

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

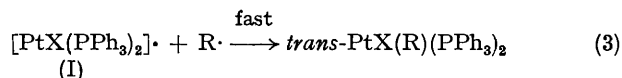
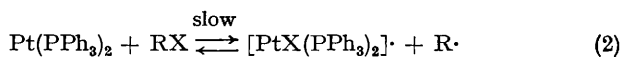
By MICHAEL F. LAPPERT\* and PETER W. LEDNOR

(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<sub>3</sub>I, EtI, or PhCH<sub>2</sub>Br) to Pt(PPh<sub>3</sub>)<sub>3</sub>, as shown by identifying (e.s.r.)

the derived nitroxide Bu<sup>t</sup>(R)NO· using Bu<sup>t</sup>NO as a spin trap; a non-chain mechanism is proposed, with the formation of [Pt<sup>IX</sup>(PPh<sub>3</sub>)<sub>2</sub>]· as rate limiting.

WE offer definitive evidence, principally e.s.r., that the formally two-electron oxidative ( $\text{Pt}^0 \rightarrow \text{Pt}^{\text{II}}$ ) addition of an alkyl halide  $\text{RX}$  to  $\text{Pt}(\text{PPh}_3)_3$  yielding *trans*- $\text{PtX}(\text{R})(\text{PPh}_3)_2$  proceeds in discrete one-electron steps, with the free radical  $\text{R}\cdot$ , and probably a halogenoplatinum(I) species such as (I), as intermediates. The following halides were examined:  $\text{MeI}$ ,  $\text{CD}_3\text{I}$ ,  $\text{EtI}$ ,  $\text{PhCH}_2\text{Br}$ , and  $\text{Ph}_3\text{CCl}$ . An important feature of this study is the use of the spin trap  $\text{Bu}^t\text{NO}$  (*cf.*, ref. 1 for its previous use in transition-metal chemistry), which with  $\text{R}\cdot$  affords the nitroxide  $\text{Bu}^t(\text{R})\text{NO}\cdot$ . The principal data to support our conclusion are (i) the identification of the nitroxide  $\text{Bu}^t(\text{R})\text{NO}\cdot$  for  $\text{R} = \text{Me}$ ,  $\text{CD}_3$ ,  $\text{Et}$ , or  $\text{PhCH}_2$ , each of which has previously been characterised by e.s.r. (ii) the demonstration that in these systems  $\text{Bu}^t\text{NO}$  does not significantly change the course of reaction yielding *trans*- $\text{PtX}(\text{R})(\text{PPh}_3)_2$ ; (iii) the formation of the stable and readily identifiable (e.s.r.) trityl radical  $\text{Ph}_3\text{C}\cdot$ , in appropriate equilibrium concentration with its dimer in the system  $\text{Pt}(\text{PPh}_3)_3 + \text{Ph}_3\text{CCl}$ , to give  $\text{PtCl}_2(\text{PPh}_3)_2$  as the metal-bearing product; and (iv) the lack of reaction between  $\text{Pt}(\text{PPh}_3)_3$  and  $\text{Ph}_3\text{C}\cdot$  in benzene at  $20^\circ$ . Additionally, (v), the suggestion that a species such as  $[\text{PtX}(\text{PPh}_3)_2]\cdot$  is an intermediate conveniently account for the formation of  $\text{PtX}_2(\text{PPh}_3)_2$  or *trans*- $\text{PtH}(\text{X})(\text{PPh}_3)_2$  in other  $\text{Pt}(\text{PPh}_3)_3$ -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 ( $\text{R} = \text{MeI}$ ),<sup>2</sup> assuming the sequence of equations (1)–(3).



For each of the halides  $\text{MeI}$ ,  $\text{EtI}$ , or  $\text{PhCH}_2\text{Br}$  three experiments were performed: A,  $\text{Pt}(\text{PPh}_3)_3 + \text{RX} + \text{Bu}^t\text{NO}$ ; B,  $\text{RX} + \text{Bu}^t\text{NO}$ ; C,  $\text{Pt}(\text{PPh}_3)_3 + \text{excess RX}$  until no further colour change, then  $+ \text{Bu}^t\text{NO}$ .  $\text{Pt}(\text{PPh}_3)_3$  and  $\text{RX}$  were used as  $5 \times 10^{-2} \text{ M}$  solutions in benzene,  $\text{Bu}^t\text{NO}$  as 5–10 mole % with respect to  $\text{Pt}(\text{PPh}_3)_3$  for A and C and to  $\text{RX}$  for B. Equimolar amounts of  $\text{Pt}(\text{PPh}_3)_3$  and  $\text{RX}$  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  $20^\circ$  in the dark. The former spectra showed for A a clean intense signal of  $\text{Bu}^t(\text{R})\text{NO}\cdot$ , 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  $\text{Bu}^t\text{NO}\cdot$  (decomposition of  $\text{Bu}^t\text{NO}$ ) had appeared. [ $\text{Pt}(\text{PPh}_3)_3$  was shown to enhance the rate of formation of  $\text{Bu}^t_2\text{NO}\cdot$  from  $\text{Bu}^t\text{NO}$  in benzene, but this process is slower than the production of  $\text{Bu}^t(\text{R})\text{NO}\cdot$  in A]. A preparative scale reaction between  $\text{Pt}(\text{PPh}_3)_3$  and excess of  $\text{RX}$ , in the presence of  $\text{Bu}^t\text{NO}$  [10 mole% with respect to  $\text{Pt}(\text{PPh}_3)_3$ ] in benzene led to the isolation of *trans*- $[\text{PtI}(\text{Me})(\text{PPh}_3)_2]$  (62%). The literature value for the same reaction, but without  $\text{Bu}^t\text{NO}$  or benzene, is 68%.

None of the alternative mechanisms<sup>3</sup> which have been proposed for oxidative addition to the  $d^{10} \text{Pt}^0$  or related  $d^8$  systems such as *trans*- $\text{IrCl}(\text{CO})(\text{PPh}_3)_2$ , including  $\text{S}_{\text{N}}2$  at C, a concerted molecular process, or a radical chain mechanism (for  $\text{Ir}^{\text{I}}$ ),<sup>4</sup> are compatible with the data for the case of  $\text{Pt}(\text{PPh}_3)_3$ . However, for oxidative addition of  $\text{RX}$  to  $[\text{Co}(\text{CN})_5]^{3-}$  or  $\text{Mg}$ ,<sup>5</sup> 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, 21st September 1973; Com. 1321.)

<sup>1</sup> D. J. Cardin, M. F. Lappert, and P. W. Lednor, *J.C.S. Chem. Comm.*, 1973, 350.

<sup>2</sup> J. P. Birk, J. Halpern, and A. L. Pickard, *J. Amer. Chem. Soc.*, 1968, **90**, 4491; *Inorg. Chem.*, 1968, **7**, 2672.

<sup>3</sup> *Cf.*, J. Halpern, *Accounts Chem. Res.*, 1970, **3**, 386.

<sup>4</sup> J. S. Bradley, D. E. Connor, D. Dolphin, J. A. Labinger, and J. A. Osborn, *J. Amer. Chem. Soc.*, 1972, **94**, 4043.

<sup>5</sup> H. W. H. J. Bodewitz, C. Blomberg, and F. Bickelhaupt, *Tetrahedron*, 1973, **29**, 719.