Manganese(II) complexes of di-2-pyridinylmethylene-1,2-diamo- 
ne di-Schiff base ligands: Structures and reactivity

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Abstract

Manganese(II) complexes \([\text{Mn}(L)X_2]\) were prepared and characterized, where \(L\) is a neutral di-Schiff base ligand incorporating pyridylmethylene donor arms, including \((1R,2R)\)-N,N\'-bis(6-methyl-2-pyridylmethylene)-1,2-diphenylethenediamine (\(L^1\)), \((1R,2R)\)-N,N\'-bis(6-methyl-2-pyridylmethylene)-1,2-cyclohexyldiamine (\(L^2\)), or \((1R,2R)\)-, \((1S,2S)\)- or racemic N,N\'-bis(2-pyri- 
dylmethylene)-1,2-cyclohexyldiamine (\(L^3\)), and X = ClO_4^- or Cl^- . Product complexes were structurally characterized, specifically including [Mn(R, 
R\_1)\_N\_Cl\_O\_4\_2] \((\text{NCCH}_3)_2\_\text{ClO}_4\_2\), [Mn(R,R\_L\_1)\_O\_2\_2\_\text{ClO}_4], and racemic [Mn(L\_1)\_Cl\_2]\_N\_Cl\_O\_4\_2. The first of these complexes 
features a heptacoordinate ligand field in a distorted pentagonal bipyramid, and the latter two are hexa- 
coordinate, but retain equatorially monovacant pentagonal bipyramidal structures. Complexes 
[Mn(L\_2)\_X\_2\_N\_Cl\_O\_4\_2] \((X = \text{Cl}^- \_ \text{ClO}_4^-)\) were reacted with the primary phosphine FeCH\_2PH\_2 (Fe = -C\_5H\_4FeC\_5H\_5), 
H\_2O and ethylidiazocacetate (EDA). The first two substrates prompted reactivity at a single ligand imine 
bond, resulting in hydrophosphinization and hydrolysis, respectively. Complexes of the derivative ligands 
were also structurally characterized. Evidence for EDA activation was obtained by electrospray ionization mass spectrometry, but catalytic carbene transfer was not obtained.

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1. Introduction

Transition metal catalysts supported by Schiff base ligands have assumed a prominent role in modern synthesis [1,2]. Perhaps the best known example is the use of chiral chloromanganese(III) salen complexes as catalysts for asymmetric epoxidations of prochiral olefins [3–5]. Distinct advantages of such ligands include their low cost, facile syntheses, and convenient incorporation of inexpensive, chiral 1,2-diamines into the ligand backbone. Moreover, the ligands generally afford air- and moisture-stable complexes. Compared to the manganese(III) complexes of dianionic salens just described, neutral di-Schiff base ligands incorporating 2-pyri- 
dylaldehydes in place of salicylates support divalent manga- 
nese(II). The constrained chelate bite resulting from replacement 
of the exocyclic phenolate oxygen donors with heterocyclic pyri- 
dines also alters the complex geometry [6–13]. Such complexes 
have been explored as chiral oxo atom transfer catalysts [6,12], 

and also as precatalysts for olefin polymerization [7]. Given the lat- 
ter as a precedent for low-valent organometallic chemistry, we 
postulated that the dipyridyldiimine Schiff base complexes 
might support group transfer reactions of softer isolobal fragments 
of oxene, such as carbenes and phosphinidenes. Manganese-cata-
lized cyclopropanation reactions are rare [14–16].

In the present work, we prepared the following ligands accord- 
ga to literature precedent: \((1R,2R)\)-N,N\'-bis(2-pyridylmethylene)- 
1,2-diphenylethenediamine (\(L^1\)), \((1R,2R)\)-N,N\'-bis(6-methyl-2-pyridylmethylene)-1,2-cyclohexyldiamine (\(L^2\)) [17,18]; \((1R, 
2R)\)-N,N\'-bis(6-methyl-2-pyridylmethylene)-1,2-cyclohexyldiamine (\(L^2\)) [19,20]; and \((1R,2R)\)-, \((1S,2S)\)- and racemic N,N\'-bis(2-pyri- 
dylmethylene)-1,2-cyclohexyldiamine (\(L^3\)) [6]. Mn(II) salts 
[MnX\_2\_N\_Cl\_O\_4\_2] \((X = \text{Cl}^- \_ \text{ClO}_4^-)\) were added in a 1:1 stoichiometry to ob- 
tain a variety of complexes [6]. \([\text{Mn}R,R\_L\_1]\_\text{N}\_\text{Cl}\_\text{O}_4\_2\_N\_\text{Cl}\_\text{O}_4\_2\), 
[Mn(R,R\_L\_2)\_O\_2\_2\_\text{ClO}_4], and racemic [Mn(L\_3)\_Cl\_2] were structurally 
characterized. Moreover, exploratory reactions with the air-
stable primary phosphine PH\_2CH\_2Fc (Fc = ferrocenyl, \(-C\_5H\_4FeC\_5H\_5\)) 
[21] and ethylidiazocacetate (EDA) [22] as potential phosphinide 
and carbene precursors were investigated. While indirect evidence 
for EDA activation was observed by mass spectrometry, group 
transfer catalysis was not obtained in solution for either precursor. Instead, novel complexes derived from ligand hydrophosphination
2. Experimental

All studies were carried out under inert atmosphere using standard techniques. Reagent grade solvents were degassed, dried by standard techniques and distilled before use. The di-Schiff base ligands (Scheme 1) were prepared by 2:1 condensation of 2-picinal or 2-methyl-6-picinal with the appropriate 1,2-diamine in EtOH solution according to literature precedent, and characterized by $^1$H NMR spectroscopy. Ferrocenylmethylphosphine (FcCH$_2$PH$_2$) [21] and $\alpha$-d$_1$-EDA [23] were prepared by literature procedures. A mixture of ordinary and d$_5$-EDA was obtained by esterification of glyicine in a 1:0.1:2 volume ratio of CH$_3$CH$_2$OH and CD$_3$CO$_2$H, followed by diazotization and extraction.

Mass spectrometry was performed on a Thermo Finnigan Polaris Q ion trap with a home-built nano-electrospray ionization source [24]. Polariometry was performed on an Autopol IV polarimeter with a 10 cm cell. Cyclic voltammetry was performed using a CH Instruments CH1730A potentiostat.$^{1}$H and $^2$H NMR spectra were obtained on a Varian Inova 500 spectrometer. Solution magnetic moments were determined by the Evans NMR method in CD$_2$OD at 298 K [25]. Elemental analyses were performed by Atlantic Microlabs, Inc. (Norcross, GA).

2.1. [Mn(L$^1$)(ClO$_4$)$_2$]$\cdot$H$_2$O

A solution of Mn(ClO$_4$)$_2$$\cdot$6H$_2$O (185 mg, 0.51 mmol) in acetonitrile (5 mL) [CAUTION: metal-organic perchlorate salts are potentially explosive!], was added dropwise to a solution of R,R,L$^1$ (203 mg, 0.51 mmol) in 5 mL acetonitrile. After stirring 15 min at room temperature, the deep yellow solution was reduced to ca. 2 mL under vacuum, and diethyl ether was added to precipitate the complex as a light-yellow solid. The solid was recovered by filtration, washed with diethyl ether and dried in vacuo. Yield: 316 mg, 94%. Anal. Calc. for C$_{20}$H$_{28}$Cl$_2$MnN$_4$O$_9$: C, 47.15; H, 3.65; N, 8.46. Found: C, 47.30; H, 3.55; N, 8.63%. $\mu_{eff} = 5.6$ $\mu_B$.

2.2. [Mn(L$^2$)(OH$_2$)$_2$](ClO$_4$)$_2$

Samples of Mn(ClO$_4$)$_2$$\cdot$6H$_2$O (200 mg, 0.55 mmol) and R,R-L$^2$ (183 mg, 0.57 mmol) were dissolved separately in CH$_3$CN (5 mL). The solution of the metal salt was added dropwise to that of the ligand. After stirring 15 min, the solvent was evaporated to yield a light-yellow solid. The product was recovered by filtration, washed with Et$_2$O and dried. Yield: 316 mg, 94%. Anal. Calc. for C$_{20}$H$_{28}$Cl$_2$MnN$_4$O$_{10}$: C, 39.36; H, 4.62; N, 9.18. Found: C, 39.71; H, 4.40; N, 9.15%. $\mu_{eff} = 5.7$ $\mu_B$. $[\chi^2]_a = -335.6$ (c 1.0, CH$_3$CN).

2.3. [Mn(L$^3$)(ClO$_4$)$_2$]$_2$H$_2$O

Complexes of racemic, R,R- and S,S-L$^3$ were prepared by a literature synthesis [6]. Anal. Calc. for C$_{41}$H$_{42}$Cl$_6$Mn$_2$N$_8$O$_8$: C, 38.32; H, 3.93; N, 9.93. Found: C, 38.32; H, 3.63; N, 9.92%. $[\chi^2]_a$ (c 1.0, CH$_3$CN) = $-308.0$ (R,R), $+311.0$ (S,S).

2.4. [Mn(L$^4$)(Cl)$_2$]$_2$H$_2$O

A solution of MnCl$_2$$\cdot$4H$_2$O (451 mg, 2.28 mmol) in methanol (20 mL) was added dropwise to a solution of racemic L$^3$ (734 mg, 2.51 mmol) in 5 mL acetonitrile. After stirring 45 min, the solution was reduced to 5 mL under vacuum, and diethyl ether was added to precipitate the complex as a yellow solid. The solid was recovered by filtration, washed with diethyl ether and dried in vacuo. Yield: 820 mg, 82%. Anal. Calc. for C$_{41}$H$_{42}$Cl$_6$Mn$_2$N$_8$O$_8$: C, 49.56; H, 5.08; N, 12.84. Found: C, 49.65; H, 5.18; N, 12.80%. $\mu_{eff} = 5.6$ $\mu_B$.

2.5. [Mn(L$^5$)(Cl)$_2$]

A 50 mL Schlenk flask was charged with solid samples of racemic [Mn(L$^5$)(Cl)$_2$]$_2$H$_2$O (100 mg, 0.23 mmol) and PH$_2$CH$_2$Fc (61 mg, 0.26 mmol). Dichloromethane (15 mL) was added, and the resulting orange solution was stirred at reflux overnight. Solvent was then removed under vacuum until approx. 3 mL remained. Excess diethyl ether was then added, affording a yellow/orange precipitate. The product was washed with diethyl ether (3 × 10 mL) and dried to constant mass. Yield: 150 mg, 94%. Anal. Calc. for C$_{22}$H$_{20}$Cl$_2$FeMn$_2$N$_4$P$_2$O$_9$Cl$_6$: C, 51.15; H, 4.95; N, 8.09. Found: C, 50.86; H, 5.06; N, 8.13%. $\mu_{eff} = 5.7$ $\mu_B$.

2.6. [Mn(L$^5$)(Cl)$_2$]

[Mn(L$^3$)(Cl)$_2$]$_2$H$_2$O (50 mg, 0.11 mmol) was dissolved in 5 mL MeOH and water was added (0.10 mL). Vapor diffusion of Et$_2$O afforded orange microcrystalline solids after several days. The product complex [Mn(L$^3$)(Cl)$_2$] was recovered by filtration, washed with Et$_2$O and dried under vacuum to constant mass. Yield: 19 mg (50%). Anal. Calc. for C$_{41}$H$_{42}$Cl$_6$Mn$_2$N$_8$O$_8$: C, 43.79; H, 5.21; N, 12.77. Found: C, 43.65; H, 5.26; N, 12.57%. $\mu_{eff} = 5.6$ $\mu_B$.

2.7. Reaction of [Mn(L$^3$)(X)$_2$] (X$^-$ = Cl$^-$, ClO$_4^-$) with EDA/styrene

In a typical reaction, racemic [Mn(L$^3$)(ClO$_4$)$_2$] (11.0 mg, 0.020 mmol) was dissolved in acetonitrile (3 mL) and heated to reflux. A solution of ethyldiazoacetate (Aldrich, 1.3 mmol in 5 mL of acetonitrile) combined with styrene (0.6 mL, 5.2 mmol) was added by syringe pump at a rate of 5.9 mL/h. Product distributions were determined by use of an HP 5890 GC–MS equipped with a Restek Corporation model RTX-OPP column. Solvent was removed under vacuum and the residue was purified by flash column chromatography (hexanes/ethyl acetate, 9:1 on silica) to yield a mixture of trans and cis cyclopropane isomers (308.0 mmol) with EDA/styrene.

In a second column (pentanes/ethyl acetate, 97:3, 1:1, chloroform) combined with styrene (0.6 mL, 5.2 mmol) was added by syringe pump at a rate of 5.9 mL/h. Product distributions were determined by use of an HP 5890 GC–MS equipped with a Restek Corporation model RTX-OPP column. Solvent was removed under vacuum and the residue was purified by flash column chromatography (hexanes/ethyl acetate, 9:1 on silica) to yield a mixture of trans and cis cyclopropane isomers (308.0 mmol) with EDA/styrene.

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combined in solution with d6-DMF added as an internal standard and heated to reflux under argon; aliquots of the reaction solution were analyzed directly without workup by 1H NMR spectroscopy. Mass spectrometric characterization of EDA activation by metal complexes was performed by direct injection of reaction solutions.

2.8. X-ray crystallography

Diffraction-quality crystals of [Mn(R,L)-L1](NCMe)3(ClO4)2(MeCN) were grown by slow diffusion of Et2O vapor onto a concentrated CH2CN solution at room temperature. The structure was determined during the 2007 Summer Crystallography School at the University of California San Diego Small Molecule Crystallography Facility, directed by Professor Arnold L. Rheingold (M.P.J.). A pale yellow block (0.20 x 0.20 x 0.20 mm) was mounted on a Bruker SMART APEX CCD diffractometer and data were collected at T = 100(2) K using Mo Kα (λ = 0.71073 Å). The SMART program package was used to determine unit cell parameters and collect data [29]. The raw frame data were processed using SADABS and a multi-scan absorption correction was applied. The linear absorption coefficient, atomic scattering factors, and anomalous dispersion corrections were calculated from values found in the International Tables of X-ray crystallography [33].

Table 1

<table>
<thead>
<tr>
<th>Complex</th>
<th><a href="NCCH3">Mn(R,L)-L1</a>_3(ClO4)_2</th>
<th><a href="OH2">Mn(R,L)-L2</a>_2(ClO4)_2</th>
<th>[Mn(L)-L2]2Cl2</th>
<th>[Mn(L)-L2]2Cl2</th>
<th>[Mn(L)-L2]2Cl2</th>
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</thead>
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<td>Empirical formula</td>
<td>C14H13Cl3MnN6O6</td>
<td>C28H32Cl4MnN8O10</td>
<td>C35H44Cl2MnN8O8</td>
<td>C31H37Cl6FeMnN4PC</td>
<td>C12H17Cl2MnN3</td>
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<td>792.12</td>
<td>1.056</td>
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<tr>
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<td>monoclinic</td>
<td>monoclinic</td>
<td>monoclinic</td>
<td>monoclinic</td>
</tr>
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<td>P21 (No. 4)</td>
<td>C2/c (No. 15)</td>
<td>P2/c (No. 4)</td>
<td>P2/c (No. 4)</td>
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<tr>
<td>a (Å)</td>
<td>8.9191(3)</td>
<td>8.9555(6)</td>
<td>13.0499(9)</td>
<td>13.0499(9)</td>
<td>13.0499(9)</td>
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<tr>
<td>b (Å)</td>
<td>11.1432(8)</td>
<td>11.2871(1)</td>
<td>16.3529(9)</td>
<td>15.8623(6)</td>
<td>15.8623(6)</td>
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<tr>
<td>c (Å)</td>
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<td>13.7974(4)</td>
<td>17.4531(6)</td>
<td>17.4531(6)</td>
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</tr>
<tr>
<td>Z</td>
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<td>2</td>
<td>4</td>
<td>4</td>
<td>4</td>
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<td>Density (calc. g/cm³)</td>
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<td>1.475</td>
<td>1.449</td>
<td>1.545</td>
<td>1.532</td>
</tr>
<tr>
<td>Absorption coefficient</td>
<td>5.73</td>
<td>7.32</td>
<td>8.63</td>
<td>12.98</td>
<td>12.85</td>
</tr>
<tr>
<td>Crystal size (mm)</td>
<td>0.20 x 0.20 x 0.20</td>
<td>0.12 x 0.32 x 0.38</td>
<td>0.40 x 0.20 x 0.10</td>
<td>0.10 x 0.10 x 0.05</td>
<td>0.20 x 0.05 x 0.05</td>
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<td>8851</td>
<td>15 149</td>
<td>74 683</td>
<td>18 1599</td>
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<tr>
<td>Independent (Rint)</td>
<td>0.05840 (0.0380)</td>
<td>0.05840 (0.0296)</td>
<td>0.05840 (0.0296)</td>
<td>0.05840 (0.0296)</td>
<td>0.05840 (0.0296)</td>
</tr>
<tr>
<td>Data/restraints/parameters</td>
<td>5684/1482</td>
<td>5680/12394</td>
<td>15 149/5 187</td>
<td>14 420/4 809</td>
<td>4355/21 225</td>
</tr>
<tr>
<td>R1 [I &gt; 2σ(I)]</td>
<td>0.0362</td>
<td>0.0457</td>
<td>0.0359</td>
<td>0.0437</td>
<td>0.0354</td>
</tr>
<tr>
<td>wR2 [I &gt; 2σ(I)]</td>
<td>0.0774</td>
<td>0.1081</td>
<td>0.0771</td>
<td>0.0696</td>
<td>0.0663</td>
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<tr>
<td>R1 (all data)</td>
<td>0.0407</td>
<td>0.0533</td>
<td>0.0538</td>
<td>0.1172</td>
<td>0.0790</td>
</tr>
<tr>
<td>wR2 (all data)</td>
<td>0.0734</td>
<td>0.1118</td>
<td>0.0815</td>
<td>0.0893</td>
<td>0.0683</td>
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<tr>
<td>Goodness-of-fit (GOF)</td>
<td>1.036</td>
<td>1.005</td>
<td>0.917</td>
<td>0.767</td>
<td>0.845</td>
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<tr>
<td>Difference peak, hole (e Å–3)</td>
<td>0.352, 0.322</td>
<td>0.384, 0.259</td>
<td>1.814, 0.271</td>
<td>0.660, 0.673</td>
<td>0.367, 0.326</td>
</tr>
</tbody>
</table>

Table 2

Pertinent bond lengths and angles are summarized in Table 1. The raw frame data were used to determine unit cell parameters and collect data [29]. Details of the refinement and crystal data are summarized in Table 1. Pertinent bond lengths and angles are summarized in Table 2. The value of the Flack parameter was 0.08(2) [31].

Table of racemic [Mn(L3)Cl2]2CH2OH were grown by Et2O vapor diffusion onto a concentrated MeOH solution. The structure was determined in Leipzig (P.L.). A suitable crystal was washed in perfluoropolyalkyl ether and mounted on an Oxford Diffraction...
Xcalibur S diffractometer equipped with a CCD detector. Data collection and processing, including multi-scan absorption correction, were carried out using the Oxford CRYSTALS software package [34]. The centrosymmetric monoclinic space group $\text{C2}/\text{c}$, with $a = 10.0$, $b = 10.1$, $c = 17.6$ Å, $\alpha = 90.0$, $\beta = 90.1$, $\gamma = 101.0$; domain ratio 0.77:0.23. The complex occupies a special position on a two-fold axis; only half of the complex and one full methanol molecule are unique. Moreover, both enantiomers occupy this position in slightly different conformations in a ratio of $0.712(4):0.288(4)$. All hydrogen atoms were placed in ideal positions except for N–H and P–H, and these bond lengths were constrained to ideal values. Details of the refinement and crystal data are summarized in Table 1. Pertinent bond lengths and angles are summarized in Table 2.

Crystals of racemic [Mn(L3)(Cl)2] were grown by diffusion of layered n-hexane into a CH2Cl2 solution at −20 °C. The structure was solved in Leipzig (S.T.) using the same equipment and techniques already described (vide supra). The centrosymmetric triclinic space group $P1$ (No. 2) was determined. A single lattice site is occupied by both enantiomers in slightly different conformations in a 0.669(4):0.331(4) ratio. All hydrogen atoms were placed in ideal positions except $H2$–$H5$ on the pyridine ring. Details of the refinement and crystal data are summarized in Table 1. Pertinent bond lengths and angles are summarized in Table 2.

### Table 2

<table>
<thead>
<tr>
<th>Complex</th>
<th>[Mn(L1)(NMe)3][ClO4]2</th>
<th>[Mn(L2)(OH2)2][ClO4]2</th>
<th>[Mn(L3)(Cl)2]$^a$</th>
<th>[Mn(L4)(Cl)2]$^b$</th>
<th>[Mn(L5)(Cl)2]$^c$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bond lengths (Å)</td>
<td></td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>Mn–N1 (py, left)$^a$</td>
<td>2.446(3)</td>
<td>2.382(2)</td>
<td>2.3767(8)</td>
<td>2.3767(8)</td>
<td>2.302(2)</td>
</tr>
<tr>
<td>Mn–N2 (imine, left)$^a$</td>
<td>2.314(3)</td>
<td>2.239(3)</td>
<td>2.299(3)</td>
<td>2.247(7)</td>
<td>2.366(3)</td>
</tr>
<tr>
<td>Mn–N3 (imine, right)$^a$</td>
<td>2.318(3)</td>
<td>2.264(2)</td>
<td>2.299(3)</td>
<td>2.247(7)</td>
<td>2.366(3)</td>
</tr>
<tr>
<td>Mn–N4 (py, right)$^a$</td>
<td>2.465(3)</td>
<td>2.406(1)</td>
<td>2.3767(8)</td>
<td>2.3767(8)</td>
<td>2.302(2)</td>
</tr>
<tr>
<td>Mn–X (ax, top)$^b$</td>
<td>2.217(3)</td>
<td>2.136(3)</td>
<td>2.4557(3)</td>
<td>2.4557(3)</td>
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</tr>
<tr>
<td>Mn–N (ax, bottom)$^b$</td>
<td>2.254(3)</td>
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<td>2.4557(3)</td>
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<td>Mn–X (equ)$^b$</td>
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<td></td>
<td>2.436(1)</td>
<td>2.458(2)</td>
<td>2.302(2)</td>
</tr>
</tbody>
</table>

### Notes

$^a$ Directionality is defined from a viewpoint at the middle of the equatorial plane opposite the cyclohexyl ring.

$^b$ Two independent molecules, with N1 pyridine donor displaced to the "axial, top" positions due to "left" N2 imine reduction.

$^c$ Vacant site.

### 3. Background and general remarks

Three di-Schiff base ligands were initially explored in the present work (L$^1$–L$^3$, Scheme 1). The coordination chemistry of L$^1$ and L$^2$ has been scarcely explored. Only bimetalllic Cu(I) complexes have been structurally characterized for L$^2$ and a bis(quinoyl) analog of L$^1$, with both ligands found in a common bridging bis-bidentate (i.e., $\mu_2$–k$^3$) mode [20,37]. Additionally, a few asymmetric reactions catalyzed by structurally undefined transition metal and lanthanide complexes of these ligands have been reported [17–20, but none of these involved manganese. L$^3$ has been more widely exploited. Six-coordinate [Mn(L3)(ClO4)2]$^6$ [6] and [Mn(L2)Br2]$^8$ [7], seven-coordinate [Mn(L3)(OH2)2Br][Br$^8$] [8] and eight-coordinate [Mn(L3)(k$^2$–OAc)2]$^13$ structures have all been characterized, as have manganese(II) complexes of several closely related ligands [8,10,11–13]. Some of these have been utilized as catalysts for asymmetric sulfoxidation [6], olefin epoxidation [12], and olefin polymerization [7].

In the present work, we prepared several manganese(II) complexes of L$^1$–L$^3$. L$^1$ and L$^2$ were prepared as enantiopure $RR$ isomers, while L$^3$ was prepared both as a racemate and as enantiopure $RR$ and $SS$-isomers. These were added to Mn(ClO4)2$\cdot$6H$2$O to prepare the manganese(II) complex salts.
strained tetradentate ligand bite of L1. Compared to dianionic salen new complexes of ligand derivatives L4 and L5 (Scheme 1) that re-precursors, respectively. Instead of metal-centered chemistry, Fig. 1.

ORTEP plots (30% ellipsoids) of the complex cations of [Mn((NCCH3)3)(ClO4)2]

Moreover, the axial N5–Mn1–N7 trans 2.254(3) and 2.217(3) Å for Mn1–N6, N5 and N7, respectively). The disparate distortional modes primarily may reflect differing geometric constraints afforded by diverging chelation within otherwise similar ligand fields [44]. However, while high-spin Mn(II) does not exhibit ligand field stabilization, orbital differentiation of axial and equatorial σ-bonding can exist under pentagonal bipyramidal symmetry [45].

A pentagonal plane is particularly accommodated by the con- strained tetradentate ligand bite of L1. Compared to diamionic salen ligands with exocyclic phenolate oxygen donor atoms that give two outer six-atom and one inner five-atom chelate rings, with average O–Mn–N and N–Mn–N cis angles of 91(2)° and 82(1)°, respectively [43], the neutral pyridylmethyldiene donors afford three contiguous five-atom chelate rings. This reduces the cis N–Mn–N bite angles to an average value of 69.0(4)° in the L1 complex (Table 2), thus circumscribing four contiguous vertices on a pen- tagonal equatorial plane (i.e., 72°). A least-squares plane calculated using the four ligand nitrogens passes through the manganese ion only 0.004 Å off-center; however, the rigid backbone introduces puffing of the nitrogen array, with respective displacements of ±0.161(1) and ±0.301(1) Å for the pyridyl and imine nitrogens. The pyridines are pinned back to a “trans” angle of 155.98(9)°, and afford somewhat longer Mn–N bonds than the imines (i.e., 2.46(1) versus 2.32(1) Å average).

The fifth equatorial position is occupied by an acetonitrile mole- cule, but the N6 donor nitrogen is displaced +0.535 Å above the N4 ligand plane just described, and exhibits a significantly elongated bond compared to the axial acetonitriles (2.419(3) versus 2.254(3) and 2.217(3) Å for Mn1–N6, N5 and N7, respectively). Moreover, the axial N5–Mn1–N7 trans angle is reduced to 159.9(1)°, specifically bending toward the equatorial solvent li-
gand; N5–Mn1–N6 and N7–Mn1–N6 cis angles are reduced to 82.3(1)° and 78.5(1)°, respectively. The acetonitrile ligands are otherwise unreasonable. A second least-squares plane passes directly through all three acetonitrile nitrogens, with the manganese ion offset by 0.137 Å toward N1, and this N5 meridional plane meets the equatorial N4 plane at nearly a right angle (86.73°). Thus, only minor distortion from a pentagonal bipyramid is evident in [Mn(L1)4(NCCH3)5]2+, principally entailing puffing of the L1 donor plane and elongation of the equatorial acetonitrile coordination.

A similar [Mn(L)(NCCH3)5]2+ complex was recently reported, with a planar tetradeinate supporting ligand and an elongated bond to a coplanar equatorial acetonitrile [39]. Two [Mn(k5- L)(k5-L)X] structures incorporating similar di-Schiff base dipropyldiimine ligands display elongated bonds to equatorial pyridines on the tetradentate ligands [9,11]. Also, a number of pentaazamacro- cyclic complexes exhibit unusually long bonds to axial co-ligands [40,42]. The disparate distortional modes primarily may reflect differing geometric constraints afforded by diverging chelation within otherwise similar ligand fields [44]. However, while high-spin Mn(II) does not exhibit ligand field stabilization, orbital differentiation of axial and equatorial σ-bonding can exist under pentagonal bipyramidal symmetry [45].

The six-coordinate structures of [Mn(L)4(OH2)2]2(ClO4)2 and [Mn(L)4Cl2] can be interpreted as monovacant pentagonal bipyramids, with the elongated equatorial site of [Mn(L)4(NCCH3)5]2+ remaining unoccupied by an exogenous ligand. In fact, this fifth equatorial site is blocked by the pyridine α-methyl substituents of L5. As a result, the axial donor atoms bend toward the equatorial site, closing down the trans angle between them from 159.9(1)° to 142.3(1)° and 130.2(1)° in the respective complexes. Similar hexa-coordinate structures were reported previously for [Mn(L2)X2] (X = ClO4, Br) [68] and the dichloride complex of a bis(quinolyl)-substituted ligand [7]. Hydrogen bonds are evident between the aquo ligand protons in the L2 complex and outer-sphere perchlo-rate oxygens (1.86–1.97 Å), and between the chloride ligands of the L3 complex and a lattice methanol proton (2.47 Å). However, the Mn–OH2 and Mn–Cl bond lengths are not atypical [43]. The Mn–N bond lengths also vary only slightly between L2 and the major con- formation of L3, notwithstanding differing charge of the axial co-li-
gands [9,11]. Hydrogen bonds are evident between the aquo ligand protons in the L2 complex and outer-sphere perchlo-rate oxygens (1.86–1.97 Å), and between the chloride ligands of the L3 complex and a lattice methanol proton (2.47 Å). However, the Mn–OH2 and Mn–Cl bond lengths are not atypical [43]. The Mn–N bond lengths also vary only slightly between L2 and the major con- formation of L3, notwithstanding differing charge of the axial co-li-
gands, but are slightly shorter compared to the heptacoordinate L1 complex. Rufflings of the N4 equatorial planes are also moderated: ±0.144 Å for the pyridines and ±0.256 Å for the imines of L2, and ±0.128 Å for the pyridines and ±0.228 Å for the imines of L3. The Mn(II) ions reside in this plane, offset by ±0.050 and 0.000 Å, respectively, while axial MnX2 (X = OH2, Cl–) planes cross at 88.37° and 87.08°.

3.3. Hydrophosphination of [Mn(L)4Cl2]

One equivalent of the air-stable primary phosphine FeCH2Ph2

[Fe = –C5H4FeC5H5] was added to racemic [Mn(L)4Cl2], with the goal of preparing an adduct [Eq. (1)] that could be utilized as a phosphinidene precursor [e.g., Eq. (2)] [46,47]. Characterization of

Fig. 1. ORTEP plots (30% ellipsoids) of the complex cations of [Mn(R,R-L)4(NCCH3)5]2(ClO4)2.CH3CN (left) and [Mn(R,R-L)4(OH2)2]2(ClO4)2 (center), as well as the major conformation of the neutral racemic complex [Mn(L)4Cl2]2CH3OH (right), arbitrarily depicted as the R,R-enantiomer. Hydrogen atoms (other than H2O) were omitted for clarity.
the product by electrospray ionization mass spectrometry gave clear evidence of adduct formation. A parent ion was observed with a mass/charge ratio of 614.1 amu, compared to a calculated exact mass of 614.09 amu for \([\text{Mn}(L^4)\text{Cl}]^+\). Moreover, the isotope pattern was consistent with the presence of one iron and one chlorine atom and the expected $^{13}\text{C}$ distribution (Fig. 2). However, FTIR spectroscopy clearly indicated that phosphine addition occurred at the electrophilic imine bond instead of metal ligation (Eq. (3)), forming a complex of a reduced monoamine ligand ($L^4$, Scheme 1). This was indicated clearly by attenuation of the corresponding $\nu(C=\text{N})$ mode at 1658 cm$^{-1}$ (Fig. 3). A $\nu(P-H)$ band at 2288 cm$^{-1}$ was unshifted from that of the free phosphine precursor [21], consistent with absence of metal ligation [48]. New modes in the $\nu(C=\text{H})$ region due to the ferrocenylmethyl substituent were also evident. Addition of a second phosphine equivalent did not result in further alteration of the FTIR spectra even after prolonged reflux.

$$\text{MnCl}_{14} \text{PH}_2R \rightarrow \text{MnCl}_{14} \text{PH}_2\text{Fc}^+$$ (1)

$$\text{MnCl}_{14} \text{PH}_2\text{Fc}^+ + 2 \text{BHCl} \rightarrow \text{MnCl}_{14} \text{PH}_2\text{Fc}^+ + 2 \text{B}^+ \text{Cl}^-$$ (2)

$$\text{MnCl}_{14} \text{PH}_2\text{Fc}^+ + \text{PH}_2R \rightarrow \text{MnCl}_{14} \text{PH}_2\text{Fc}^+ + \text{PH}_2R^- + \text{Cl}^-$$ (3)

The novel hydrophosphination product complex $[\text{Mn}(L^4)\text{Cl}_2]$ was further characterized by X-ray crystallography, which revealed details of the imine reduction. Two independent molecules were observed that differ only trivially in the orientation of their respective ferrocenylmethyl substituents, which are unremarkable (Fig. 4). Imine reduction forces refolding of the ligand from the planar configuration of $L^3$ into a cis-$\beta$ geometry [49], with the pyridine on the reduced arm displaced to an axial position and the other retained in the equatorial plane. Diastereoselectivity of the product complex must be determined by the preexisting chirality imposed by the cyclohexyl backbone. Addition of $\text{FcCH}_2\text{PH}_2$ to the $R,R$-enantiomer of $[\text{Mn}(L^3)\text{Cl}_2]$ occurred at the imine $\text{si}$ face to extend chirality across the imine bond, yielding $S$-carbon and $R$-nitrogen. This was reversed at the $S,S$-enantiomer. The selectivity results from folding of the reduced pyridinylmethyl arm into an equatorial position on the amine nitrogen, which is locked by fusion of two five-atom chelate rings. Addition to the opposite face would thus entail formation of a minor axial diastereomer, but its relative yield was not determined.

Approximate pentagonal bipyramidal geometry is still maintained, with one open equatorial site vacated by the displaced pyridine. The chlorides are retained in cis-equatorial and trans-axial positions, with nearly equal bond lengths, approaching those of the $[\text{Mn}(L^3)\text{Cl}_2]$ precursor. However, the equatorial chloride bends approximately 20° toward the open equatorial site, so the equatorial Cl–Mn–N angles to the pyridine and amine, respectively, average 92(4)° and 122(5)° in both unique molecules, compared to the ideal 72° and 144°. Owing to the constrained pyridylmethyl arm, the axial trans angle from the second chloride to the pyridine aver-

![Fig. 2](image1.png)

**Fig. 2.** Observed (black) and calculated (white) isotope pattern for the parent ion of the addition product $[\text{Mn}(L^3)\text{Cl}_2\text{PH}_2\text{CH}_2\text{Fc}]^+$, observed by electrospray ionization mass spectrometry.

![Fig. 3](image2.png)

**Fig. 3.** Excerpts of FTIR spectra for $[\text{Mn}(L^3)\text{Cl}_2]$ (bottom) and the $\text{FcCH}_2\text{PH}_2$ addition product (top), illustrating (from high to low energy) new $\nu(C=\text{H})$ and $\nu(P-H)$ modes and attenuation of the imine $\nu(C=\text{N})$ mode.

![Fig. 4](image3.png)

**Fig. 4.** ORTEP drawings (30% ellipsoids) of the two independent molecules of $[\text{Mn}(L^4)\text{Cl}_2]$, arbitrarily depicted as $R,R$-enantiomer. Hydrogen atoms are omitted for clarity, except those relating to the reduced imine bond.
ages 155(1)°, while the N–Mn–Cl and Cl–Mn–Cl cis angles average 86(2)° and 100(1)°, respectively. The axial pyridine bond length is 0.07(3) Å shorter in the cis-β L₄ configuration than in the precursor, while the equatorial amine bond is markedly lengthened compared to the imine. The imine C=N bond averages 1.264(4) Å in the two L⁴ complexes, compared to 1.277(3) Å in the major isomer of the L³ precursor complex, and 1.474(4) Å for the reduced amine C–N bond.

3.4. Reaction of [Mn(L³)(X)₂] with EDA

We also investigated reactivity of the L³ complexes with ethyl diazoacetate (EDA) as a carbene precursor. Addition of EDA to a dilute solution of [Mn(L³)(ClO₄)₂] in CH₃CN produced no obvious effervescence. Monitoring of the reaction solution by electrospray mass spectrometry, in the absence of a convenient solution-phase spectroscopic probe, gave evidence of EDA activation upon extended thermolysis. The parent ion corresponding to [Mn(L³)ClO₄]⁺ at 446 amu was observed along with heavier ions consistent with carbene addition. Using a mixture of ordinary and d₅-labeled EDA enriched on the ethyl substituent, a pair of product ions were observed at 468 and 473 amu, consistent with assignment as a carbene adduct [Mn(L³)(OH₂)(OH)(CH(C(O)OEt))⁺] (vide supra) (Fig. 5). Prolonged thermolysis resulted in exhaustion of precursor ion at 446 amu and appearance of further derivative peaks at 379 amu and 290 amu, corresponding to consecutive imine hydrolyses with loss of 89 amu (Fig. 6). Reaction of [Mn(L³)Cl₂] with EDA gave analogous peaks at 382 amu, corresponding to [Mn(L³)Cl]⁺, and 468 amu, corresponding to [Mn(L³)Cl(CH(C(O)OEt))⁺] (Fig. 7).

The various ions produced from [Mn(L³)(ClO₄)₂] were further probed by selective ion trapping and fragmentation by collision-induced dissociation (CID). Both the normal and d₅-enriched product ions at 468 and 473 amu gave a common major fragment at 365 amu, consistent with [Mn(L³)(OH₂)]⁺. In contrast, the imine-hydrolyzed ions at 379 and 290 amu gave major fragmentation products with mass losses of 46 amu, implying loss of EtOH to form ketenylidene (i.e., C≡C=O); this was also confirmed by CID fragmentation of the d₅-enriched peak at 384 amu with loss of 51 amu. The various derivative ions are summarized in Scheme 2, in which complex geometries are arbitrary and formation of a metallocarbene is assumed, rather than Mn–N bond insertion, due to observation of ions with hydrolyzed imine linkages. As a test for EDA activation in solution, excess styrene was added to capture any incipient carbenoid fragment. Cyclopropane formation (29% yield, 1.0:1.7 syn:anti) was observed, along with the minor insertion product cis-ethyl-4-phenyl-3-butenoate. However, several lines of evidence indicated a lack of significant metal-catalyzed carbene transfer: (i), in the absence of catalyst, a significant yield (54%) of 3-carboxy-5-phenyl-2-pyrazoline ethyl ester was observed by 1H NMR spectroscopy, consistent with direct 1,3-dipolar addition of EDA to styrene; (ii), the reaction timescale was consistent with known rates for such a reaction [50]; (iii), olefinic carbene coupling products (i.e., diethylmaleate and fumarate) were not observed; (iv) cyclopropanes still formed in the absence of catalyst; and (v), chiral induction into the cyclopropanes was not observed in the presence of a single L³ complex enantiomer. Thus, we conclude that the [Mn(L³)X₂] complexes were not active as carbene transfer catalysts, at least under the conditions utilized in the present study (vide supra).

3.5. Reaction of [Mn(L³)Cl₂] with H₂O

Extended thermolysis of [Mn(L³)Cl₂] with EDA also engendered a deep orange color in solution, which we attributed to reversible imine bond hydrolysis [Eq. (4)]. Water was added to a yellow solution of [Mn(L³)Cl₂] in methanol to afford orange crystals upon ether vapor diffusion. Elemental analysis and X-ray crystallography confirmed the formulation of the orange derivative complex as [Mn(L⁵)Cl₂], where L⁵ is the tridentate hydrolysis product of one imine linkage of L³ (Fig. 8). The structure of [Mn(L³)Cl₂] is interesting insofar as penta-coordinate manganese(II) complexes
are comparatively rare \[51,52\]. The structure can be viewed as an equatorially cis-divacet pentagonal bipyramid, with axial chlorides bent toward the open sites and the Cl–Mn–Cl angle accordingly reduced to 115.11(2)°. More conventionally, a square pyramidal structure can be assigned, with “trans” angles in the equatorial plane of 145.15(5)° from the remaining pyridine (N1) to the amine (N3), and 138.49(9)° from the imine nitrogen (N2) to Cl1 in the major conformation. This gives a \( \tau \) value of 0.11 \[53\]. The three remaining N–Mn–Cl angles to the axial Cl2 average 102.4(4)°. All five metal–ligand bond lengths are shorter than their counterparts in the hexacoordinate [Mn(L3)Cl2] (Table 2).

\[ \text{Scheme 2.} \]

### 4. Summary and conclusions

Inspired by the use of di-Schiff base pyridylmethylene manganese(II) complexes for catalysis of stereoselective oxo atom transfer and olefin polymerization, we prepared a series of three ligand complexes and investigated their potential for transfer catalysis of soft isolobal oxene analogues, including an air-stable primary phosphine as a phosphinidene precursor and ethyldiazoacetate as a carbene precursor. However, the reactive ligand imine bonds instead yielded respective hydrophosphination and hydrosis reactions. Such reactivity can be expected to constrain the use of these complexes as group transfer catalysts. Imine reduction would overcome these limitations, but also enable a high degree of conformational flexibility, as demonstrated previously \[49,54\] and illustrated again by the L5 complex herein. Nonetheless, we did obtain novel ligand derivatives L5 and L3, and X-ray crystallographic studies of the L1–L3 complexes gave a series of five-, six-, and seven-coordinate structures related by the pentagonal bipyramidal geometry imposed by ligand constraints in the equatorial plane.

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### Appendix A. Supplementary material

CCDC 645115 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. Supplementary data associated with this article can be found in the online version, at doi:10.1016/j.icca.2010.06.041.

### References

