Activation of Platinum Complexes by Methyl Fluorosulphonate: Olefin Isomerization and Alkyne Insertion

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Summary Isomerization of oct-1-ene is very effectively catalysed by *trans*-[PtClH$(PMe_2Ph)_2$]–$MeSO_3F$ in dichloromethane, while diphenylacetylene reacts readily with *trans*-[PtClH$(PPh_3)_2$]–$MeSO_3F$ to give *trans*-[Pt(SO_3F)(PhC=CHPh)$(PPh_3)_2$].

WE recently demonstrated that methyl fluorosulphonate can act as a very effective halogen-abstractor towards appropriate transition-metal complexes, and that the diolefin ligand in the cationic complex bis(cyclo-octa-1,5-diene)di-μ-chloro-dipalladium(II) formed from methyl fluorosulphonate and *cis*-dichloro(cyclo-octa-1,5-diene)palladium(II) shows a very high reactivity towards nucleophiles, readily giving bis-(2-methoxycyclo-oct-5-enyl)di-μ-chloro-dipalladium(II) on treatment with neutral MeOH.[1]† We now report that the (presumably solvated) cationic platinum(II) complexes $[PtH(PR_3)_2]^+(SO_3F)^-$ formed from $[PtHCl(PR_3)_2]$ complexes and methyl fluorosulphonate can show high activity towards alkyne-insertion and as catalysts in olefin-isomerization.‡

Methyl fluorosulphonate (0·5 ml) was added to a mixture of oct-1-ene (10 ml) and *trans*-[PtClH$(PMe_2Ph)_2$] (50 mg) in dichloromethane at 35° under nitrogen. After 30 min the olefin composition was oct-1-ene 1%, *trans*-oct-2-ene 93%, and oct-3-ene 6%. The equilibrium composition of 0:46:54 was reached in 300 min. (It is possible that some oct-4-ene was also formed, since this would have not been separated from the 2-ene in our g.l.c. system.) Under the same conditions, isomerization of hex-1-ene to hex-2-ene was complete within 1·5 h, and this compares with the 22% of

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† It also reacts analogously with water in acetone. A very high reactivity towards nucleophiles of the olefin ligands of the cationic dienyl complex $[C_6H_7Fe(CO)_3]^+BF_4^-$ has since been reported.[2]

‡ For a recent summary of reactions of cationic platinum(II) complexes see ref. 3. The complex *trans*-$[PtH(PMePh_2)_2(acetone)]^+$-$(PF_6)^-$ is known to be reactive in olefin insertion.[4]

isomerization during 22 h at 180° observed for catalysis by *trans*-$[PtClH(PEt_3)_2]$ alone.[5] Use of benzene as solvent or hydrogen as the atmosphere led to markedly lower activity of the $[PtClH(PMe_2Ph)_2]$–$MeSO_3F$ system in isomerization of oct-1-ene. Use of *trans*-$[PtClH(PPh_3)_2]$ in place of *trans*-$[PtClH(PMe_2Ph)_2]$ gave a much less effective catalyst.

The only published examples of insertions of alkynes into Pt–H bonds involve the activated acetylenes $CF_3C\vdots CH$ and $CF_3C\vdots CCF_3$, either in prolonged reaction at elevated temperature or under u.v. irradiation,[6] but the latter acetylene is known to insert readily into the Pt–Me bond of $[PtMe(acetone)L_2]^+PF_6^-$ species.[7] We find that treatment of a mixture of diphenylacetylene (0·375 mmol) and *trans*-$[PtClH(PPh_3)_2]$ (0·375 mmol) in benzene (25 ml) with methyl fluorosulphonate (0·08 g), gives during 2 h a precipitate of the known $[Pt_2Cl_2(PPh_3)_4](FSO_3)_2$ (15%) (indicating the occurrence of some hydrogen-abstraction), and addition of n-hexane to the solution gives $[Pt(OSO_2F)(PhC{=}CHPh)(PPh_3)_2]$ (65%), m.p. 112—114° (decomp.), $\nu_{asym}(FSO_2\text{–}O_{uncoord})$ 1350vs; $\nu_{sym}(FSO_2\text{–}O_{uncoord})$ 1230vs; $\delta_{asym}(FSO_2\text{–}O_{uncoord})$ 586m; $\delta_{sym}(FSO_2\text{–}O_{uncoord})$ 582m; $\nu(FSO_2\text{–}O_{coord})$ 1070; $\nu(C{=}C)$ 1550w cm^{-1}; τ(CH) 4·8. Treatment of this with $Et_4N^+Cl^-$ in chloroform gives quantitatively the known[8] *trans*-$[PtCl(PhC{=}CHPh)(PPh_3)_2]$ m.p. 217—218°, $\nu(C{=}C)$ 1560w cm^{-1}. Such use of methyl fluorosulphonate thus seems to offer a new and convenient route to alkenyl–platinum complexes.

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