Formation of Metal Carbonyl Complexes in Reactions with Tetrafluoroethylene

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A recent crystal structure determination[1] has shown that one of the products of the reaction from tetrafluoroethylene and *trans*-$(Et_3P)_2PtHCl$, originally[2] formulated as a π-bonded tetrafluoroethylene complex $(Et_3P)_2PtHCl(\pi\text{-}C_2F_4)$, is in fact a carbonyl complex, *trans*-$(Et_3P)_2PtCOCl^+BF_4^-$. This unusual reaction prompts us to report our experiments on the formation of metal carbonyl complexes in reactions with tetrafluoroethylene and to comment on possible mechanisms for these reactions.

Reaction of $[(C_6F_5)_3P]_4Rh_2Cl_2$[3] in sodium-dried benzene in a sealed glass tube with tetrafluoroethylene at 120° gives a very high yield of *trans*-$[(C_6F_5)_3P]_2RhCOCl$[3] identified by analyses, m.p., and i.r. spectra. Similarly, reaction of tetrafluoroethylene with the complexes $L_4Rh_2Cl_2$ [L = $(C_6F_5)_2(C_6H_5)P$ or $(C_6F_5)(C_6H_5)_2P$] gives high yields of the complexes *trans*-$L_2RhCOCl$ which can also be prepared from the phosphines and $[Rh(CO)_2Cl]_2$. Tetrafluoroethylene and $(Ph_3P)_3RhCl$ in benzene at 120° also gives the carbonyl *trans*-$(Ph_3P)_2RhCOCl$.

The complexes $L_4Rh_2Cl_2$ [L = $(C_6F_5)_3P$ or $(C_6F_5)_2(C_6H_5)P$] in benzene solution do not react with tetrafluoroethylene at room temperature. However, reaction of the complex, L = $(C_6F_5)(C_6H_5)_2P$, with tetrafluoroethylene at room temperature gives the tetrafluoroethylene complex, $L_2Rh(C_2F_4)Cl$, analogous to the complex obtained from $(Ph_3P)_3RhCl$ and tetrafluoroethylene at room temperature.[4]

It has been suggested[1] that the carbon monoxide formed in the reaction of the platinum complex is produced by attack of the tetrafluoroethylene on the glass surface of the sealed tube since silicon tetrafluoride is detected in the gaseous products of reaction. In agreement with this we find silicon tetrafluoride is formed as a by-product in the reactions and that the carbonyl complex $[(C_6F_5)_3P]_2RhCOCl$ is not formed in reactions with tetrachloroethylene or in blank experiments with no added olefin. However, reaction of tetrafluoroethylene with $[(C_6F_5]_3P]_4Rh_2Cl_2$ in benzene in a stainless steel autoclave also gives the carbonyl complex, $[(C_6F_6)_3P]_2RhCOCl$, and it is likely that there is another competing mechanism for the formation of carbon monoxide. Similarly, reaction of tetrafluoroethylene with $(Ph_3P)_3RhCl$ under identical conditions gives $(Ph_3P)_2RhCOCl$ although the yield is less than that obtained in a sealed glass tube. It is possible that the amount of carbonyl complex obtained may be dependent on the type of phosphine bonded to the rhodium.

The amounts of carbonyl complexes isolated can be reduced when the reactions carried out in the stainless steel autoclave are repeated under more rigorous anhydrous conditions suggesting that water may take a part in the formation of the carbonyls. Solvolysis of the tetrafluoroethylene complex, acac $Rh(C_2F_4)(C_2H_4)$, in acetic acid has been reported[5] to give carbon monoxide. Similarly we find that on heating the complex $(Ph_3P)_2Rh(C_2F_4)Cl$ to 120° in wet benzene in a sealed glass tube or steel autoclave $(Ph_3P)_2RhCOCl$ is obtained. In the absence of water only very small amounts of the carbonyl are produced.

Presumably in the reaction of tetrafluoroethylene with the rhodium complexes an olefin complex is formed initially. It is known[4] that tetrafluoroethylene is readily displaced from $(Ph_3P)_2Rh(C_2F_4)Cl$ by carbon monoxide to give $(Ph_3P)_2RhCOCl$. Thus once carbon monoxide has been formed in the sealed glass tube the co-ordinated tetrafluoroethylene would be displaced to give the complexes, $L_2RhCOCl$. In addition, traces of water present could hydrolyse the co-ordinated olefin to give the carbonyl complex and the hydrogen fluoride formed would attack the glass to give silicon tetrafluoride. Since the scale of these experiments involves 0·2 to 0·3 g of rhodium complex only very small amounts of water would be necessary for the hydrolysis.

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