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REACTIONS OF FLUORO-OLEFINS, CHLORO-OLEFINS AND RELATED MOLECULES WITH CARBONATOBIS(TRIPHENYLARSINE)PLATINUM(II) IN ETHANOL

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SUMMARY

Tetrafluoroethylene, hexafluoropropene, trifluoroethylene or tetracyanoethylene, react with carbonatobis(triphenylarsine)platinum(II) in ethanol at 40° to give the zerovalent platinum–olefin complexes Pt(Olefin)$(AsPh_3)_2$. Hexafluoro-2-butyne similarly gives $Pt(CF_3C{\equiv}CCF_3)(AsPh_3)_2$. Corresponding reactions with chlorotrifluoroethylene, bromotrifluoroethylene or tetrachloroethylene give the vinyl complexes, $PtX(CF{=}CF_2)(AsPh_3)_2$ (X = Cl or Br) and $PtCl(CCl{=}CCl_2)(AsPh_3)_2$ respectively, but tetrabromoethylene and tetraiodoethylene give $PtY_2(AsPh_3)_2$ (Y = Br or I). The olefin complexes $Pt(CF_2{=}CFX)(AsPh_3)_2$ rearrange to vinyl complexes in ethanol at 40° and it is apparent that the triphenylarsine complexes undergo the vinyl rearrangement more readily than the corresponding triphenylphosphine complexes. Lithium iodide is also shown to react with $Pt(C_2F_4)(PPh_3)_2$ in benzene/ethanol at 95° to give $PtI(CF{=}CF_2)(PPh_3)_2$.

INTRODUCTION

We have shown[1] that triphenylarsine is readily displaced from complexes of the type, Pt(Fluoro-olefin)$(AsPh_3)_2$, by a variety of donor ligands to give a convenient synthesis of zerovalent platinum olefin complexes, Pt(Fluoro-olefin)L_2, (L = tertiary phosphine, pyridine; L_2 = 2,2′-bipyridine, 1,10-phenanthroline, 2,5-dithiahexane). The parent triphenylarsine complexes can be obtained by the reaction of a fluoro-olefin with tetrakis(triphenylarsine)platinum(0), but since it has recently been shown[2] that both thermal and photochemical reactions of carbonatobis(triphenylarsine)-platinum(II) in alcoholic solvents provides a convenient source of bis(triphenylarsine)platinum(0) we therefore decided to investigate the usefulness of this system for the synthesis of zerovalent platinum halo-olefin complexes.

RESULTS AND DISCUSSION

Tetrafluoroethylene, hexafluoropropene, trifluoroethylene, tetracyanoethylene and hexafluoro-2-butyne readily react with an ethanolic suspension of carbonatobis(triphenylarsine)platinum(II) at 40° to give high yields of the appropriate olefin complexes, $Pt(olefin)(AsPh_3)_2$ and $Pt(CF_3C{\equiv}CCF_3)(AsPh_3)_2$ which are identical to the complexes previously prepared via tetrakis(triphenylarsine)platinum(0). However, whilst both chlorotrifluoroethylene and bromotrifluoroethylene react with $Pt(AsPh_3)_4$ in benzene solution at room temperature to produce olefin complexes, $Pt(C_2F_3X)(AsPh_3)_2$, (X=Cl[3] or Br), the reactions of these olefins with $Pt(CO_3)(AsPh_3)_2$ in ethanol at 40° give vinyl complexes $PtX(CF{=}CF_2)(AsPh_3)_2$ which are readily characterised by the appearance of a C=C stretching vibration of the trifluorovinyl ligand in their IR spectra as well as platinum–chlorine stretching vibration in the product when X=Cl.

The reactions of both chlorotrifluoroethylene and bromotrifluoroethylene with the carbonate complex could involve an ionic intermediate $(Ph_3As)_2Pt^+{-}CFX{-}CF_2^-$, prior to the formation of the vinyl complexes as has been suggested for some analogous systems[4]. Alternatively intermediate olefins could be formed which subsequently undergo a vinyl rearrangement in the solvent ethanol[5,6]. Some evidence for this latter scheme is provided by the observation that both $Pt(CF_2{=}CFCl)(AsPh_3)_2$ and $Pt(CF_2{=}CFBr)(AsPh_3)_2$ give the corresponding vinyl complexes when suspended in ethanol at 40°. Further since we also find that the reaction of tetrakis(triphenylarsine)platinum(0) with either chloro- or bromotrifluoroethylene in benzene solution at 40° give only vinyl complexes whereas it is known that the corresponding reactions with tetrakis(triphenylphosphine)platinum(0) give olefin complexes[6] it is clear that the triphenylarsine ligands enhance this vinyl rearrangement. In other investigations it has been shown that $Pt(CF_2{=}CFBr)(PMePh_2)_2$ undergoes rearrangement to the vinyl complex more readily than $Pt(CF_2{=}CFBr)(PPh_3)_2$[7].

In some previous studies[8] we have shown that tetrachloroethylene reacts with $Pt(PhC{\equiv}CPh)(PPh_3)_2$ to produce the olefin complex, $Pt(Cl_2C{=}CCl_2)(PPh_3)_2$. However, the analogous reaction with $Pt(PhC{\equiv}CPh)(AsPh_3)_2$ in benzene solution at room temperature gives the vinyl $PtCl(CCl{=}CCl_2)(PPh_3)_2$. In view of these findings it is therefore not surprising to find that tetrachloroethylene reacts with $Pt(CO_3)(AsPh_3)_2$ in ethanol at 40° to give $PtCl(CCl{=}CCl_2)(AsPh_3)_2$. The corresponding reactions with tetrabromoethylene and tetraiodoethylene give the dihalo complexes, $PtX_2(AsPh_3)_2$.

Although triphenylarsine enhances the olefin–vinyl rearrangement it is noteworthy that we have obtained no evidence for the isomerisation of the tetrafluoroethylene complex, $Pt(C_2F_4)(AsPh_3)_2$, to a vinyl complex, the high strength of the carbon–fluorine bond presumably inhibiting this rearrangement. However, treatment of $Pt(C_2F_4)(PPh_3)_2$ with lithium iodide in benzene/ethanol at 95° does produce a vinyl complex, $PtI(CF{=}CF_2)(PPh_3)_2$, [ν(C=C) 1735 cm^{-1}], since the high lattice energy of lithium fluoride formed provides a driving force for the reaction. Below 95°, however, a mixture of $Pt(C_2F_4)(PPh_3)_2$ and $PtI(CF{=}CF_2)(PPh_3)_2$ is obtained.

In conclusion it is apparent that the reactions of fluoro-olefins with the easily prepared $Pt(CO_3)(AsPh_3)_2$ does provide a useful alternative synthesis of fluoro-olefin platinum(0) complexes. However, chloro and bromo substituted olefins lead to vinyl complexes and their formation is enhanced by the presence of triphenylarsine ligands.

EXPERIMENTAL

IR spectra were recorded on a Perkin–Elmer Model 225 spectrophotometer in Nujol mulls between KBr plates (4000–400 cm^{-1}) and polythene discs (400–200 cm^{-1}). M.p.'s were recorded on a Reichert hot-stage apparatus and are uncorrected.

Preparation of carbonatobis(triphenylarsine)platinum(II)

A solution of *cis*-dichlorobis(triphenylarsine)platinum(II)[9] (0.88 g, 1 mmol) in methylene chloride (50 ml) was shaken at room temperature with an excess of freshly prepared silver carbonate (2.0 g, 9 mmol). After 2 h the deep yellow solution became pale yellow and the precipitated silver chloride was filtered off. The filtrate was evaporated under reduced pressure until the complex just began to crystallise. Diethyl ether (100 ml) was then added slowly to the vigorously shaken solution to give white crystals of carbonatobis(triphenylarsine)platinum(II) (0.82 g, 95%). The complex becomes yellow at 190°, decomposes with evolution of gas at 205° and finally melts to an orange-brown oil at 225° and is identical to an authentic sample[10].

Reaction of tetrafluoroethylene with carbonatobis(triphenylarsine)platinum(II)

Excess tetrafluoroethylene was condensed (−196°) into a Carius tube containing a suspension of carbonatobis(triphenylarsine)platinum(II) (0.89 g, 1.0 mmol) in degassed ethanol (20 ml). After mechanical shaking of the tube at 40° for 2 days the colourless crystals which had been deposited were collected and washed with methanol (3 × 5 ml). The product (0.85 g, 94%) was identified as (tetrafluoroethylene)-bis(triphenylarsine)platinum(0) by comparison of its IR and ^{19}F NMR with that of an authentic sample[1]. In a similar manner trifluoroethylene after 3 h gave $Pt(CF_2{=}CHF)(AsPh_3)_2$ (70%). M.p. 142–143°. (Found: C, 51.3; H, 3.6; F, 6.2. $C_{38}H_{31}AsF_3Pt$ calcd.: C, 51.3; H, 3.5; F, 6.4%.) Hexafluoropropene after 2 days gave $Pt(CF_2{=}CFCF_3)(AsPh_3)_2$ (95%)[3]. Tetracyanoethylene after 2 days gave white crystals of $Pt[(CN)_2C{=}C(CN)_2](AsPh_3)_2$ (90%). M.p. >300°. ν(CN), 2152 s. (Found: C, 52.8; H, 3.6; N, 5.3. $C_{42}H_{30}As_2N_4Pt$ calcd.: C, 52.9; H, 3.6; N, 6.0%.) Hexafluoro-2-butyne after 18 h gave $Pt(CF_3C{\equiv}CCF_3)(AsPh_3)_2$ (92%)[11]. Chlorotrifluoroethylene after 18 h gave white crystals of $PtCl(CF{=}CF_2)(AsPh_3)_2$ (74%). M.p. 217–218°. ν(C=C) 1736 m cm^{-1}. ν(Pt–Cl) 315 s cm^{-1}. (Found: C, 49.9; H, 3.4; Cl, 3.9; F, 6.5. $C_{38}H_{30}As_2ClF_3Pt$ calcd.: C, 49.4; H, 3.3; Br, 3.8; F, 6.2%.) Bromotrifluoroethylene gave after 12 h white crystals of $PtBr(CF{=}CF_2)(AsPh_3)_2$ (72%). M.p. 229–230°. ν(C=C) 1733 m cm^{-1}. (Found: C, 47.0; H, 3.1; Br, 8.4; F, 5.8. $C_{38}H_{30}As_2BrF_3Pt$ calcd.: C, 47.1; H, 3.1; Br, 8.3; F, 5.9%.) Tetrachloroethylene gave after 18 h sandy-yellow crystals of $PtCl(CCl{=}CCl_2)(AsPh_3)_2$ (63%). M.p. 156–158°. ν(C=C) 1732 m cm^{-1}, ν(Pt–Cl) 306 cm^{-1}. (Found: C, 46.7; H, 3.2; C, 14.4. $C_{38}H_{30}As_2Cl_4Pt$ calcd.: C, 46.9; H, 3.1; Cl, 14.6%.) Tetrabromoethylene gave after 2 days $PtBr_2(AsPh_3)_2$ (100%). M.p. >300°. (Found: C, 43.9; H, 3.1; Br, 16.9. $C_{36}H_{30}As_2Br_2Pt$ calcd.: C, 44.7; H, 3.1; Br, 17.8%.) Tetraiodoethylene gave after 2 days $PtI_2(AsPh_3)_2$ (100%)[12]. No pure products could be isolated from the reactions of fumaronitrile or 1/1 difluoroethylene with $Pt(CO_3)(AsPh_3)_2$ and no reaction was observed to take place with trifluoroacetonitrile.

Reaction of bromotrifluoroethylene with tetrakis(triphenylarsine)platinum(0)

Excess of bromotrifluoroethylene was condensed (−196°) into a Carius tube containing a suspension of tetrakis(triphenylarsine)platinum(0)[12] (0.72 g, 0.5 mmol) in degassed benzene (20 ml). After shaking the tube for 5 h at room temperature the solution was filtered to remove a small deposit of platinum metal and the filtrate was evaporated to dryness under reduced pressure at room temperature. The white residue was dissolved in methylene chloride (10 ml) and diethyl ether (10 ml) was added. Dropwise addition of petroleum spirit (b.p. 60–80°) and vigorous shaking gave white crystals of (bromotrifluoroethylene)bis(triphenylarsine)platinum(0) which were washed with diethyl ether (0.28 g, 58%) m.p. partially melts at 160° and resolidifies then softens at 230° (dec). (Found: C, 46.9; H, 3.1; Br, 8.3; F, 5.8. $C_{38}H_{30}As_2BrF_3Pt$ calcd.: C, 47.1; H, 3.1; Br, 8.4; F, 5.9%.)

When the above reaction was repeated at 40° a pale yellow solution was obtained. This solution was evaporated to dryness and recrystallisation of the residue from methylene chloride/diethyl ether/petroleum spirit (b.p. 60–80°) gave white crystals of $PtBr(CF{=}CF_2)(AsPh_3)_2$ (0.34 g, 70%) which was identified by its m.p. and IR spectrum.

In a similar manner chlorotrifluoroethylene gave $PtCl(CF{=}CF_2)(AsPh_3)_2$ (0.33 g, 72%).

Isomerisation of the olefin complexes, $Pt(CFX{=}CF_2)(AsPh_3)_2$ *(X = Cl*[3] *or Br) in ethanol.*

A suspension of the olefin complex (0.35 mmol) in ethanol (25 ml) was shaken at 40° for 2 days. During this time long fine white needle-shaped crystals separated. The solution was evaporated to dryness and recrystallisation of the residue from methylene chloride/ethanol gave white crystals of the vinyl complex which was identified by its m.p. and IR spectrum. X = Cl (0.21 g, 91%); X = Br (0.21 g, 87%).

Reaction of tetrachloroethylene with (diphenylacetylene)bis(triphenylarsine)platinum(0)

An excess of tetrachloroethylene (1 ml) was added to a solution of $Pt(PhC{\equiv}CPh)(AsPh_3)_2$[2] in benzene (30 ml). After standing for 15 h at room temperature the solution was evaporated to dryness and the residue was recrystallised from methylene chloride/diethyl ether to give $PtCl(CCl{=}CCl_2)(AsPh_3)_2$ (0.15 g, 62%) which was identified by its m.p. and IR spectrum.

Reaction of (tetrafluoroethylene)bis(triphenylarsine)platinum(0) with lithium iodide

Lithium iodide (0.5 g) and $Pt(C_2F_4)(PPh_3)_2$ (0.6 g) in benzene (20 ml) and ethanol (20 ml) were heated in an evacuated Carius tube for 1 day at 95°. The solution was filtered and the filtrate was evaporated to dryness under reduced pressure. The orange residue was washed with water and the product was recrystallised from methylene chloride/ethanol to afford yellow needles of $PtI(CF{=}CF_2)(PPh_3)_2$ (0.58 g, 85%) m.p. 248–251°. (Found: C, 48.9; H, 3.2; F, 6.0. $C_{38}H_{30}F_3P_2PtI$ calcd.: C, 49.2; H, 3.3; F, 6.1; I, 13.7%) $\nu(C{=}C)$ 1735 m cm^{-1}.

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