Three-fragment Oxidative Addition of Chloroform-iminium or -amidinium Chlorides to Rh^I or Pt^{II} Substrates; Complexes of the Secondary Carbene $CHNMe_2$

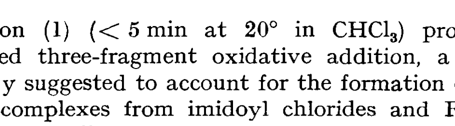
By B. Çetinkaya, M. F. Lappert,* and K. Turner
(School of Molecular Sciences, University of Sussex, Brighton BN1 9QJ)

Summary Chloroform-iminium or -amidinium chlorides oxidatively add to Rh^I or Pt^{II} compounds to give Rh^{III} or Pt^{IV} carbene complexes; of particular interest are the Cr^0, Fe^0, Rh^{III}, Ir^{III}, and Pt^{IV} complexes of the secondary carbene $CHNMe_2$, in which the hydrogen atom attached to C(carbene) is deshielded (τ $-1{\cdot}2$ to $+0{\cdot}9$).

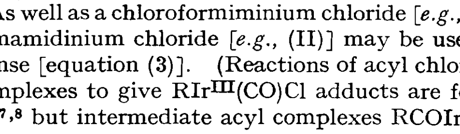
A large number of transition metal carbene complexes has now been described.[1] These derive from nucleophilic carbenes and hitherto have been tertiary derivatives: we suggest that the types having the ligands $-CH_2$ (identified only as transient species),[2] $-CH(X)$, and $-CXY$ be termed primary, secondary, and tertiary carbene complexes, respectively.

We now report the synthesis and characterisation of a number of secondary complexes (see Table). Two methods of synthesis have been employed [equation (1) (for Rh^{III} and Pt^{IV} products) and (2) (for Cr^0 and Fe^0)]. The Pt^{IV} carbene complex is noteworthy (only a few Pt^{IV} compounds were known, from Pt^{II} carbenes and halogens).[3] Chelating ligands incorporating a secondary carbene moiety, such as $\pi\text{-}C_5H_5(OC)\overline{Fe\text{-}CHNMe\text{-}BH_2\text{-}CHNMe}$, have been described for Mo^{II}, Mn^I, and Fe^{II}.[4] In connection with formimidoylruthenium(II) compounds, mention has been made of a Ru^{II} secondary carbene complex.[5]

Reaction (1), using *trans*-$IrCl(N_2)(PPh_3)_2$, afforded a compound, m.p. 285—290°, believed to be the Ir^{III} carbene complex, $IrCl_3(CHNMe_2)(PPh_3)_2$.

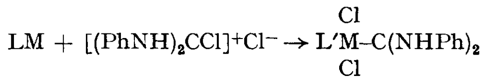


$$LM + \underset{(I)}{[Me_2NCHCl]^+Cl^-} \rightarrow L'\overset{Cl}{\underset{Cl}{M}}\text{-}C{\overset{H}{\underset{NMe_2}{}}} \qquad (1)$$



$$[L''M]^{2-}2Na^+ + (I) \rightarrow L''\,M\text{-}C{\overset{H}{\underset{NMe_2}{}}} + 2NaCl \qquad (2)$$

Reaction (1) (< 5 min at 20° in $CHCl_3$) provides a generalised three-fragment oxidative addition, a process previously suggested to account for the formation of Rh^{III} carbene complexes from imidoyl chlorides and Rh^I precursors.[6] As well as a chloroformiminium chloride [*e.g.*, (I)], a chloroformamidinium chloride [*e.g.*, (II)] may be used in the same sense [equation (3)]. (Reactions of acyl chlorides with Ir^I complexes to give $RIr^{III}(CO)Cl$ adducts are formally similar,[7,8] but intermediate acyl complexes $RCOIr^{III}Cl$ are isolable.[8]) We do not wish to imply that the three fragments are added synchronously.



$$LM + [(PhNH)_2CCl]^+Cl^- \rightarrow L'\overset{Cl}{\underset{Cl}{M}}\text{–}C(NHPh)_2 \qquad (3)$$

(II)

A related reaction to equation (2) has been used for the synthesis of another Cr^0 complex.[9]

Transition metal–carbene complexes are characterised by an electrophilic C(carbene).[1] Consistent with this, we find that for secondary carbene complexes the hydrogen atom attached to C(carbene) is deshielded (τ −1·2 to +0·9, see Table).

Evidence for the formulations shown in the Table rests on (*i*) satisfactory elemental analyses, (*ii*) parent molecular ions in the mass spectra of the Cr^0 and Fe^0 complexes and of $RhCl_3(CHNMe_2)(PEt_3)_2$, (*iii*) the identification of ν(NH), ν(CN), and ν(CO) where appropriate, and (*iv*) consistent ^1H n.m.r. data. The secondary carbene ligand $CHNMe_2$ is characterised at 34 °C by a broad C(carbene)–H signal and a doublet of doublets due to magnetic non-equivalence of the two sets of *N*-methyl protons (high CN bond order), with each set coupled to C(carbene)–H[*J*(H–H) 0·8 Hz] (see ref. 10, for data on tertiary complexes).

TABLE

Compound	M.p. (°C)[b]	ν(CN)[c]	Selected ^1H n.m.r. data[d]
$Cr(CHNMe_2)(CO)_5$[a]	64—66	1545	−0·86 (CH); 6·25 (NMe); 6·43 (NMe)
$Fe(CHNMe_2)(CO)_4$	55—56	1555	−1·10 (CH); 6·35 (NMe); 6·48 (NMe)
$RhCl_3(CHNMe_2)(PEt_3)_2$[e,f]	169—173	1587	−1·13 (CH); 6·06 (NMe); 6·40 (NMe)
$RhCl_3(CO)[C(NHPh)_2](PPh_3)$[g]	139—145	1531	8·75 (NH); 9·14 (NH)
$PtCl_4(CHNMe_2)(PEt_3)$	138—140[h]	1630	Insoluble

[a] Yields range from 50 to 95%. [b] Under nitrogen in a sealed capillary. [c] As Nujol mulls. [d] Expressed in τ value relative to Me_4Si in $CDCl_3$; satisfactory integration. [e] $RhCl_3(CHNMe_2)(PPh_3)_2 + PEt_3$. [f] Phosphines are *trans* to one another. [g] ν(CO) = 2090, 2100 cm^{-1}. [h] Partial melt.

We thank the S.R.C. for their support, B.P. Ltd. for a bursary (to K.T.), and Dr. C. G. Smith and Englehard Ltd., for loan of platinum metals.

(*Received*, 15*th May* 1972; *Com.* 821.)

---

[1] D. J. Cardin, B. Çetinkaya, and M. F. Lappert, *Chem. Rev.*, 1972, **72**, in the press.

[2] P. W. Jolly and R. Pettit, *J. Amer. Chem. Soc.*, 1966, **88**, 5044; M. L. H. Green, M. Ishaq, and R. N. Whiteley, *J. Chem. Soc.* (*A*), 1967, 1508.

[3] A. L. Balch, *J. Organometallic Chem.*, 1972, **37**, C19.

[4] P. M. Treichel, J. P. Stenson, and J. J. Benedict, *Inorg. Chem.*, 1971, **10**, 1183.

[5] D. F. Christian, G. R. Clark, W. R. Roper, J. M. Waters, and K. R. Whittle, *J.C.S. Chem. Comm.*, 1972, 458.

[6] M. F. Lappert and A. J. Oliver, *J.C.S. Chem. Comm.*, 1972, 274.

[7] B. L. Shaw and E. Singleton, *J. Chem. Soc.* (*A*), 1967, 1683 and subsequent papers.

[8] M. Kubota and D. M. Blake, *J. Amer. Chem. Soc.*, 1971, **93**, 1368; ($ArSO_2Cl$) M. Kubota and B. M. Loeffler, *Inorg. Chem.*, 1972, **11**, 469.

[9] K. Öfele, *Angew. Chem. Internat. Edn.*, 1968, **7**, 950.

[10] C. G. Kreiter and E. O. Fischer, 'XXIIIrd International Congress of Pure and Applied Chemistry (Boston)', Butterworths, 1971, vol. 6, p. 151.