A π-Bonded Trifluoroacetonitrile Complex of Platinum(0)

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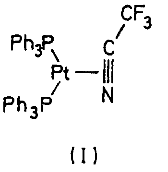
Trifluoroacetonitrile displaces *trans*-stilbene from Pt(*trans*-stilbene)$(PPh_3)_2$ to give $Pt(\pi\text{-}CF_3CN)(PPh_3)_2$, (I). The trifluoroacetonitrile ligand in (I) is labile and is displaced by diphenylacetylene and carbon monoxide to give $Pt(PhC{\equiv}CPh)(PPh_3)_2$ and $Pt_3(CO)_3(PPh_3)_4$ respectively. Other displacement reactions indicate that the complexes $Pt(L)(PPh_3)_2$ decrease in stability in the order of ligands (L), $(CF_3)_2CO > PhC{\equiv}CPh > CF_3C{\equiv}N > CF_2{=}CH_2 >$ *trans*-PhCH=CHPh. In addition to $Pt\{(CF_3)_2CO\}(PPh_3)_2$, a five-membered ring complex $(Ph_3P)_2\overline{PtC(CF_3){=}N{-}C(CF_3)_2{-}O}$ may also be isolated from the reaction of (I) with hexafluoroacetone. Treatment of (I) with trifluoroacetic acid gives a mixture of *trans*-$PtH(OCOCF_3)(PPh_3)_2$ and *trans*-$Pt(OCOCF_3)\{C(CF_3){=}NH\}(PPh_3)_2$.

TRIFLUOROACETONITRILE reacts with *trans*-stilbenebis(triphenylphosphine) platinum(0) suspended in diethyl ether to afford a white air-stable complex (I)[1] *via* a reaction which involves displacement of *trans*-stilbene by trifluoroacetonitrile. The i.r. spectrum of (I)



(I)

exhibited a strong band at 1734 cm^{-1} in the region normally assigned to C=N stretching frequencies. In free trifluoroacetonitrile $\nu(C{\equiv}N)$ occurs at 2271 cm^{-1}.[2] The magnitude of the change in $\nu(C{\equiv}N)$ upon co-ordination of trifluoroacetonitrile to the platinum is similar to the change observed when acetylenes co-ordinate to platinum(0).[3] The i.r. spectrum of (I) is therefore consistent with a structure in which the nitrile is π-complexed *via* its *p*π–*p*π bonds to the metal atom, the large reduction in $\nu(C{\equiv}N)$ implying considerable back-bonding from metal to ligand. In simple *N*-bonded nitrile complexes of the type $RCN \longrightarrow M$ there is usually an increase of $\nu(C{\equiv}N)$ upon co-ordination.[4]

The ^{19}F n.m.r. spectrum of (I) showed three doublets centred at 2·37 p.p.m. on the low-field side of benzotrifluoride [$J(PF) = 6{\cdot}7$ and $J(PtF) = 57{\cdot}3$ Hz]. The presence of only one PF coupling in (I) implies a rigid planar or near-planar structure for the two phosphorus atoms, the platinum, and the carbon and nitrogen atoms of the nitrile as has been proposed for the related hexafluoroacetone complex.[5] The PF coupling in (I) presumably results from coupling with the *trans*-phosphorus atom since in related hexafluoroacetone[5] and hexafluorobut-2-yne complexes[6] it is found that $J(P_{trans}F) \gg J(P_{cis}F)$. Confirmation of the proposed structure for (I) has been provided by a single-crystal *X*-ray structure determination which reveals a near-planar arrangement

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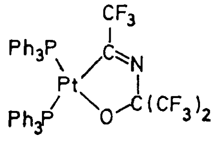
of atoms around the platinum,[7] as has been observed in the related complexes, $Pt(PhC{\equiv}CPh)(PPh_3)_2$,[8] $Pt(CS_2)(PPh_3)_2$,[9] and $Pt\{C_2(CN)_4\}(PPh_3)_2$.[10]

The trifluoroacetonitrile ligand in (I) is labile and attempted recrystallisation of the complex from acetone in the presence of atmospheric oxygen afforded the five-membered ring complex, $\overline{PtOCMe_2OO}(PPh_3)_2$.[11,12] Displacement of the trifluoroacetonitrile ligand was also found to occur when (I) was treated separately with diphenylacetylene and carbon monoxide gas at room temperature and atmospheric pressure. These reactions afforded $Pt(PhC{\equiv}CPh)(PPh_3)_2$ and $Pt_3(CO)_3(PPh_3)_4$ [13] respectively, the trinuclear carbonyl complex presumably being formed *via* $Pt(CO)_2(PPh_3)_2$.[13] The reaction of hexafluoroacetone with (I) afforded two complexes, $Pt\{(CF_3)_2CO\}(PPh_3)_2$ and a small amount of a product of molecular formula $[Pt(CF_3CN)\{(CF_3)_2CO\}(PPh_3)_2]$, (II). Studies on metal complexes of trifluoroacetyl cyanide suggest that the C=O group co-ordinates more strongly *via* its $P\pi$–$P\pi$ orbitals, to iridium(I) and rhodium(I) than does the C≡N group.[14] The displacement of trifluoroacetonitrile from (I) by hexafluoroacetone provides more evidence for this point. Further since trifluoroacetonitrile will displace 1,1-difluoroethylene from its platinum complex, $Pt(CF_2CH_2)(PPh_3)_2$, these complexes may be placed in the following order of decreasing stability:

$$(CF_3)_2CO > PhC{\equiv}CPh > CF_3CN > CF_2{=}CH_2 > \textit{trans}\text{-}PhCH{=}CHPh$$

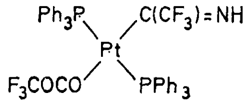
The i.r. spectrum of the second product, (II), which is formed in the reaction of (I) with hexafluoroacetone exhibited a medium strong band at 1558 cm^{-1}, but no bands could be detected in the region associated with $\nu(C{=}O)$, $\nu(C{\equiv}N)$, or $\nu(N{-}H)$. The ^{19}F n.m.r. spectrum of the complex showed two resonances of relative intensity 1 : 2. The low field resonance (intensity 3) consisted of a central triplet with additional ^{195}Pt satellite peaks, the triplet arising since $J_{PF\mathit{cis}}$ and $J_{PF\mathit{trans}}$ may be of similar magnitude. The ^{19}F resonance at $Pd\{(CF_3)_2CO\}\{P(OPh)_3\}_2$ also appears as a triplet[15] but whilst the palladium complex is dissociated in solution so that $J_{PF\mathit{cis}}$ and $J_{PF\mathit{trans}}$ may be averaged on the n.m.r. time scale, the molecular weight of (II) was found to be normal. Further the spectrum of (II) was unchanged at −90°. The high field resonance of (II), (intensity 6) appeared as a singlet with platinum satellites. This data provides support for the proposed structure of (II), the i.r. band at 1558 cm^{-1} being assigned to a C=N stretching frequency of (II). A somewhat similar ring system has also been shown to result from the action of the imine, $(CF_3)_2C{=}NH$, on the hexafluoroacetone complex, $[Ni\{OC(CF_3)_2\}(CNBu^t)_2]$.[16,17]



(II)

It has been suggested[18] that the formation of this latter nickel complex involves an intermediate in which both fluorocarbon molecules are co-ordinated to the nickel. A similar mechanism may well operate in the formation of (II).

Treatment of (I) with trifluoroacetic acid gave two products, *trans*-$PtH(OCOCF_3)(PPh_3)_2$ and *trans*-$Pt(OCOCF_3)(CCF_3{=}NH)(PPh_3)_2$, (III). The hydride–trifluoroacetate complex is identical to the complex which has been isolated from the action of trifluoroacetic acid upon $Pt(C_2H_4)(PPh_3)_2$.[19] The i.r. spectrum of the second product (III) exhibited a weak band at 3385 cm^{-1} which may be assigned to an N–H stretching frequency, and a broad absorption between 1700 and 1600 cm^{-1} in the region of $\nu(C{=}N)$ and ν_{asym} (CO_2) of a co-ordinated trifluoroacetate ligand. The ^{19}F n.m.r. of (III) showed a resonance at +4·8 p.p.m. with ^{195}Pt satellite peaks and a singlet at +12·8 p.p.m. relative to benzotrifluoride, the low-field resonance being assigned to the CF_3 group of the ligand, $-C(CF_3){=}NH$. This i.r. and n.m.r. data is consistent with the proposed structure for (III) in which the protonation has taken place at the nitrogen of the co-ordinated trifluoroacetonitrile. The absence of ^{31}P–^{19}F coupling provides good evidence for a *trans*-configuration about the platinum(II).[20] Similar protonation reactions have been shown to take place with the related hexafluorobut-2-yne complexes, $Pt(CF_3C{\equiv}CCF_3)(PR_3)_2$.[20]



(III)

Attempts to obtain complexes analogous to (I) using trichloroacetonitrile, chloromethylcyanide, or pentafluorobenzonitrile have not been successful.

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The trifluoroacetonitrile complex (I) provides one of the few definite examples of a simple π-bonded metal nitrile complex. The aliphatic dinitrile complexes, $MX(CO)_3(NC[CH_2]_2CN)$ (M = Mn or Re; X = Cl or Br), were suggested[21,22] to contain chelating π-bonding nitrile systems but recently these complexes have been reformulated as *N*-bonded σ-bonded complexes.[23] * *Dihapto* nitrile bonding is considered to be present[24] in the complex $[(PMe_2Ph)_2(Me)Pt\{h^2{-}NC{\cdot}C_6F_4{\cdot}C(OEt){:}NH\}{-}Pt(Me)(PMe_2Ph)_2][BF_4]_2$ and has been shown to be present in $Ni(CO)(C_5H_{10}NCN)$.[25] This type of bond may also be involved in the metal catalysed cyclotrimerisation of benzonitrile[26,27] and the molybdenum catalysed reduction of nitriles.[28]

EXPERIMENTAL

I.r. spectra were recorded with a Perkin-Elmer 225 spectrophotometer using Nujol and Fluorolube mulls. ^1H and ^{19}F N.m.r. spectra were recorded on Varian Associates T60 and DA60 spectrometers respectively. The ^{19}F n.m.r. spectra were measured relative to benzotrifluoride as internal standard and were recorded at 56·4 MHz. M.p.s were determined on a Reichart hot-stage apparatus and are uncorrected.

The complex $Pt(\textit{trans}\text{-stilbene})(PPh_3)_2$ was prepared as described in the literature.[29] Trifluoroacetonitrile was prepared by dehydration of trifluoroacetamide.[30]

(π-Trifluoroacetonitrile)bis(triphenylphosphine)platinum-(0).—An excess of trifluoroacetonitrile was condensed onto a suspension of $Pt(\textit{trans}\text{-stilbene})(PPh_3)_2$ (1·2 g, 1·34 mmol) in diethyl ether (50 ml) contained in a Carius tube (150 ml) which was cooled in liquid nitrogen. The tube was sealed and the reaction mixture was allowed to warm to room temperature and then vigorously shaken for 72 h. The resulting pale yellow precipitate was washed with ether to afford the *product* (0·90 g, 1·0 mmol, 82%), m.p. 130—133° (dec.) [Found: C, 55·6; H, 4·4; F, 6·9; N, 1·9. $C_{38}H_{30}F_3NP_2Pt$ requires C, 56·0; H, 4·4; F, 7·0; N, 1·7%]. ν(C≡N) 1734 cm^{-1}. The ^{19}F n.m.r. spectrum (acetone) showed a resonance at −2·37 p.p.m. (3F, d with ^{195}Pt satellites, *J*(PF) 6·7, *J*(PtF) 57·3 Hz). Dissolution of the complex (0·71 g, 0·21 mmol) in acetone (10 ml) at 50° followed by evaporation to a small volume and addition of hexane gave a pale yellow precipitate. The precipitate was washed with hexane and dried *in vacuo* and identified as $Pt\overline{OCMe_2OO}{-}(PPh_3)_2$ (0·1 g, 60%). M.p. 168—172° (lit.,[12] 172—174°) (Found: C, 57·8; H, 4·5. Calc. for $C_{39}H_{36}O_3P_2Pt$: C, 57·9; H, 4·5%).

Reactions of Complex (I).—(a) *With diphenylacetylene.* Diphenylacetylene (0·11 g, 0·62 mmol) and (I) (0·50 g, 0·61 mmol) and benzene (20 ml) were sealed together in a Carius tube. After 1 h the solid had dissolved to give a pale yellow solution, and after two weeks the tube was opened. The i.r. spectrum of the vapour present in the tube exhibited a peak at 2271 cm^{-1} characteristic of free trifluoroacetonitrile.[2] The yellow solution was evaporated under reduced pressure to a small volume and addition of ethanol gave pale yellow crystals of $Pt(PhC{\equiv}CPh)(PPh_3)_2$ (0·41 g, 75%) identical (analysis, m.p., and i.r.) with an authentic sample.[31]

(b) *With carbon monoxide.* Carbon monoxide was passed slowly through a suspension of (I) (0·36 g, 0·44 mmol) in benzene (40 ml). The complex immediately dissolved to give an orange solution. After 5 h the solution was evaporated to a small volume under reduced pressure. Addition of methanol gave an orange-red precipitate which was washed with methanol and dried *in vacuo* to give $Pt_3(CO)_3(PPh_3)_4$ identical with an authentic sample.[13]

(c) *With hexafluoroacetone.* An excess of hexafluoroacetone and a suspension of (I) (1·20 g, 1·5 mmol) in benzene (40 ml) were allowed to react at room temperature for 2 weeks. The white product which formed was filtered and washed with a small volume of benzene and recrystallised from methylene chloride–ethanol to give white crystals of (II) (0·21 g, 15%), m.p. 255—258° (dec.) (Found: C, 50·3; H, 3·0; F, 17·0; N, 1·6. *M* ($CHCl_3$), 960. $C_{41}H_{30}F_9NOP_2Pt$ requires C, 50·2; H, 3·1; F, 17·4; N, 1·4%; *M*, 981). ν(C=N), 1547 cm^{-1}. The ^{19}F n.m.r. spectrum (CH_2Cl_2) showed resonances at +1·4 p.p.m. [t, 3F, CF_3C, with ^{195}Pt satellites, *J*(PF *trans*) = *J*(PF *cis*) 5, *J*(PtF) 25 Hz] and +14·2 p.p.m. [s, 6F, $(CF_3)_2C$, with ^{195}Pt satellites, *J*(PtF) 21 Hz].

The pale yellow filtrate and benzene washings from above were evaporated to a small volume under reduced pressure. Addition of hexane gave a cream coloured precipitate which was washed with ether to form $[Pt\{(CF_3)_2CO\}(PPh_3)_2]$ (0·74 g, 57%), identical with authentic sample.[5]

(d) *With trifluoroacetic acid.* An ether solution of trifluoroacetic acid (1 ml, 0·29M) was pipetted onto a suspension of (I) (0·23 g, 0·29 mmol) in ether (10 ml) and the reaction mixture was shaken for 2 h. The white crystals which formed were filtered off, washed with ether, dried *in vacuo*, and recrystallised from methylene chloride–ethanol to give $\textit{trans}\text{-}PtH(OCOCF_3)(PPh_3)_2$ identical (analysis, m.p., i.r., and ^{19}F n.m.r.) to an authentic sample.[19]

The filtrate and washings from above were combined, hexane added, and the mixture was evaporated to a small volume under reduced pressure. The pale yellow solid which formed was washed with hexane and dried *in vacuo*, to give (III) (0·12 g, 45%), m.p. 210—220° (dec.) (Found: C, 49·7; H, 3·5; F, 11·7; N, 1·4. $C_{40}H_{31}F_6NO_2P_2Pt$ requires C, 51·7; H, 3·4; F, 12·6; N, 1·5%). The i.r. spectrum showed a very weak band at 3385 cm^{-1}, {ν(N–H)} and a very broad band at *ca.* 1685 cm^{-1}, {$\nu_{asym}(CO_2)$ + ν(C=N)}. The ^{19}F n.m.r. spectrum (CH_2Cl_2) showed resonances at +4·8 p.p.m. (s, 3F, CCF_3 with ^{195}Pt satellites, *J*(PtF) 52 Hz) and +12·4 p.p.m. (s, CF_3, $OCOCF_3$). The complex decomposed upon attempted recrystallisation from methylene chloride–hexane.

Reaction of Trifluoroacetonitrile with $Pt(CF_2{=}CH_2)(PPh_3)_2$, (*with* G. W. LITTLECOTT).—Trifluoroacetonitrile and Pt-

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* *Note added in proof:* Both monomeric π-bonded dinitriles and σ-bonded dinitriles may be present in these systems. M. F. Farona and K. F. Kraus, *J.C.S. Chem. Comm.*, 1972, 513.

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$(CF_2{=}CH_2)(PPh_3)_2$[32] (0·2 g, 2·6 mmol) suspended in diethyl ether (10 ml) in a Carius tube were allowed to react at room temperature for 2 days. The white solid was collected, washed with diethyl ether, and dried *in vacuo* and identified as (I) (0·18 g, 72%).

Reactions of Pt(trans-PhCH=CHPh)$(PPh_3)_2$.—(a) *With trichloroacetonitrile.* Trichloroacetonitrile (0·4 g, 9·6 mmol) was added to a suspension of Pt(*trans*-PhCH=CHPh)$(PPh_3)_2$ (0·39 g, 0·3 mmol) in ether (30 ml). The solution became brown and after 12 h the greyish precipitate was collected, washed with ether, and recrystallised from methylene chloride–methanol to give *cis*-$PtCl_2(PPh_3)_2$ (0·11 g, 43%) identified by analysis and m.p.[33]

(b) *With pentafluorobenzonitrile.* As above to give unchanged Pt(*trans*-PhCH=CHPh)$(PPh_3)_2$.

(c) *With monochloromethylcyanide.* Monochloromethylcyanide (1·2 g, 15·7 mmol) was added to a solution of $Pt(PPh_3)_4$ (1 g, 0·8 mmol) in benzene (30 ml) and the mixture was heated under reflux for 15 h. Evaporation of the brown-yellow solution to a small volume and addition of methanol gave white crystals of *trans*-$PtCl(CH_2CN)(PPh_3)_2$ which was recrystallised from methylene chloride–methanol (0·48 g, 73%), m.p. 252—255° (dec.) (Found: C, 57·3; H, 4·2; Cl, 4·3; N, 1·6%. $M(CHCl_3)_2$, 820. $C_{38}H_{32}ClNP_2Pt$ requires C, 57·4; H, 4·1; Cl, 4·5; N, 1·8%. *M*, 795). ν(C≡N), 2217; ν(Pt–Cl), 291 cm^{-1}. Oxidative additions of chloromethylcyanide to complexes of the type *trans*-$IrCl(CO)(L)_2$ have similarly been reported.[34]

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