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Preliminary Communication

OXIDATIVE ADDITION REACTIONS OF ORGANOTIN AND ORGANOLEAD COMPOUNDS TO THE PLATINUM(0) COMPLEX $[Pt(C_2H_4)(PPh_3)_2]$. INSERTION OF PLATINUM INTO Sn-C1, Sn-C, and Pb-C BONDS[†]

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SUMMARY

The products of the reactions between $[Pt(C_2H_4)(PPh_3)_2]$ and a wide range of compounds SnR₃X, SnArMe₃, SnR₂X₂, SnRX₃ and SnX₄ have been determined; insertion of platinum into the Sn-R, Sn-Ar or Sn-X bond occurs depending on the nature of the tin substrate. The compounds Sn₂Ph₆ and Pb₂Ph₆ give products <u>cis</u>-[PtPh(PPh₃)₂(M₂Ph₅)] (M = Sn, Pb).

Reactions of platinum(0) complexes with SnPh_3Cl and SnMe_3Cl were first reported to give complexes [PtCl(PPh}_3)_2(SnR}_3)] (R = Ph, Me) [1,2], but work in this laboratory [3] has shown that these and other tin compounds SnR_3X [R = Ph, X = Cl, Br, I, OH, ONO₂; R = Me, X = Cl] react with [Pt(C_2H_4)(PPh}_3)_2] to give products <u>cis-[PtR(PPh}_3)_2(SnR}_2X)</u>] which result from insertion of platinum into the Sn-R bonds and not the Sn-X bonds as was previously assumed. It was also shown that SnPh₄ gave <u>cis-[PtPh(PPh}_3)_2(SnPh}_3)</u>], and that an analogous complex could be obtained from SnMe₄ and a more reactive platinum(0) complex [3]. We have now extended our study of the reactions (in dichloromethane) of [Pt(C_2H_4)(PPh_3)_2] with organic derivatives of Group IV elements SnR}_3X (R = Ph, X = OMe, OSnPh}_3; R=Me,

⁷No reprints available.

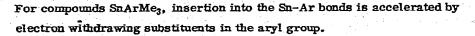
X = Br, NMe₂, OAc; R=Et, X = Cl, Br; R = n-Bu, n-heryl, benzyl, X = Cl), SnArMe₃ (Ar = o-Me-, p-Me-, o-MeO-, m-MeO, p-MeO-, o-Cl-, m-Cl-, p-Cl-, m-F-, p-F-, p-Br-, m-Me₃Sn-, p-Me₃Sn-, p-Ph-, p-MeS-C₆H₄), SnR₂X₂ (R = Ph, Me, n-Bu, X = Cl, Br; R = Et, n-heryl, benzyl, X = Cl), SnRX₃ (R = Ph, Me, X = Cl), and SnX₄ (X = Cl, Br). The structure of the products could be reliably inferred from the form and the parameters of the ³¹P- $\{^{1}H\}$ n. m. r. spectra [3]; analytical results were also satisfactory in all cases examined.

The listed compounds SnR_3X gave complexes $\underline{cis} - [PtR(PPh_3)_2(SnR_2X)]$ and the compounds $SnArMe_3$ reacted in a manner consistent with that found previously for $SnMe_nPh_{3-n}$ Cl (n = 1,2) [3] giving $\underline{cis} - [PtAr(PPh_3)_2(SnMe_3)]$. The compounds $SnPh_2X_2$ (X=Cl, Br) reacted in a similar manner to give $\underline{cis} - [PtPh(PPh_3)_2(SnPhX_2)]$, but the compounds SnR_2X_2 in which R was an alkyl group gave mixtures of \underline{cis} - and \underline{trans} -isomers of $[Pt(PPh_3)_2(SnR_2X)X]$. Insertion of platinum into the Sn-X bonds also occurred for $SnRX_3$ for R = Ph or alkyl, and for SnX_4 .

It has been reported that Pb_2Ph_6 reacts with $[Pt(PPh_3)_4]$ to give $[Pt(PPh_3)_2(PbPh_3)_2]$ (PbPh_3)₂] which decomposes in chlorinated solvents to give $[PtPh(PPh_3)_2(PbPh_3)]$ [4]. We have shown that <u>cis</u>- $[PtPh(PPh_3)_2(PbPh_3)]$ may be obtained directly from PbPh₄ and $[Pt(C_2H_4)(PPh_3)_2]$ and that it is also obtained in the manner previously described from the product of the reaction between Pb_2Ph_6 and $[Pt(C_2H_4)(PPh_3)_2]$. However, the ³¹P- $\{^iH\}$ n.m.r. spectrum shows that this latter reaction gives a complex with non-equivalent phosphorus nuclei with coupling constants $^1J(Pt-P)$ which indicate the formulation <u>cis</u>- $[PtPh(PPh_3)_2(Pb_2Ph_5)]$, and a similar product cis- $[PtPh(PPh_3)_2(Sn_2Ph_5)]$, has been obtained from $[Pt(C_2H_4)(PPh_3)_2]$ and Sn_2Ph_6 .

Competition experiments in which 1 mol $[Pt(C_2H_4)(PPh_3)_2]$ are mixed with 1 mol each of two tin compounds in dichloromethane and the products examined <u>via</u> the ³¹P- $\{^{1}H\}$ spectra have enabled us to draw a number of conclusions about these reactions:-

- 1. The rates of insertion of platinum into Sn-C or into Sn-Cl bonds of R_nSn-Cl_{4-n} (R=Ph, Me) increase with increasing number of chlorine atoms on tin; the insertion into Sn-Cl is more sensitive to the number of chlorine atoms and is faster for R=Me than for R=Ph.
- 2. The Sn-Ar bonds are always more reactive than Sn-alkyl bonds in the same compound or in compounds that are otherwise identical. The changes in the nature of the products in the series $R_n SnCl_{4-n}$ (R = Ph, Me) are consistent with these trends in rate.



3.

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