A Two-carbon Atom Insertion into a Metal–Metal Bond

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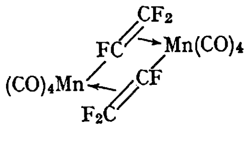
PREVIOUS reports describing metal–metal bonded systems have emphasized synthetic aspects, and few studies have been made of the chemical behaviour of metal–metal bonds. We have previously[1] described the addition of tetrafluoroethylene to compounds containing Sn–Sn bonds, and have now extended this study to a more detailed investigation concerning the conditions under which addition can most readily occur, and involving reactions with a variety of fluoro-olefins. For example, hexamethylditin and perfluoropropene were allowed to react for 8 hr. in a sealed silica tube at 70° under ultraviolet irradiation. The main product was 1,2-bis(trimethylstannyl) hexafluoropropane, $Me_3Sn{\cdot}CF_2{\cdot}CF(CF_3){\cdot}Sn{\cdot}Me_3$, with $Me_3Sn{\cdot}CF_2{\cdot}CFH{\cdot}CF_3$ being characterised as a secondary product. Such insertions into the Sn–Sn bond also occur slowly under ultraviolet irradiation at 20°, and are accelerated by raising the temperature, but do not take place with heating alone, thus suggesting a free-radical mechanism.

More significantly, we have now extended this novel type of reaction to the Sn–Mn bond. The compound[2] $Me_3Sn{\cdot}Mn(CO)_5$ reacted with tetrafluoroethylene in pentane on being heated at 50° under ultraviolet irradiation for 6 hr. The desired product $Me_3Sn{\cdot}CF_2{\cdot}CF_2{\cdot}Mn(CO)_5$ was isolated as a pale yellow solid, and other products included a small amount of carbon monoxide, and some trimethyltin fluoride. In addition, at least three components containing fluorocarbon and manganese carbonyl groups were separated. These are still under investigation; one, on the basis of analytical and molecular weight data and infrared spectrum, is tentatively assigned structure (I).



The reaction probably proceeds in two stages:

$$(a)\quad Me_3Sn{\cdot}Mn(CO)_5 + C_2F_4 \rightarrow Me_3Sn{\cdot}CF_2{\cdot}CF_2{\cdot}Mn(CO)_5$$

$$(b)\quad 2Me_3Sn{\cdot}CF_2{\cdot}CF_2{\cdot}Mn(CO)_5 \rightarrow 2Me_3SnF + [(CO)_4Mn{\cdot}CF{=}CF_2]_2 + 2CO$$

The driving force for reaction (*b*) under the above conditions may be the great stability of crystalline trimethyltin fluoride.[3]

It is significant that the above reaction of tetrafluoroethylene with $Me_3Sn{\cdot}Mn(CO)_5$ does not occur in the absence of ultraviolet irradiation. A mixture of the two reactants heated in pentane at 70° for 10 days gave only polymerized olefin and unchanged $Me_3Sn{\cdot}Mn(CO)_5$. Not only does this appear to be the first instance of direct insertion into a group IVA metal–transition metal bond, but also the qualitative evidence now available indicates that it may occur by a free-radical mechanism.

Adequate analytical data were obtained for the compounds described.

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[3] H. C. Clark, R. J. O'Brien, and J. Trotter, *J. Chem. Soc.*, 1964, 2332.