Activation and Transfer of Oxygen Atom from Dioxygen–Metal Complexes. Epoxidation of Olefins Induced by Electrophiles

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Summary Oxygen transfer from dioxygenbis(triphenylphosphine) platinum to form cyclohexene and norbornene oxides from olefins is induced by acid halides under mild conditions.

Dioxygen–metal complexes are potentially viable intermediates for the direct activation of molecular oxygen, particularly with regard to the desired catalytic epoxidation of olefins.[1] However, despite the large number and structural varieties of dioxygen-metal complexes,[2] there are no unambiguous examples reported in which an oxygen atom is transferred to an unactivated olefin.† We have surmised that such a transfer may be promoted by electrophiles, and report the effect of acyl halides on the otherwise stable dioxygen complex $[(Ph_3P)_2PtO_2]$[2,3] as a prototype for such an electrophilic activation.

Dioxygenbis(triphenylphosphine)platinum (I) [^{31}P n.m.r.: δ 14·68 (s, J_{Pt-P} 4030 Hz) p.p.m.] reacts instantaneously at -78 °C with 1 mol of benzoyl chloride in methylene chloride solution to afford *cis*-chloroperoxybenzoatobis-

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† Peroxomolybdenum(VI) (H. Mimoun, I. Seree de Roch, and L. Sajus, *Tetrahedron*, 1970, **26**, 37) and related species are not considered in this context (see ref. 1). For reactions with activated olefins see: R. A. Sheldon and J. A. Van Doorn, *J. Organometallic Chem.*, 1975, **94**, 115.

TABLE. Epoxidation of olefins by [L_2PtO_2] complexes induced by acid halides[a]

[L_2PtO_2] L (10 mmol)		RCOCl R (10 mmol)		Solvent	Olefin[b] mmol		Epoxide/%[c]
Ph_3P	(1·35)	none		CH_2Cl_2	NB	(12·4)	0
Ph_2P	(1·35)	Ph	(1·37)	CH_2Cl_2	NB	(12·4)	48
Ph_3P	(1·28)[d]	Ph	(1·29)	CH_2Cl_2	NB	(15·4)	50
Ph_3P	(1·51)	Ph	(1·51)	C_6H_6	NB	(13·9)	50
Ph_3P	(1·31)	Ph	(1·31)	C_6H_{12}	NB	(13·8)	41
Cy_3P[e]	(0·74)	Ph	(0·74)	C_6H_6	NB	(10·7)	31
Ph_3P	(1·34)	none		none	C	(19·6)	0
Ph_3P	(1·34)	Ph	(1·72)	none	C	(19·6)	29
Ph_3P	(1·20	Ph	(1·20)	CH_2Cl_2	C	(9·9)	20
Ph_3P	(1·49)	Me	(1·69)	none	C	(19·6)	15

[a] Reactions carried out by the addition of RCOCl to a mixture of olefin and (I) unless noted otherwise. [b] NB = norbornene, C = cyclohexene. [c] Yield based on [L_2PtO_2]. [d] Olefin added to (II) at − 78 °C; stirred for 20 min and reaction mixture allowed to warm to room temperature. [e] Tricyclohexylphosphine.

(triphenylphosphine)platinum (II) [equation (1)] as a metastable intermediate. Complex (II) is identified at low temperatures by its ^{31}P {^1H} n.m.r. spectrum [two doublets

$$\underset{\text{(I)}}{[(Ph_3P)_2PtO_2]} + PhCOCl \xrightarrow{-78^\circ C} \underset{\text{(II)}}{[(Ph_3P)_2Pt(OOCOPh)Cl]} \quad (1)$$

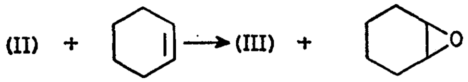
of equal intensity with ^{195}Pt satellites: δ 19·19 ($J_{\mathrm{Pt-P}}$ 4013 and $J_{\mathrm{P-P}}$ 19·8 Hz) and 4·95 ($J_{\mathrm{Pt-P}}$ 3240 and $J_{\mathrm{P-P}}$ 19·8 Hz) p.p.m., rel. to external H_3PO_4 reference], and the presence of the peroxybenzoato–ligand is confirmed by its characteristic i.r. bands at ν 1730 (antisym. CO) and 1335 (sym. CO) cm^{-1}.[4]

Intermediate (II) is quite unstable thermally. However, at −78 °C it reacts rapidly with 1 mol of added triphenylphosphine to afford triphenylphosphine oxide which can be isolated in 85% yield [equation (2)].‡ The

$$\text{(II)} + PPh_3 \rightarrow \underset{\text{(III)}}{[(Ph_3P)_2Pt(OCOPh)Cl]} + OPPh_3 \quad (2)$$

platinum-containing product (III) can also be isolated in high yields (90%) from the reaction mixture, and characterized as *cis*-chlorobenzoatobis(triphenylphosphine)platinum by ^{31}P n.m.r. [two doublets of equal intensity with ^{195}P satellites: δ 17·35 ($J_{\mathrm{Pt-P}}$ 3937 and $J_{\mathrm{P-P}}$ 18·9 Hz) and 2·29 ($J_{\mathrm{Pt-P}}$ 3598 and $J_{\mathrm{P-P}}$ 18·9 Hz) p.p.m.], and i.r. [ν 1632 (antisym. CO) and 1333 (sym. CO) cm^{-1}] spectroscopy and satisfactory elemental analysis.

Transfer of oxygen from (I) to olefinic substrates is also possible. Thus, the addition of norbornene to the intermediate (II) at −78 °C, followed by the removal of the cold bath, led to norbornene oxide in 50% yields in <0·5 h. The same results were obtained if a mixture of (I) and norbornene was treated with benzoyl chloride at room temperature as described in the Table. Similarly, cyclohexene afforded cyclohexene oxide. [The less-than-quantitative yields of



epoxides are due to the concomitant decomposition of (II) which occurs spontaneously at the higher temperature required for oxygen transfer to olefins]. In both cases the platinum-containing product was identified as *cis*-chlorobenzoatobis(triphenylphosphine)platinum. Acetyl chloride could be used in place of benzoyl chloride, but trimethylchlorosilane and methyl iodide were not effective in promoting oxygen transfer.

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‡ Complex (I) itself does not react with triphenylphosphine under these conditions.

[1] R. A. Sheldon and J. K. Kochi, *Adv. Catalysis*, **1976**, **25**, 272; R. A. Budnik and J. K. Kochi, *J. Org. Chem.*, 1976, **41**, 1384.

[2] L. Vaska, *Accounts Chem. Res.*, 1976, **9**, 175, and references cited therein.

[3] S. Takahashi, K. Sonogashira, and N. Hagihara, *J. Chem. Soc. Japan*, 1966, **87**, 610; G. Wilke, H. Schott, and P. Heimbach, *Angew. Chem. Internat. Edn.*, 1967, **6**, 92; C. D. Cook and G. S. Jauhal, *Inorg. Nuclear Chem. Letters*, 1967, **3**, 31; C. J. Nyman, C. E. Wymore, and G. Wilkinson, *J. Chem. Soc.*, (*A*), 1963, 561; J. P. Birk, J. Halpern, and A. L. Pickard, *J. Amer. Chem. Soc.*, 1968, **90**, 4491; P. T. Cheng, C. D. Cook, S. C. Nyburg, and K. Y. Wan, *Canad. J. Chem.*, 1971, **49**, 3772; D. A. Phillips, M. Kubota, and J. Thomas, *Inorg. Chem.*, 1972, **15**, 118.

[4] *Cf.* L. Vaska, *Science*, 1963, **740**, 809; S. Otsuka, A. Nakamura, Y. Tatsuno, and M. Miki, *J. Amer. Chem. Soc.*, 1972, **94**, 3761; S. Muto and Y. Kamiya, *Bull. Chem. Soc. Japan*, 1976, **49**, 2587; P. J. Hayward, D. M. Blake, G. Wilkinson, and C. J. Nyman, *J. Amer. Chem. Soc.*, 1970, **92**, 5873 for examples of peroxide formation; N. W. Alcock, V. M. Tracy, and T. C. Waddington, *J.C.S. Dalton*, 1976, 2243; T. A. Stephenson, S. M. Morehouse, A. R. Powell, J. P. Heffer, and G. Wilkinson, *J. Chem. Soc.*, 1965, 3632; R. Kavcic, B. Plesnicar, and B. Hadzi, *Spectrochim. Acta*, 1967, **23A**, 2483 for i.r. spectra.