

Mechanisms of Reactions between Organotin Compounds and Platinum Complexes

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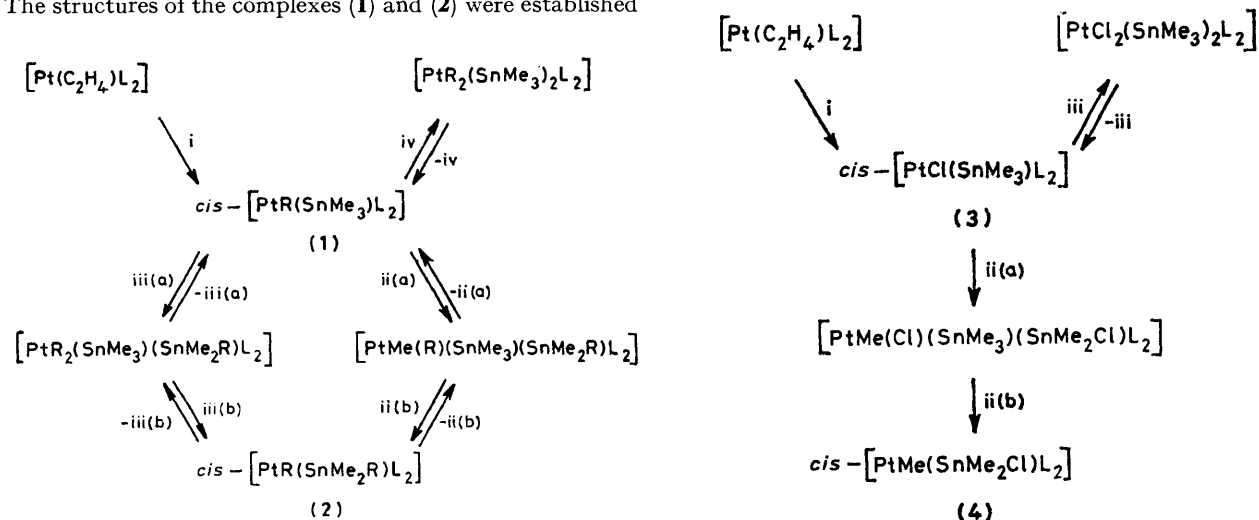
Summary Mechanisms involving Pt^{IV} intermediates are proposed for the homogeneous catalysis by platinum(II) complexes of the redistribution reaction $2\text{SnMe}_3\text{R} \rightleftharpoons \text{SnMe}_4 + \text{SnMe}_2\text{R}_2$ (R = aryl), and for the formation of *cis*-[PtMe(SnMe₂Cl)L₂] (L = PPh₃) from [Pt(C₂H₄)L₂] and SnMe₃Cl.

TREATMENT of [Pt(C₂H₄)L₂] (L = PPh₃) with an excess of an aryltrimethylstannane SnMe₃R in dichloromethane at room temperature gives a mixture of the platinum(II) complexes *cis*-[PtR(SnMe₃)L₂] (1) and *cis*-[PtR(SnMe₂R)L₂] (2), and for R = Ph the mixture catalyses the redistribution reaction (1). Whilst redistribution is well known for $2\text{SnMe}_3\text{R} \rightleftharpoons \text{SnMe}_4 + \text{SnMe}_2\text{R}_2$ (1)

organotin halides, it is known for tetraorganotin compounds only at 50 °C in the presence of Friedel-Crafts catalysts.¹ The structures of the complexes (1) and (2) were established

by ³¹P-¹H and ¹H n.m.r. spectroscopy, which were also used to examine the products of reactions in which (1) or (2) were treated with a variety of tin compounds, *viz.* SnMe₄, SnMe₃R', SnMe₂R', and SnEt₃R' (R' = aryl). The results are consistent with the reactions shown in Scheme 1, in which (2) is formed from (1) *via* addition and elimination processes involving platinum(IV) intermediates. A significant feature is that although the insertion of (1) into the active Sn-R bond of SnMe₃R (step iv) is expected to be faster than the insertion into the Sn-Me bond [step ii(a)], the elimination of a tetraorganotin compound from the platinum(IV) intermediate leads to a new product (2) only in step ii(b).

A similar mechanism involving platinum(IV) intermediates (Scheme 2) accounts for the surprising products from reactions between platinum(0) complexes and triorganotin halides. These reactions were originally reported



SCHEME 1. (L = PPh₃) i, +SnMe₃R, -C₂H₄, ii, (a) +SnMe₃R, (b) -SnMe₄, iii, (a) +SnMe₃R₂, (b) -SnMe₃R, iv, +SnMe₃R.

SCHEME 2. (L = PPh₃) i, +SnMe₃Cl, -C₂H₄, ii, (a) +SnMe₃Cl, (b) -SnMe₃Cl, iii, +SnMe₃Cl.

to form $[\text{PtCl}(\text{SnR}_3)_2\text{L}_2]$ ($\text{L} = \text{phosphine}$, $\text{R} = \text{Me}$, Ph),² but the products are now known to have the isomeric formula $\text{cis-}[\text{PtR}(\text{SnR}_2\text{Cl})(\text{PPh}_3)_2]$ (**4**).³ At temperatures above *ca.* 10 °C, $[\text{Pt}(\text{C}_2\text{H}_4)_2\text{L}_2]$ ($\text{L} = \text{PPh}_3$) reacts with SnMe_3Cl to give $\text{cis-}[\text{PtMe}(\text{SnMe}_2\text{Cl})\text{L}_2]$ (**4**) [$^1J(\text{PtP})$ 2092 and 2474 Hz], but we suggest that the initial product is $\text{cis-}[\text{PtCl}(\text{SnMe}_3)\text{L}_2]$ (**3**), which is rapidly converted into $\text{cis-}[\text{PtMe}(\text{SnMe}_2\text{Cl})\text{L}_2]$ (**4**) *via* insertion of (**3**) into the Sn–Me bond of SnMe_3Cl . The presumably faster reaction of (**3**) with the Sn–Cl bond of SnMe_3Cl is unproductive (steps iii, –iii), and neither (**3**) nor platinum(IV) intermediates are detectable in reaction mixtures by ^{31}P - $\{^1\text{H}\}$ n.m.r. spectroscopy. The complex (**3**) [$^1J(\text{PtP})$ 1939 and 4520 Hz] has been obtained by treatment of a dichloromethane solution of $[\text{PtCl}(\text{SnMe}_3)(\text{cod})]$ {from $[\text{Pt}(\text{cod})_2]$

and SnMe_3Cl ; $\text{cod} = \text{cyclo-octa-1,5-diene}$ } with PPh_3 at –70 °C. Complex (**3**) slowly forms the *trans* isomer in CH_2Cl_2 at –50 °C and the mixture of isomers is rapidly converted into (**4**) in the presence of SnMe_3Cl at temperatures substantially below the lowest at which (**4**) forms from $[\text{Pt}(\text{C}_2\text{H}_4)_2\text{L}_2]$.

The Schemes are consistent with the expected reactivity order $\text{Sn-Cl} > \text{Sn-R} > \text{Sn-Me}$, and the results suggest that catalysis of organotin redistributions or the formation of thermodynamically favoured complexes such as (**4**) are to be expected for transition metal complexes only when a higher oxidation state such as platinum(IV) is accessible.

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