Free Radicals as Intermediates in the Oxidative Addition of Alkyl Halides to Platinum(0)

By MICHAEL F. LAPPERT* and PETER W. LEDNOR
(*School of Molecular Sciences, University of Sussex, Brighton* BN1 9QJ)

Summary Free radicals are implicated in the oxidative addition of an alkyl halide RX (MeI, CD_3I, EtI, or $PhCH_2Br$) to $Pt(PPh_3)_3$, as shown by identifying (e.s.r.) the derived nitroxide $Bu^t(R)NO\cdot$ using Bu^tNO as a spin trap; a non-chain mechanism is proposed, with the formation of $[Pt^IX(PPh_3)_2]\cdot$ as rate limiting.

We offer definitive evidence, principally e.s.r., that the formally two-electron oxidative ($\mathrm{Pt^0} \rightarrow \mathrm{Pt^{II}}$) addition of an alkyl halide RX to $\mathrm{Pt(PPh_3)_3}$ yielding *trans*-$\mathrm{PtX(R)(PPh_3)_2}$ proceeds in discrete one-electron steps, with the free radical R·, and probably a halogenoplatinum(I) species such as (I), as intermediates. The following halides were examined: MeI, $\mathrm{CD_3I}$, EtI, $\mathrm{PhCH_2Br}$, and $\mathrm{Ph_3CCl}$. An important feature of this study is the use of the spin trap $\mathrm{Bu^tNO}$ (*cf.*, ref. 1 for its previous use in transition-metal chemistry), which with R· affords the nitroxide $\mathrm{Bu^t(R)NO}$·. The principal data to support our conclusion are (i) the identification of the nitroxide $\mathrm{Bu^t(R)NO}$· for R = Me, $\mathrm{CD_3}$, Et, or $\mathrm{PhCH_2}$, each of which has previously been characterised by e.s.r. (ii) the demonstration that in these systems $\mathrm{Bu^tNO}$ does not significantly change the course of reaction yielding *trans*-$\mathrm{PtX(R)(PPh_3)_2}$; (iii) the formation of the stable and readily identifiable (e.s.r.) trityl radical $\mathrm{Ph_3C}$·, in appropriate equilibrium concentration with its dimer in the system $\mathrm{Pt(PPh_3)_3} + \mathrm{Ph_3CCl}$, to give $\mathrm{PtCl_2(PPh_3)_2}$ as the metal-bearing product; and (iv) the lack of reaction between $\mathrm{Pt(PPh_3)_3}$ and $\mathrm{Ph_3C}$· in benzene at 20°. Additionally, (v), the suggestion that a species such as $[\mathrm{PtX(PPh_3)_2}]$· is an intermediate conveniently account for the formation of $\mathrm{PtX_2(PPh_3)_2}$ or *trans*-$\mathrm{PtH(X)(PPh_3)_2}$ in other $\mathrm{Pt(PPh_3)_3}$–halide systems, by halogen or hydrogen atom abstraction reactions of (I); and (vi) a radical mechanism is compatible with the kinetic data of Halpern and his co-workers (R = MeI),[2] assuming the sequence of equations (1)—(3).

$$\mathrm{Pt(PPh_3)_3} \rightleftharpoons \mathrm{Pt(PPh_3)_2} + \mathrm{PPh_3} \tag{1}$$

$$\mathrm{Pt(PPh_3)_2} + \mathrm{RX} \overset{\text{slow}}{\rightleftharpoons} [\mathrm{PtX(PPh_3)_2}]\cdot + \mathrm{R}\cdot \tag{2}$$

$$\underset{\text{(I)}}{[\mathrm{PtX(PPh_3)_2}]\cdot} + \mathrm{R}\cdot \xrightarrow{\text{fast}} \textit{trans}\text{-}\mathrm{PtX(R)(PPh_3)_2} \tag{3}$$

For each of the halides MeI, EtI, or $\mathrm{PhCH_2Br}$ three experiments were performed: A, $\mathrm{Pt(PPh_3)_3} + \mathrm{RX} + \mathrm{Bu^tNO}$; B, $\mathrm{RX} + \mathrm{Bu^tNO}$; C, $\mathrm{Pt(PPh_3)_3}$ + excess RX until no further colour change, then + $\mathrm{Bu^tNO}$. $\mathrm{Pt(PPh_3)_3}$ and RX were used as 5×10^{-2} M solutions in benzene, $\mathrm{Bu^tNO}$ as 5—10 mole % with respect to $\mathrm{Pt(PPh_3)_3}$ for A and C and to RX for B. Equimolar amounts of $\mathrm{Pt(PPh_3)_3}$ and RX were used for A. All experiments were carried out in the dark under argon, and for A and B mixing between reagents took place in the e.s.r. tube. Spectra were then recorded immediately, and again after $\frac{1}{2}$ h at 20° in the dark. The former spectra showed for A a clean intense signal of $\mathrm{Bu^t(R)NO}$·, but no signal for B or C. The spectra for A were unchanged after $\frac{1}{2}$ h; for B and C only a signal corresponding to $\mathrm{Bu^tNO}$· (decomposition of $\mathrm{Bu^tNO}$) had appeared. [$\mathrm{Pt(PPh_3)_3}$ was shown to enhance the rate of formation of $\mathrm{Bu^t_2NO}$· from $\mathrm{Bu^tNO}$ in benzene, but this process is slower than the production of $\mathrm{Bu^t(R)NO}$· in A]. A preparative scale reaction between $\mathrm{Pt(PPh_3)_3}$ and excess of RX, in the presence of $\mathrm{Bu^tNO}$ [10 mole% with respect to $\mathrm{Pt(PPh_3)_3}$] in benzene led to the isolation of *trans*-$[\mathrm{PtI(Me)(PPh_3)_2}]$ (62%). The literature value for the same reaction, but without $\mathrm{Bu^tNO}$ or benzene, is 68%.

None of the alternative mechanisms[3] which have been proposed for oxidative addition to the d^{10} $\mathrm{Pt^0}$ or related d^8 systems such as *trans*-$\mathrm{IrCl(CO)(PPh_3)_2}$, including S_N2 at C, a concerted molecular process, or a radical chain mechanism (for $\mathrm{Ir^I}$),[4] are compatible with the data for the case of $\mathrm{Pt(PPh_3)_3}$. However, for oxidative addition of RX to $[\mathrm{Co(CN)_5}]^{3-}$ [3] or Mg,[5] radical mechanisms similar to equations (2) and (3) have been suggested on the basis of other types of evidence.

We thank S.R.C. for the award of a studentship to P.W.L.

(*Received*, 21*st September* 1973; *Com.* 1321.)

---

[1] D. J. Cardin, M. F. Lappert, and P. W. Lednor, *J.C.S. Chem. Comm.*, 1973, **350**.

[2] J. P. Birk, J. Halpern, and A. L. Pickard, *J. Amer. Chem. Soc.*, 1968, **90**, 4491; *Inorg. Chem.*, 1968, **7**, 2672.

[3] *Cf.*, J. Halpern, *Accounts Chem. Res.*, 1970, **3**, 386.

[4] J. S. Bradley, D. E. Connor, D. Dolphin, J. A. Labinger, and J. A. Osborn, *J. Amer. Chem. Soc.*, 1972, **94**, 4043.

[5] H. W. H. J. Bodewitz, C. Blomberg, and F. Bickelhaupt, *Tetrahedron*, 1973, **29**, 719.