*Journal of Organometallic Chemistry*, 144 (1978) C23—C25
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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-Cl, Sn-C, and Pb-C BONDS†

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(Received November 1st, 1977)

## SUMMARY

The products of the reactions between [Pt($C_2H_4$)($PPh_3$)$_2$] and a wide range of compounds $SnR_3X$, $SnArMe_3$, $SnR_2X_2$, $SnRX_3$ and $SnX_4$ 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 $Sn_2Ph_6$ and $Pb_2Ph_6$ give products cis-[PtPh($PPh_3$)$_2$($M_2Ph_5$)] (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, $ONO_2$ ; R = Me, X = Cl ] react with [Pt($C_2H_4$)($PPh_3$)$_2$] to give products cis-[PtR($PPh_3$)$_2$($SnR_2X$) ] 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 $SnPh_4$ gave cis-[PtPh($PPh_3$)$_2$($SnPh_3$)], and that an analogous complex could be obtained from $SnMe_4$ 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,

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† No reprints available.

$X = Br, NMe_2$, OAc; R = Et, X = Cl, Br; R = n-Bu, n-hexyl, benzyl, X = Cl), $SnArMe_3$ (Ar = o-Me-, p-Me-, o-MeO-, m-MeO, p-MeO-, o-Cl-, m-Cl-, p-Cl-, m-F-, p-F-, p-Br-, m-$Me_3Sn$-, p-$Me_3Sn$-, p-Ph-, p-MeS-$C_6H_4$), $SnR_2X_2$ (R = Ph, Me, n-Bu, X = Cl, Br; R = Et, n-hexyl, benzyl, X = Cl), $SnRX_3$ (R = Ph, Me, X = Cl), and $SnX_4$ (X = Cl, Br). The structure of the products could be reliably inferred from the form and the parameters of the $^{31}P-\{^1H\}$ n.m.r. spectra [3]; analytical results were also satisfactory in all cases examined.

The listed compounds $SnR_3X$ gave complexes 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 cis-$[PtAr(PPh_3)_2(SnMe_3)]$. The compounds $SnPh_2X_2$ (X=Cl, Br) reacted in a similar manner to give cis-$[PtPh(PPh_3)_2(SnPhX_2)]$, but the compounds $SnR_2X_2$ in which R was an alkyl group gave mixtures of cis- and 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 $[Pt(PPh_3)_2(PbPh_3)_2]$ which decomposes in chlorinated solvents to give $[PtPh(PPh_3)_2(PbPh_3)]$ [4]. We have shown that cis-$[PtPh(PPh_3)_2(PbPh_3)]$ may be obtained directly from $PbPh_4$ 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 $^{31}P-\{^1H\}$ 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 cis-$[PtPh(PPh_3)_2(Pb_2Ph_5)]$, 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 via the $^{31}P-\{^1H\}$ 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 $R_nSnCl_{4-n}$ (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 $R_nSnCl_{4-n}$ (R=Ph, Me) are consistent with these trends in rate.
3. For compounds $SnArMe_3$, insertion into the Sn-Ar bonds is accelerated by electron withdrawing substituents in the aryl group.

## ACKNOWLEDGEMENTS

We thank the Science Research Council for the award of a Research studentship, and Chugoku Marine Paints, Ltd., for a generous gift of dichlorodimethyltin.

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