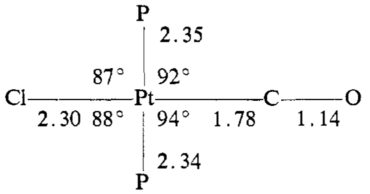
An Unexpected Product in the Reaction of $PtHCl(P(C_2H_5)_3)_2$ with C_2F_4. The Structure of the $PtCl(CO)(P(C_2H_5)_3)_2^+$ Cation and Evidence for the Existence of the SiF_5^- Ion

Sir:

In a recent paper[1] one of us described the reaction of *trans*-$PtHCl(P(C_2H_5)_3)_2$ with C_2F_4 and postulated that one of the low-yield products isolated was a reaction intermediate, $PtHCl(\pi\text{-}C_2F_4)(P(C_2H_5)_3)_2$. We now report that studies of this compound by X-ray diffraction techniques, and further chemical characterization, have not confirmed the structure postulated. The compound is now known to contain the new cation *trans*-$PtCl(CO)(P(C_2H_5)_3)_2^+$, which is isoelectronic with Vaska's compound[2] $IrCl(CO)(PR_3)_2$, where R may be alkyl or aryl. We present evidence here that the anion is SiF_5^- when the reactions are carried out in silica tubes, and that both SiF_5^- and BF_4^- are formed when reactions are carried out in Pyrex glass tubes. The formation of SiF_4 as a by-product had been noted previously,[1] indicating attack by HF on the glass walls of the reaction vessel, but apparently the glass is degraded more thoroughly than had been thought.

A sample of the compound isolated from reactions in Pyrex glass tubes was recrystallized from methyl acetate. The unit cell, as determined from a number of crystals, is orthorhombic, with $a = 9.17$, $b = 16.01$, $c = 14.97$ A; space group: either Pbcm or Pbc2$_1$. A formula weight of 574 is derived from the observed density of 1.73 ± 0.01 g/cm^3 and the assumption of four formula units in the cell. Three-dimensional X-ray data were collected from a crystal of maximum dimension 0.15 mm, with the use of Mo Kα radiation, by procedures previously described.[3] Comparison of the intensities of the hkl and $hk\bar{l}$ reflections indicated that the space group is the polar noncentric one Pbc2$_1$, and this was confirmed by the positions of the Pt, Cl, and P atoms, as determined by Patterson and Fourier methods. By comparison of two least-squares refinements of the positions of the heavy atoms it proved possible to determine the direction of the polar axis at this stage, because of the anomalous scattering of the Pt atom. The positions of the ethyl carbon atoms could now be determined. The P atoms were seen to be *trans*, and the Pt–Cl direction was at right angles to the P–Pt–P axis. Structure factors calculated for this $PtCl(P(C_2H_5)_3)_2$ fragment led to a conventional R factor of 0.104. Inspection of the resulting difference Fourier map revealed no evidence of a π-bonded C_2F_4 fragment. Two strong peaks close to the Pt of heights 4.5 and 6.5 e/A^3 suggested a carbonyl group linearly bound to the Pt atom and completing a planar four-coordinate arrangement around the Pt. At a distance of at least 4 A from the Pt atom was a group of four peaks in tetrahedral arrangement, heights 2–3 e/A^3, and there was a small peak at their center of gravity. These facts suggested refinement of a model corresponding to $PtCl(CO)(P(C_2H_5)_3)_2^+BF_4^-$, and this resulted in an R factor of 0.055. Refinement continues, but at this stage the bond lengths and angles in the cation are



Apart from the ethyl groups, the cation is essentially planar. The small deviations make the coordination tend toward a flattened tetrahedron rather than a square pyramid, and it is thus extremely unlikely that there is a hydrogen atom coordinated to the Pt atom. We conclude that recrystallization of the original sample gave a pure BF_4^- salt, and this is confirmed by comparisons of the infrared spectra of the recrystallized sample with both the original sample (containing both BF_4^- and SiF_5^-) and a sample containing SiF_5^- only.

Further chemical and analytical studies have confirmed the chemical formulation suggested by the X-ray investigation. The original reactions were carried out in Pyrex glass tubes, which are now known to yield a mixture of BF_4^- and SiF_5^- anions, as noted above. On the basis of the analyses reported previously[1] (Found: Pt, 34.4; P, 10.7; F, 12.7), it is not possible to distinguish between the original postulate (Calcd for $PtHCl(C_2F_4)(P(C_2H_5)_3)_2$: Pt, 34.3; P, 10.9; F, 13.4) and the structure suggested by the X-ray study (Calcd for $PtCl(CO)(P(C_2H_5)_3)_2^+BF_4^-$: Pt, 33.5; P, 10.6; F, 13.1). However, treatment of the product with sodium tetraphenylboron led to a water-soluble fraction that contained $NaBF_4$ and Na_2SiF_6. Conductivity studies[1] were consistent with a formulation as a 1:1 electrolyte. The infrared spectrum[1] confirms the presence of the *trans*-$PtCl(P(C_2H_5)_3)_2$ fragment.[4,5] The absorption at 2100 cm^{-1} may equally well be assigned as ν(Pt–H) or ν(C≡O), but the high-resolution mass spectrum of the pyrolysis products of the SiF_5^- salt confirms the presence of carbon monoxide. The sharp absorptions at 1094, 1060, and 881 cm^{-1}, which were previously assigned to C–F modes, are now known to be due to the anions. These spectra will be discussed in detail elsewhere, but we note that a splitting of the tetrafluoroborate ν_3 mode into two sharp absorptions (1094 and 1060 cm^{-1}) has not been reported previously.

The final confirmation of the structure is the rational synthesis of the tetrafluoroborate salt. *trans*-$PtHCl(P(C_2H_5)_3)_2$ reacts with carbon monoxide and aqueous tetrafluoroboric acid under pressure to yield *trans*-bis(triethylphosphine)chlorocarbonylplatinum(II) tetrafluoroborate, $[PtCl(CO)(P(C_2H_5)_3)_2]BF_4$. *Anal.* Calcd for $PtClC_{13}H_{30}P_2OBF_4$: C, 26.9; H, 5.2; B, 1.86; F, 13.1. Found: C, 27.4; H, 5.4; B, 2.0; F, 13.4.

When the original reaction between $PtHCl(P(C_2H_5)_3)_2$ and C_2F_4 is carried out in a silica tube, then the pure SiF_5^- salt can be isolated. That this is a SiF_5^- salt, rather than a SiF_6^{2-} salt, is strongly suggested both by the analytical data and the X-ray molecular weight. *Anal.* Calcd for $PtCl(CO)(P(C_2H_5)_3)_2SiF_5$: C, 25.3; H, 4.9; Si, 4.5; F, 15.4; Pt, 31.6; P, 10.0; Cl, 5.7. Found: C, 24.9; H, 4.6; Si, 4.7; F, 15.2; Pt, 32.2; P, 9.9; Cl, 5.8. This salt is not isomorphous with the BF_4^- analog, although the unit cells are related. The

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[5] H. C. Clark and K. R. Dixon, unpublished observations.

space group is Pbca, with $a = 16.9$, $b = 18.9$, $c = 14.7$ A. The formula weight from these data and the observed density is 611 ($\pm 1\%$) (calcd for $[PtCl(CO)(P(C_2H_5)_3)_2]SiF_5$: 618; calcd for $0.5[PtCl(CO)(P(C_2H_5)_3)_2]_2SiF_6$: 566).

Although the previous conclusions[1] are now known to be incorrect, the reactions described above are remarkable in several ways. (a) The formation of a platinum carbonyl and BF_4^- under such mild conditions, presumably by interaction of C_2F_4 with the glass surface in contact with the hydride, is remarkable. It can be related to, but is more extreme than, the ability of the isoelectronic Ir(I) and Rh(I) systems to abstract carbon monoxide from oxygen-containing organic solvents.[2,6] (b) The cation is isoelectronic with Vaska's compound[2] and may show similar properties. These are being investigated. (c) This is the first reported isolation of the SiF_5^- ion. Further detailed studies of this species are currently in progress.

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Opening the $B_{10}H_{10}^{2-}$ Cage to Produce $B_{10}H_{12}(Et_2S)_2$

Sir:

The preparations of $B_{10}H_{12}(base)_2$ derivatives have been reported from reactions of decaborane with soft bases.[1,2] These have been converted further to the $B_{10}H_{10}^{2-}$ structure by action of more or harder base.[3] We wish to report the synthesis of $B_{10}H_{12}(Et_2S)_2$ from $(NH_4)_2B_{10}H_{10}$, which is the first time, to our knowledge, that the $B_{10}H_{10}^{2-}$ cage has been opened to clearly reestablish the decaborane skeleton.

This reaction takes on further significance with the recent preparation in these laboratories of the $B_{10}H_{10}^{2-}$ ion from simple borohydrides.[4] $B_{10}H_{12}(Et_2S)_2$, other $B_{10}H_{12}(base)_2$ compounds,[2,3] and carboranes,[5] for example, can now be prepared from simple starting materials, by-passing decaborane as an intermediate.

The product is obtained from the reaction of $(NH_4)_2B_{10}H_{10}$ and anhydrous HCl in ethyl sulfide (eq 1).

$$3(NH_4)_2B_{10}H_{10} + 2HCl + 2Et_2S \longrightarrow B_{10}H_{12}(Et_2S)_2 + 2NH_4Cl\cdot(NH_4)_2B_{10}H_{10} \quad (1)$$

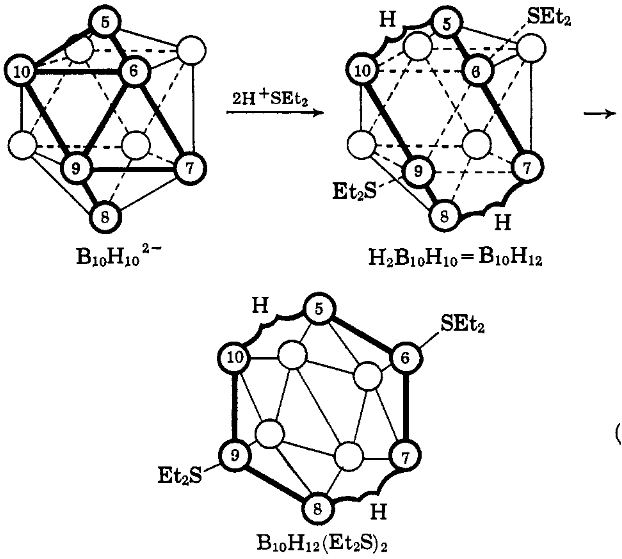
Reaction occurs readily at room temperature. A double salt, $NH_4Cl\cdot(NH_4)_2B_{10}H_{10}$, insoluble in ethyl sulfide, is produced as the by-product. $B_{10}H_{12}(Et_2S)_2$ is recovered in approximately 92% yield based on the above equation from the filtrate by vacuum evaporation of the excess ethyl sulfide. Infrared, X-ray, and nmr comparisons with authentic samples left no doubt as to its identity. The product was somewhat impure but gave elemental analyses approximating the desired compound.

Anal. Calcd for $[(C_2H_5)_2S]_2B_{10}H_{12}$: B, 36.0; C, 31.9; H, 10.6; S, 21.3. Found: B, 34.7; C, 29.6; H, 10.3; S, 20.3.

Work on recovery of the $(NH_4)_2B_{10}H_{10}$ from the double salt by use of other solvents is in progress. With large excesses of HCl the reaction gives some free NH_4Cl and correspondingly higher quantities of $B_{10}H_{12}(Et_2S)_2$. Several samples have been allowed to react with propargyl bromide, and the expected bromomethylcarborane derivative was obtained.[5]

Muetterties has reported obtaining a bridge-hydrogen structure from the $B_{10}H_{10}^{2-}$ ion.[6] Dehydration of an aqueous solution of $(H_3O)_2B_{10}H_{10}$ gave a white solid from which a material could be sublimed. The sublimate showed evidence for bridge hydrogens in its infrared pattern. The unknown had the approximate composition of $B_{10}H_{12}OH_2$. He concluded that the solid belonged to the $B_{10}H_{12}(base)$ or $B_{10}H_{13}^-$ structural class. A referee has pointed out that the formation of $B_{18}H_{22}$ from $B_{20}H_{18}^{2-}$ plus acid involves opening $B_{10}H_{10}$ cages. However, degradation with loss of boron also obviously occurred.[7]

Mechanistically the synthesis of $B_{10}H_{12}(Et_2S)_2$ from $(NH_4)_2B_{10}H_{10}$ can be pictured as just the reverse of the $B_{10}H_{12}(base)_2$ conversion to $B_{10}H_{10}^{2-}$ derivatives. Hawthorne suggests that this latter conversion occurs by the removal of protons from the bridge positions in the $B_{10}H_{12}(base)_2$ structure, and that the resulting filled two-center orbitals undergo a nucleophilic displacement of the coordinated bases. In our reaction, protons which are presumably supplied *via* the ethylsulfonium ion, Et_2SH^+, probably attack in the apex region of the $B_{10}H_{10}^{2-}$ cage. Nmr studies with deuterium chloride have established that hydrogen exchange occurs at the apex borons.[6,8,9] Single crystal X-ray



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