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Asymmetric alkene epoxidation with chromium oxo salen complexes
Effect of π-rich and other types of additives

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Abstract

The stoichiometric asymmetric epoxidation of *E*-β-methylstyrene with cationic chromium–salen oxo complexes was studied. It was found that enantiomeric excess (ee) could be strongly affected (±20% ee) by the presence of compounds containing extended π-electron systems. In certain cases, such additives appeared to stabilize the active oxidant slowing reaction. Unsubstituted and methyl-substituted imidazoles were found to be beneficial additives but imidazoles with aromatic substituents were very detrimental. These results are interpreted as providing support for Katsuki's views on the importance of π-interactions in the analogous manganese–salen catalyzed epoxidations. Compounds containing S=O and C=O bonds also affected enantioselectivity but to a lesser extent. Phosphine sulfides an borane could survive contact with the oxidant depending on the salen substitution pattern and in the latter case the enantioselectivity was raised. A phosphorus ylide was found to stabilize a Cr(V) oxo species, approximately doubling its lifetime.

Keywords: Asymmetric epoxidation; Chromium; Salen; π-Donor ligands

1. Introduction

The use of metal complexes of chiral salen ligands in catalytic asymmetric synthesis has been widespread in recent years [1]. Especially useful is the manganese–salen catalyzed asymmetric epoxidation of conjugated *Z*-alkenes (Fig. 1, M = Mn) studied extensively by Jacobsen [2] and Katsuki [3]. We have reported [4–9] on the complementary chiral chromium–salen complexes which give good selectivity for *E*-alkenes (Fig. 1, M = Cr and Scheme 1) and have the useful feature that the SalCr(V)=O species is stable [10] unlike the SalMn(V)=O species, which is a fleeting intermediate [11–16]. Use of the isolated Cr(V)=O species (stoichiometric reaction) then enables separate study of the stereoselectivity and catalysis issues. We showed that the high enantiomeric excesses (ees) obtained stoichiometrically were not fully maintained in the catalytic version of the reaction although the latter gave a higher yield [5,6,8]. We proposed an explanation [8] based on reaction of the Cr(V)=O with its reduced Cr(III) form to give an unreactive μ-oxo dimer, Cr(IV)–O–Cr(IV) (Fig. 1) the manganese version of which is considered to be the resting state of the catalyst in the manganese series [11,17].

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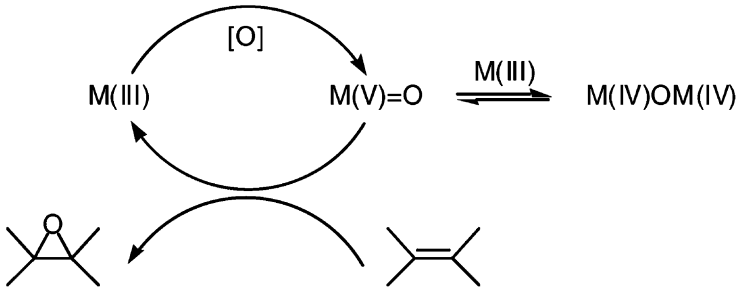
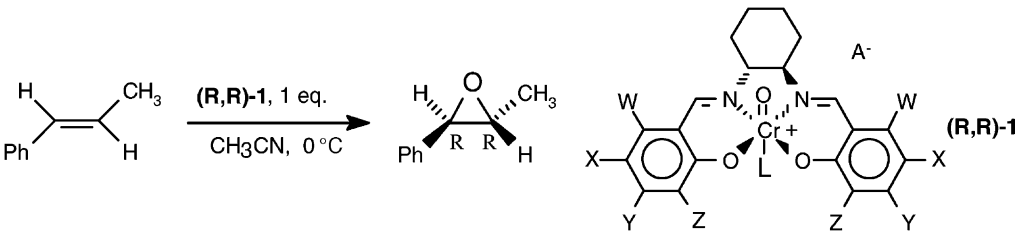


Fig. 1. The catalytic for chromium and salen.

A notable aspect of our system was the change in ee by as much as 30% on addition of certain achiral oxo-type ligands (L), such as phosphine oxides and amine *N*-oxides [5,6,9]. It was known [10,18] that such additives are co-ordinated by the oxygen atom in the apical position (L in complex **1**, Scheme 1) which weakens the Cr=O bond and increases epoxidation rate. Apart from our own work [5,6,8,9,19,20] and one contribution from Imanishi and Katsuki [21], we are not aware of any other studies of additives in the chromium series. In contrast, additives, especially *N*-oxides, have a wide range of reported effects on the chiral manganese–salen epoxidation [2,3,16,22,23].

We hoped that the stoichiometric variants of the reaction available in the chromium series might provide an understanding of the manganese system. Our first studies showed that there is a complex relationship between the effect of L addition and the salen substituents W–Z in **1**. Thus, ee can be increased when substituents are present at X/Z but not at W/Y [9]. Since then, we have embarked on more comprehensive studies and we have recently reported on phosphoryl (R_3P=O) and *N*-oxide additives [19,20]. In all of our work, we have found that the substitution at the Z-position in complex **1** is essential for high enantioselectivity. However, the substituent does not have to be large (F is as effective as ^{t}Bu) in contrast to the manganese series.

We found that the phosphoryl compounds behaved in a consistent manner in our test reaction (Scheme 1) across a range of chromium–salen complexes, with the tri-aryl derivatives being most effective [19]. They always accelerate the reaction slightly, usually improve epoxide yields and consistently cause an ee elevation. The latter is subject to a ceiling, decreasing as the salen substitution pattern itself becomes more beneficial. An important point is that the effect of phosphoryl additives reaches its maximum at well below one equivalent of additive relative to complex (0.2 equivalents in the case of Ph_3PO). Bulky phosphine oxides were less effective additives, especially *ortho*-substituted tri-aryl cases. In notable contrast to these results with phosphoryl compounds, *N*-oxides as additives usually caused a decrease in epoxide yield. They also had an effect on ee that varied with concentration in a different manner to that of the phosphoryl additives. Thus, ee elevation passed through a maximum with increasing concentration and fell quite dramatically with more than one equivalent of additive [20]. Also the number of equivalents required to elicit the maximum ee elevation varied with the pattern of substitution on the salen ring. For example, 0.4 equivalents of pyridine *N*-oxide



Scheme 1.

Table 1
Results of stoichiometric epoxidation[a] of *E*-β-methylstyrene according to Scheme 1 with various chiral non-racemic substituted oxo-chromium(V) salen complexes[b] in the presence of various phosphine oxides as added ligand L[c]

Complex			Time[d]	ee (%) (Δee)[e] in the presence of				Yield (%) in the presence of			
W	X	Z		No L	TPPO[f]	DBPO	DDPO	No L	TPPO[f]	DBPO	DDPO
H	H	H	12 h	58	72 (12)	80 (22)	nr	22	46	40	nr
H	H	Ph	2 days	66	85 (19)	73 (7)	nr	15	14	15	nr
H	Cl	Cl	60 min	67	83 (16)	56 (−11)	48 (−19)	18	40	20	10
H	^{t}Bu	^{t}Bu	1 week	67	69 (2)			10	25		
Cl	Cl	Cl	10 min	68	72 (4)	76 (8)		19	29	14	
H	F	F	20 min	71	83 (12)			41	46		
H	H	Bz	2 days	74	82 (8)	73 (−1)		14	15	8	
H	H	Cl	60 min	80	86 (6)	80 (0)		20	35	15	
H	H	^{t}Bu	1 week	84	79 (−5)	81 (−3)		20	17	22	
H	H	CF_3	90 min	90[g]	92[g] (2)	86[g] (−4)		16	33	16	

[a] Procedure (Caution) as described in Section 3; ee yield determined by CSP GC.
[b] A = hexafluorophosphate unless noted otherwise.
[c] 1 equivalent used.
[d] Time to discharge of dark green color to brown/orange.
[e] ee with L minus ee without L.
[f] Previously reported by us [4–9].
[g] A = nitrate.

caused the maximum ee with complex **1**: W = X = Z = Cl whereas 1.0 equivalents were required in the case of complex **1**: W = H, X = Z = F. These results showed that the catalysis system was more complex than originally thought [10], as represented in Fig. 1. Our working hypothesis [19,20] includes an additional set of equilibria involving the additive and both the Cr(V)=O oxidant and Cr(III) reaction product.

We now report that a wide range of other additive-types, including both oxo- and non-oxo species, influence the epoxidation.

2. Results and discussion

Tables 1–4 show results for the epoxidation in Scheme 1 using a selection of our oxo-chromium(V)

Table 2
Results of stoichiometric epoxidation[a] of *E*-β-methylstyrene according to Scheme 1 with various chiral non-racemic substituted oxo-chromium(V) salen complexes[b] in the presence of various π-rich compounds as added ligands L[c]

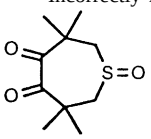
Entry	Additive L	Δee[e] (yield %) for complexes 1: WXZ				
		HHH	H^{t}Bu^{t}Bu	ClClCl	HHCl	HHCF_3
	No additive[d]	58 (22)	67 (10)	68 (19)	80 (20)	88 (25)
1	Fluorenone (**2**)	−5 (47)	8 (17)	−8 (2)	−7 (2)	−3 (5)
2	Fluorene (**3**)	−4 (14)	6 (13)	4 (18)	−14 (<1)	
3	Dibenzosuberone (**4**)	−5 (22)	6 (11)	7 (6)	−6 (2)	−12 (13)
4	Dibenzosuberane (**5**)		6 (14)			
5	Naphthalene	9 (25)			1 (10)	
6	Ferrocene			−42 (<1)		

The triplets HHH, H^{t}Bu^{t}Bu, etc. denote substituents for WXZ (see Scheme 1).
[a] Procedure (Caution) as described in Section 3; ee yield determined by CSP GC.
[b] A = hexafluorophosphate.
[c] 1 equivalent added, unless noted otherwise.
[d] Previously reported by us, references [4–9].
[e] ee with L – ee without L.

Table 3
Results of stoichiometric epoxidation[a] of *E*-β-methylstyrene according to Scheme 1 with various chiral non-racemic substituted oxo-chromium(V) salen complexes[b] in the presence of various oxo-compounds as added ligands L[c]

Entry	Additive L	Complex 1: WXZ	ee	Δee[d] (%)	Yield (%)
	No additive	HHH	58		22
		ClClCl	68		19
		HHCl	80		20
		$HHCF_3$	88		25
	With DMSO	HHH		8[e]	–
		ClClCl		2[e]	12
		HHCl		2[e]	10
		$HHCF_3$		−2	16
	With DMF	HHH		11[e,f]	–
		ClClCl		3[e]	10
		HHCl		−2[e]	46
				−2[e,f]	56
		$HHCF_3$		−6	15
				−10[g,h]	8
With additive L					
1	Benzyltert-butylsulfoxide	HHH	62	4	–
2	Anisyltoluylsulfoxide	HHH	66	8	–
3	Sulfoxide (8)	ClClCl	77	9	15
4	Sulfolane	HHCl	71	−9	–
5	Dibenzothiophenesulfone	H^{t}Bu^{t}Bu	73	6	7
6	*p*-Toluenesulfonamide	HHCl	78	−2	20
7	Methyl *p*-toluenesulfonate	HFF	69	−3	27
8	Methyl *p*-toluenesulfonate	HH^{t}Bu	87	3	20
9	1-Methyl-2-pyrrolidinone	HHCl	81	1	30
10	1-Methyl-2-pyrrolidinone	HFF	80	9	27
11	Urea	$HHCF_3$	86	−2	13
12	Ethyl acetate	HHCl	70	−10	–
13	Acetone	HHCl	73	−7	–
14	Diphenyl tin chloride	ClClCl	78	10	3
15	18-Crown-4	HHCl	85	5	5

[a] The triplets HHH, CICICI etc. denote substituents for WXZ (see Scheme 1). Procedure (Caution) as described in Section 3; ee yield determined by CSP GC.
[b] A = hexafluorophosphate unless noted otherwise.
[c] 1 equivalent added, unless noted otherwise.
[d] ee with L minus ee without L (Table 1).
[e] Previously reported by us, references [4–9].
[f] 2 eqvivalents of additive.
[g] A = nitrate.
[h] Incorrectly reported as −23 in [8]



sulfoxide **8**.

salen complexes in combination with various types of additives. We had previously [19] confirmed that the influence of small amounts of water and atmospheric oxygen on the reaction was minimal. We have also shown [8] that the effects of extended reaction times and possible kinetic resolution effects are not significant under these conditions. Successful epoxidation requires [10] a non-nucleophilic counterion, A in Scheme 1, and we had previously [4–6] used hexafluorophosphate. We have recently found [8,9] that

Table 4
Results of stoichiometric epoxidation[a] of *E*-β-methylstyrene according to Scheme 1 with various chiral non-racemic substituted oxo-chromium(V) salen complexes[b] in the presence of various imidazoles and phosphorus compounds as added ligands L[c]

Entry	Additive L	Δee[e] (yield %) for complexes 1: WXZ		
		HHH	ClClCl	HHCl
	No additive[d]	58 (22)	68 (19)	80 (20)
1	Imidazole			2 (37)
2	1-Methylimidazole			3 (48)
3	2-Methylimidazole			2 (38)
4	1-Benzylimidazole	−1 (23)		−36 (8)
5	4,5-Diphenylimidazole	−5 (11)		−5 (11)
6	4-Phenylimidazole	−2 (18)		−13 (4)
7	4-Nitroimidazole	1 (20)		−1 (7)
8	Ph_3PS	2 (29), 5[f] (5)	nr	nr
9	(±)-*o*-AnMePhPS[f]	−1 (4)		nr
10	(±)-*o*-AnMePhPNH[f]	nr		nr
11	(±)-*o*-AnMePhPBH3[f]	10 (40)		nr
12	Ph_3P=CHAr[g]		68 (19)	
13	Ph_3P		nr	

The triplets HHH, H^{t}Bu^{t}Bu, etc. denote substituents for WXZ (see Scheme 1).

[a] Procedure (Caution) as described in the Section 3; ee yield determined by CSP GC; nr denotes that no epoxide was formed even though the green color of Cr(V) = O was discharged.

[b] A = hexafluorophosphate unless noted otherwise.

[c] 1 equivalent added, unless noted otherwise.

[d] Previously reported by us, references [4–9].

[e] ee with L minus ee without L.

[f] 2 equivalents of additive.

[g] Ar = 4-bromophenyl.

nitrate gives better selectivity, and therefore, some results with it are included in the tables but they are qualitatively similar. The solvent used was acetonitrile but, in previous additive studies [5,9] we showed that dichloromethane gave similar results to acetonitrile. We found no influence of additive concentration in any of the work reported here. The tables include, for comparison purposes, some results previously published by us.

2.1. General observations

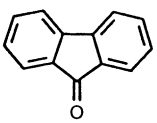
The first entries in Table 1 give the (previously reported) reaction times, yields, and ee with no additive for each complex [4–9]. It is well established that electron-withdrawing groups are required for reasonable reaction times [5,6,9,10] and this can be seen clearly in Table 1. The time quoted is that for the discharge of the very dark green color of the Cr(V)=O species to the brown/orange color of Cr(III) when there is no additive present. Because the Cr(III) product may also consume the oxidant, these reaction times do not necessarily reflect the reaction rate of Cr(V)=O with epoxide. The yields of epoxide produced vary markedly with the salen substitution pattern and the ligand added but it is very noticeable that they are never much greater than 50%. We attribute this to the reaction of the Cr(V)=O species with the Cr(III) product [8], which can occur more readily in the stoichiometric reaction. The presence of additive usually decreased the reaction time, sometimes by as much as half, indicating a weak ligand accelerated catalysis effect [24].

We found triphenylphosphine oxide (TPPO) to be one of the most effective at raising the ee and yield and our previously reported results for it are included in Table 1. A general trend in enantioselectivity with TPPO is visible. The complexes are arranged in order of increasing ee without additive, and it can be seen very clearly that the beneficial effect of TPPO as additive becomes less as the ee without additive increases. Thus, the values of the Δee entries (ee with L minus

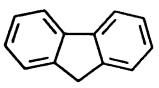
ee without L) become smaller or go negative downwards in Table 1. We refer to this as a *ceiling effect of additive* and we have discussed it [4,9] in the context of how the additives L can influence ee despite the fact that they are co-ordinated on the opposite side of the metal atom from the proposed alkene approach trajectory. Thus, our working hypothesis is that the metal salen complexes **1** are not planar and that both Z-substituents and additives L can favorably influence their conformation to give better selectivity. In complexes with suitable Z-substituents, the conformation without L reaches an optimum and the effect of L is, thus, minimal. Wiest and Plattner and co-workers [12–15], have proposed a similar explanation for the same types of additive effects in the manganese series.

2.2. Additives with extended π-systems

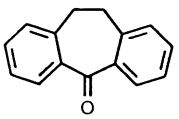
Table 2 shows results with some additives that have extended aromatic π-systems. We initially became interested in these because of the result with naphthalene and complex **1**: W = X = Z = H (entry 5) which showed a significant elevation of ee. We were not entirely surprised by this because Katsuki and co-workers [3,25–27] have pointed out consistently that the success of the manganese epoxidation system may be partly to do with π–π interaction of one of the salen aromatic rings and the conjugated portion of the incoming alkene. Imanishi and Katsuki had also reported notable effects of aromatic solvents on the chromium system [21]. We also knew [5,6] that carbonyl additives could effect the selectivity (Table 3). So we chose to examine some systems (**2**–**5**) which we thought might interact with both salen aromatic rings (entries 1–4). However, it can be seen that although all four compounds give noticeable effects when added to the epoxidation reaction, they are mostly detrimental to ee and to yield, especially with the more reactive complexes.



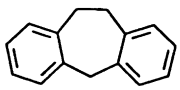
fluorenone **2**



fluorene **3**

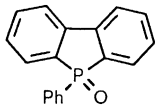


dibenzosuberone **4**

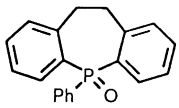


dibenzosuberane **5**

Then, aware that TPPO was the best additive, we considered the compound 5-phenyl-5*H*-dibenzo[b,d]-phosphole 5-oxide (DBPO-**6**) which results from the fusion of two of the phenyl rings in TPPO to give a flat π-system. As can be seen from Table 1, DBPO does indeed give very strong elevations of ee but the effect is not as consistent as that for TPPO. Indeed these effects could be characterized as wildly variable because DBPO gives the highest ee obtained by us with one complex (**1**: W = X = Z = H), the lowest with another (**1**: W = H, X = Z = Cl) and almost no effect in other cases. We speculated that this might be due to the reduction in *o*-effects upon fusion and/or the creation of the flat π-rich system capable of interacting with the salen rings. Thus, in interaction with the additive, the complex may attain a more or less favorable conformation depending on the salen substitution pattern.



DBPO **6**



DDPO **7**

To try to probe these issues a little further, we examined the effect of 10,11-dihydro-5-phenyl-5*H*-dibenzo[b,f]phosphepin-5-oxide (DDPO-**7**) which has interrupted conjugation and a fairly strong *peri*-effect. Surprisingly it reduced the reaction rate by stabilizing the Cr(V)=O species, which was apparent from the persistence of its green color for a much longer period during the experiment. There was effectively no reaction with previously sluggish complexes, Table 1, and a further reduction of ee with complex **1**: W = H, X = Z = Cl. We assume that the flexibility of species **7** allows it to fit into the non-planar shape of the complex [9] and establish π–π interactions with both aromatic salen rings.

From these results we concluded that the beneficial effects of DBPO were a result of both the PO bond and extended π-moieties. However, since all of these compounds showed the ceiling effect quite strongly,

we did not pursue their study any further. Another discouragement was that we could not detect any clear trends in the yields with the various additives. One other notable effect of a π-rich compound was with ferrocene (Table 2, entry 6) which effectively shut down the epoxidation reaction.

2.3. Additives with other oxo-group types

We had previously shown that dimethylsulfoxide (DMSO) and dimethylformamide (DMF) were beneficial to ee and yield in a manner similar to TPPO but to a lesser extent. The first part of Table 3 shows some of these previous results along with further results for related compounds using the same set of complexes. Entries 1–8 are various sulfur compounds having at least one S=O bond and it can be seen that no variant provides much improvement over DMSO. The only notable case is entry 8 where methyl *p*-toluenesulfonate provides an increase in ee with complex **1**: W = X = H, Z = ^{t}Bu, which is the only instance of an increase with that complex. Entries 9–13 are various carbonyl compounds, which, again, provide no improvement over DMF. Two other additives merit brief mention. It had been suggested in the manganese series that spin crossover effects might be significant in the epoxidation reaction [28]. We, therefore, added diphenyl tin dichloride to an epoxidation reaction. Such tin compounds are known to form bimetallic co-ordination compounds with salen complexes [29,30] and we thought the heavy tin atom might influence the spin properties of the chromium atom. Indeed this additive did have a noticeable effect in a test reaction, giving one of the highest ees to be obtained with complex **1**: W = X = Z = Cl, although the yield was poor (entry 14). We feel that this effect deserves further study. Finally, the addition of a crown ether was also quite beneficial to ee (entry 15).

2.4. Imidazoles as additives

Katsuki and co-workers [31] had shown that imidazoles were very beneficial additives in certain cases in the manganese series. We, therefore, assayed a number of them in our system, Table 4 (entries 1–7). The unsubstituted and methyl-substituted cases do indeed provide some modest ee increases and substantial improvements in yield for the cases studied (entries 1–3). On the other hand, substitution with aromatic groups provides large decreases in both yield and ee (entries 4–6). This striking result would seem to bear out the importance of π-interactions in these systems and we speculate again that the possession of two aromatic rings enables the molecule to interact effectively with both salen aromatic rings, thereby causing the effects noted.

2.5. Other phosphorus chalogenides as additives

Phosphine sulfides were potentially interesting as additives because there is a likely competitive conversion to oxide. In the event (Table 4, entry 8), triphenylphosphine sulfide survived the less active unsubstituted complex, which then gave some epoxidation with ee elevation. The yield of epoxide with one equivalent sulfide was 30%, dropping to 5% with 2 equivalents of additive, so the effect is real. With other more active complexes, conversion to phosphine oxide predominated. A more easily oxidized sulfide did not survive even the less active complex (entry 9). This was also the case with phosphinimine (entry 10) but the phosphine borane also survived contact with the less active complex and gave reasonable ee elevation (entry 11). Remarkably a phosphorus ylide added to the epoxidation reaction had no deleterious effect (entry 12). In fact, in the absence of substrate, addition of the ylide prolonged the lifetime of the hexachloro-chromium–salen oxo complex. Thus, the complex usually decomposed over a 3-day period as evidenced by a reversion to the orange color of Cr(III) and a black precipitate. In the presence of the ylide the decomposition took one week to complete. Other products in the latter case included TPPO, 4-bromobenzaldehyde and 4-bromotoluene presumably by oxidation/hydrolysis of the ylide. Unsurprisingly, triphenylphosphine was instantaneously oxidized to its oxide (entry 13).

3. Experimental

3.1. Precursor chromium(III) complexes and additives

We have previously described [8] the method of synthesis of the precursor Cr(III) complexes (deoxy-**1**, A = NO_3, PF_6, L = none). Commercially available

additives were used as purchased. 5-Phenyl-5*H*-dibenzo[b,d]phosphole 5-oxide (DBPO) was made according to the precise procedure of Reutov and co-workers [32] and 10,11-dihydro-5-phenyl-5*H*-dibenzo[b,f] phosphepin-5-oxide (DDPO) was prepared by the one-pot procedure of Warren and co-workers [33].

3,3,6,6-Tetramethyl-1-thiacycloheptan-4,5-dione 1-oxide (sulfoxide **8**) was prepared from its precursor sulfide which in its turn was prepared from 3-chloropivalic acid in four steps by the method of de Groot and Wynberg [34]. The oxidation was performed as follows: to a solution of 3,3,6,6-tetramethyl-1-thiacycloheptan-4,5-dione (0.30 g, 1.5 mmol) in dichloromethane (10 ml) was added *m*-chloroperbenzoic acid (0.38 g, 2.2 mmol). The solution was stirred overnight and was concentrated in vacuo leaving a white solid, recrystallized from diethyl ether yielding (0.26 g, 78%) of (**8**) white needles: m.p. 119–120 °C; δH($CDCl_3$) 3.14 (s, 2H, CH_2), 3.13 (s, 2H, CH_2), 1.41 (s, 3H, CH_3), 1.41 (s, 3H, CH_3); δC($CDCl_3$) 210.1, 60.8, 44.2, 25.2 and 24.2. υ_{max} (KBr) cm^{-1}: 2967, 1712, 1466, 1384, 1262, 1089, 1032, 923, 874, 802, 711, 599 and 478. Anal. Calcd. for $C_{10}H_{16}SO_3$: C, 55.53; H, 7.55. Found: C, 54.99; H, 7.33.

(±)-*o*-Anisylmethylphenylphosphine [35,36] and its sulfide [37], *N*-phenylimine [38] and borane adduct [39] were made according to literature methods. [(4-Bromophenyl)methylidene]triphenylphosphorane was prepared by the action, under nitrogen, of dimsyl sodium on the precursor salt, itself prepared from triphenylphosphine and 4-bromobenzyl bromide.

3.2. Epoxidation reactions

Complexes **1** were generated and used in situ (Caution—Cr(V) compounds are known carcinogens) by reaction of the precursor Cr(III) complex with iodosylbenzene and subsequent addition of the relevant ligand L, followed by the alkene. Thus, iodosylbenzene [40] (1–2 equivalents) was added to a stirred solution of the appropriate (salen) Cr(III) complex (30 mg, 1 equivalent) in CH_3CN (5 ml). A deep green/black color appeared almost immediately. After stirring for 30 min this solution was filtered and the filtrate cooled to 0 °C using an ice/water bath. The relevant ligand L (usually 1 equivalent) was added followed 5 min later by *E*-β-methylstyrene (1 equivalent). The reaction mixture was stirred at 0 °C until the brown/orange color of the (salen)Cr(III) complex returned completely. This usually took 0.5–1.5 h, except in the unsubstituted and alkyl/aryl-substituted cases (1–2 days) and the *tert*-butyl cases (up to 1 week). The solvent was removed in vacuo and the residue treated with Et_2O. The Et_2O washings were flushed through a short alumina column with Et_2O and concentrated in vacuo to a small volume (∼1 ml). After addition of *n*-decane (1 μl) as internal standard, this sample was analyzed by chiral stationary phase gas chromatography on a Supelco α-cyclodextrin capillary column (alphadex 120), 30 m × 0.25 mm i.d., 0.25 μm film operated at an injection temperature of 230 °C and a column temperature of 93 °C, with a column pressure of 18 psi. Retention times for the epoxides were 15.9 min (*S*,*S*) and 16.5 min (*R*,*R*) approximately under these conditions. Yields of epoxide varied with complex and additive used but were usually in the ranges as follows: W–Z = H: 20–45%; X = Z = Cl: 10–35%; Z = Cl: 5–50%; Z = CF_3: 10–30%; W = X = Z = Cl: 5–20%; X = Z = ^{t}Bu: 5–15%. Reduced yields are approximately accounted for by recovered alkene, along with some benzaldehyde and benzyl methyl ketone. Burn ratios used and determination of absolute configurations have been given previously [8]. Investigations into the effects of extended reaction times and possible kinetic resolution effects indicated that these are not significant under these conditions [8].

4. Conclusions

Taking into account our previous work, a large number of additives have now been found to influence the selectivity of asymmetric alkene epoxidation with oxo chromium(V) salen complexes. These can be divided into two groups: those with and without oxo functional groups. Of the former triarylphosphine oxides are still the best additives both for raising the selectivity and the yield. Of the latter, those with extended π-systems are effective. A combination of the two types does give some spectacular changes in selectivity but, unfortunately, these do not occur for those complexes that already give a high ee in the absence of additive. Most significantly, these obser-

vations lend support to the general ideas of Katsuki [3] regarding the importance of π-interactions for selectivity in the manganese system.

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