Novel Cleavage of a Phosphinoacetylene by Palladium(II) and Platinum(II): Preparation and Structure of Complexes of 1,3-Bis(diphenylphosphino)-2-trifluoromethylpropene Derived from 3,3,3-Trifluoropropynyldiphenylphosphine

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Summary Unsymmetrical ditertiary phosphine complexes $[Ph_2PCH_2C(CF_3){=}CHPPh_2]$-$MX_2$ (M=Pd or Pt and X=Cl or SCN) have been prepared by reaction of $Ph_2PC{\equiv}CCF_3$ with MX_4^{2-} salts and characterized by an *X*-ray study of the $Pd(SCN)_2$ derivatives.

Acetylenes react with metal carbonyls to give organometallic complexes formed *via* acetylene oligomerisation,[1] Pd^{II} and Pt^{II} salts also oligomerise acetylenes, yielding in addition to organic products, complexes containing cyclobutadiene, cyclobutenyl, and σ,π-octatriene ligands.[2] However, in some cases it is necessary to postulate cleavage of the acetylenic bond in order to account for the products.[1,2] We have found that the activated phosphinoacetylene, $Ph_2PC{\equiv}CCF_3$, reacts with MX_4^{2-} ions (M=Pd or Pt, X=Cl or SCN) to produce unusual ditertiary phosphine complexes $[Ph_2PCH_2C(CF_3){=}CHPPh_2]MX_2$, (I). The result is an unprecedented example of the reaction of an acetylene with Pd^{II} or Pt^{II} which results in bond cleavage and the formation of a three-carbon chain from two acetylene groups. The i.r. spectra of (I; M = Pd, X = Cl) showed no absorption in the range 1600—2500 cm^{-1} assignable to $\nu(C{\equiv}C)$ of a co-ordinated acetylene; $\nu(C{\equiv}C)$ in $Ph_2PC{\equiv}CCF_3$ occurs at 2200 cm^{-1}. A square planar *cis*-arrangement was suggested by two strong ν(Pd–Cl) bands at 317 and 299 cm^{-1} which were absent in the corresponding thiocyanate complex. A sharp doublet at 2117 cm^{-1} assignable to $\nu(C{\equiv}N)$ was consistent with a *cis*-S-bonded isomer for the thiocyanate. A 100 MHz ^1H n.m.r. spectrum of (I; M = Pd, X = Cl) in CD_2Cl_2 [δ-scale; 3·0 (dd) CH_2, $^2J_{P-H}$ 11·0 Hz, $^4J_{P-H}$ 4·0 Hz; 6·9 (d) CH, $^2J_{P-H}$ 6·0 Hz; 7·7 (m) due to phenyl H] suggested the presence of both CH_2 and =CH groups. ^{19}F n.m.r. spectra for all the compounds exhibited a singlet. In view of the unusual nature of the complex we undertook an *X*-ray investigation of the thiocyanate derivative (I; M = Pd and X = SCN).

Crystal data: $PdC_{30}H_{23}F_3N_2P_2S_2,CH_2Cl_2$, yellow monoclinic crystals from CH_2Cl_2–EtOH, $M = 782{\cdot}9$, $a = 11{\cdot}019(1)$, $b = 17{\cdot}180(2)$, $c = 17{\cdot}800(2)$ Å, $\beta = 102{\cdot}46(1)^\circ$, D_m(flotation) $= 1{\cdot}58$, $D_c = 1{\cdot}580$ g cm^{-3}, $Z = 4$, Cu-K_α radiation ($\lambda = 1{\cdot}5418$ Å), space group $P2_1/c$. The structure was solved by the heavy-atom method and the present R value is 0·072.†

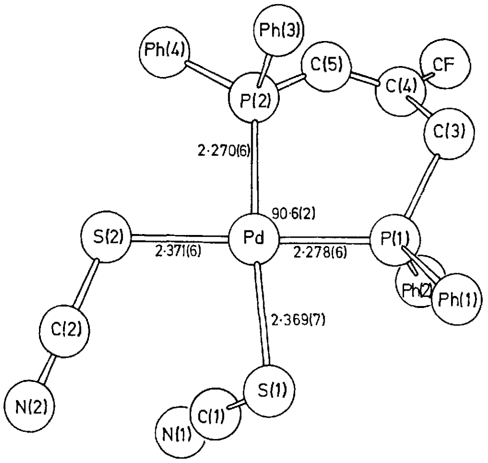

FIGURE. *A view approximately normal to the co-ordination plane, giving the atomic numbering and some pertinent distances. The S*(1)–*C*(1)–*N*(1) *group is bent* 48° *out of the plane defined by Pd–S*(1)–*S*(2)–*P*(1)–*P*(2).

The molecular structure, atomic numbering, and pertinent bond distances are shown in the Figure. The palladium atom is co-ordinated in a square planar fashion by two S-bonded thiocyanates and the two phosphorus atoms of the diphosphine. The C(4)–C(5) distance of 1·375(27) Å is longer than a pure double-bond but the difference is not significant due to the large e.s.d. The Pd–P distances (avg. 2·274 Å) are similar to those found in *cis*-$Pd(SCN)_2(Ph_2PCH_2PPh_2)$ of 2·277 Å[4] and *cis*-$Pd(NCS)(SCN)[Ph_2PC{\equiv}CBu^t]_2$ of 2·279 Å[5] but are longer than in *cis*-$Pd(NCS)(SCN)(Ph_2PCH_2CH_2PPh_2)$.[6] The P–Pd–P angle of 90·0(2)° is somewhat larger than the 89·31° in *cis*-$Pd(NCS)_2(Ph_2PCH_2CH_2CH_2PPh_2)$.[7] Thus the 'bite' of $Ph_2PCH_2CH_2CH_2PPh_2$ and $Ph_2PCH_2C(CF_3){=}CHPPh_2$ appear to be similar although the thiocyanates are S-bonded in the latter and N-bonded in the former. The more rigid propene chain alters the orientations of the four phenyl groups sufficiently to allow the thiocyanates to S-bond in the present complex. However, the steric interactions are still sufficiently important so that the thiocyanate, S(1)–C(1)–N(1) is tipped 48° out of the co-ordination plane. The equality of the two Pd–S and Pd–P distances suggests that either π-bonding involving the Pd atom is minimal or that the π-bonding is independent of the tip of the thiocyanate ion. In any case, the presence of two S-bonded thiocyanates *trans* to phosphorus atoms is contrary to the π-bonding hypothesis of Turco and Pecile.[8] These π-bonding arguments have been used extensively by others to rationalize thiocyanate linkage isomers in palladium and other systems.[9] The characterization of the present complex together with additional studies of palladiumphosphine–thiocyanate complexes,[4,7,10,11] suggest that π-bonding arguments should be viewed very critically.

The conversion of $Ph_2PC{\equiv}CCF_3$ into the ligand in (I) occurs in protonic solvents in the presence of metal salts. Reaction of $Ph_2PC{\equiv}CCF_3$ with $PdCl_2(PhCN)_2$ in dry benzene, for example, gives *cis*-$PdCl_2(Ph_2PC{\equiv}CCF_3)_2$ with only the phosphorus atoms of the ligand co-ordinated. Furthermore, *cis*-$PdCl_2(Ph_2PC{\equiv}CCF_3)_2$ is not an intermediate in the formation of (I; M = Pd, X = Cl) since treatment of this complex with $EtOH–H_2O$ afforded a third complex, at present under X-ray study, containing no fluorine and neither $=CH–$ nor CH_2 protons. There was no evidence for σ-bonded complexes similar to those formed in the reaction of $PtCl_2(Ph_2PCH_2C{\equiv}CMe)_2$ with methoxide ion[12] nor complexes derived from simple addition of solvent across the triple bonds of the phosphinoacetylene. Although the detailed mechanism of the reaction has yet to be established, these results confirm previous indications[12] of enhanced reactivity for unco-ordinated $–C{\equiv}C$-bonds held in the proximity of a metal in phosphinoacetylene complexes.

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† The relatively high R value and the large estimated standard deviations are due to the loss of solvent (CH_2Cl_2) during data collection. The drop in the standard reflections of *ca.* 50% limited the data collection to a maximum 2θ value of 90°.

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