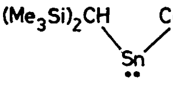
Catalysis and Solvent Participation in Organometallic Oxidative Additions ($Pt^0 \rightarrow Pt^{II}$ and $Sn^{II} \rightarrow Sn^{IV}$)†

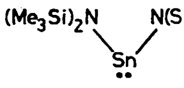
By MICHAEL J. S. GYNANE, MICHAEL F. LAPPERT,* STUART J. MILES, and PHILIP P. POWER
(*School of Molecular Sciences, University of Sussex, Brighton* BN1 9QJ)

Summary The oxidative addition of (i) PhBr to SnR_2 or $Sn(NR'_2)_2$, or (ii) Bu^nCl to $Sn(NR'_2)_2$ [R = $(Me_3Si)_2CH$, R′ = Me_3Si] is catalysed by a trace of the more reactive halide EtBr, and when tetrahydrofuran is the solvent, rather than C_6H_6, a larger proportion of the product is the Sn^{IV}-dihalide rather than the Sn^{IV}–1:1 adduct; the solvent effect is also shown in the $[Pt(PPh_3)_3]$–MeI system, and both catalysis (for $Pt^0 \xrightarrow{PhBr} Pt^{II}$ by azobisisobutyronitrile) and solvent effects are interpreted in terms of radical-chain processes.

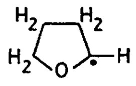
WE report two new factors (catalytic and solvent) which are relevant to discussions of mechanisms of organometallic oxidative additions. These are illustrated by the reaction of an alkyl or aryl halide with an Sn^{II} (s^2) or Pt^0 (d^{10}) substrate to give an Sn^{IV} (d^{10}) or Pt^{II} (d^8) product. Thus, a trace of a 'reactive' alkyl halide catalyses the addition of a less-reactive halogeno-hydrocarbon R″X to an Sn^{II} alkyl or amide to give a Sn^{IV}–R″X adduct, a trace of azobisisobutyronitrile (AIBN) under u.v. irradiation catalyses the addition of PhBr to $[Pt(PPh_3)_3]$, and the use of tetrahydrofuran (thf) as solvent in such a reaction, rather than a hydrocarbon, favours the formation of a dihalogeno–Sn^{IV} (or –Pt^{II}) adduct. We were led to the alkyl halide catalyst effect by noting that the formation of a Grignard reagent (*i.e.*, a $Mg^0 \rightarrow Mg^{II}$ oxidative addition) may be initiated by a trace of ethyl iodide.



(1)



(2)



(3)

Both the tin(II) alkyl (**1**), SnR_2, and amide (**2**), $Sn(NR'_2)_2$ were previously shown to undergo oxidative addition of an alkyl or aryl halide R″X to give $SnR_2(R'')X$ or $Sn(NR'_2)_2$-(R″)X by a free-radical pathway.[1] We now report that the presence of a trace (*ca.* 2 mole %) of ethyl bromide (i) enhances the rate of reaction of an aryl bromide with (**1**) or (**2**), and (ii) permits the reaction of n-butyl chloride with (**2**) to be observed; there is no reaction at 20 or 80 °C in n-hexane in the absence of EtBr. Point (i) is further illustrated by the first-order plot in the Figure; the catalysed reaction has the significantly higher (2·3-fold) rate constant. Similar pairs of plots, but using molar ratios of 9, 11, or 13PhBr : 1SnR_2, afforded comparable results. The corresponding reaction between $Sn(NR'_2)_2$ and PhBr in molar ratio 1:8 in C_6H_6 (0·4 M in amide) at 32 °C is appreciably slower, $k = 7 \times 10^{-5}\ s^{-1}$; in the presence of EtBr ($2{\cdot}5 \times 10^{-3}$ M per 1 mol amide), $k = 1{\cdot}8 \times 10^{-4}\ s^{-1}$.

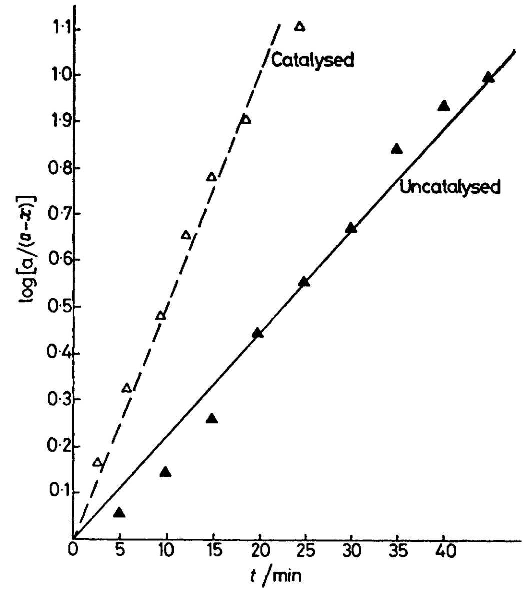
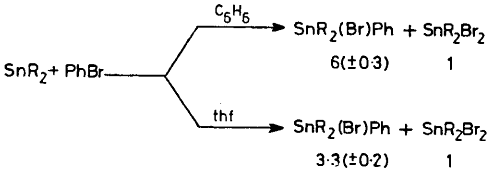
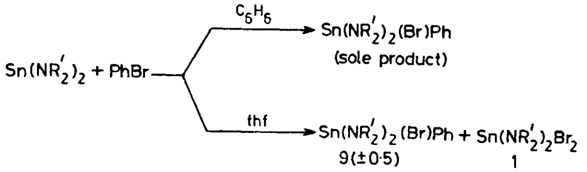


FIGURE. First-order plot for the reaction of PhBr (1 M) with SnR_2 (0·143 M) in benzene at 32 °C in the absence (———: *k* 9 × $10^{-4}\ s^{-1}$) or presence (- - - -) of a trace (*ca.* 2 × 10^{-3} M) of EtBr.

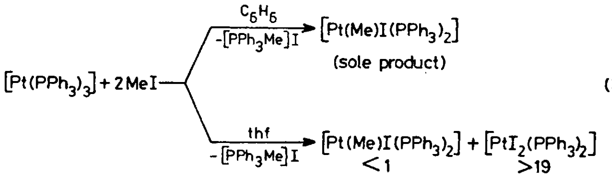
Solvent participation in oxidative addition is exemplified by equations (1)—(3), showing product ratios (obtained from



(1)



(2)



(3)

---

† No reprints available.

^{1}H n.m.r. spectroscopy; average of 6 runs, e.s.d.'s in parentheses) using equimolar [equations (1) or (2)] or excess [2 mol of MeI, equation (3), to allow for phosphonium salt formation] portions of R″X; these were reactions in absence of EtBr.

The above data, together with earlier results (e.s.r. or optical activity) for a free radical process,[1] leads to the suggested main pathway in reactions (a)—(d) for the catalysis (illustrated for SnR_2–PhBr in the presence of EtBr). Further evidence is: step (d) is expected to be fast

$$\left.\begin{aligned} SnR_2 + EtBr &\xrightarrow{(a)} \cdot SnR_2Br + Et\cdot \\ \cdot SnR_2Br + PhBr &\xrightarrow{(b)} SnR_2Br_2 + Ph\cdot \end{aligned}\right\}\text{Initiation}$$

$$\left.\begin{aligned} SnR_2 + Ph\cdot &\xrightarrow{(c)} \cdot SnR_2Ph \\ \cdot SnR_2Ph + PhBr &\xrightarrow{(d)} SnR_2(Br)Ph + Ph\cdot \end{aligned}\right\}\text{Propagation}$$

e.g.,[2] the absolute rate constant for the analogous $\cdot SnBu^n{}_3$–alkyl bromide reaction in cyclohexane at 25 °C is *ca.* 10^7 mol^{-1} s^{-1}), (ii) the reaction rate is increased by illumination (250 W medium-pressure Hg lamp) [*cf.*[3] $Sn(\eta\text{-}C_5H_5)_2$–R″X system], and (iii) $\cdot SnR_3$ (*cf.* ref. 4) reacts instantly with PhBr to give SnR_3Br, which has clear analogy with step (d).

An alternative to the above mechanism involves step (a) followed by PhBr + Et$\cdot \xrightarrow{(e)}$ Ph$\cdot$ + EtBr, when (a) and (e) comprise the propagation cycle and Ph$\cdot$ + $\cdot SnR_2Br \xrightarrow{(f)} SnR_2(Br)Ph$ becomes the principal path to Sn^{IV} adduct.

The oxidative addition of an aryl halide to a Pt^0 complex appears to have no precedent.[5] The reaction of $[Pt(PPh_3)_3]$ + 8PhBr in benzene (*ca.* 2×10^{-1} M) gave *cis*-$[PtBr(PPh_3)_2Ph]$ (> 70%) + PPh_3 in *ca.* 40 h at 20 °C; in the presence of AIBN (*ca.* 6×10^{-3} M) under photolysis after *ca.* 5 h, the reaction was *ca.* 30% complete, and in the absence of AIBN *ca.* 20% complete. These percentages were obtained from 3 pairs (*i.e.*, with or without AIBN) of experiments and each yield (obtained by gravimetry; the 1:1 adduct is the sole C_6H_6-insoluble component) was ±2% from the quoted mean. Neither I_2 nor MeI appeared to behave as a catalyst in the $[Pt(PPh_3)_3]$–PhBr reaction, probably because the formation of $[PtI(PPh_3)_2X]$ (X = I or Me) was instantaneous at 20 °C. In control experiments, the reaction of $[Pt(PPh_3)_3]$ (*ca.* 0.33 mmol) with PhBr (*ca.* 30 mmol) in C_6H_6 (10 ml) was allowed to proceed for 16 h at 20 °C (a) with and (b) without irradiation; there was only a slight (*ca.* 10%) rate enhancement for (a) compared with (b), in contrast (see above) to (c) the *ca.* 50% for AIBN and irradiation.

AIBN gave non-radical products both with SnR_2 (*cf.* ref. 4) or $Sn(NR'_2)_2$, and not unexpectedly AIBN was not a catalyst in the SnR_2–PhBr or $Sn(NR'_2)_2$–Bu^{n}Cl systems.

The intervention of tetrahydrofuran in the reaction pathway is conveniently accommodated within the proposed mechanisms: thus, the radical Et$\cdot$ or Ph$\cdot$ rapidly abstracts a hydrogen atom from thf to generate (**3**). The radical (**3**) is more bulky than a primary alkyl radical and hence the 1:1 adduct formation competes less effectively with dihalide formation than if a hydrocarbon is used as solvent. Another recent example of such a 'thf effect' is in the reaction $[Mo(N_2)_2(dppe)_2] \xrightarrow{R''X} [Mo(N_2R'')(X)(dppe)_2]$ (in C_6H_6) or $[Mo\{N_2\overline{CH(CH_2)_3O}\}(dppe)_2X]$ (in thf) (dppe = $Ph_2PCH_2CH_2PPh_2$); thus, either R″$\cdot$ or (**3**) attacks the ligating dinitrogen.[6]

We thank I.C.I. Ltd. for the award of a Fellowship to M.J.S.G., the S.R.C. for a studentship to S.J.M. and other support, and Drs. M. H. Ford-Smith and R. A. Jackson for discussions.

(*Received*, 13*th September* 1977; *Com.* 955.)

---

[1] M. J. S. Gynane, M. F. Lappert, S. J. Miles, and P. P. Power, *J.C.S. Chem. Comm.*, 1976, 256.

[2] D. L. Carlsson and K. U. Ingold, *J. Amer. Chem. Soc.*, 1968, **90**, 7047.

[3] K. D. Bos, E. J. Bulten, and J. G. Noltes, *J. Organometallic Chem.*, 1975, **99**, 397.

[4] A. Hudson, M. F. Lappert, and P. W. Lednor, *J.C.S. Dalton*, 1976, 2369.

[5] M. F. Lappert and P. W. Lednor, *Adv. Organometallic Chem.*, 1976, **14**, 345.

[6] J. Chatt, R. A. Head, G. J. Leigh, and C. J. Pickett, *J.C.S. Chem. Comm.*, 1977, 299.