Catalytic Epoxidation of Alkenes by Co-ordinatively Unsaturated Phosphino Complexes of Ruthenium(II) and Osmium(II)

Mario Bressan and Antonino Morvillo

Dipartimento di Chimica Inorganica, Metallorganica e Analitica, Centro C.N.R., Universita di Padova, via Marzolo 1, 35131 Padova, Italy

Ruthenium(II) and osmium(II) complexes $[MCl(LL)_2]Y$, where LL is 1,3-bis(diphenylphosphino)propane or 1-diphenylphosphino-2-(2′-pyridyl)ethane, promote the oxidation of a number of alkenes by PhIO, hypochlorites, and H_2O_2.

In recent years oxygen-atom transfers by non-metal oxides to effect selective oxidations of hydrocarbons in the presence of transition metal complexes, both porphyrinic[1] and others[2] have been throughly investigated. Ruthenium and osmium based catalysts typically promote the oxidative cleavage of double bonds,[3] but selectivity in the epoxides has been shown to improve significantly in the presence of polydentate nitrogen donors,[4,5] indicating that the nature of ligands has a definite influence upon the catalytic behaviour of these metals.

To investigate a different co-ordination environment, we have tested the effect of a number of phosphino complexes of ruthenium(II) and osmium(II) on the epoxidation of alkenes by iodosylbenzene and other single-oxygen oxidants (Scheme 1).

We used the five-co-ordinate $[MCl(LL)_2]^+$ cations (M = Ru, Os), easily prepared by dissociation of the conventional six-co-ordinate $[MCl_2(LL)_2]$ derivatives, where LL is 1,3-bis(diphenylphosphino)propane (DPPP),[6a,b] 1-diphenylphosphino-2-(2′-pyridyl)ethane (PPY),[6c] or other related bidentate phosphinic ligands[6d,e] capable of generating six-membered chelate rings upon co-ordination.

In a typical catalytic experiment, a dichloromethane solution containing the catalyst (2×10^{-3} mol dm^{-3}) and the alkene (0.1 mol dm^{-3}) was stirred vigorously with excess of PhIO, with aliquots monitored by gas chromatography. The catalysts are apparently active for week-long periods, either exposed to air or under a nitrogen atmosphere.

It is noteworthy that the $[MCl(LL)_2]^+$ catalysts are completely poisoned by the presence of strong donors (L′) such as carbon monoxide and acetonitrile, which add to the complexes, forming stable six-co-ordinate $[MCl(L')(LL)_2]^+$ adducts,[6] thus effectively competing with the oxidants (PhIO, ClO^-) at the available co-ordination site. Significantly, the corresponding co-ordinatively saturated $[MCl_2(LL)_2]$ species do not exhibit catalytic activity.

Conversions with iodosylbenzene are reported in Table 1. Product distribution is similar, when hypochlorites (0.2 M aqueous solutions) or dilute hydrogen peroxide are used. Yields, based on the amount of alkene converted, are indicative of the efficiency of the oxygen-transfer reaction. Excess oxidant was always necessary, since iodosylbenzene, hypochlorites, and hydrogen peroxide decomposed extensively even in the absence of the alkenes.

The osmium catalysts appear to be more active than the ruthenium complexes, but definitely less selective for epoxide formation. The ruthenium complexes, almost regardless of the nature of the ligand, exhibit good selectivities for the conversion of norbornene, cyclo-octene, and linear alkenes to their respective epoxides, but other oxidation pathways are dominant in the cases of cyclohexene (allylic attack) and of styrene, β-methylstyrene, and stilbenes (oxidative cleavage). Epoxide production parallels the formation of the other products from the onset of oxidation, suggesting that all oxidation pathways are operating simultaneously and ruling out the possibility that cleavage of the alkene involves initial conversion of the alkene into the related epoxide, followed by further oxidation.[4b,5b] Indeed, styrene oxide was recovered unchanged, when treated with PhIO in the presence of the title catalysts.

Scheme 1

Cis-stilbene undergoes extensive loss of stereoselectivity upon epoxidation, the thermodynamically stable *trans*-epoxide being formed in higher yields (Table 1). No accumulation of *trans*-stilbene is observed, even in anaerobic conditions where stilbene cation radicals, possibly formed during the reaction, could isomerize to the *trans* configuration.[7] However, since in our experiments *trans*- and *cis*-stilbene epoxidize at comparable rates (Table 1), we suggest that the observed change in the stereochemistry might occur during the breakdown of an oxo-metal–alkene intermediate, probably radicaloid in character.[6]

The course of the $[RuCl(DPPP)_2]ClO_4$-catalysed epoxidation of norbornene by iodosylbenzene, in dichloromethane,

Table 1. Ruthenium- and osmium-catalysed epoxidation of alkenes with iodosylbenzene.[a]

	% Conversion (% Epoxide)[b]		
	M = Ru		M = Os
Alkene	LL = DPPP	LL = PPY	LL = DPPP
Norbornene	7(58)[c]	13(46)[c]	7(55)[c]
Cyclo-octene	4(67)[d]	7(55)[d]	4(24)[d]
Cyclohexene	3(<1)[e]	nd	5(<1)[f]
Styrene	7(37)[g]	12(34)[g]	19(18)[g]
trans-β-Methylstyrene	21(25)[g,h]	nd	79(3)[g,h]
trans-Stilbene	16(20)[g,h]	15(25)[g,h]	76(2)[g,h]
cis-Stilbene	20(35)[g,i]	17(38)[g,j]	43(1)[g,k]
trans-Hex-2-ene	2(60)[h,m]	nd	2(14)[h,m]
Hex-1-ene	1(67)	nd	3(5)[n]

[a] Alkene (0.1 M) and $[MCl(DPPP)_2]ClO_4$ (2 mM) treated with PhIO (molar ratio PhIO catalyst, 100:1) in dichloromethane, at 22 °C. [b] Conversion of the alkene into various oxidation products, after 10 h (selectivity in epoxide). [c] Together with small amounts of cyclopentane-1,3-bis(carboxyaldehyde). [d] Together with cyclo-octen-2-one. [e] Cyclohexen-2-one (65%) and minor amounts of cyclohexen-2-ol, cyclohexane-1,2-dione, and 1-hydroxycyclohexanone. [f] Cyclohexanol-2-one (60%) and minor amounts of cyclohexen-2-one, cyclohexene-2 ol and cyclohexane-1,2-dione. [g] Together with benzaldehyde. [h] Only *trans*-epoxide. [i] *cis*- and *trans*- epoxide (40:60 molar ratio). [j] *cis*- and *trans*-epoxide (60:40 molar ratio). [k] *cis*- and *trans*-epoxide (45:55 molar ratio). [m] Together with hex-2-enal and hexenones. [n] Together with 1-hydroxy-2-one (75%).

was also followed in the presence of 90% ^{18}O-water (25-fold excess of catalyst). The product consisted of 33% labelled norbornene oxide. Assuming that ^{18}O-water exchanges neither with PhIO nor with norbornene oxide,[8] water must be incorporated during the catalytic transfer, namely in an oxo-derivative of Ru^{IV}, probably formed *via* the following reaction sequence.[9]

$$[Ru^{II}Cl(LL)_2]^+ \xrightarrow{PhIO} [Ru^{II}Cl(OIPh)(LL)_2]^+ \xrightarrow{-PhI} [Ru^{IV}Cl(O)(LL)_2]^+$$

$$[Ru^{IV}Cl(O)(LL)_2]^+ \underset{}{\overset{H_2{}^{18}O}{\rightleftharpoons}} [Ru^{IV}Cl(^{18}O)(LL)_2]^+$$

Attempts to isolate, or to identify, these oxo-species have been unsuccessful so far. Treatment of $[RuCl(LL)_2]^+$ with PhIO, NaClO, or H_2O_2, slowly turns the original red (LL = DPPP) or orange (LL = PPY) solutions green, while in the ^{31}P n.m.r. spectra, the diagnostic resonance patterns [A_2B_2(δ 45.7 and 2.95 p.p.m., J_{pp} 30 Hz), or AB (δ 36.8 p.p.m.), respectively] are replaced by broad unstructured signals in the 50—60 p.p.m. region. Green paramagnetic materials (χ_g 7.5 × 10^{-12}) with erratic composition, no longer active as catalysts, were recovered from the reaction mixtures. These products were probably Ru^{III} derivatives resulting from the common reaction between ruthenium(II) and oxo-ruthenium(IV) derivatives, and were tentatively assigned oxo-bridging structures [Ru^{IV}=O + Ru^{II} → $Ru^{III}ORu^{III}$ → products].[10]

The technical assistance of Mr. A. Ravazzolo is gratefully acknowledged.

Received, 7th December 1987; Com. 1754

References

1 J. P. Collman, T. Kodakek, and J. I. Brauman, *J. Am. Chem. Soc.*, 1986, **108**, 2588, and references therein; I. Tabushi, M. Kodera, and M. Yokoyama, *ibid.*, 1985, **107**, 4466, B. Meunier, E. Guilmet, M. DeCarvalho, and R. Poilblanc, *ibid.*, 1984, **106**, 6668; J. T. Groves and T. E. Nemo, *ibid.*, 1983, **105**, 5786.

2 J. D. Koola and J. K. Kochi, *Inorg. Chem.*, 1987, **26**, 908, and references therein; R. B. VanAtta, C. C. Franklin, and J. S. Valentine, *ibid.*, 1984, **23**, 4121.

3 W. J. Mijs and C. R. H. I. deJonge, 'Organic Synthesis by Oxidation with Metal Compounds,' Plenum; New York, 1986.

4 (a) C. Eskenazi, G. Balavoine, F. Meunier, and H. Riviere, *J. Chem. Soc., Chem. Commun.*, 1985, 1111; (b) G. Balavoine, C. Eskenazi, F. Meunier, and H. Riviere, *Tetrahedron Lett.*, 1984, **25**, 3187.

5 (a) J. C. Dobson, W. K. Seok, and T. J. Meyer, *Inorg. Chem.*, 1986, **25**, 1513; (b) C. L. Bailey and R. S. Drago, *J. Chem. Soc., Chem. Commun.*, 1987, 179.

6 (a) M. Bressan and P. Rigo, *Inorg. Chem.*, 1975, **14**, 2286; (b) M. Bressan, R. Ettorre, and P. Rigo, *Inorg. Chim. Acta*, 1977, **24**, L57; (c) M. Bressan and P. Rigo, *J. Inorg. Nucl. Chem.*, 1976, **38**, 592; (d) J. C. Briggs, C. A. McAuliffe, and G. Dyer, *J. Chem. Soc., Dalton Trans.*, 1984, 423; (e) M. Bressan and A. Morvillo, *Inorg. Chim. Acta*, 1987, **132**, 1.

7 D. C. Heimbrook, R. L. Mulholland, Jr., and S. M. Hecht, *J. Am. Chem. Soc.*, 1986, **108**, 7839.

8 See also, K. Srinivasan, P. Michaud, and J. K. Kochi, *J. Am. Chem. Soc.*, 1986, **108**, 2309.

9 B. A. Moyer and T. J. Meyer, *Inorg. Chem.*, 1981, **20**, 436; C. Che, K. Wong, and T. C. W. Mak, *J. Chem. Soc., Chem. Commun.*, 1985, 546; M. E. Mormion and K. J. Takeuchi, *J. Am. Chem. Soc.*, 1986, **108**, 510.

10 J. A. Gilbert, D. S. Eggleston, W. R. Murphy, Jr., D. A. Geselowitz, S. W. Gersten, D. J. Hodgson, and T. J. Meyer, *J. Am. Chem. Soc.*, 1985, **107**, 3855.