

Perhalocarboxylato Complexes of the Platinum Group Metals. Facile Fragmentation Reactions

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Thermal fragmentation of perhaloacetate anions, $CX_3CO_2^-$ ($X = Cl, Br$), is well established as an important route to the corresponding dihalo-carbenes ($:CX_2$) [1]. There is also much interest in the thermal fragmentation of perhalocarboxylate ligands bound to transition metals [2–5]. We now report a new series of reactions in which certain perhaloacetate complexes of the platinum group metals undergo a remarkably facile series of spontaneous fragmentation reactions at ambient temperature.

The nitrosyl complexes $M(NO)(PPh_3)_3$ ($M = Rh, Ir$) react with excess perhalocarboxylic acid CX_3CO_2H ($X = Cl, Br$) under very mild conditions (*ca* 5–10 min, 25 °C, acetone or benzene sol.) to afford the known dihalides $MX_2(NO)(PPh_3)_2$ in essentially quantitative yield. The reaction is accompanied by liberation of carbon dioxide (2 mole per mole of complex) and formation of a phosphorus containing species [^{31}P NMR singlet δ 33.44 ($X = Cl$), δ 30.76 ($X = Br$)] which we believe to be $Ph_3P=CX_2$ or some hydrolysis product thereof.

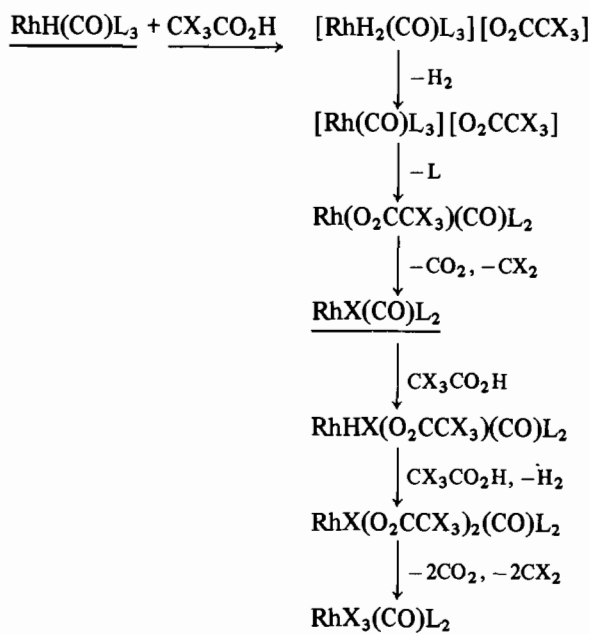
By terminating the rhodium reaction after 1–4 min then quickly filtering off and washing the precipitated product it is possible to isolate in good yield the green carboxylato complexes $Rh(O_2CCX_3)_2(NO)(PPh_3)_2$. These products prove to be thermally stable when returned to *clean* solvent but rapidly fragment to afford the dihalides $MX_2(NO)(PPh_3)_2$ even in cold solvent when free triphenylphosphine *and* acid, CX_3CO_2H , are added. In contrast other halocarboxylic acids RCO_2H ($R = CF_3, CF_2Cl, CHCl_2$ and CH_2Cl) afford carboxylato complexes $M(O_2CR)_2(NO)(PPh_3)_2$ which show no tendency to react further even in the presence of excess phosphine and free acid (toluene reflux, 1h).

We suggest that conversion of the carboxylates to the corresponding halo complexes involves extrusion of carbon dioxide and dihalocarbene. The role of the free phosphine and acid in this process remains to be determined. Decarboxylation of platinum group metal perhaloarylcarboxylates to yield the corresponding perhaloaryl complexes is well established [2–4], and the extrusion of dihalocarbenes CX_2 from coordinated CX_3 ligands has recently been reported [6]. However, both of these processes require

reaction conditions considerably more vigorous than those described here.

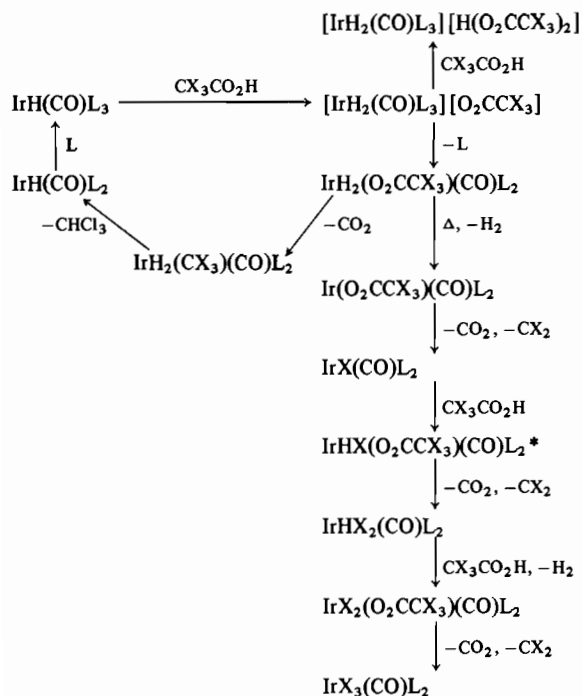
Perhalocarboxylic acids also undergo fragmentation in their reactions with the rhodium and iridium carbonyl complexes $MH(CO)(PPh_3)_3$ and $MCl(CO)(PPh_3)_2$. In each case differences in the relative stabilities of the I and III oxidation states for rhodium and iridium are reflected in the reaction pathways, and in the products isolated.

In cold or refluxing benzene, $RhH(CO)(PPh_3)_3$ reacts with one mole of CCl_3CO_2H to liberate carbon dioxide (1 mol) and form $RhCl(CO)(PPh_3)_2$. The ^{31}P NMR spectrum of the solution obtained when this reaction was performed in cold benzene showed a doublet [δ 29.05, $^1J(RhP) = 128$ Hz] attributable to $RhCl(CO)(PPh_3)_2$, and a second weaker doublet [δ 29.87, $^1J(RhP) = 132.4$ Hz] which we tentatively attribute to $Rh(O_2CCCl_3)(CO)(PPh_3)_2$ or possibly $Rh(CCl_3)(CO)(PPh_3)_2$. All attempts to detect hydridic intermediates by high field proton NMR were unsuccessful. Formation of the observed products can be explained in terms of the reactions shown in Scheme 1.



Scheme 1 ($L = PPh_3$).

The corresponding iridium complex, $IrH(CO)(PPh_3)_3$, reacts in a rather different manner (Scheme 2), presumably because of the greater reluctance of the iridium(III) cation $[IrH_2(CO)(PPh_3)_3]^+$ to reductively eliminate dihydrogen. For reactions involving *ca.* one mole of acid, CCl_3CO_2H , per mole of iridium complex, formation of chloroform and liberation of carbon dioxide has been confirmed by proton NMR/



*plus isomers and disproportionation products (see text).

Scheme 2 (L = PPh₃).

GLC and gravimetric methods respectively. Successive formation of $[\text{IrH}_2(\text{CO})(\text{PPh}_3)_3]^+$ and $\text{IrH}(\text{CO})(\text{PPh}_3)_3$ has been established by high field proton NMR. Although the reaction leads to the regeneration of $\text{IrH}(\text{CO})(\text{PPh}_3)_3$ it does not lend itself to the establishment of a catalytic process since the addition of excess acid ($\text{CCl}_3\text{CO}_2\text{H}$) leads to the stabilisation of the intermediate salt $[\text{IrH}_2(\text{CO})(\text{PPh}_3)_3][\text{H}(\text{O}_2\text{CCl}_3)_2]$ by hydrogen bonding within the anion, and thus breaks the catalytic cycle. Quantitative formation of the cation $[\text{IrH}_2(\text{CO})(\text{PPh}_3)_3]^+$ in the presence of excess acid has been confirmed by high field proton NMR [7].

Attempts to render the system catalytic by raising the temperature of reaction (boiling toluene) led to a complex series of reactions (Scheme 2) from which $\text{IrCl}_3(\text{CO})(\text{PPh}_3)_2$ emerged as the major product. The treatment of $\text{IrH}(\text{CO})(\text{PPh}_3)_3$ with $\text{CBr}_3\text{CO}_2\text{H}$ leads to the liberation of some bromoform; however,

the major products are $\text{IrHBr}_2(\text{CO})(\text{PPh}_3)_2$ and $\text{IrBr}_3(\text{CO})(\text{PPh}_3)_2$ even when the reaction is performed at ambient temperature.

Treatment of $\text{RhCl}(\text{CO})(\text{PPh}_3)_2$ with excess $\text{CCl}_3\text{CO}_2\text{H}$ in cold or boiling benzene affords $\text{RhCl}_3(\text{CO})(\text{PPh}_3)_2$ plus two moles of carbon dioxide. This system, in common with many others involving rhodium(I), is very labile and all attempts to detect intermediate hydride species under milder conditions (25 °C, 1 mol $\text{CCl}_3\text{CO}_2\text{H}$) by ^1H NMR were unsuccessful.

In contrast treatment of $\text{IrCl}(\text{CO})(\text{PPh}_3)_2$ with one mole of $\text{CCl}_3\text{CO}_2\text{H}$ in deuteriobenzene at ambient temperature affords a solution containing four hydridic species [$\delta(\text{IrH}) = -12.6(\text{t}), -14.6(\text{t}), -17.1(\text{t}), -18.8(\text{t})$]. These products appear to be simple perhalocarboxylato complexes or disproportionation products [8] directly analogous to those reported by Wilkinson *et al.* [9] for the corresponding $\text{IrCl}(\text{CO})(\text{PPh}_3)_2/\text{CF}_3\text{CO}_2\text{H}$ system [$\delta(\text{Ir-H}) = -14.5(\text{t}), -16.3(\text{t}), -18.1(\text{t}), -19.5(\text{t})$]. Prolonged treatment of $\text{IrCl}(\text{CO})(\text{PPh}_3)_2$ with excess $\text{CCl}_3\text{CO}_2\text{H}$ in boiling benzene induces a complex sequence of reactions (Scheme 2) leading to formation of a mixture of $\text{IrHCl}_2(\text{CO})(\text{PPh}_3)_2$ and $\text{IrCl}_3(\text{CO})(\text{PPh}_3)_2$.

The mechanisms of these reactions and some similar ones involving perhalocarboxylato complexes of the other platinum metals are under investigation and will be reported elsewhere.

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