Free-radical Displacement Reactions at a Transition-metal Centre: Bimolecular Homolytic Substitution (S_H2) at Square-planar Pt^{II}

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Summary The displacement of the free radical R· from the complex *cis*-PtR_2X_2 (R = Me, Et, Me_3SiCH_2, or $PhCH_2$; X = $PAlk_3$ or PMe_2Ph; Alk = Et, Pr^n, or Bu^n) by Bu^tO· or PhS· is demonstrated by e.s.r. spectroscopy (direct detection or spin-trapping) or by initiation of a chain reaction involving R·.

WE present the first unequivocal demonstration of the occurrence of radical substitution reactions at a transition-metal site. The attacking radical was either an oxygen- or a sulphur-centred species, displacing an alkyl radical R·. The evidence rests in part on e.s.r. spectra by identification either of R· or the derived nitroxide radical $Bu^t(R)NO$·, using Bu^tNO as a spin-trapping reagent. Additionally, on a preparative scale, we have used a chain reaction in which R· is involved in a propagation step, the reaction being initiated by $(Bu^tON)_2$. The realisation of bimolecular homolytic substitution reactions (S_H2) at a transition-metal site may provide a new dimension for transition-metal chemistry (for example in understanding the autoxidation of alkyls[1]), and complements recent discoveries for some Main Group element compounds.[2]

When a saturated solution of the compound *cis*-PtR_2X_2 (I) (R = Me, X = PEt_3) in di-t-butyl peroxide was irradiated with high-intensity u.v. light in the cavity of an e.s.r. spectrometer at −40° (procedure *A*), an Me· signal was detected. Photolytic cleavage was ruled out, by replacing the peroxide with tetrahydrofuran, when no signal was seen. For (I) (R = Et, X = PPr^n_3), using procedure *A*, Et· was observed; this eliminates the possibility of Me· having originated from β-scission of Bu^tO· (with Me_2CO as the other product). The probable mechanism is shown in equations (1) and (2), with the latter the S_H2 process.

$$Bu^tO{-}OBu^t \xrightarrow{h\nu} 2Bu^tO\cdot \tag{1}$$

$$\underset{\text{(I)}}{cis\text{-}PtR_2X_2} + Bu^tO\cdot \longrightarrow PtR(OBu^t)X_2 + R\cdot \tag{2}$$

The spin-trapping technique[3] was employed to characterise further the S_H2 reaction, using $(Bu^tON)_2$ (*ca.* 20 mol %) as a thermal (40°) source of Bu^tO· and Bu^tNO (*ca.* 20 mol %) as the spin-trap in benzene (procedure *B*). Thus, R· from reaction (2) was allowed to react with Bu^tNO to give $Bu^t(R)NO$·, identified from the hyperfine splitting For (I) (R = Me, X = PEt_3 or PBu^n_3), all twelve lines[3c] of the expected triplet of quartets of $Bu^t(Me)NO$· were readily detected. Control experiments [in the absence of (I)] showed only $Bu^t(Bu^tO)NO$· and Bu^t_2NO·, neither of which interfere with the detection of $Bu^t(Me)NO$·, thus demonstrating that Me· originates from (I). For (I) (R = $PhCH_2$, X = PEt_3), benzyl radical was detected only by procedure *B* (7-line spectrum[2c]) but not *A* (54 lines for $Ph\dot{C}H_2$).

Attempts to replicate R–Bu^tO exchange on a preparative scale have not yet been successful: this may be associated with the lability of the alkoxides of late transition elements. However, such a process has been demonstrated for the corresponding R–PhS exchange. Using (I) (R = Me_3SiCH_2, X = PMe_2Ph) three experiments have been carried out. Neither procedure *A* nor *B* yielded evidence for *R*·; from *A* an e.s.r. spectrum attributed to the phosphoranyl radical $Pt(CH_2SiMe_3)_2(\dot{P}Me_2PhOBu^t)(PMe_2Ph)$ was observed. However with PhSSPh in the presence of $(Bu^tON)_2$ (6·8 mol %) as initiator, in benzene at *ca.* 60° under nitrogen in the dark (procedure *C*), the compound yielded *trans*-$Pt(SPh)_2X_2$ and $PhSCH_2SiMe_3$, identified by g.l.c.–mass spectrometry: τ 7·95 (CH_2) and 9·82 (Me). The rate of reaction was followed from these n.m.r. signals, which flank those of (I). Use of procedure *C*, but without initiator, afforded *ca.* 2% of $PhSCH_2SiMe_3$ under the conditions which gave complete reaction with $(Bu^tON)_2$. The proposed mechanism is shown in equations (3)—(6) [X· = Me· from Bu^tO·, or R· (equation 2)], and has precedent in organoboron chemistry.[4]

$$(Bu^tON)_2 \rightarrow 2Bu^tO\cdot + N_2 \tag{3}$$

$$\text{Initiation:}\quad PhS{-}SPh + X\cdot \rightarrow PhS\cdot + XSPh \tag{4}$$

$$\text{Propagation:}\ \left\{\begin{array}{ll} PhS\cdot + PtR_2X_2 \rightarrow PtR(SPh)X_2 + R\cdot & (5) \\ R\cdot + PhSSPh \rightarrow RSPh + PhS\cdot & (6) \end{array}\right.$$

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