A Structurally Characterized Dichloro-manganese(IV) Complex Capable of Halogenating Alkenes

Neil A. Law, Timothy E. Machonkin, Joel P. McGorman, Erlund J. Larson, Jeff W. Kampf and Vincent L. Pecoraro*

Department of Chemistry, The University of Michigan, Ann Arbor, MI 48109-1055, USA

$Mn^{IV}(salpn)Cl_2$ regioselectively *trans*-halogenates alkenes in a reaction for which the Mn-containing product is also identified; this is the first Mn-based halogenating system for which the reactive and final Mn-containing products are structurally characterized.

Several reagents exploiting moderate or high valent manganese are known that *trans*-chlorinate alkenes. These include $Mn^{IV}O_2$–Me_3SiCl in THF (40–60 °C)[1–2] and Mn^{III} acetate–$CaCl_2$ (5:6)[3] or Mn^{III} acetate–acetyl chloride[3] in acetic acid at 177 or 0 °C, respectively. Other examples are $Mn^{IV}O_2$–$Mn^{II}Cl_2$–acetyl chloride (1:1:4) in DMF at −45 °C,[4] and $KMnO_4$–oxalyl chloride (1:2) in dichloromethane.[5] While these systems are of practical importance, little is known about the actual active chlorinating agent. We now report dichloro-$(N,N'$-(salicylidene)-1,3-propanediamino)manganese(IV), Mn^{IV}-(salpn)Cl_2, as the first moderate valent manganese complex that selectively *trans* chlorinates alkenes, for which both the active and the product manganese complexes have been crystallographically characterized.

Deep forest green $Mn^{IV}(salpn)Cl_2$ 1, was synthesized by the addition of 2 mol. equiv. of dry HCl gas in distilled acetonitrile to a 30 ml solution of $Mn^{III}(salpn)Cl$ in distilled dichloromethane or acetonitrile. After stirring for 1 min, a solid impurity was removed by gravity filtration. Diethyl ether (anhydrous) or distilled hexanes were then added to the stirring filtrate to precipitate microcrystalline 1. The material was dried *in vacuo* for 2 h and stored at −70 °C under argon. Single crystals of 1 for X-ray analysis were grown by vapour diffusion of diethyl ether into a dichloromethane solution of 1 at −70 °C. $Mn^{III}(salpn)Cl$ was prepared *via* the procedure reported for $Mn^{III}(salen)Cl$ by substituting 1,3-diaminopropane for ethylenediamine.[6] $Mn^{III}(salpn)(MeOH)Cl$ 2, was synthesized by the addition of 10 mmol $Mn^{II}Cl_2\cdot4H_2O$ to a solution of 10 mmol of H_2salpn in 250 ml of MeOH to which 1 molar equiv. of a 25% by mass sodium methoxide solution had been added. Single crystals of 2 were grown by vapour diffusion of diethyl ether into a methanol solution of 2.

Fig. 1 presents the crystal structures† of 1 and 2. In both cases, the salpn[2−] ligand binds to the manganese so that all four of its donor atoms are in the equatorial plane, with the chloride(s) axial. Despite the difference in manganese oxidation states, the equatorial metal–ligand distances are nearly the same for 1 and 2. However, the Mn^{IV}–Cl bond lengths of 2.290(1) and 2.253(1) Å lengthen significantly upon reduction to Mn^{III}, which has a Mn^{III}–Cl bond length of 2.493(1) Å. Such pseudo-Jahn–Teller elongations for the high-spin Mn^{III} ion (d^4) are consistent with a $d_{x^2-y^2}$ LUMO. Thus, addition of an electron to a Mn^{IV} occurs along the z-axis in the d_{z^2} orbital. This indicates that 1 is perfectly poised to generate 2 plus Cl· which suggests that 1 might be capable of chlorinating alkenes.

A deep green solution forms when 1 dissolves in either dry acetonitrile or dichloromethane. $Mn^{IV}(salpn)Cl_2$ is water sensitive, as with similar $Mn^{IV}Cl_2$ Schiff base complexes.[7] The EPR spectrum of 1 at 77 K exhibits a set of features with resolved Mn hyperfine that is indicative of an axial Mn^{IV} ion (d^3). A characteristic UV–VIS absorption of 1 in dichloromethane is found at 650 nm ($\varepsilon = 6000$ dm³ mol⁻¹ cm⁻¹). Complex 1 also exhibits a quasi-reversible reduction wave (Mn^{IV}–Mn^{III}) at +890 mV *vs.* SCE in dichloromethane. This reduction potential is also suggestive of the ability for this complex to halogenate alkenes. $Mn^{III}(salpn)(MeOH)Cl$ is EPR silent at 77 K and forms green–brown to brown coloured solutions in acetonitrile or dichloromethane.

Upon addition of an alkene-containing substrate, *e.g.* cyclohexene, to a solution of 1 in stoppered flasks to exclude light, the solution gradually changes to a reddish-brown colour, while the Mn^{IV} EPR signal disappears. After completion of the reaction (18–48 h), isolation of the manganese product by precipitation with hexanes yields a Mn^{III} species with chemical properties that closely match those of compound 2. This demonstrated that 2 or a complex closely similar to 2 is the Mn-containing product of this reaction. The exact chemical composition of this product depends on whether or not a solvent molecule is present that could coordinate to the Mn^{III} to give the six-coordinate structure like that shown for 2 or to give the five-coordinate $Mn^{III}(salpn)Cl$ analogue of $Mn^{III}(salen)Cl$.[6] Additionally, chlorination of alkenes by 2 was not observed.

Complex 1 is capable of chlorinating alkenes (Scheme 1) with a high degree of selectivity for *anti*-addition. The Mn-products were separated on 10 cm³ hexanes-packed Florisil columns. Products were analysed by GC-MS with o-di-
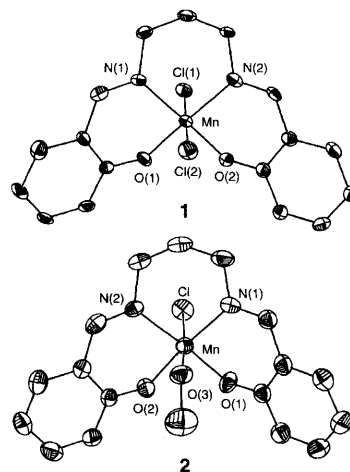

Fig. 1 ORTEP diagrams of $Mn^{IV}(salpn)Cl_2$ 1 and $Mn^{III}(salpn)(MeOH)Cl$ 2. Selected bond distances (Å) and angles (°). For 1: Mn–Cl(1) 2.290(1), Mn–Cl(2) 2.253(1), Mn–O(1) 1.871(3), Mn–O(2) 1.860(2), Mn–N(1) 2.019(3), Mn–N(2) 2.027(4), Cl(1)–Mn–Cl(2) 174.94(6), Cl(1)–Mn–O(1) 91.5(1), Cl(1)–Mn–O(2) 94.0(1), Cl(1)–Mn–N(1) 89.4(1), Cl(1)–Mn–N(2) 88.6(1), Cl(2)–Mn–O(1) 91.9(1), Cl(2)–Mn–O(2) 89.8(1), Cl(2)–Mn–N(1) 89.6(1), Cl(2)–Mn–N(2) 88.1(1), O(1)–Mn–O(2) 88.9(1), O(1)–Mn–N(1) 89.6(1), O(1)–Mn–N(2) 177.8(1). For 2: Mn–Cl(1) 2.493(1), Mn–O(3) 2.407(3), Mn–O(1) 1.874(3), Mn–O(2) 1.895(3), Mn–N(1) 2.020(3), Mn–N(2) 2.042(3), Cl(1)–Mn–O(3) 169.98(9), Cl(1)–Mn–O(1) 97.3(1), Cl(1)–Mn–O(2) 97.5(1), Cl(1)–Mn–N(1) 92.4(1), Cl(1)–Mn–N(2) 89.8(1), O(3)–Mn–O(1) 91.8(1), O(3)–Mn–O(2) 86.8(1), O(3)–Mn–N(1) 83.7(1), O(3)–Mn–N(2) 81.2(1), O(1)–Mn–O(2) 88.8(1), O(1)–Mn–N(1) 88.2(1), O(1)–Mn–N(2) 172.8(1) (Thermal ellipsoids are at 50% probability).
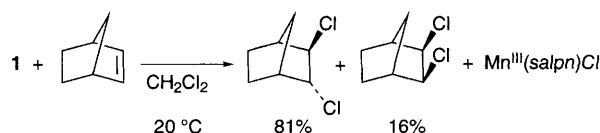
Scheme 1

Table 1 Selected results from reactions of **1** with alkenes

Substrate	Solvent	Product(s)^a	Yield (%)	1 : Substrate
Cyclohexene	CH_2Cl_2	trans-1,2-dichlorocyclohexane	95	5 : 1
Cyclohexene	CH_2Cl_2	trans-1,2-dichlorocyclohexane	68	2 : 1
Cyclohexene	CH_2Cl_2	trans-1,2-dichlorocyclohexane	41	1 : 1
Cyclohexene	CH_3CN	trans-1,2-dichlorocyclohexane	8	1 : 1
Norbornene	CH_2Cl_2	trans-2,3-dichloronorbornane	81	2 : 1
		cis-2,3-dichloronorbornane	16	
(R)-Limonene	CH_2Cl_2	(R)-1,2-dichloro-1-methyl-4-isopropenylcyclohexane	29	2 : 1
		(R)-4-(1,2-dichloroisopropyl)-1-methylcyclohex-1-ene	42	
4-Vinyl cyclohexene	CH_2Cl_2	1,2-dichloro-4-vinylcyclohexane	40	2 : 1
		4-(1,2-dichloroethyl)cyclohex-1-ene	7	
3-Methylcyclohex-1-ene	CH_2Cl_2	3-methyl-1,2-dichlorocyclohexane	14	1 : 1

^{a} Absolute configurations for the new stereocentres were not determined.

chlorobenzene as a standard, and ^1H NMR. The data for some representative compounds are presented in Table 1. Complex **1** also trans-halogenated trans-stilbene, cyclohex-2-en-1-ol and cyclooctene. (R)-Limonene was chlorinated in a 71% overall yield, but with the opposite alkene site preference from that reported for the proposed in situ $Mn^{IV}Cl_4$ of Bellesia et al.[1–2] For comparison, **1** gave up to a 5:1 ratio of trans:cis-2,3-dichloronorbornane, whereas iodobenzene dichloride generated a 3:1 ratio,[8] while $Mn^{IV}O_2$–Me_3SiCl produced a 10.6:1 ratio of products.[1] Complex **1** does not chlorinate cyclopropane rings, terminal alkynes and deactivated alkenes such as 3,3-dimethylbut-1-ene. With the exception of a low yield of p-chlorophenol from phenol, chlorination of other activated benzene rings by **1** does not occur, e.g. p-cresol, phenol red, 2,6-dimethylphenol and methoxybenzene. In contrast, some other Mn-based reagents have been reported to chlorinate aromatics,[9] while $Mn^{IV}O_2$–Me_3SiCl will chlorinate 3,3-dimethylbut-1-ene.[1] Therefore, **1** is capable of halogenating certain alkenes in the presence of functional groups that may be susceptible to attack by other manganese reagents.

Although the exact mechanism of chlorination by **1** is not yet known, there is some evidence for what that pathway might be. When chlorination occurs via an ionic pathway,[8] cis and trans 2,3-dichloronorbornane are not the major products. Instead, nortricyclenyl chloride and exo-2-syn-7-dichloronorbornane predominate due to skeletal rearrangements. This suggests that **1** probably reacts via a radical or caged radical pathway. Similarly, Bellesia et al. suggested that their proposed in situ $Mn^{IV}Cl_4$, formed from $Mn^{IV}O_2$ and Me_3SiCl, reacted with alkenes via a non-chain radical mechanism.[1,2] Further, the dichloromethane solvent does not provide the chlorine in the product, since this reaction occurs in acetonitrile using **1** prepared in acetonitrile. No brominated products were detected for reactions run in 99% dibromomethane. These observations are consistent with those made for other Mn-based systems.[1–5]

While the previously reported manganese-containing chlorination systems chlorinate substrates more efficiently, it is still desirable to develop easily handled coordination complexes to facilitate such transformations. We have described a system which is a competent reagent for the chlorination of alkenes. $Mn^{IV}(salpn)Cl_2$ shows a preference for halogenating at electron rich alkene sites with a high degree of selectivity for trans products to give yields that approach or equal those of other previously reported manganese-based systems. The active $Mn^{IV}(salpn)Cl_2$ complex itself is easily prepared and is of known composition, and may be stored for months at $-70\,^{\circ}C$. The final Mn-containing product from the chlorination reaction is easily separated from the reaction mixture, and has been identified as a Mn^{III} complex similar to the $Mn^{III}(salpn)$-(MeOH)Cl complex reported here.

Footnote

† *Crystal data* for **1** and **2**. $Mn^{IV}(salpn)Cl_2$ **1**: $C_{17}H_{16}Cl_2MnN_2O_2$, M = 406.19, monoclinic, space group $P2_1/c$ (No. 14), a = 13.113(4), b = 9.635(3), c = 14.313(4) Å, β = 113.15°, V = 1662.7(9) Å^3, D_c = 1.62 g cm^{-3}, Z = 4, T = $-90\,^{\circ}C$, $F(000)$ = 828, Mo-Kα (λ = 0.70173), μ = 10.98 cm^{-1}. For $Mn^{III}(salpn)(MeOH)Cl$, **2**: $C_{18}H_{20}ClMnN_2O_3$, M = 402.79, orthorhombic, space group $P2_12_12_1$ (No. 19), a = 6.705(7), b = 14.46(1), c = 18.51(1) Å, V = 1795(3) Å^3, D_c = 1.49 g cm^{-3}, Z = 4, T = ambient, $F(000)$ = 832, Mo-Kα (λ = 0.70173), μ = 8.75 cm^{-1}. Intensity data were obtained on a Siemens R3m/v diffractometer, equipped with LT-2 for **1**. Three standard reflections were measured every 97 reflections. The data were collected using θ–2θ scans. The 2θ scan range was 5–50 and 3–50 for **1** and **2** respectively. The structures were solved on a VAX Station 3500 using the Siemens SHELXTL PLUS program package and were refined using full-matrix least squares. In subsequent refinement, the function $\Sigma w(|F_o| - |F_c|)^2$ was minimized. For **1**, 2532 reflections with $F_o \geqslant 2\sigma(F)$ were refined; 1754 for **2**. The agreement indices R = $\Sigma||F_o - F_c|| / |F_o|$ and R_w = $[\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2}$ were used to evaluate the results. For **1**, R = 0.0567, R_w = 0.0310 with GOF = 2.81. For **2**, R = 0.0356, R_w = 0.0248 with GOF = 2.45. Atomic scattering factors are from ref. 10. Atomic coordinates, bond lengths and angles, and thermal parameters for both compounds have been deposited at the Cambridge Crystallographic Data Centre. See Information for Authors, Issue No. 1.

References

1 F. Bellesia, F. Ghelfi, U. M. Pagnoni and A. Pinetti, J. Chem. Res.(S), 1989, 108.
2 F. Bellesia, F. Ghelfi, U. M. Pagnoni and A. Pinetti, J. Chem. Res.(S), 1989, 360.
3 K. D. Donnelly, W. E. Fristad, B. J. Gellerman, J. R. Peterson and B. J. Selle, Tetrahedron Lett., 1984, 25, 607.
4 F. Bellesia, F. Ghelfi, U. M. Pagnoni and A. Pinetti, Synth. Commun., 1991, 21, 489.
5 I. E. Markó and P. F. Richardson, Tetrahedron Lett., 1991, 32, 1831.
6 V. L. Pecoraro and W. M. Butler, Acta Crystallogr., Sect. C, Cryst. Struct. Commun., 1986, 42, 1151.
7 T. Matsushita, H. Kono and T. Shono, Bull. Chem. Soc. Jpn., 1981, 54, 2646.
8 B. Uemara, N. Okazaki, A. Onoe and M. Okano, Bull. Chem. Soc. Jpn., 1978, 51, 3568; D. D. Tanner and G. C. Gidley, J. Org. Chem., 1968, 33, 38; M. L. Poutsma, J. Am. Chem. Soc., 1965, 87, 4285.
9 F. Bellesia, F. Ghelfi, U. M. Pagnoni and A. Pinetti, J. Chem. Res.(S), 1991, 284.
10 International Tables for Crystallography, ed. Theo Hahn, D. Reidel Publishing Co., Boston, 1987, vol. A.