichloromethane. Similarly, $\nu(\text{Rh-Cl})$ was identified in complexes (II) and (IV) by spectroscopic examination of the iodo-analogue (IVa). $\nu(\text{Rh-Cl})$ in (III) was identified by comparison with the Rh carbenes prepared in parts V⁵ and VI.¹

The secondary carbene complexes are characterised by a broad $C_{\text{carb}}\text{-H}$ signal in the ^1H n.m.r. spectra, arising from coupling with ^{103}Rh ($I = \frac{1}{2}$) and in (IV) [also presumably in (III) though insolubility prevents observation] coupling with ^{31}P ($I = \frac{1}{2}$). In (IV), the *trans*-phosphines are virtually coupled and they couple

¹⁰ (a) S. Masamune, M. Sakia, and N. Darby, *J.C.S. Chem. Comm.*, 1972, 471; (b) W. G. Dauben and A. J. Keilbania, *J. Amer. Chem. Soc.*, 1972, **94**, 3669.

¹¹ P. G. Gassman and R. R. Reitz, *J. Organometallic Chem.*, **52**, C51.

¹² E. J. Gallay, D. de Montaulon, and R. Poilblanc, *J. Organometallic Chem.*, 1972, **38**, 179; D. F. Steel and T. A. Stephenson, *J.C.S. Dalton*, 1972, 2161.

with the carbene proton to give a virtual triplet which is split by Rh to give a doublet of triplets. The signal actually observed is a 1 : 3 : 3 : 1 quartet and from ^{103}Rh two different signals are observed (Table 2). In the case of complex (IVa) it has also been possible to observe the coupling between N-CH₃ and C_{carb}-H which is

TABLE 1
Analytical data, melting points, and yields (all compounds are yellow or yellow-orange)

Compounds	M.p. (t/°C)	Yield (%)	Found (%)			Required (%)		
			C	H	N	C	H	N
(Ia) [RhCl ₃ (CO)CHNMe ₂] ₂	> 300 (dec.)	100	16.4	2.38	4.60	16.3	2.39	4.76
(Ib) [RhCl ₃ (CO)CHNET ₂] ₂	170-171	100	22.4	3.42	4.31	22.3	3.44	4.34
(Ic) [RhCl ₃ (CO)CHNPr ¹ ₂] ₂ , 2CHCl ₃ ^e	205-215 (dec.)	95	23.4	3.65	3.13	23.0	3.43	2.98
(Id) [RhCl ₃ (CO)CHNBu ² ₂] ₂ ^b	119-123 (dec.)	95	31.8	5.13	3.75	31.7	5.06	3.70
(IIa) [RhCl ₃ (PPh ₃) ₂ CHNMe ₂]	242-243 (dec.)	81	59.2	5.09	1.84	59.1	4.70	1.77
(IIb) [RhCl ₃ (PPh ₃) ₂ CHNET ₂], CHCl ₃	201-203 (froths)	95	53.7	4.80	1.55	53.8	4.51	1.49
(IIc) [RhCl ₃ (PPh ₃) ₂ CHNPr ¹ ₂], CHCl ₃	175-183 (froths)	90	54.6	5.16	1.43	54.7	4.69	1.45
(IIIa) [RhCl ₃ (PPh ₃) ₂ (CO)CHNMe ₂] ^c	> 150 (dec.)	95	46.4	4.31	2.90	47.5	3.99	2.52
(IIIb) [RhCl ₃ (PPh ₃) ₂ (CO)CHNET ₂], CHCl ₃ ^{c,d}	160-163 (froths)	100	42.5	3.82	2.21	42.9	3.89	2.00
(IIIc) [RhCl ₃ (PPh ₃) ₂ (CO)CHNPr ¹ ₂] ^c	213-218 (dec.)	92	49.7	5.13	2.28	51.0	4.93	2.29
(IVa) [RhCl ₃ (PEt ₃) ₂ CHNMe ₂] ^e	169-173	85	36.1	7.29	2.75	35.8	7.42	2.78
(IVb) [RhCl ₃ (PEt ₃) ₂ CHNET ₂] ^e	146-149	84	38.3	7.70	2.75	38.5	7.79	2.64
(IVc) [RhCl ₃ (PEt ₃) ₂ CHNPr ¹ ₂] ^e	141-145	81	41.1	8.45	2.56	40.8	8.12	2.51
(Va) [RhCl ₃ (PMe ₂ Ph) ₂ CHNMe ₂], CHCl ₃ ^f	230-232	64	36.4	4.79	2.37	36.2	4.52	2.11
(Vb) [RhBr ₃ (PMe ₂ Ph) ₂ CHNMe ₂]	237-239	68	34.0	4.39	2.03	33.7	4.29	2.07
(VIa) [RhI ₃ (CO)CHNMe ₂] ₂ ^g	210-218 (dec.)	50	8.7	1.28	2.69	8.5	1.24	2.46
(VIb) [RhI ₃ (PEt ₃) ₂ CHNMe ₂] ^{g,h}	> 175 (dec.)	68	22.8	4.31	1.88	23.2	4.80	1.81

^a Found: Cl, 46.0%. C₁₈H₃₅Cl₁₂N₂O₂Rh₂^d requires 45.3%. ^b Osmometric molecular weight determined in CHCl₃. Found: 758. Required 757. ^c From [RhCl(CO)PPh₃]₂. Found: Cl, 30.1%. C₂₂H₃₀Cl₆NOPRh requires 30.4%. ^e Prepared from (I). ^f Prepared from (IIa). ^g Colour is red-brown. ^h Prepared from (IVa).

TABLE 2
Spectroscopic data for new complexes

Compound	$\nu(\text{C}-\text{O})$ ^a	$\nu(\text{C}-\text{N})$ ^a	$\nu(\text{Rh}-\text{Cl})$ ^a	Selected ¹ H n.m.r. data
(Ia)	2140vs	1620vs	365vs, 325s, 303m, 284w	Insoluble
(Ib)	2129vs	1608vs	351vs, 330s, 286br,m	Insoluble
(Ic)	2116vs	1601vs	348s, 323ms, 294w, 271w	-0.85d (C _{carb} -H); ^b 2.00s (CHCl ₃); 8.53m (CH ₃)
(Id)	2120vs	1601vs	347s, 333ms, 306m, 280w	-0.33d (C _{carb} -H); ^b 6.05m (CH ₂ -N); 9.01m (CH ₃ -CH ₂ CH ₂ -CH ₂ N)
(IIa)	1590s	1590s	340m, 280w	Insoluble
(IIb)	1570s	1570s	331s, 271w	1.47br (C _{carb} -H); 2.40m (PhP); 6.60qa (CH ₂ N); 6.74qa (CH ₂ N); 8.84t (CH ₃ -CH ₂ N); 8.88t (CH ₃ -CH ₂ N)
(IIc)	1550s	1550s	332s, 267m	0.05br (C _{carb} -H); 2.83m (PhP); 3.85br (CH); 5.89br (CH); 8.42d (CH ₃); 9.08d (CH ₃)
(IIIa)	2102vs	1615vs	336m, 270s	0.90br (C _{carb} -H); 2.53m (PhP); 6.27s (NMe); 6.73s (NMe)
(IIIb)	2105vs	1594vs	332m, 280s	Insoluble
(IIIc)	2090vs	1582vs	329m, 287s	Insoluble
(IVa)	1590s	1590s	339s, 281m	{ -1.11qa (C _{carb} -H); ^c 6.06d (NMe); ^d 6.40d (NMe); ^e 7.90m (CH ₂ P); 8.83qi (CH ₃ -CH ₂ P)
(IVb)	1545s	1545s	324s, 280w	{ -1.26qa (C _{carb} -H); ^f 5.64qa (CH ₂ N); ^g 6.10qa (CH ₂ N); ^h 7.95m (CH ₂ P); 8.72m (CH ₃ -CH ₂ P) and (CH ₃ -CH ₂ N)
(IVc)	1535s	1535s	333s, 292w, 280w	{ -1.32qa (C _{carb} -H); ⁱ 4.15se (CH); 5.88se (CH); 7.93m (CH ₂ P); 8.68m (CH ₃ -CH ₂ P) and [(CH ₃) ₂ CHN]
(Va)	1590vs	1590vs	330m, 290w	{ 0.23br (C _{carb} -H); 2.57m (PhP); 2.30s (NMe); 7.68s (NMe); 7.95t (PMe)
(Vb)	1590vs	1590vs	330m, 290w	{ 0.34br (C _{carb} -H); 2.60m (PhP); 7.32s (NMe); 7.50s (NMe); 7.90t (PMe)
(VIa)	2064vs	1591vs	330m, 290w	Insoluble
(VIb)	1589s	1589s	330m, 290w	{ -1.09br (C _{carb} -H); 6.13s (NMe); 6.45s (NMe); 7.67m (CH ₂ P); 8.89qi (CH ₃ -CH ₂ P)

^a Expressed in cm⁻¹, in Nujol. ^b ²J(Rh-H) = 3.5 Hz. ^c ²J(Rh-H) = 3.5 Hz, ³J(P-H) = 2.0 Hz. ^d J(H-H) = 0.7 Hz. ^e J(H-H) = 0.9 Hz. ^f ²J(Rh-H) = 3.0 Hz, ³J(P-H) = 3.0 Hz. ^g J(H-H) = 7.0 Hz. ^h J(H-H) = 7.2 Hz. ⁱ ²J(Rh-H) = 3.4 Hz. ^j ³J(P-H) = 2.8 Hz; abbreviations: s = singlet; d = doublet; qa = quartet; qi = quintet; se = septet; m = complex multiplet, most intense peak given.

and ³¹P decoupling experiments,* and direct observation, it has been possible to determine the values of ²J(¹⁰³Rh-¹H) and ³J(³¹P-¹H) for the complexes (IV) (see Figure 1).

The high C_{carb}-N bond order causes magnetic non-equivalence of the two N-alkyl groups and accordingly

different for each methyl group as is the case in dimethylformamide and -thioformamide.¹³ The high-field N-Me signal in (IVa) has a greater coupling (J = 0.9 Hz) than the low-field N-Me signal (J = 0.7 Hz). This, as well as its relative position, indicates that the latter is *cis*

* We thank Dr. W. McFarlane of the Sir John Cass School of Science and Technology, London, for these results.

¹³ R. C. Neuman, jun., W. Snider, and V. Jonas, *J. Phys. Chem.*, 1968, **72**, 2469.

to the $C_{\text{carb}}-H$ and the former *trans*. This is exactly analogous to the effect observed in *NN*-dimethylamides.¹³

High-temperature n.m.r. studies on (IVa) in α -bromonaphthalene showed that even at temperatures up to 150° no coalescence, or indeed change of line shape, of the 2-NMe signals occurred, thus confirming the high C-N bond order. (It is noted, however, that in variable-temperature n.m.r. studies on the related dimethylformamide and -thioformamide the coalescence temperature of the NMe signals is higher in aromatic than aliphatic solvents, since the two signals are shifted further apart.¹⁴) It is likely, therefore, that for secondary carbene complexes the barrier to C-N rotation is greater than for tertiary complexes.³ This situation is paralleled by that for secondary and tertiary carboxylic acid amides, such as HCONMe₂ and RCONMe₂, and for both series is attributable mainly to a higher degree of ground-state stabilisation for the HC derivatives.

Consistent with the electrophilic nature of the C_{carb} atom, the attached H is deshielded (see Table 2), more so than in the corresponding *NN*-dialkylformamides (see Table 3). The stereochemistry of complex (IV) is revealed by the phosphine resonances. In complex (IV),

TABLE 3
Spectroscopic data for dialkylformamides and chloromethyleneammonium chlorides

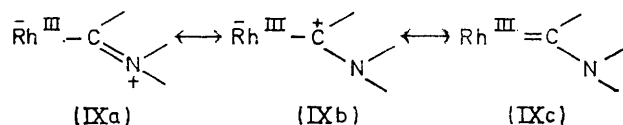
	$\nu(C-N)$ ^a	CH n.m.r. chemical shift (τ) ^{b,c}	NR n.m.r. chemical shift (τ) ^{b,c}
Me ₂ NCHO		1.93s	7.05s (CH ₃); 7.21 (CH ₃)
(Me ₂ NCHCl) ⁺ Cl ⁻	1664	-1.11s	6.00s (CH ₃)
Et ₂ NCHO		1.90s	6.67qa (CH ₂); 8.86t (CH ₃); 8.93t (CH ₃)
(Et ₂ NCHCl)Cl	1664	-1.12s	5.60qa (CH ₂); 8.40t (CH ₃)
Pr ₂ NCHO		1.80s	6.03se (CH); 6.32se (CH); 8.75d (CH ₃); 8.79d (CH ₃)
(Pr ₂ NCHCl)Cl	1670	-1.17s	5.07se (CH); 8.39d (CH ₃)
Bu ₂ NCHO		1.92s	6.72m (N-CH ₂); 9.08m (CH ₂ CH ₂ CH ₃)
(Bu ₂ NCHCl)Cl	1662	-1.13s	5.70m (N-CH ₂); 8.98m (CH ₂ CH ₂ CH ₃)

^a In CHCl₃ solution. ^b R₂NCHO neat; (R₂NCHCl)⁺Cl⁻ in CDCl₃ solution. ^c For abbreviations, see footnotes of Table 2.

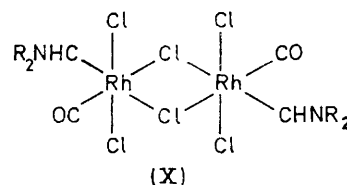
the Me groups of the Et₃P ligands appear as a quintet showing that the phosphines are mutually *trans* and the stereochemistry is therefore unambiguous. The same stereochemistry is observed in complex (VI) as revealed by the n.m.r. of the Me group of PMe₂Ph which appears as a doublet. Although not shown by n.m.r., the stereochemistry of (II) is also presumed to be *trans*-phosphine from i.r. data (see below).

In the i.r. spectra of the complexes (Table 2) a very strong absorption appears in the range 1580–1630 cm⁻¹ due to $\nu(C_{\text{carb}}-N)$. This is significantly higher than in some rhodium tertiary carbene complexes,³ as is consistent with a higher degree of $p_{\pi}-p_{\pi}$ overlap in this bond for the former; further confirmation is provided by the

bond length [in (IVa), see later] and n.m.r. data. The i.r. characterisation for the chloromethyleneammonium chlorides are given for comparison in Table 3 and it can be seen that there is only a slight fall in $\nu(C-N)$ in going from (R₂NCHCl)⁺Cl⁻ to the co-ordinated secondary carbene Rh^{III}-CHNR₂. It appears (also from CH τ values, see above) that CN double-bond character and associated C electrophilicity decreases in the order (R₂NCHCl)⁺Cl⁻ > (R₂N)CHRh^{III} > (R₂N)CR'^{III}Rh^{III} > R₂NCH(:O). This is consistent with a bonding scheme for carbene complexes which, in valence-bond terms, requires a higher significance to structures (IXa) and (IXb), rather than (IXc).⁸ In the carbonyl-containing



complexes (I) and (III), strong absorptions above 2000 cm⁻¹ indicate the presence of Rh^{III} species. For the series of complexes (Ia–d), on the basis of $\nu(CO)$ and $\nu(Rh-Cl)$, we tentatively assign the configuration (X).



In the i.r. spectra of (II) and (IV), in the region 400–250 cm⁻¹, bands due to $\nu(Rh-Cl)$ were identified by comparison with the iodo-analogue of (IVa) (*vide supra*). The configurations of (II) and (IV) are thought to be equivalent by comparison of their i.r. spectra. [Definitive evidence from n.m.r. data is lacking owing to the greater insolubility of (II) over (IV).] There should be three peaks due to $\nu(Rh-Cl)$ in the proposed configuration of (II) and (IV) and only two are observed. This may be due to the high *trans*-influence of the secondary carbene ligand (see below) causing the value of $\nu(Rh-Cl)$ *trans* to -CHNR₂ to fall below 250 cm⁻¹, which is the instrumental limit. Comparison with the i.r. spectra of (IV) and [RhCl₃(PET₃)₂L] is instructive: $\nu(Rh-Cl)$ *trans* to CO and PET₃ has been reported¹⁵ as 270 and 264 cm⁻¹,¹⁶ respectively. From X-ray data (see below) it is clear that the secondary carbene has a greater *trans*-influence in Rh^{III} than either CO or PET₃, and therefore $\nu(Rh-Cl)$ *trans* to -CHNR₂ in (IV) is likely to be below 264 cm⁻¹.

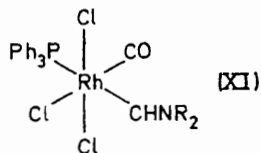
For (III), the assignment of $\nu(Rh-Cl)$ was achieved by comparison with the iodo-analogue of (IIIa). The configuration of (III) cannot be assigned definitively because n.m.r. data are not available because of insolubility, but by comparison with earlier work on Rh^{III} a tentative suggestion is made. The position and intensity of $\nu(Rh-Cl)$ in complex (III) is similar in *cis*-

¹⁴ R. C. Neuman, jun., and L. B. Young, *J. Phys. Chem.*, **1965**, **69**, 1777; also M. F. Robin, F. A. Bovey, and H. Basch in 'The Chemistry of Amides,' Interscience, New York, 1970, p. 19.

¹⁵ M. A. Bennett, R. J. H. Clark, and D. L. Milner, *Inorg. Chem.*, **1967**, **6**, 1647.

¹⁶ P. R. Brookes and B. L. Shaw, *J. Chem. Soc. (A)*, **1967**, 1079.

$[\text{RhCl}_3(\text{PhMe}_2\text{P})_2\text{C}(\text{Ph})\text{N}(\text{Me})\text{C}(\text{Ph})\text{NMe}]^1$ and the configuration of (III) may therefore be based on the meridional configuration of Cl ligands. The constant value of $\nu(\text{CO})$ in the series $[\text{RhCl}_3(\text{PPh}_3)(\text{CO})\text{C}(\text{Ph})\text{NHR}]$ ($\text{R} = \text{Me, Et, or Pr}^i$)⁵ and similar values in (III) as well as in *mer*- $[\text{RhCl}_3(\text{PPh}_3)_2\text{CO}]$ ¹⁷ support the proposal shown in (XI).



In the i.r. spectrum of (Ia) (Nujol) there is a weak band at 3050 cm^{-1} which we suggest is due to $\nu(\text{C}_{\text{carb}}\text{-H})$. The deuteriated analogue $[\text{RhCl}_3\text{CO}(\text{CO})\text{CDNMe}_2]_2$ was prepared and showed a weak but sharp band at 2216 cm^{-1} which is assigned to $\nu(\text{C}_{\text{carb}}\text{-D})$ [$\nu(\text{CH})/\nu(\text{CD}) = 1.376$]. In the i.r. spectrum of (IVa) in hexachlorobutadiene a weak sharp band at 3045 cm^{-1} is present which we suggest is due to $\nu(\text{C}_{\text{carb}}\text{-H})$. The spectrum of $[\text{RhCl}_3(\text{PET}_3)_2\text{CDNMe}_2]$ does not contain this peak, but has a weak one at 2209 cm^{-1} assignable to $\nu(\text{C}_{\text{carb}}\text{-D})$ [$\nu(\text{CH})/\nu(\text{CD}) = 1.378$]. By comparison, the value of $\nu(\text{C-H})$ for dimethylformamide has been reported as 2928 cm^{-1} ,^{18a} and $\nu(\text{C-D})$ for ^2H dimethylformamide as 2170 cm^{-1} ,^{18b} [$\nu(\text{CH})/\nu(\text{CD}) = 1.349$].

CRYSTAL AND MOLECULAR STRUCTURE OF
 $[\text{RhCl}_3(\text{PET}_3)_2\text{CHNMe}_2]$ (IVa)

Crystal Data.— $\text{C}_{15}\text{H}_{37}\text{Cl}_3\text{NP}_2\text{Rh}$, $M = 502.68$, $a = 11.84(1)$, $b = 12.26(1)$, $c = 15.72(2)\text{ \AA}$, $U = 2281.9\text{ \AA}^3$, $D_m = 1.46$, $Z = 4$, $D_c = 1.463\text{ g cm}^{-3}$, $F(000) = 1040$. Space group $P2_12_12_1$ (D_2^7 , No. 19) from systematic absences: $h00$ for h odd, $0k0$ for k odd, and $00l$ for l odd. Lattice parameters were derived from precession photographs taken with $\text{Mo-K}\alpha$ radiation (silicon crystal monochromator), $\lambda = 0.71069\text{ \AA}$, $\mu(\text{Mo-K}\alpha) = 12.13\text{ cm}^{-1}$.

Crystals were yellow parallelepipeds, the data crystal being $0.031 \times 0.028 \times 0.016\text{ cm}$. Integrated intensities were measured on a PAILRED diffractometer by use of $\text{Mo-K}\alpha$ radiation and a silicon crystal monochromator. The crystal was oriented so that its c axis coincided with the instrument ω axis. The layers $hk0$ —21 were surveyed by the stationary-counter-moving-crystal method. Intensities of reflection with $2\theta \leq 60^\circ$ were measured, the ω scan-range through the reflections varying from 2.0° on the zero layer to 3.6° on layer 21, at a scan velocity of 1° min^{-1} . Stationary-background counts were measured at the extremities of each scan for 40 s.

Reflections whose independent background intensities differed by more than 3σ were discarded, as were those

¹⁷ B. F. G. Johnson, J. Lewis, and P. W. Robinson, *J. Chem. Soc. (A)*, 1970, 1100.

¹⁸ (a) G. Kaufmann and M. J. F. Leroy, *Bull. Soc. chim. France*, 1967, 402; (b) O. N. Efimov and V. B. Panov, *Izvest. Akad. Nauk S.S.S.R., Ser. khim.*, 1970, 491.

¹⁹ J. M. Stewart, F. A. Kundell, and J. C. Baldwin, 'X-Ray '67' System of programs, 1970 version, University of Maryland Technical Report 67 58, 1967, adapted for Atlas Computer Laboratory, Chilton.

which had $I/\sigma(I) < 2.0$. Those with $I/\sigma(I) > 3.0$ were classed as observed (2112 independent reflections in all), whereas those with $2.0 < I/\sigma(I) < 3.0$ were classed as less than minimum observed intensity (394 in all). The intensities were corrected for Lorentz-polarisation effects but not for absorption.

Structure Analysis.—The co-ordinates of the rhodium atom were initially obtained from a three-dimensional Patterson synthesis and subsequent electron-density distribution yielded positions for all non-hydrogen atoms. The structure was refined by use of the least-squares programme CRYLSQ¹⁹ in the full-matrix mode, minimising the function $\sum w(|F_o| - |F_c|)^2$, where $w = 1/\sigma^2(F)$. Atomic scattering factors were taken from ref. 20, except those for hydrogen.²¹ The effects of anomalous dispersion from the rhodium, chlorine, and phosphorus atoms were included in the calculations by using values of Δ_f' and Δ_f'' (for $\text{Mo-K}\alpha$ radiation) taken from ref. 22.

Refinement of positional and isotropic thermal parameters of all non-hydrogen atoms gave R 0.076. Allowance was then made for the anisotropic thermal vibration of the rhodium, chlorine, and phosphorus atoms which decreased

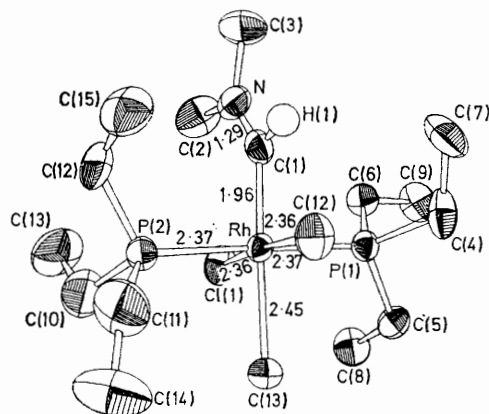


FIGURE 2 Diagram of the molecule showing the numbering system used, and anisotropic thermal motion (ellipsoids are scaled to enclose 50% probability)

R to 0.057. Positions of the hydrogen atoms attached to the six methylene carbon atoms were then calculated and assigned isotropic thermal parameters of B 5.0. There was no reduction in R on subsequent refinements when the hydrogen atoms were not allowed to vary. The highest peak in the resulting difference synthesis (0.6 e) corresponded to the hydrogen attached to the carbene carbon. Subsequent least-squares refinements, including this hydrogen and those previously calculated as fixed-atom contributors with B 5.0, reduced the statistical residual, R' [$= (\sum w\Delta^2 / \sum wF_o^2)^{1/2}$], from 0.065 to 0.064. The hydrogen atoms attached to the methyl carbons were not very well resolved in the difference synthesis and were not included in the calculations. All non-hydrogen atoms were then allowed to refine with anisotropic temperature factors when R converged at 0.052.

As $P2_12_12_1$ is a non-centrosymmetric space group, Friedel's law should break down when anomalous scatterers

²⁰ D. T. Cromer and J. T. Waber, *Acta Cryst.*, 1965, **18**, 104.

²¹ R. F. Stewart, E. R. Davidson, and W. T. Simpson, *J. Chem. Phys.*, 1965, **42**, 3175.

²² D. T. Cromer, *Acta Cryst.*, 1965, **18**, 17.

are present. To see if the two configurations could be distinguished, the alternative to the one used up until this point (obtained by changing the signs of all x co-ordinates

TABLE 4

(a) Final fractional co-ordinates ($\times 10^4$), with standard deviations in parentheses

	x	y	z
Rh	7363(1)	1149(1)	1696(1)
Cl(1)	6156(3)	2198(2)	829(2)
Cl(2)	8449(3)	111(2)	2664(2)
Cl(3)	6239(3)	1795(2)	2900(2)
P(1)	6101(2)	-321(2)	1469(2)
P(2)	8580(2)	2652(2)	1946(2)
N	8611(8)	716(8)	26(6)
C(1)	8362(10)	558(8)	814(6)
C(2)	8091(12)	1505(13)	-545(8)
C(3)	9530(14)	78(13)	-399(9)
C(4)	6597(10)	-1666(9)	1791(8)
C(5)	4739(9)	-231(10)	2026(8)
C(6)	5672(10)	-521(9)	344(7)
C(7)	7531(12)	-2174(9)	1273(10)
C(8)	3949(9)	701(10)	1713(10)
C(9)	4824(10)	-1411(10)	192(8)
C(10)	7962(11)	3975(12)	1711(11)
C(11)	9078(15)	2825(13)	3017(8)
C(12)	9869(11)	2675(12)	1344(10)
C(13)	8032(16)	4383(15)	863(11)
C(14)	8446(16)	3347(16)	3664(10)
C(15)	10 733(10)	1743(12)	1556(10)
H(1) *	8924	-139	1042
H(4a)	6884	-1620	2447
H(4b)	5887	-2218	1809
H(5a)	4304	-984	1960
H(5b)	4894	-113	2688
H(6a)	5353	251	113
H(6b)	6429	-668	-22
H(10a)	7092	3953	1908
H(10b)	8362	4566	2121
H(11a)	9298	2002	3261
H(11b)	9913	3216	2983
H(12a)	9654	2613	693
H(12b)	10 257	3440	1446

* Hydrogen atom parameters were not refined.

(b) Anisotropic thermal parameters ($\text{\AA}^2 \times 10^3$) in the form: $\exp [-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{12}hka^*b^* + 2U_{13}hla^*c^* + 2U_{23}kfb^*c^*)]$

	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Rh	31(1)	30(1)	35(1)	1(1)	2(1)	6(1)
Cl(1)	52(2)	51(2)	71(2)	4(2)	-11(2)	22(2)
Cl(2)	58(2)	47(2)	50(2)	4(1)	-12(1)	14(1)
Cl(3)	61(2)	47(2)	62(2)	-6(2)	23(2)	-11(1)
P(1)	34(2)	34(1)	46(1)	-3(1)	-1(1)	2(1)
P(2)	39(2)	34(1)	48(1)	-3(1)	2(1)	-1(1)
N	58(6)	62(6)	46(4)	-24(5)	13(5)	-17(5)
C(1)	56(7)	32(6)	45(5)	-8(5)	0(5)	-7(5)
C(2)	85(10)	104(12)	49(6)	5(9)	-2(6)	26(7)
C(3)	115(13)	84(11)	76(8)	7(10)	48(9)	-24(8)
C(4)	54(7)	40(6)	93(9)	-8(6)	-24(8)	26(7)
C(5)	38(6)	54(7)	74(7)	-9(6)	17(5)	-2(6)
C(6)	56(7)	52(7)	48(5)	0(6)	-3(6)	-1(5)
C(7)	69(9)	44(6)	122(11)	20(8)	-5(9)	-15(7)
C(8)	37(6)	64(8)	108(9)	11(6)	2(8)	4(8)
C(9)	66(8)	67(9)	69(7)	-18(7)	-28(7)	-19(6)
C(10)	75(9)	76(9)	106(10)	-5(8)	3(9)	5(10)
C(11)	125(13)	108(13)	60(7)	-32(12)	-21(9)	-23(8)
C(12)	65(9)	80(10)	108(11)	-44(8)	22(8)	-22(8)
C(13)	129(15)	105(12)	81(10)	0(12)	25(10)	38(9)
C(14)	124(15)	149(17)	77(10)	38(14)	-5(10)	-41(11)
C(15)	41(7)	85(10)	103(11)	8(7)	-1(8)	10(9)

and associated thermal parameters) was refined. The result was to lower R to 0.050 and R' to 0.056 for observed reflections. According to Hamilton's test²³ this drop is significant to a level < 0.005 , and this is the configuration referred to in the Tables. Bond-length and -angle differences

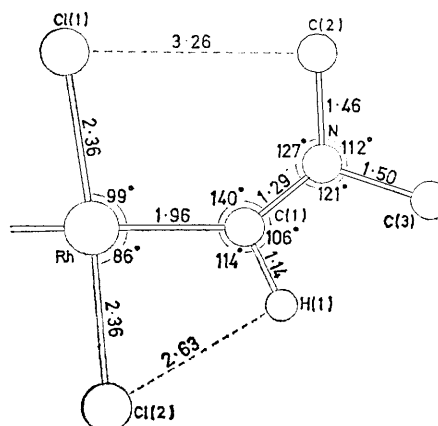


FIGURE 3 View looking down the P(2)-Rh-P(1) bonds, showing the geometry around the carbene ligand

TABLE 5

Bond lengths, angles, and intermolecular contacts, with standard deviations in parentheses

(a) Bond Lengths (Å)

Rh-Cl(1)	2.357(4)	N-C(1)	1.289(14)
Rh-Cl(2)	2.364(3)	N-C(2)	1.455(17)
Rh-Cl(3)	2.445(4)	N-C(3)	1.497(19)
Rh-P(1)	2.368(3)	C(1)-H(1)	1.14
Rh-P(2)	2.372(3)	C(4)-C(7)	1.508(19)
Rh-C(1)	1.961(11)	C(5)-C(8)	1.556(18)
P(1)-C(4)	1.822(12)	C(6)-C(9)	1.503(18)
P(1)-C(5)	1.838(12)	C(10)-C(13)	1.425(24)
P(1)-C(6)	1.856(11)	C(11)-C(14)	1.416(24)
P(2)-C(10)	1.817(15)	C(12)-C(15)	1.569(21)
P(2)-C(11)	1.796(14)		
P(2)-C(12)	1.796(15)		

(b) Bond angles ($^\circ$)

Cl(1)-Rh-Cl(2)	174.8(1)	Rh-P(2)-C(10)	114.5(5)
Cl(1)-Rh-C(3)	86.6(1)	Rh-P(2)-C(11)	116.5(6)
Cl(1)-Rh-P(1)	86.9(1)	Rh-P(2)-C(12)	116.2(5)
Cl(1)-Rh-P(2)	92.3(1)	C(10)-P(2)-C(11)	102.6(8)
Cl(1)-Rh-C(1)	99.1(3)	C(10)-P(2)-C(12)	102.8(7)
Cl(2)-Rh-Cl(3)	88.4(1)	C(11)-P(2)-C(12)	102.3(8)
Cl(2)-Rh-P(1)	91.7(1)	C(1)-N-C(2)	126.6(10)
Cl(2)-Rh-P(2)	88.9(1)	C(1)-N-C(3)	121.1(11)
Cl(2)-Rh-C(1)	85.9(3)	N-C(2)-C(3)	112.3(10)
Cl(3)-Rh-P(1)	91.1(1)	Rh-C(1)-N	139.6(9)
Cl(3)-Rh-P(2)	87.2(1)	Rh-C(1)-H(1)	114
Cl(3)-Rh-C(1)	174.2(3)	N-C(1)-H(1)	106
P(1)-Rh-P(2)	178.2(1)	P(1)-C(4)-C(7)	117.4(10)
P(1)-Rh-C(1)	89.6(3)	P(1)-C(5)-C(8)	114.9(9)
P(2)-Rh-C(1)	92.2(3)	P(1)-C(6)-C(9)	115.5(8)
Rh-P(1)-C(4)	116.3(4)	P(2)-C(10)-C(13)	118.7(12)
Rh-P(1)-C(5)	115.9(4)	P(2)-C(11)-C(14)	123.6(14)
Rh-P(1)-C(6)	114.6(4)	P(2)-C(12)-C(15)	115.5(11)
C(4)-P(1)-C(5)	101.8(6)		
C(4)-P(1)-C(6)	103.5(6)		
C(5)-P(1)-C(6)	102.8(6)		

(c) Intermolecular contacts (Å) < 3.9 Å

Cl(2) ... C(2 ^I)	3.896(13)	C(15) ... C(2 ^{III})	3.866(20)
Cl(3) ... C(3 ^I)	3.640(13)	Cl(3) ... C(4 ^{III})	3.833(12)
C(13) ... C(9 ^{III})	3.665(22)	Cl(3) ... C(5 ^{III})	3.828(13)
C(12) ... Cl(1 ^{III})	3.743(14)	C(5) ... C(10 ^{III})	3.889(23)

Roman numeral superscripts refer to the following coordinate transformations:

$$\text{I } \frac{1}{2} - x + 1, -y, \frac{1}{2} + z \quad \text{II } \frac{1}{2} + x, \frac{1}{2} - y, -z$$

$$\text{III } \bar{1} - x, \frac{1}{2} + y, \frac{1}{2} - z$$

between the final parameters from the two refinements differed by $< 0.5\sigma$, though, as expected, some thermal parameters varied to a slightly greater extent.

²³ W. C. Hamilton, *Acta Cryst.*, 1965, **18**, 502.

During the final cycle of refinement there were no parameter shifts $>0.1\sigma$. The adequacy of the weighting scheme was confirmed by an analysis of the mean $w\Delta^2$ with F_o and $\sin \theta/\lambda$. The function values in the final difference synthesis were in the range ± 0.3 e. Observed and calculated structure factors are listed in Supplementary Publication No. SUP 20955 (4 pp., 1 microfiche).^{*} Results are shown in Tables 4–6 and Figures 2 and 3.

TABLE 6

Least-squares planes expressed in the form: $Px + Qy + Rz = S$, with displacements (Å) of atoms from these planes

(a) Displacements

Plane (a): Rh, C(1), N, H(1)

Rh 0.001, C(1) -0.005, N 0.002, H(1) 0.001, Cl(3) 0.081,
C(2) -0.037, C(3) 0.082

Plane (b): N, C(1)–(3)

N -0.006, C(1) 0.002, C(2) 0.002, C(3) 0.002, Rh 0.088, H(1)
0.042

Plane (c): N, C(1)–(3), H(1)

N -0.001, C(1) 0.019, C(2) -0.008, C(3) 0.007, H(1) -0.016,
Rh 0.111

Plane (d): Rh, Cl(1), Cl(2), Cl(3)

Rh 0.020, Cl(1) -0.011, Cl(2) -0.011, Cl(3) 0.001, C(1) 0.053

(b) Equations

	<i>P</i>	<i>Q</i>	<i>R</i>	<i>S</i>	σ^*
(a)	8.375	8.032	4.171	7.796	0.003
(b)	7.945	8.446	4.307	7.463	0.004
(c)	7.966	8.380	4.449	7.472	0.013
(d)	7.369	9.513	1.610	6.771	0.015

* σ is the root-mean-square deviation of the atoms (those defining the plane) from the plane.

DISCUSSION OF STRUCTURE

Previous crystallographic studies on carbene complexes have been confined to tertiary-carbene complexes,³ though there has recently been a report of the structural details of a chelating bis-secondary-carbene complex of Fe^{II}.⁷ The compound has two significantly different C_{carb} bond lengths but this appears to be due to the relative positions of each C_{carb} -N grouping with the other ligands on the Fe atom. As may have been expected, the bonding environment of the secondary over the tertiary carbene³ is greatly modified. The atoms Rh, C(1), N, and H(1) are planar to within 0.005 Å [Table 6 plane (a)] and this plane is twisted by 12.6° from the RhCl_3 plane [plane (d)].

The Rh-C(1)-N(1) bond angle [139.6(9)°] is much larger than the idealised value of 120° for trigonal carbon. This is much larger than bond angles in other carbene complexes though a value as high as 134 (2)° has been reported for the Cr-C_{carb}-O angle in $\text{Cr}(\text{CO})_5\text{C}(\text{OMe})\text{Ph}$.²⁴ As can be seen from Figure 3, the Cl(1)-Rh-C(1) and C(1)-N-C(2) angles are both larger than expected and it would seem that the geometry of the carbene

ligand is modified by steric interaction between Cl(1) and the C(2) methyl group [Cl(1) ··· C(2) 3.26 Å].

A second possibility for the large changes in the carbene bond angles could be the intramolecular interaction Cl(2) ··· H(1) 2.63 Å, which would decrease the Cl(2)-Rh-C(1) angle (Figure 3). This interaction would also have the effect observed in the n.m.r. spectrum of deshielding the $C_{\text{carb}}\text{-H}$ more than may have been expected when not considering such interaction. However, similar compounds which do not contain *cis*-carbene-chlorine moieties have not been extensively studied. The only examples here are $[\text{RhI}_3(\text{PEt}_3)_2\text{CHNMe}_2]$ and $[\text{RhBr}_3(\text{PMe}_2\text{Ph})_2\text{CHNMe}_2]$, both of which have $C_{\text{carb}}\text{-H}$ chemical shifts not too unexpectedly different from those of their trichloro-analogues which may tend to suggest their interaction is not too significant. The Rh-C(1) distance [1.961(11) Å] compares favourably with the $\text{Rh}^{\text{III}}\text{-C}_{\text{carb}}$ bond length [1.968(13) Å] in the only other Rh^{III} carbene complex studied

$[\text{RhI}_3(\text{CO})\text{CPhNMeCPhNMe}]$,¹ but is significantly longer than the Rh-C(0) distance [1.892(14) Å] in the same compound. This is attributed to a decrease in the π -acceptor character of the carbene ligands as compared with carbonyl ligands, because of competition from $p_{\pi}\text{-}p_{\pi}$ bonding between C_{carb} and N. This large $p_{\pi}\text{-}p_{\pi}$ contribution to the stability of the carbene is borne out by the extremely short C(1)-N distance of 1.289(14) Å which is shorter than the lengths of 1.31–1.38 Å of similar bonds in other monocarbene complexes³ but compares well with the shortest $C_{\text{carb}}\text{-N}$ bond [1.293(17) Å] in the only other secondary-carbene complex studied crystallographically,⁷ and is shorter than C-N bond lengths in typical organic amides, *e.g.*, 1.317 and 1.351(18) Å in two independent molecules of acetamide.²⁵ It is, in fact, similar in value to the formal C-N double bond in glyoxime, 1.284(5) Å.²⁶ The large spread of C-C bond lengths of the ethyl groups (1.416–1.569 Å) indicates the possibility of slight disorder.

The $C_{\text{carb}}\text{-H}$ distance (1.14 Å) is tentative, as H(1) was not refined. The N-Me bond lengths of 1.455(17) and 1.497(19) Å are not significantly different from typical N-C single bonds in, *e.g.*, diethylamine 1.47(2) Å.²⁷

The mutually *trans*-Rh^{III}-P distances [2.368(3) and 2.372(3) Å] are significantly shorter than the sum of the covalent radii (2.44 Å), though there are only limited data for Rh^{III}-P bond lengths,²⁸ and compare well with other determinations of mutually *trans*-Rh^{III}-P bond lengths: 2.379(5) and 2.400(5) for Bu_3P in $[\text{RhCl}_3(\text{PBu}_3)_2\text{P}(\text{OMe})_3]$,^{29a} and 2.382(4) and 2.415(4) Å for Et_2PhP in $[\text{RhCl}_3(\text{PEt}_2\text{Ph})_3]$.^{29b}

The Rh^{III}-Cl mutually *trans*-bond lengths [2.357(4)

²⁷ V. Schomaker, quoted in P. Allen and L. E. Sutton, *Acta Cryst.*, 1950, **3**, 46.

²⁸ Cf. M. J. Doyle, M. F. Lappert, G. M. McLaughlin, and J. McMeeking, *J.C.S. Dalton*, 1974, 1494.

²⁹ (a) F. H. Allen, G. Chang, K. K. Cheung, T. F. Lai, L. M. Lee, and A. Pidcock, *Chem. Comm.*, 1970, 1297; (b) A. C. Skapski and F. A. Stephens, *J.C.S. Dalton*, 1973, 1789; (c) J. A. Evans, D. R. Russel, A. Bright, and B. L. Shaw, *Chem. Comm.*, 1971, 841.

* See Notice to Authors No. 7 in *J.C.S. Dalton*, 1973, Index issue (items less than 10 pp. are sent as full-size copies).

²⁴ O. S. Mills and A. D. Redhouse, *J. Chem. Soc. (A)*, 1968, 642.

²⁵ W. C. Hamilton, *Acta Cryst.*, 1965, **18**, 866.

²⁶ M. Calleri, G. Ferraris, and D. Viterbo, *Acta Cryst.*, 1966, **20**, 73.

and 2.364(3) Å] are in good agreement with other similar determinations: 2.339(5) and 2.349(5) in $[\text{RhCl}_3(\text{PBU}_3)_2\text{P}(\text{OMe})_3]$,^{29a} 2.362(3) and 2.362(3) in $[\text{RhCl}_3(\text{PEt}_2\text{Ph})_3]$,^{29b} and 2.347(6) and 2.365(6) Å in $[\text{RhCl}_3(\text{C}_8\text{H}_{15}\text{O})(4\text{-Mepy})_2]$.^{29c}

The Rh^{III}-Cl(3) distance [2.445(3) Å] is much longer than the Rh-Cl(1) and Rh-Cl(2) distances and this is due to the *trans*-influence of the secondary-carbene ligand. From data on Rh^{III}-Cl bond lengths^{29,30,31} it is possible to compare the *trans*-influence of the secondary carbene with other ligands as: σ -alkyl > σ -phenyl > s-carbene > tertiary phosphine > tertiary phosphite > tertiary arsine \sim π -olefin > chlorine \sim amine \sim pyridine > ROH. It can be seen that the secondary carbene ligand occupies the highest position in the series [for Rh^{III}] of neutral ligands, although similar data on Rh^{III} tertiary carbene complexes are not available. However, for the latter and Pt^{II}, crystallographic studies relating to *trans*-Pt-Cl lengths give the order: σ -C > tertiary carbene \sim tertiary phosphine > CO \sim isonitrile \sim chlorine.

Although tertiary-carbene complexes have an extensive and varied chemistry³ the secondary-carbene complexes described here as yet show no sign of reactivity at the carbene ligand. The following reactions were attempted and all proved unsuccessful (see Experimental section for details): (1) exchange of C_{carb}-D for C_{carb}-H with D₂O or DCl, (2) reaction with C₂H₄, and (3) reaction with CO. The unreactivity of the secondary-carbene ligand is in keeping with the inertness of -CH of the dialkylformamides.

EXPERIMENTAL

General procedures.—All reactions were carried out under an atmosphere of dry nitrogen. Hydrocarbon and ether solvents were dried over sodium wire and distilled before use and chlorinated solvents were distilled from phosphorus pentoxide. Molecular weights were determined in chloroform using a Mechrolab 301A vapour-pressure osmometer and analyses were carried out in our Microanalytical Laboratory by Mr. and Mrs. A. G. Olney. I.r. spectra (4000–250 cm⁻¹) were examined as Nujol or hexachlorobutadiene mulls using a Perkin-Elmer 457 grating spectrophotometer, and ¹H n.m.r. spectra were recorded on Varian Associates HA 100, A 60, or T 60 spectrometers. Melting points were determined in an evacuated sealed tube and are uncorrected.

Chloromethyleneammonium chlorides were prepared by the method of Ulrich³² from redistilled, commercially available, dialkylformamides.

Other starting materials were prepared by standard literature procedures: $[\text{RhCl}(\text{CO})_2]_2$,³³ $[\text{RhCl}(\text{PPh}_3)(\text{CO})]_2$,¹² and $[\text{RhCl}(\text{PPh}_3)_3]$.³⁴

Synthesis of [²H]Dimethylformamide.—A mixture of sodium cyanide (3.75 g) and deuterium oxide (10 ml) was heated in a sealed tube for 20 h at 160°. The tube was cooled to -196° and opened and the ND₃ and excess of D₂O removed *in vacuo* to leave DCO₂Na; this was dis-

solved in distilled water and passed through a Dowex 50W-X8 cation (H) exchange column in distilled water. To the aqueous solution of [²H]formic acid was added an aqueous solution of dimethylamine (30 ml containing ca. 25% Me₂NH); the solution was gently heated under reflux overnight.

The excess of water was then carefully distilled through a 75-cm helical packed column and the crude [²H]dimethylformamide was finally distilled under reduced pressure (b.p. 82° at 79 mmHg). An n.m.r. spectrum of the sample showed an approximate ratio of Me₂NCHO : Me₂NCDO of 1 : 3. This was used to prepare the (Me₂NCDO)⁺Cl⁻ in exactly the same way as for (Me₂NCHCl)⁺Cl⁻.³²

Reactions of [RhCl(CO)₂]₂.—(a) *With chloromethylenedimethylammonium chloride.* To a solution containing the ammonium chloride (0.351 g, 2.752 mmol) in chloroform (15 ml) was added the solid rhodium complex (0.535 g, 1.376 mmol). An immediate evolution of gas occurred to produce a yellow solution from which a fine yellow amorphous precipitate was deposited in ca. 2 min. This was collected, washed in chloroform (5 ml), dried *in vacuo*, and identified as *carbonyl(trichloro)dimethylaminomethylenerrhodium(III)* (100%).

(b) *With chloromethylenediethylammonium chloride.* Similarly the ammonium chloride (0.225 g, 1.444 mmol) and the rhodium complex (0.281 g, 0.722 mmol) afforded a quantitative yield of *carbonyl(trichloro)diethylaminomethylenerrhodium(III)* as a yellow powder.

(c) *With chloromethylenediisopropylammonium chloride.* Similarly, the ammonium chloride (0.355 g, 2.042 mmol) and the rhodium complex (0.397 g, 1.021 mmol) gave *carbonyl(trichloro)diisopropylaminomethylenerrhodium(III)* (95%) as a yellow orange powder, containing 2 mol of chloroform of crystallisation which even after drying *in vacuo* for several hours was not removed.

(d) *With dibutyl(chloromethylene)ammonium chloride.* The ammonium chloride (0.196 g, 0.926 mmol) and the rhodium complex (0.180 g, 0.463 mmol) in chloroform afforded a gas but no solid. Addition of diethyl ether and cooling to -30° afforded yellow needles of *carbonyl(trichloro)di-n-butylaminomethylene)rhodium(III)* (95%).

Reactions of [RhCl(PPh₃)(CO)]₂.—(a) *With chloromethylenedimethylammonium chloride.* To a solution of the ammonium chloride (0.209 g, 1.633 mmol) in chloroform (15 ml) was added the solid rhodium complex (0.700 g, 0.816 mmol). From the yellow solution, yellow *carbonyl(trichloro)dimethylaminomethylene(triphenylphosphine)rhodium(III)* (95%) was precipitated, collected by filtration, washed in cold chloroform, and dried.

(b) *With chloromethylenediethylammonium chloride.* Similarly, the ammonium chloride (0.268 g, 1.719 mmol) and the rhodium complex (0.737 g, 0.859 mmol) gave a pale yellow precipitate, which on washing with chloroform gave *carbonyl(trichloro)diethylaminomethylene(triphenylphosphine)rhodium(III)* (100%) containing 1 mol of chloroform of crystallisation.

(c) *With chloromethylenediisopropylammonium chloride.* Similarly, the ammonium chloride (0.131 g, 0.752 mmol) and the rhodium complex (0.322 g, 0.376 mmol) gave *carbonyl(trichloro)diisopropylaminomethylene(triphenylphosphine)rhodium(III)* (92%) as a pale yellow precipitate which was washed in chloroform and dried.

³⁰ R. Mason and A. D. C. Towl, *J. Chem. Soc. (A)*, 1970, 1601.

³¹ R. J. Hoare and O. S. Mills, *J.C.S. Dalton*, 1972, 2141.

³² H. Ulrich, 'The Chemistry of Imidoyl Halides,' Plenum, New York, 1968.

³³ J. A. McCleverty and G. Wilkinson, *Inorg. Synth.*, 1966, **8**, 211.

³⁴ J. A. Osborne and G. Wilkinson, *Inorg. Synth.*, 1967, **10**, 67.

Reactions of [RhCl(PPh₃)₃].—(a) *With chloromethylenedimethylammonium chloride.* To a solution of the ammonium chloride (0.309 g, 2.414 mmol) in chloroform (20 ml) the rhodium complex (2.232 g, 2.414 mmol) was slowly added. The yellow solution turned orange-red and after being stirred for 12 h a yellow solid had precipitated. Diethyl ether was added to complete the precipitation and the solid was collected, washed in ice-cold chloroform, then diethyl ether, and finally dried *in vacuo* to give *trichloro(dimethylaminomethylene)bis(triphenylphosphine)rhodium(III)* (81%).

(b) *With chloromethylenediethylammonium chloride.* The ammonium chloride (0.107 g, 0.683 mmol) and the rhodium complex (0.496 g, 0.536 mmol) gave a golden orange solution but no solid. The chloroform was removed *in vacuo*, the orange residue washed in diethyl ether and crystallisation (CHCl₃-n-C₆H₁₄) gave *trichloro(diethylaminomethylene)bis(triphenylphosphine)rhodium(III)* (95%).

(c) *With chloromethylenediisopropylammonium chloride.* Similarly the ammonium chloride (0.095 g, 0.543 mmol) and the rhodium complex (0.453 g, 0.490 mmol) gave *trichloro(diisopropylaminomethylene)bis(triphenylphosphine)rhodium(III)* (from CHCl₃-n-C₆H₁₄) in 90% yield.

It was found that using the above rhodium complex an excess of the ammonium chloride was required for completion of the reaction and maximum product yields.

Reactions of [RhCl₃(PPh₃)₂CHNMe₂].—(a) *With triethylphosphine.* To a suspension of the rhodium complex (0.975 g, 1.217 mmol) in benzene (20 ml) was added triethylphosphine (0.4 g, ca. 3.4 mmol) and the mixture was heated under reflux until a clear yellow solution was obtained. After cooling, the benzene was removed *in vacuo*, the orange residue washed several times (n-C₆H₁₄) and crystallisation (CHCl₃-n-C₆H₁₄) gave *trichloro(dimethylaminomethylene)bis(triethylphosphine)rhodium(III)* (70%).

(b) *With dimethyl(phenyl)phosphine.* Similarly the rhodium complex (0.674 g, 0.852 mmol) and dimethylphenylphosphine (0.4 ml) gave *trichloro(dimethylphenylphosphine)rhodium(III)* (from CHCl₃-n-C₆H₁₄) in 64% yield.

Reaction of [RhCl₃(PMe₂Ph)₂CHNMe₂] with Lithium Bromide.—The rhodium complex (0.070 g, 0.13 mmol) and lithium bromide (0.24 g, 0.2 mmol) were shaken in acetone (10 ml) for 20 h. The solvent was then removed *in vacuo* and the residue washed with water (10 ml) and diethyl ether (10 ml). Recrystallisation (from CHCl₃-n-C₆H₁₄) gave *tribromo(dimethylaminomethylene)bis(dimethylphenylphosphine)rhodium(III)* as orange crystals in 68% yield.

Reaction of [RhCl₃(CO)CHNR₂]₂ with Triphenylphosphine.—(a) R = Me. To a suspension of the dimer (0.496 g, 0.843 mmol) in chloroform (10 ml) a solution of triphenylphosphine (0.442 g, 1.686 mmol) in chloroform (5 ml) was added dropwise. After stirring for 16 h at room temperature, the solvent was removed *in vacuo* and the residue was washed in benzene (× 2). Recrystallisation (CHCl₃-n-C₆H₁₄) gave [RhCl₃(PPh₃)(CO)CHNMe₂] (90%).

(b) R = Et or Prⁱ. Similarly, the ethyl dimer (0.443 g, 0.688 mmol) and triphenylphosphine (0.361 g, 1.376 mmol) gave [RhCl₃(PPh₃)(CO)CHNEt₂].CHCl₃ (from CHCl₃-Et₂O) (89%), and the isopropyl dimer (0.266 g, 0.379 mmol) and triphenylphosphine (0.199 g, 0.758 mmol) gave [RhCl₃(PPh₃)(CO)CHNPrⁱ]₂ (93%).

Reaction of [RhCl₃(CO)CHNR₂]₂ with Triethylphosphine.—(a) R = Me. To a suspension of the dimer (0.487 g, 0.829 mmol) in benzene (15 ml) was added an excess of triethylphosphine (ca. 0.4 g, 3.4 mmol) and the mixture was heated under reflux for 30 min, whereafter the solid had dissolved. The solution was cooled and benzene removed *in vacuo*. The orange residue was washed several times (n-C₆H₁₄); recrystallisation (CHCl₃-n-C₆H₁₄) afforded *trichloro(dimethylaminomethylene)bis(triethylphosphine)rhodium(III)* (85%).

(b) R = Et or Prⁱ. Similarly, the ethyl (0.229 g, 0.356 mmol) or isopropyl (0.312 g, 0.332 mmol) dimer and triethylphosphine (0.12 ml, 1.4 mmol) gave *trichloro(diethyl- or diisopropyl-aminomethylene)bis(triethylphosphine)rhodium(III)* (from CHCl₃-n-C₆H₁₄) in 84% (Et) or 81% (Prⁱ) yield, respectively.

Synthesis of Some Iodorhodium(III) Carbene Complexes.—(a) [RhI₃(CO)CHNMe₂]₂. A suspension of [RhCl₃(CO)CHNMe₂]₂ (0.413 g, 0.701 mmol) in dichloromethane and finely powdered lithium iodide (0.8 g, ca. 4.5 mmol) was stirred in the dark at room temperature for 3 days. The mixture was filtered and hexane added to the dark red filtrate to give dark-red crystals of *carbonyl(dimethylaminomethylene)tri-iodorhodium(III)* (50%).

(b) [RhI₃(PEt₃)₂CHNMe₂]. Using the procedure of (a), [RhCl₃(PEt₃)₂CHNMe₂] (0.164 g, 0.327 mmol) and lithium iodide (0.752 g, 4.00 mmol) yielded *(dimethylaminomethylene)tri-iodobis(triethylphosphine)rhodium(III)* (68%).

Synthesis of Deuteriated Secondary Carbene complexes.—(a) [RhCl₃(CO)CDNMe₂]₂. Using the method for [RhCl₃(CO)CHNMe₂]₂ above, [RhCl(CO)]₂ (0.104 g, 0.267 mmol) and the deuterioammonium chloride (0.690 g, 0.535 mmol) gave 92% of [RhCl₃(CO)CDNMe₂]₂/[RhCl₃(CO)CHNMe₂]₂.

(b) [RhCl₃(PEt₃)₂CDNMe₂]. Using the same procedure as for (IVa), triethylphosphine (0.14 g, 1.15 mmol) and the deuteriated dimer (0.129 g, 0.230 mmol) gave 80% of [RhCl₃(PEt₃)₂CDNMe₂]/[RhCl₃(PEt₃)₂CHNMe₂].

Reactions of [RhCl₃(PEt₃)₂CHNMe₂].—(a) *With DCl.* A solution of the rhodium complex in deuteriochloroform in an n.m.r. tube was saturated with DCl. No change in the spectrum was observed after 24 h.

(b) *With D₂O.* The n.m.r. spectrum of a solution of the rhodium complex in [2H₆]acetone containing D₂O showed no change after 3 days at 34 °C.

(c) *With ethylene.* Ethylene was bubbled through a solution of the rhodium complex (0.078 g, 0.113 mmol) in chloroform (10 ml) at 20 °C for 3 h. No change in colour was apparent. The solvent was removed *in vacuo* and the i.r. and ¹H n.m.r. spectra of the residue showed it to be unchanged.

(d) *With carbon monoxide.* Carbon monoxide was bubbled through a suspension of the rhodium complex in refluxing ethanol until the solid had dissolved. Removal of solvent and recrystallisation of the residue from CHCl₃-n-C₆H₁₄ afforded unchanged starting compound as shown by i.r. and n.m.r. spectra.

We thank the S.R.C. for the award of a studentship to K. T. and for other support, and Englehard Ltd., for loan of rhodium.

[3/1954 Received, 24th September, 1973]