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Preliminary communication

ARYL—TIN COMPOUNDS AS REAGENTS FOR THE FORMATION OF ARYL—TRANSITION METAL BONDS

COLIN EABORN*, KEVIN ODELL and ALAN PIDCOCK*
School of Molecular Sciences, University of Sussex, Brighton BN1 9QJ (Great Britain)
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Summary

In complexes of platinum and rhodium, active anionic ligands can be replaced by aryl groups by use of aryltrimethyltin reagents under mild conditions.

The complex $[PtCl_2(COD)]$ (COD = cycloocta-1,5-diene) reacts with a wide range of aryltrimethyltin compounds in dichloromethane according to Scheme 1.

$$[PtCl_2(COD)] + ArSnMe_3 \rightarrow [PtClAr(COD)] + SnClMe_3$$

$$[PtClAr(COD)] + Ar'SnMe_3 \rightarrow [PtArAr'(COD)] + SnClMe_3$$

SCHEME 1

Mono-aryl complexes (Ar = 2-benzo[*b*]furyl, 2-benzo[*b*]thienyl, 3-(1,2-dihydrobenzo)cyclobutenyl, 2-furyl, 2-thienyl, 4-chlorophenyl, 4-methylphenyl, 4-methoxyphenyl, 4-(trimethylsilyl)phenyl) have been obtained by use of stoichiometric proportions of reactants, bis-aryl complexes (Ar = Ar′ = 2-benzo[*b*]furyl, 2-benzo[*b*]thienyl, 3-(1,2-dihydrobenzo)cyclobutenyl, 2-furyl, 2-thienyl, phenyl, 4-bromophenyl, 4-t-butylphenyl, 3-fluorophenyl, 2-, 3-, and 4-methoxyphenyl, 4-methylphenyl, 3-(trifluoromethyl)phenyl, 4-(trimethylsilyl)phenyl) by use of 2.5 molar proportions of tin reagents, and mixed aryl complexes (Ar = 2-benzo[*b*]furyl, Ar′ = 4-methylphenyl; Ar = 2-thienyl, Ar′ = 2-furyl, 4-methoxyphenyl) by use of 1.5 molar proportions of $Ar'SnMe_3$ with the complexes $[PtClAr(COD)]$. The complex $[Pt\{(C_6H_4Me\text{-}4\text{-}\eta)Cr(CO)_3\}_2COD]$ has also been obtained from the tricarbonylchromium derivative of $4\text{-}MeC_6H_4SnMe_3$. Yields are high (> 80%), and almost pure products are obtained directly by taking off the solvent under vacuum and washing the residue with a small quantity of ether to remove $SnClMe_3$ and unchanged $ArSnMe_3$. Use of the aryl—tin compounds clearly has special

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*Authors to whom correspondence should be addressed.

importance (in addition to general advantages such as cleaner reactions, higher yields, and avoidance of any hydrolysis step) when the corresponding aryl—Grignard or —lithium reagents are not available, as for example, for Ar = 3-(1,2-dihydrobenzo)cyclobutenyl [1] or $(C_6H_4Me\text{-}4\text{-}\eta)CrCO_3$ [2].

The reactivities of the $ArSnMe_3$ compounds vary widely, and the qualitative sequence of the ease of reaction parallels that established for cleavage of the Ar—MMe_3 bonds (M = Si, Ge, Sn) by a range of electrophiles [3], suggesting that the reactions may be regarded as electrophilic aromatic substitutions. Reactions of active tin compounds (Ar = 2-benzo[*b*]furyl, 2-benzo[*b*]thienyl, 2-furyl, 2-thienyl) are complete at room temperature within a few hours. With less active tin compounds it is necessary to reflux the reaction mixtures, since reactions at room temperature take several days and may give only the mono-aryl complexes (Ar = phenyl, substituted phenyl).

Aryl complexes with ligands L such as phosphines, arsines, 2,2′-bipyridyl and the carbene $CN(Me)CH_2CH_2NMe$ [4] are easily obtained by displacement of COD. The ^{31}P—$\{^1H\}$ NMR spectra of the phosphine complexes in dichloromethane show that the bis-aryl complexes are *cis*, but the mono-aryl complexes $[PtClArL_2]$ are *trans* or predominantly *trans* in solution, except when L_2 = 1,2-bis(diphenylphosphino)ethane.

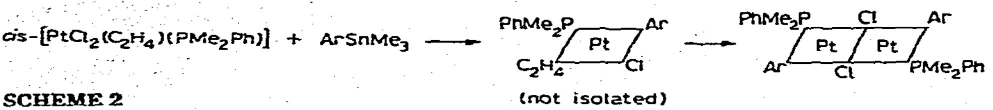
The complexes *cis*-$[PtCl_2L_2]$ (L = phosphine) do not react with $ArSnMe_3$, perhaps due to the lower *trans* effect of phosphine compared with olefin ligands [5]. The complexes *cis*-$[Pt(O_2CCF_3)_2L_2]$ (L = PMe_2Ph, PEt_2Ph) are much more reactive, forming *trans*-$[Pt(O_2CCF_3)ArL_2]$ with $ArSnMe_3$ (Ar = XC_6H_4, with X = *o*-Me, *p*-OMe, or *m*-F) at room temperature. A small proportion of *cis*-$[PtAr_2L_2]$ is also formed, and this product is favoured in reactions carried out under reflux. The *cis*-$[Pt(O_2CCF_3)_2L_2]$ complexes will react even with alkyl—Sn bonds, as shown by the interaction of *cis*-$[Pt(O_2CCF_3)_2](PMe_2Ph)_2]$ and Me_4Sn to give *trans*-$[PtMe(O_2CCF_3)(PMe_2Ph)_2]$ quantitatively after 16 h at room temperature or after 4 h under reflux in benzene.

In some other systems to be described later, the $ArSnMe_3$ compounds appear to transfer Me ligands even more readily than Ph ligands to Pt.

As expected, the reactivity of Group IV compounds in this type of reaction appears to decrease in the sequence Pb > Sn > Ge > Si. We obtained $[PtPh_2(COD)]$ from $[PtCl_2(COD)]$ and $PhPbMe_3$ after a few hours at room temperature, whereas $ArGeMe_3$ gave $[PtAr_2(COD)]$ (Ar = 2-benzo[*b*]furyl) from $[PtCl_2(COD)]$ after 23 h at 90°; at room temperature [PtArCl(COD)] was formed in only 10% yield after 5 days. Treatment of $[PtCl_2(COD)]$ with $ArSiMe_3$ having Ar = 2-methoxyphenyl for 15 h at 90° gave no indication of reaction, but with Ar = 2-furyl a 15% yield of [PtClAr(COD)] was obtained after 30 h at 90°.

The labilizing effect of olefins is also indicated by reaction of *cis*-$[PtCl_2(C_2H_4)(PMe_2Ph)]$ with $ArSnMe_3$ (Scheme 2, Ar = 3-t-butylphenyl, 2-benzo[*b*]furyl). The complexes *cis*-$[PtCl_2(CO)(PR_3)]$ form analogous chlorine-bridged complexes, but with ArCO ligands instead of Ar. From the ^{31}P—$\{^1H\}$spectra both classes of bridged complexes appear to be comprised of *cis* and *trans* isomers in solution, and both undergo the usual bridge cleavage reaction with two molar equivalents of donors such as amines or phosphines.

Although *mer*-$[RhCl_3(PMe_2Ph)_3]$ does not react with $2\text{-}MeOC_6H_4SnMe_3$, the complex *mer*-$[RhCl_2(SO_3F)(PMe_2Ph)_3]$ [6], which has the better leaving group



SCHEME 2

SO_3F^- *trans* to phosphorus, gives a product with two sets of ^{31}P resonances with parameters $^1J(Rh—P) = 95$ Hz (doublets, $I = 2$), $^1J(Rh—P) = 78$ Hz (triplets, $I = 1$, $^2J(PRhP) = 24$ Hz. The small magnitude of $^1J(Rh—P)$ for the unique phosphine indicates that the complex should be formulated *mer*-[$RhCl_2(C_6H_4OMe$-*o*)-$(PMe_2Ph)_3$] with the aryl group *trans* to the unique phosphine. It is noteworthy that Grignard and organolithium reagents do not give identifiable products with Rh^{III} complexes [7].

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