The Reaction of Trifluoroacetonitrile with Tetrakistriphenylphosphineplatinum(0): *X*-ray Analysis of One of the Products and the Preparation of $(Ph_3P)_2Pt(CF_3CN)$

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VARIOUS transition metals[1,2] have been shown to catalyse the trimerisation of benzonitrile to triphenyltriazine. However, although π-bonded metal-nitrile complexes are presumably involved in these reactions, no such mono-nitrile complex has been isolated. We now report the preparation of a π-bonded trifluoroacetonitrile complex which may be intermediate in the formation of other new complexes containing polymerised trifluoroacetonitrile fragments.

Treatment of bis(triphenylphosphine)platinum *trans*-stilbene with excess of trifluoroacetonitrile gives the complex bis(triphenylphosphine)platinum(trifluoroacetonitrile) (I). The proposed structure is based on the 56·4 MHz ^{19}F n.m.r. spectrum {three doublets centred at 2·37 p.p.m. on the low-field side of benzotrifluoride, $J(^{195}Pt-^{19}F)$ 57·3 and $J(^{31}P-^{19}F)$ 6·7 Hz, similar to that of $(Ph_3P)_2Pt[(CF_3)_2CO]$},[3] and an intense i.r. absorption of 1734 cm.$^{-1}$ in the region normally assigned to the C=N stretching frequency. Although metal nitrile π-bonds have been reported to exist[4] in the complexes $Mn(CO)_3(NC{\cdot}CH_2{\cdot}CH_2{\cdot}CN)X$ (X = Cl, Br, or I), i.r. data suggest that the carbon–nitrogen bonds have a significant amount of triple-bond character.

A second product, isolated from the reaction of trifluoroacetonitrile and $Pt(PPh_3)_4$, for which chemical analysis indicates the molecular formula $(PPh_3)_2Pt(CF_3CN)_2N$, was subjected to a single-crystal *X*-ray structure determination.

The compound crystallises in space group $P2_1/c$, $a = 12{\cdot}27$, $b = 13{\cdot}91$, $c = 23{\cdot}86$ Å, $\beta = 116{\cdot}3^{\circ}$; $U = 3651$ Å, $Z = 4$, $D_m = 1{\cdot}70$, D_c for $4(C_{40}H_{31}F_6N_3P_2Pt) = 1{\cdot}68$. 1746 Independent reflections were measured by an integrating microdensitometer from Weissenberg and precession films, and at the present stage of refinement $R = 0{\cdot}11$. The overall molecular stereochemistry is shown in the Figure. The platinum, phosphorus and atoms 1—7 are all virtually coplanar (maximum deviation from plane 0·18 Å for atom 6).

It is not possible from the *X*-ray data to distinguish between carbon and nitrogen atoms. However, structure (II) is indicated for the complex by a single, sharp i.r. absorption at 3358 cm.$^{-1}$, which may be assigned to the N–H stretching frequency, and by the ^{19}F n.m.r. spectrum which shows the presence of two non-equivalent CF_3 groups. A strong peak corresponding to the fragment $(CF_3{\cdot}CN)_2NH$ appears in the mass spectrum of the complex, although the parent ion is not observed.

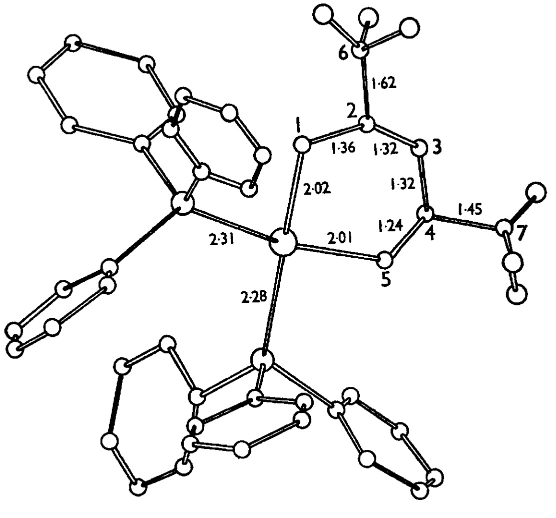
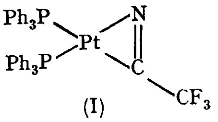
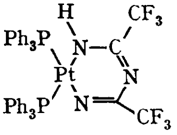


FIGURE. *Molecular structure of* $(Ph_3P)_2Pt(CF_3CN)_2NH$. *Bond lengths in* Å, *e.s.d.'s of* Pt–P ± 0·03; Pt-*atoms* 1,5 ± 0·04; C–C, C–N ± 0·08 Å.



(I)



(II)

The source of the NH group is presumably the result of hydrolytic degradation of $CF_3{\cdot}CN$ since there is probably sufficient water in sodium-dried benzene, and on the walls of the glass reaction vessel, for this to occur. In agreement with this we find that addition of water to the initial reaction mixture results in an increased yield of (II).

From this latter reaction we have isolated further complexes containing trifluoroacetonitrile in varying degrees of polymerisation. Preliminary chemical investigation suggests that two of the compounds may be formulated $Ph_3PPtC_6F_9N_3H_2$ and $(Ph_3P)_2PtC_6F_9N_3H$. Their i.r. and n.m.r. spectra show that both compounds contain N–H bonds and three non-equivalent CF_3 groups.

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