

CHEMISTRY OF METAL HYDRIDES IX. REACTIONS OF *trans*-PtHCl(Et₃P)₂ WITH PERFLUOROCYCLOBUTENE AND PERFLUOROPROPENE AND THE CONVERSION OF A CYCLOBU- TENYL TO A FURYL GROUP

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SUMMARY

Reactions of perfluoropropene and perfluorocyclobutene with *trans*-PtHCl(Et₃P)₂ are described. A product obtained from perfluorocyclobutene is characterized as *trans*-PtCl(Et₃P)₂(C₄F₃O) and probably possesses a furyl group, formed by an unusual rearrangement of a cyclobutenyl group.

INTRODUCTION

We have described previously^{1,2} the unusual reaction of *trans*-PtHCl(Et₃P)₂ with tetrafluoroethylene, leading to the cationic carbonyl salt *trans*-[PtCl(CO)-(Et₃P)₂]⁺X⁻ where X = BF₄⁻ or SiF₅⁻, and two vinylic products, *trans*-PtCl(Et₃P)₂-(CF=CF₂) and *trans*-PtCl(Et₃P)₂[C(CF₂H)=CF₂]. The sequence of reactions involves formation of the tetrafluoroethyl-platinum derivative which loses hydrogen fluoride forming the perfluorovinyl product, *trans*-PtCl(Et₃P)₂(CF=CF₂). This is followed by the SiF₄-catalyzed addition of water to this latter perfluorovinyl compound, with rearrangement to give the carbonyl salt and the second vinylic product. The occurrence of such complex reactions under mild conditions was so unexpected that, as part of our continuing study of hydride and carbonyl compounds of platinum(II), we have explored the extent to which such behavior is general. We now describe in more detail the reactions of perfluoropropene and perfluorocyclobutene with *trans*-PtHCl(Et₃P)₂ and related compounds; because of its cyclic nature, the behavior of perfluorocyclobutene should be of particular interest.

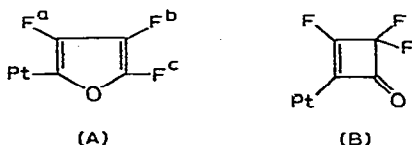
RESULTS AND DISCUSSION

The reaction of perfluoropropene with *trans*-PtHCl(Et₃P)₂ in cyclohexane at 120° gave³ (perfluoropropenyl)chlorobis(triethylphosphine)platinum(II) in reasonable yield, while under comparable conditions perfluorocyclobutene gave (perfluoro-1-cyclobutenyl)chlorobis(triethylphosphine)platinum(II). Neither in these early experiments nor in the current studies was evidence obtained for the addition compounds (e.g. the hexafluoropropyl derivative from the propene), although the formation in

both reactions of silicon tetrafluoride suggests that alkyl compounds are formed but that these readily lose hydrogen fluoride. Treatment of this propenyl product, *trans*-PtCl(Et₃P)₂(CF=CFCF₃) with silicon tetrafluoride and a small amount of water, in benzene in a silica tube, gives *trans*-PtCl(Et₃P)₂(CO)⁺SiF₅⁻. By analogy with the corresponding tetrafluoroethylene reaction, a new vinylic product containing the grouping Pt-C(CFHCF₃)=CFCF₃ might also be formed, but no evidence for its formation has been obtained.

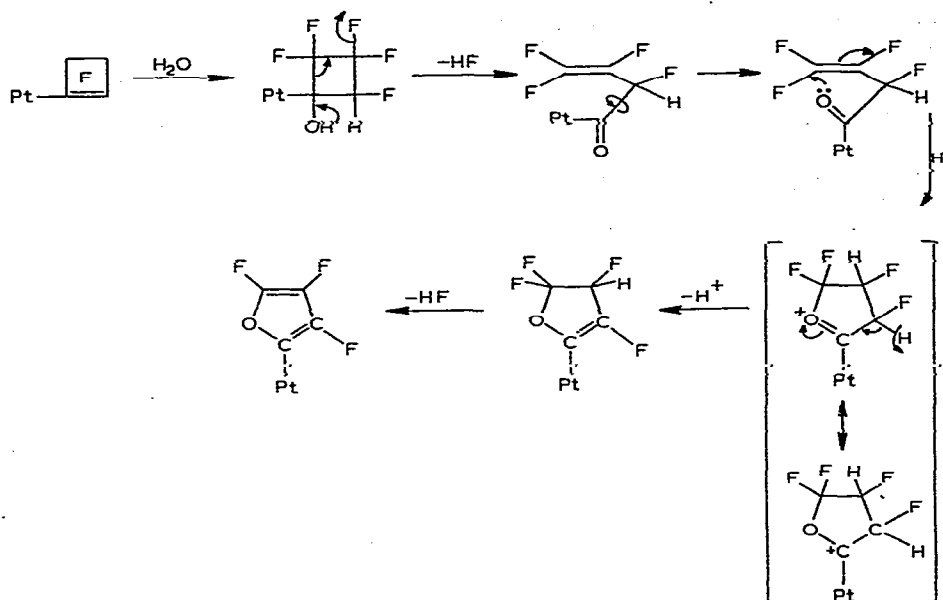
(Perfluoro-1-cyclobutenyl)chlorobis(triethylphosphine)platinum(II) on treatment with silicon tetrafluoride and water gave a good yield of a white crystalline solid, melting at 106–107°, for which the elemental analyses suggested the formula PtCl(Et₃P)₂(C₄F₃O). Additionally, *trans*-PtCl(Et₃P)₂CO⁺SiF₅⁻ was formed, indicating that the same SiF₄-catalyzed addition of water had occurred.

The formation of the grouping PtC₄F₃O is of some interest and two structural possibilities exist, namely (A) and (B).



The IR spectrum of the compound showed strong absorptions at 1578 and 1780 cm⁻¹; these compare with absorptions⁴ at 1480 and 1750 cm⁻¹ for tetrafluorofuran. The ¹⁹F NMR spectrum in CFCl₃ showed absorptions at 104 ppm and 106 ppm in the ratio 1/2. The low field absorption consisted of two doublets arising from coupling of F_a with F_b and F_c (separation 24 Hz), each component of which was further split into a 1/2/1 triplet by phosphorus [*J*(P-F_a) = 3.4 Hz] and a 1/4/1 triplet by ¹⁹⁵Pt [*J*(Pt-F_a) = 65 Hz]. The higher field absorption could not be adequately interpreted, suggesting that some second order splitting effects were also present. The mass spectrum showed an ion at *m/e* = 588 in agreement with a theoretical molecular weight of 587.8 for the formulation, C₁₆H₃₀F₃P₂OClPt. Moreover, a computer-generated mass spectral pattern based on the natural abundance of isotopes in a compound of this formula gave excellent agreement with the overall spectrum, as well as with the relative peak intensities of the components of the absorption centred at *m/e* = 588. Other prominent complex peaks of similar shape to the 588 peak were observed at *m/e* = 495 and *m/e* = 467, corresponding to the loss of C₃F₃ and CO respectively from the parent ion. In addition, the predicted metastable peak (*m/e* = 416.6) arising from the loss of the C₃F₃ fragment is observed at *m/e* = 416–417. It is also of interest that the mass spectrum of tetrafluorofuran shows an intense peak at *m/e* = 93, indicating that a stable C₃F₃⁺ fragment is involved in the fragmentation of tetrafluorofuran.

While some of the above evidence is also consistent with structure (B), these data suggest that the compound most probably has structure (A) and that the mass spectroscopic fragmentation involves loss of a C₃F₃ fragment and formation of a carbonyl species. This unusual reaction therefore involves the conversion on platinum of a cyclobutenyl group to a furyl grouping, for which the following mechanism can be written.



EXPERIMENTAL

The general procedures including instrumentation and analytical facilities have been described previously¹⁻³. The preparation of *trans*-PtHCl(Et₃P)₂ was by Chatt's method⁵. Perfluoropropene was obtained from Columbia Organic Chemical Co. and perfluorocyclobutene from Peninsular ChemResearch Inc. The reactions of *trans*-PtHCl(Et₃P)₂ with these two olefins were performed as described earlier³, leading to the isolation of *trans*-PtCl(Et₃P)₂(CF=CFCF₃) and *trans*-PtCl(Et₃P)₂(C₄F₅), hereafter referred to as (I) and (II) respectively.

(a). Silicon tetrafluoride (1.5 g), (I) (206 mg), and several drops of water with 8 ml benzene were heated in a silica tube at 120° for 48 h. Evaporation of the solvent and extraction of the dark residue with chloroform, followed by recrystallization from ethyl acetate gave a small yield (ca. 40 mg) of *trans*-[PtCl(Et₃P)₂CO]⁺SiF₅⁻ identified spectroscopically¹. The volatile materials from the reaction mixture contained only benzene and some silicon tetrafluoride.

(b). Silicon tetrafluoride (1.0 g), (II) (1.10 g) and several drops of water were heated with benzene in a silica tube at 120° for 48 h. An insoluble white solid was filtered off and the residue was extracted first with ethyl acetate and then with petroleum ether. The petroleum ether extract gave on evaporation, a light yellow solid which showed strong IR absorptions at 1780 and 1578 cm⁻¹. This material was purified by chromatography on a Florisil column with benzene as elutant, to give on evaporation a white crystalline solid, *trans*-PtCl(Et₃P)₂(C₄F₃O) (0.20 g). (Found: C, 33.00; H, 5.13; F, 10.26; osmometric mol.wt., 584. C₁₆H₃₀ClF₃OP₂Pt calcd.: C, 32.70; H, 5.12; F, 9.73%; mol.wt., 587.8.) The second product obtained chromatographically was identified spectroscopically as *trans*-PtCl(Et₃P)₂(C₄F₅) (0.25 g). The ethyl acetate extract of the reaction residue gave, after recrystallization from di-

chloromethane/diethyl ether, *trans*-[PtCl(Et₃P)₂(CO)]⁺SiF₅⁻ (0.035 g), identified by its IR spectrum¹.

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