

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

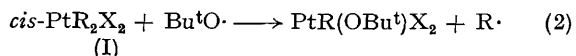
By DAVID J. CARDIN, MICHAEL F. LAPPERT,* and PETER W. LEDNOR

(School of Molecular Sciences, University of Sussex, Brighton BN1 9QJ)

Summary The displacement of the free radical $R\cdot$ 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 $Bu^tO\cdot$ or $PhS\cdot$ is demonstrated by e.s.r. spectroscopy (direct detection or spin-trapping) or by initiation of a chain reaction involving $R\cdot$.

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 $R\cdot$. The evidence rests in part on e.s.r. spectra by identification either of $R\cdot$ or the derived nitroxide radical $Bu^t(R)NO\cdot$, using Bu^tNO as a spin-trapping reagent. Additionally, on a preparative scale, we have used a chain reaction in which $R\cdot$ 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 alkyls¹), and complements recent discoveries for some Main Group element compounds.²

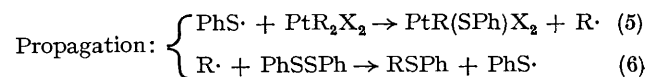
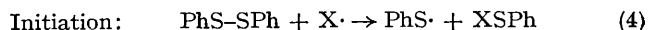
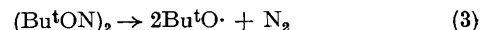
When a saturated solution of the compound $cis-PtR_2X_2$ (I) ($R = Me, X = PEt_3$) in di-*t*-butyl peroxide was irradiated with high-intensity u.v. light in the cavity of an e.s.r. spectrometer at -40° (procedure A), an $Me\cdot$ signal was detected. Photolytic cleavage was ruled out, by replacing the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



The spin-trapping technique³ was employed to characterise further the S_H2 reaction, using $(Bu^tON)_2$ (ca. 20 mol %) as a thermal (40°) source of $Bu^tO\cdot$ and Bu^tNO (ca. 20 mol %) as the spin-trap in benzene (procedure B). Thus,

$R\cdot$ from reaction (2) was allowed to react with Bu^tNO to give $Bu^t(R)NO\cdot$, identified from the hyperfine splitting. For (I) ($R = Me, X = PEt_3$ or PBu_3^n), all twelve lines^{3c} of the expected triplet of quartets of $Bu^t(Me)NO\cdot$ were readily detected. Control experiments [in the absence of (I)] showed only $Bu^t(Bu^tO)NO\cdot$ and $Bu^t_2NO\cdot$, neither of which interfere with the detection of $Bu^t(Me)NO\cdot$, thus demonstrating that $Me\cdot$ 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 $R\cdot$; from A an e.s.r. spectrum attributed to the phosphoranyl radical $Pt(CH_2SiMe_3)_2(PMe_2PhOBu^t)(PMe_2Ph)$ 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 $Bu^tO\cdot$, or $R\cdot$ (equation 2)], and has precedent in organoboron chemistry.⁴



We thank Professor A. G. Davies and Dr. B. P. Roberts for useful discussions, and the S.R.C. for a studentship (to P.W.L.).

(Received, 9th April 1973; Com. 501.)

¹ P. B. Brindley and J. C. Hodgson, *J. C. S. Dalton*, submitted for publication.

² A. G. Davies and B. P. Roberts, *Accounts Chem. Res.*, 1972, 5, 387; K. U. Ingold and B. P. Roberts, 'Free Radical Substitution Reactions,' Wiley-Interscience, New York, 1971.

³ (a) E. G. Janzen, *Accounts Chem. Res.*, 1971, 4, 31; (b) C. Lagercrantz, *J. Phys. Chem.*, 1971, 75, 3466; (c) M. J. Perkins, *Chem. Soc. Spec. Publ.*, No. 24, 1970, p. 97.

⁴ H. C. Brown and M. M. Midland, *J. Amer. Chem. Soc.*, 1971, 93, 3291.