A Three-fragment Oxidative Addition Reaction as a Route to Transition Metal Carbene Complexes: Imidoyl Halides and Rhodium(I) Compounds as Precursors for Rhodium(III) Carbenes

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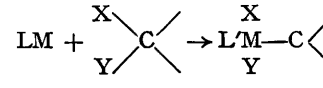
Summary A number of imidoyl chlorides has been found to react with chlororhodium(I) complexes to yield substituted rhodium(III) chlorides having an organic fragment attached to the metal as a carbene moiety.

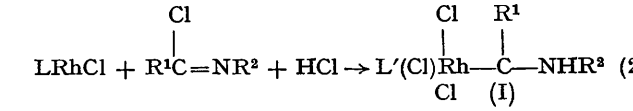
VARIOUS methods are available for the synthesis of transition metal carbene complexes. Most of these are based on reactions of co-ordinated carbonyl or alkyl isocyanide groups; but organic precursors, such as electron-rich olefins, have also recently been used.[1]

We now report a new synthesis, which promises to be of some generality. It may formally be regarded as a three fragment oxidative addition, as illustrated by equation (1), where L and L′ are the remaining ligands, other than X^- and Y^-, attached to the metal M. Oxidative addition reactions, both without and with two-part fragmentation, are well-known.[2]

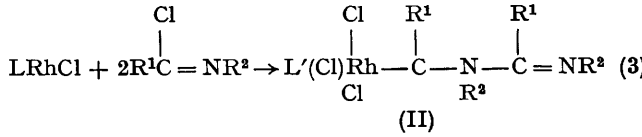
In the present instance, the organic precursor is an imidoyl chloride and the transition metal complex to be oxidised is a rhodium(I) compound. Two types of behaviour have been noted, exemplified by equations (2) and (3) (see Table footnotes b and f.)



(1)



(2)



(3)

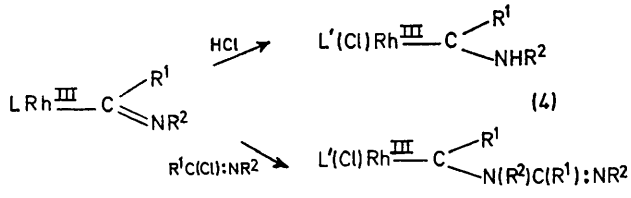
Compounds of types (I) and (II) which have been characterised are listed in the Table. A crystal structure of one of these, $[(OC)I_3Rh\text{–}C(Ph)N(Me)C(Ph)=NMe]$, is in progress.

TABLE

Compound	M.p.	Yield	Selected data[a]
$[(OC)Cl_3Rh-C(Ph)N(Me)-C(Ph)=NMe]_2$[b]	>300	73	Pale yellow crystals. Also + $2CH_2Cl_2$; *X*-ray Mol. wt.: ν(CO), 2120; ν(CN), 1656, 1502; ν(RhCl), 355vs, 332m, 315w cm^{-1}; n.m.r.
$[(OC)Cl_3Rh-C(Ph)N(Et)-C(Ph)=NMe]_2$	>300	69	Yellow crystals. ν(CO), 2120; ν(CN), 1648, 1497; ν(RhCl), 349s, 316m cm^{-1}; n.m.r.
$[(OC)Br_3Rh-C(Ph)N(Me)-C(Ph)=NMe]_2$[c]	>300	82	Orange crystals. ν(CO), 2115; ν(CN), 1648, 1492 cm^{-1}; n.m.r.
$[(OC)I_3Rh-C(Ph)N(Me)-C(Ph)=NMe]_2$[c]	240—2	57	Deep red cubes. ν(CO), 2080; ν(CN), 1638, 1470 cm^{-1}; n.m.r.
$(Me_2PhP)_2Cl_3Rh-C(Ph)N-(Me)C(Ph)=NMe$[d]	187—9	34	Yellow crystals. ν(CN), 1651, 1470; ν(RhCl), 323w, 298m cm^{-1}; n.m.r.
$[(OC)Cl_3Rh-C(Ph)NHMe]_n$	>190 (dec.)	69	Yellow crystals. ν(NH), 3165; ν(CO), 2120; ν(CN), 1612; ν(RhCl), 355m, 340w, 324w, 297w cm^{-1}.
$[(OC)Cl_3Rh-C(Ph)NHPr^i]_n$	160 (dec.)	59	Yellow crystals. ν(NH), 3110; ν(CO), 2120; ν(CN), 1602; ν(RhCl), 360s, 320m, 301w, 255m cm^{-1}.
$[(OC)Cl_3Rh-C(Me)NH-C_6H_4Me-o]_n$	>200 (dec.)	49	Orange-yellow crystals. ν(NH), 3115; ν(CO), 2125; ν(CN), 1570; ν(RhCl), 369m, 355w, 325m, 304m, 288m, 252m cm^{-1}.
$(Me_2PhP)_2Cl_3Rh-C(Me)-NHC_6H_4Me-o$[e]	289—91	29	Yellow crystals. ν(NH), 3110; ν(CN), 1529; ν(RhCl), 330m, 301w, 273m cm^{-1}; n.m.r.
$(Ph_3P)(OC)Cl_3Rh-C(Ph)NMHe$[f]	168—71	85	White crystals. ν(NH), 3120; ν(CO), 2105; ν(CN), 1598; ν(RhCl), 324m, 293s cm^{-1}; n.m.r.
$(Ph_3P)(OC)Cl_3Rh-C(Ph)NHEt$	164—7	65	White crystals. ν(NH), 3130; ν(CO), 2105; ν(CN), 1599; ν(RhCl), 330w, 299m, 283w cm^{-1}; n.m.r.

[a] I.r. spectra refer to 'Nujol' mulls; osmometric molecular weights in $CHCl_3$ confirm the dimeric assignments. [b] From $[Rh(CO)_2Cl]_2$ (0·447 g), PhC(=NMe)Cl (0·784 g) (J. von Braun and W. Pinkernelle, *Ber.*, 1934, **67**, 1218), dichloromethane (20 ml) and, after 16 h at 20°, Et_2O (15 ml), cooling to 0°, and filtration. [c] From the corresponding chloride + LiHal. [d] From $[(OC)Cl_3Rh-C(Ph)N(Me)C(Ph):NMe]_2$ + Me_2PPh. [e] From $[(OC)Cl_3Rh-C(Me)NHC_6H_4Me-o]_n$ + Me_2PPh. [f] By addition at 20° of PhC(=NMe)Cl (0·195 g) in C_6H_6 (5 ml) to $(Ph_3P)(OC)_2ClRh$ (0·155 g) in C_6H_6 (15 ml), passage of HCl gas through the stirred mixture, addition of Et_2O (20 ml), and filtration.

For the present, the principal spectroscopic diagnostic features are, where appropriate, (Table), (i) the high ν(CO), characteristic of Rh^{III} rather than Rh^{I}; (ii) the identification of ν(NH), ν(CN), and ν(RhCl); (iii) consistent ^1H n.m.r.



data; and (iv) a preliminary single crystal *X*-ray analysis of one compound, which confirms the molecular weight and which requires a centrosymmetric molecular structure.

The mechanism of reactions such as (2) and (3) may involve initial oxidative addition of the imidoyl chloride and subsequent reaction of the co-ordinated imidoyl ligand as shown in equation (4). Alternatively, especially for reaction (2), the organic reagent may be $[R^1C(Cl)-NHR^2]^+Cl^-$, which then reacts with LRhCl. Experiments which should settle this issue are in progress. An oxidative addition product, $P_2Pt(Cl)C(R^1):NR^2$ (P = PPh_3, R^1 = Ph, R^2 = Me), has been identified from the reaction of P_4Pt and $R^1C(Cl):NR^2$.[3] Previously, transition metal imidoyl complexes have been obtained by insertion of R^2NC into M–R bonds;[4] they are isomeric with imides $M-N:CR^1R^2$.[5]

Additional features of interest arising from this work are: (i) the chemistry of imidoyl chlorides, $R^1C(Cl):NR^2$,[6] in relation to transition metal complexes, and the extensive chemistry of the corresponding acyl chlorides RC(Cl):O;[7] (ii) the isolation of stable carbene complexes of a metal in a high oxidation state (Rh^{III});[8] and (iii) reactions of the co-ordinated imidoyl group of possible synthetic value in organic chemistry. The addition of 3,3-dichloro-1,2-diphenylcyclopropene to palladium metal[9] may clearly be regarded as a three-fragment oxidative addition.

We thank the S.R.C. for the award of a Fellowship to A.J.O.

(*Received*, 14*th December* 1971; *Com.* 2124.)

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