Reactions of Hexafluorobut-2-yne with Some Methylplatinum(II) Complexes

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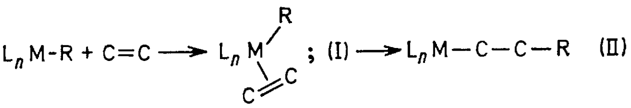
Summary Hexafluorobut-2-yne with several methylplatinum(II) compounds gives both 1 : 1 complexes and 1 : 1 insertion products, of types important in catalytic polymerization processes.

THE catalytic polymerization of unsaturated organic compounds by transition-metal complexes is believed to proceed by a series of reactions involving complex formation followed by insertion,

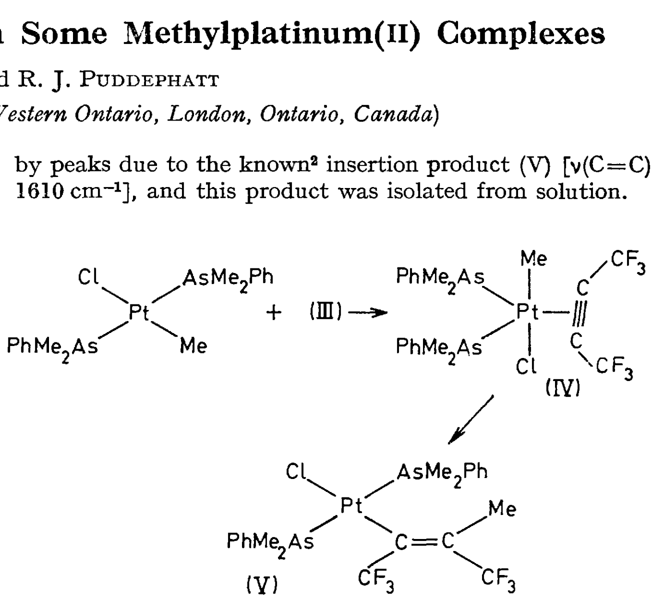


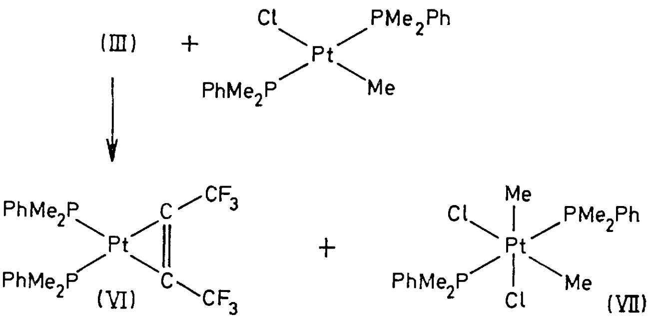
$$L_nM\text{-}R + C{=}C \longrightarrow L_nM\begin{smallmatrix}R\\ \\ C{=}C\end{smallmatrix} \;;\; (I) \longrightarrow L_nM{-}C{-}C{-}R \quad (II)$$

where R is a σ-bonded organic group. However, only rarely[1] have either the intermediate complex (I) or the product of a single insertion (II) been isolated. We report the formation of complexes of type (I) and their rearrangement to insertion products of type (II), both being formed in the reactions of hexafluorobut-2-yne, $CF_3{-}C{\equiv}C{-}CF_3$, (III), with some methylplatinum(II) complexes.

A concentrated solution of *trans*-$PtClMe(AsMe_2Ph)_2$ in benzene, on reaction with a large excess of (III) in a sealed tube, gave a precipitate of the white complex $PtClMe(AsMe_2Ph)_2C_4F_6$, (IV) [$\nu(C{\equiv}C)$ 1870 cm^{-1}]. This complex was stable at room temperature but decomposed to its constituents on heating to 70—80° or on dissolution in benzene.

The ^1H and ^{19}F n.m.r. spectra of a solution of *trans*-$PtClMe(AsMe_2Ph)_2$ in chloroform containing an excess of (III) at first indicated the presence of (IV) [$\delta(CH_3Pt)$ $-$ 0·45 p.p.m., $J(Pt{-}CH_3)$ 68·0 Hz; $\delta(C_4F_6$ complexed) 55·3 p.p.m. from $CFCl_3$, $J(Pt{-}F)$ 41·0 Hz]. However, after three weeks at room temperature, these peaks had been replaced by peaks due to the known[2] insertion product (V) [$\nu(C{=}C)$ 1610 cm^{-1}], and this product was isolated from solution.





The spectroscopic evidence is consistent with the initial complex having the trigonal bipyramidal structure (IV), though other structures cannot be entirely discounted.

A similar complex of (III) with *trans*-PtIMe(AsMe$_2$Ph)$_2$ was observed in solution [ν(C≡C) 1868 cm^{-1}; δ(C$_4$F$_6$ complexed) 55·5 p.p.m., *J*(PtF) 40·5 Hz], but attempts to isolate the complex led to reversion to its constituents.

With *cis*-PtMe$_2$(AsMe$_2$Ph)$_2$, (III) very rapidly gave a mixture of insertion products so that no intermediate complex could be observed. Similarly, *cis*-PtMe$_2$(PMe$_2$Ph)$_2$ in ether solution gave insertion products Pt[C(CF$_3$)=C(CF$_3$)-CH$_3$]$_2$(PMe$_2$Ph)$_2$. However, in benzene solution a different reaction took place giving Pt(C$_4$F$_6$)(PMe$_2$Ph)$_2$, (VI), a known compound[3] as the only platinum-containing product.

I.r. and n.m.r. spectra indicated that there was no interaction between *trans*-PtClMe(PMe$_2$Ph)$_2$ and (III) in CHCl$_3$ after 1 hr. at room temperature. However, after one week the ^{1}H and ^{19}F n.m.r. spectra indicated formation of equimolar proportions of (VI) and (VII); these products being isolated and identified by comparison with the authentic compounds.[3,4]

(*Received, November 3rd*, 1969; *Com.* 1676.)

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