Supplementary Material (ESI) for Chemical Communications
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Supporting Information

For

NiII(TPA) as an efficient catalyst for alkane hydroxylation with m-CPBA

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Experimental

General

Reagents and solvents used in this study except the ligand and the complexes were commercial products of the highest available purity and were further purified by the standard methods, if necessary.\textsuperscript{1} Tris(2-pyridylmethyl)amine (TPA) was prepared according to the reported procedures.\textsuperscript{2} FT-IR spectra were recorded with a Jasco FT/IR-4100. Mass spectra were recorded with a JEOL JMS-700T Tandem MS station or a PE SCIEX API 150EX (for ESI-MS).\textsuperscript{1} H NMR spectra were recorded on a JEOL LMN-ECP300WB or a LMX-GX400. UV-vis spectra were measured using a Hewlett-Packard HP8453 diode array spectrophotometer or a Jasco V-570. Elemental analyses were performed on a Perkin-Elmer or a Fisons instruments EA 1108 Elemental analyzer.

Synthesis

\textbf{[Ni\textsuperscript{II}(TPA)(OAc)(H\textsubscript{2}O)]BPh\textsubscript{4} (1).} A methanol solution (5 mL) of Ni\textsuperscript{II}(OAc)\textsubscript{2}•4H\textsubscript{2}O (62.3 mg, 0.25 mmol) was added into a methanol solution (5 mL) of TPA (72.6 mg, 0.25 mmol) with stirring at room temperature. The solution was turned to brown. After the solution was stirred for 2 h, NaBPh\textsubscript{4} (86 mg, 0.25 mmol) was added. Then, the mixture was stirred further for 1 h at room temperature. The resulting insoluble materials were removed by filtration and the filtrate was concentrated by evaporation. The resulting residue was dissolved into CH\textsubscript{2}Cl\textsubscript{2}, and insoluble materials were removed by filtration again. The filtrate was concentrated to 2 mL in volume, and the solution was poured into ether-hexane (1:1 v/v, 100 mL) to give pale gray precipitates, which were collected by filtration and dried. Recrystallization of the crude product from CH\textsubscript{2}Cl\textsubscript{2}-cyclohexane gave pure complex 1 as purple crystals. (80.9 mg, 43%). FT-IR (KBr): 3300 (O–H, very broad), 1605, 1560, 1425 (COO\textsuperscript{−}), 733, 706 cm\textsuperscript{−1} (BPh\textsubscript{4}\textsuperscript{−}); HRMS (FAB\textsuperscript{+}): \textit{m/z} 407.1003 [M–BPh\textsubscript{4}–H\textsubscript{2}O]\textsuperscript{+}, calcd for C\textsubscript{20}H\textsubscript{21}N\textsubscript{4}O\textsubscript{2}Ni 407.1018; Anal. Caled for [Ni(TPA)(OAc)(H\textsubscript{2}O)]BPh\textsubscript{4}, C\textsubscript{44}H\textsubscript{43}N\textsubscript{6}O\textsubscript{3}NiB: C, 70.90; H, 5.81; N, 7.52. Found: C, 70.69; H, 5.82; N, 7.41.
Single crystals suitable for X-ray crystallographic analysis were obtained by slow diffusion of cyclohexane into a CH₂Cl₂ solution of the complex.

\([\text{Co}^{II}(\text{TPA})(\text{OAc})]\text{BPh}_4\) (2). A methanol solution (3 mL) of Co^{II}(\text{OAc})₂•4H₂O (70.0 mg, 0.28 mmol) was added into a methanol solution (3 mL) of TPA (81.5 mg, 0.28 mmol) with stirring at room temperature. The solution was turned to dark green. After the solution was stirred for 8 h, NaBPh₄ (96 mg, 0.28 mmol) was added to the mixture to give green precipitates, which were collected by filtration and dried (139.7 mg, 68%). FT-IR (KBr): 1609, 1481, 1439 (COO⁻), 735, 708 cm⁻¹ (BPh₄⁻); HRMS (FAB⁺): m/z 408.1012 [M–BPh₄]⁺, calcd for C₂₀H₂₁N₄O₂Co 408.0996; Anal. Calcd for [Co(TPA)(OAc)]BPh₄•C₆H₁₂•0.5CH₂Cl₂, C₅₀.₅H₅₄N₄O₂CoBCl: C, 71.01; H, 6.37; N, 6.56. Found: C, 71.08; H, 6.30; N, 6.56.

Single crystals suitable for X-ray crystallographic analysis were obtained by slow diffusion of cyclohexane into a CH₂Cl₂ solution of the complex.

\([\text{Fe}^{II}_2(\text{TPA})_2(\mu-\text{OAc})_2]\text{BPh}_4)_2\) (3).³ The complex was synthesized under anaerobic conditions (in a glove box). A methanol suspension (3 mL) of Fe^{II}(\text{OAc})₂ (35 mg, 0.20 mmol) was added into a methanol solution (2 mL) of TPA (58.1 mg, 0.20 mmol) with stirring at room temperature. The mixture was turned to brown. After stirring for 30 min, a methanol solution (1 mL) of NaBPh₄ (69 mg, 0.20 mmol) was added to the mixture and stirring for further 30 min. The mixture was filtered through a KimWipe plugged pipette to insoluble materials and the filtrate was stand for several hours to afford orange crystals, which were collected by filtration and dried (96.3 mg, 70%). FT-IR (KBr): 1602, 1441, 1425 (COO⁻), 733, 703 cm⁻¹ (BPh₄⁻); HRMS (FAB⁺): m/z 405.1008 [0.5M–BPh₄]⁺, calcd for C₂₀H₂₁N₄O₂Fe 405.1014; Anal. Calcd for [Fe₂(TPA)(OAc)₂](BPh₄)₂, C₈₈H₈₂N₈O₄Fe₂B₂: C, 72.95; H, 5.70; N, 7.73. Found: C, 72.80; H, 5.67; N, 7.74.

Single crystals suitable for X-ray crystallographic analysis were obtained from a methanol solution of the complex as described above.

\([\text{Mn}^{II}_2(\text{TPA})_2(\mu-\text{OAc})_2]\text{BPh}_4)_2\) (4). The complex was synthesized under anaerobic conditions (in a glove box). A methanol solution (2 mL) of Mn^{II}(\text{OAc})•4H₂O (49.1 mg, 0.20 mmol) was added into a methanol solution (2 mL) of TPA (58.0 mg, 0.20 mmol) with stirring
at room temperature. The mixture was stirring for 30 min, then a solution (2 mL) of NaBPh₄ (75 mg, 0.22 mmol) was added to the mixture and stirring for further 30 min. The mixture was filtered through a KimWipe plugged pipette to insoluble materials and the filtrate was stand for several hours to afford pale yellow crystals, which were collected by filtration and dried (101.7 mg, 70%). FT-IR (KBr): 1591, 1480, 1426 (COO⁻), 733, 704 cm⁻¹ (BPh₄⁻); HRMS (FAB⁺): m/z 404.1049 [0.5M–BPh₄]⁺, calcd for C₂₀H₂₁N₄O₂Mn 404.1045; Anal. Calcd for [Mn₂(TPA)₂(OAc)₂(BPh₄)₂], C₈₈H₈₂N₈O₄Mn₂B₂: C, 73.04; H, 5.71; N, 7.74. Found: C, 72.87; H, 5.69; N, 7.65.

Single crystals suitable for X-ray crystallographic analysis were obtained from a methanol solution of the complex as described above.

**X-ray Structure Determination.** The single crystal was mounted on a glass-fiber. Data of X-ray diffraction were collected by a Rigaku RAXIS-RAPID imaging plate two-dimensional area detector using graphite-monochromated MoKα radiation (λ = 0.71069 Å) to 2θ max of 55°. All the crystallographic calculations were performed by using Crystal Structure software package of the Molecular Structure Corporation [Crystal Structure: Crystal Structure Analysis Package version 3.7.0, Molecular Structure Corp. and Rigaku Corp. (2005)]. The crystal structures were solved by the direct methods and refined by the full-matrix least squares using SIR92. All non-hydrogen atoms and hydrogen atoms were refined anisotropically and isotropically, respectively. Atomic coordinates, thermal parameters, and intramolecular bond distances and angles are deposited in the supplementary materials (CIF file format).

**Catalytic Oxygenation of Alkanes. Caution! The reaction was very exothermic in the case of using complex 3(Fe) or 4(Mn) as a catalyst.** All procedures of the catalytic reaction were carried out under anaerobic conditions (in a glove box, [O₂] < 1 ppm, [H₂O] < 1 ppm). Typically, complex 1 (2 μmol) in CH₃CN-CH₂Cl₂ (1:1 v/v, 2 ml) was added to a CH₂Cl₂ (2 ml) solution containing alkane (15 mmol), m-CPBA (2 mmol), and nitrobenzene or o-dichlorobenzene (50 μmol) as an internal standard with vigorous stirring at room temperature. An aliquot of the reaction mixture was taken at a certain reaction time and...
quenched with PPh$_3$ for the GLC analysis using a Shimadzu GC–14A gas chromatograph equipped with a Restek Rtx–1701 capillary column (30 m x 0.25 mm). All peaks of interest were identified by comparison of the retention times and co-injection with the authentic samples. The products were quantified by comparison against a known amount of internal standard using a calibration curve consisting of a plot of mole ratio (moles of organic compound/moles of internal standard) versus area ratio (area of organic compound/area of standard).

**Determination of Kinetic Deuterium Isotope Effect.** Typically, complex 1 (2 µmol) in CH$_3$CN-CH$_2$Cl$_2$ (2 ml) was added to a CH$_2$Cl$_2$ (2.4 ml) solution containing cyclohexane (0.81 ml, 7.5 mmol) and cyclooctane (0.81 ml, 6.0 mmol) and m-CPBA (2 mmol) with vigorous stirring for 1 h at room temperature. The oxidation products were analyzed by the GLC method described above. The reaction was also carried out using cyclohexane-$d_{12}$ instead of cyclohexane. The $k_H/k_D$ value for cyclohexanol was calculated by dividing the value of $\{(\text{moles of the products of cyclohexane})/(\text{moles of the products of cyclooctane})\}$ by $\{(\text{moles of the products of cyclohexane-$d_{12}$})/(\text{moles of the products of cyclooctane})\}$.

**Determination of Oxidant Efficiency.** After the catalytic reaction of cyclohexane for 1 h, the reaction mixture was diluted with methanol to a total volume of 20 ml. The mole of remaining oxidant was determined by iodometric titration as follows. A portion (1.0 ml) of the diluted methanol solution was added to 1 M H$_2$SO$_4$ aqueous solution (20 ml) containing 1 mmol potassium iodide and a small amount of starch. The mixture turned purple due to generation of I$_2$. Then, the mixture was titrated with 0.02 M Na$_2$S$_2$O$_3$ aqueous solution until the color disappeared.
References


Table S1. Summary of X-ray Crystallographic Data of Complex 1

<table>
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<tr>
<th>Compound</th>
<th>[Ni^{II}(TPA)(OAc)(H_2O)]BPh_4 (1)</th>
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<td>14.028(4)</td>
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<td>c, Å</td>
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<tr>
<td>γ, deg</td>
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<td>goodness of fit indicator</td>
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^aR = \frac{\sum ||F_o| - |F_c|| \Sigma |F_o|}{R_w = \left[ \Sigma w (|F_o| - |F_c|)^2 / \Sigma w F_o^2 \right]^{1/2}}
Table S2. Summary of X-ray Crystallographic Data of Complex 2

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<th>Compound</th>
<th>[Co\textsuperscript{II}(TPA)(OAc)]BPh\textsubscript{4} (2)</th>
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<td>C\textsubscript{44}H\textsubscript{41}N\textsubscript{4}O\textsubscript{2}CoB</td>
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<td>(b), Å</td>
<td>13.010(7)</td>
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<td>(c), Å</td>
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<td>(\mu) (MoK(\alpha)), cm(^{-1})</td>
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\(R = \Sigma \left| F_o \right| - \left| F_c \right| / \Sigma \left| F_o \right| \quad \text{\(RW = \left[ \Sigma w \left( \left| F_o \right| - \left| F_c \right| \right)^2 / \Sigma w \left| F_o \right|^2 \right]^{1/2}\)} \)
Table S3. Summary of X-ray Crystallographic Data of Complex 3

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<th>Compound</th>
<th>(<a href="%5Ctext%7BBPh%7D_4">\text{Fe}^{II}_2(\text{TPA})_2(\text{OAc})_2</a>_2) (3)</th>
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<td>C(<em>{88})H(</em>{82})N(_8)O(_4)Fe(_2)B(_2)</td>
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<td>(b), Å</td>
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<td>(c), Å</td>
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<td>(\alpha), deg</td>
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<td>(\beta), deg</td>
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<td>(\gamma), deg</td>
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\(^aR = \Sigma ||F_o| - |F_c|| / \Sigma |F_o| \quad ^bR_W = [ \Sigma w (|F_o| - |F_c|)^2 / \Sigma w F_o^2 ]^{1/2}\)
**Table S4. Summary of X-ray Crystallographic Data of Complex 4**

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<tr>
<th>Compound</th>
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\[^a\]R = \Sigma ||F_o| - |F_c|| / \Sigma |F_o|  \hspace{1cm} \[^b\]R_w = [\Sigma w (|F_o| - |F_c|)^2 / \Sigma w F_o^2]^{1/2}
Table S5. Selected Bond Lengths (Å) and Angles (deg) of [NiII(TPA)(OAc)(H2O)]BPh4 (1)a

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<th>Length (Å)</th>
<th>Bond</th>
<th>Length (Å)</th>
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<td>N(1)-Ni(1)-N(4)</td>
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<td>N(1)-Ni(1)-N(3)</td>
<td>83.6(2)</td>
</tr>
<tr>
<td>N(2)-Ni(1)-N(3)</td>
<td>88.5(2)</td>
<td>N(2)-Ni(1)-N(4)</td>
<td>161.3(2)</td>
<td>N(2)-Ni(1)-N(3)</td>
<td>88.5(2)</td>
</tr>
<tr>
<td>N(3)-Ni(1)-N(4)</td>
<td>89.7(2)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

aEstimated standard deviations are given in parentheses.
Table S6. Selected Bond Lengths (Å) and Angles (deg) of [Co\textsuperscript{II}(TPA)(OAc)]\textsubscript{4} (2)\textsuperscript{a}

<table>
<thead>
<tr>
<th>Bond</th>
<th>Length (Å)</th>
<th>Bond</th>
<th>Length (Å)</th>
<th>Bond</th>
<th>Length (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Co(1)-O(1)</td>
<td>2.0434(15)</td>
<td>Co(1)-O(2)</td>
<td>2.3757(17)</td>
<td>Co(1)-N(1)</td>
<td>2.2337(18)</td>
</tr>
<tr>
<td>Co(1)-N(1)</td>
<td>2.2337(18)</td>
<td>Co(1)-N(2)</td>
<td>2.086(2)</td>
<td>Co(1)-N(3)</td>
<td>2.0809(18)</td>
</tr>
<tr>
<td>Co(1)-N(3)</td>
<td>2.0809(18)</td>
<td>Co(1)-N(4)</td>
<td>2.096(2)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>O(1)-Co(1)-O(2)</td>
<td>59.09(6)</td>
<td>O(1)-Co(1)-N(1)</td>
<td>174.01(7)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>O(1)-Co(1)-N(2)</td>
<td>102.14(7)</td>
<td>O(1)-Co(1)-N(3)</td>
<td>98.63(6)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>O(1)-Co(1)-N(4)</td>
<td>108.06(7)</td>
<td>O(2)-Co(1)-N(1)</td>
<td>125.32(6)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>O(2)-Co(1)-N(2)</td>
<td>79.81(6)</td>
<td>O(2)-Co(1)-N(3)</td>
<td>157.65(6)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>O(2)-Co(1)-N(4)</td>
<td>83.21(7)</td>
<td>N(1)-Co(1)-N(2)</td>
<td>75.73(7)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>N(1)-Co(1)-N(3)</td>
<td>77.03(7)</td>
<td>N(1)-Co(1)-N(4)</td>
<td>77.21(7)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>N(2)-Co(1)-N(3)</td>
<td>109.00(7)</td>
<td>N(2)-Co(1)-N(4)</td>
<td>130.50(8)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>N(3)-Co(1)-N(4)</td>
<td>104.17(8)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

\textsuperscript{a}Estimated standard deviations are given in parentheses.
Table S7. Selected Bond Lengths (Å) and Angles (deg) of \([\text{Fe}^{\text{II}}_2(\text{TPA})_2(\text{OAc})_2](\text{BPh}_4)_2\) (3)\(^a\)

<table>
<thead>
<tr>
<th>Bond Pair</th>
<th>Length/Angle</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\text{Fe}(1)-\text{O}(1))</td>
<td>1.9972(17)</td>
</tr>
<tr>
<td>(\text{Fe}(1)-\text{O}(2)^*)</td>
<td>2.1482(15)</td>
</tr>
<tr>
<td>(\text{Fe}(1)-\text{N}(1))</td>
<td>2.2671(18)</td>
</tr>
<tr>
<td>(\text{Fe}(1)-\text{N}(2))</td>
<td>2.146(2)</td>
</tr>
<tr>
<td>(\text{Fe}(1)-\text{N}(3))</td>
<td>2.2622(17)</td>
</tr>
<tr>
<td>(\text{Fe}(1)-\text{N}(4))</td>
<td>2.138(2)</td>
</tr>
<tr>
<td>(\text{Fe}(1)-\text{Fe}(1)^*)</td>
<td>4.2868(4)</td>
</tr>
<tr>
<td>(\text{O}(1)-\text{Fe}(1)-\text{O}(2)^*)</td>
<td>110.02(6)</td>
</tr>
<tr>
<td>(\text{O}(1)-\text{Fe}(1)-\text{N}(1))</td>
<td>160.77(6)</td>
</tr>
<tr>
<td>(\text{O}(1)-\text{Fe}(1)-\text{N}(2))</td>
<td>110.04(8)</td>
</tr>
<tr>
<td>(\text{O}(1)-\text{Fe}(1)-\text{N}(3))</td>
<td>87.10(6)</td>
</tr>
<tr>
<td>(\text{O}(1)-\text{Fe}(1)-\text{N}(4))</td>
<td>97.83(7)</td>
</tr>
<tr>
<td>(\text{O}(2)^*-\text{Fe}(1)-\text{N}(1))</td>
<td>87.51(6)</td>
</tr>
<tr>
<td>(\text{O}(2)^*-\text{Fe}(1)-\text{N}(2))</td>
<td>98.69(6)</td>
</tr>
<tr>
<td>(\text{O}(2)^*-\text{Fe}(1)-\text{N}(3))</td>
<td>162.33(6)</td>
</tr>
<tr>
<td>(\text{O}(2)^*-\text{Fe}(1)-\text{N}(4))</td>
<td>82.39(6)</td>
</tr>
<tr>
<td>(\text{N}(1)-\text{Fe}(1)-\text{N}(2))</td>
<td>76.24(6)</td>
</tr>
<tr>
<td>(\text{N}(1)-\text{Fe}(1)-\text{N}(3))</td>
<td>76.09(7)</td>
</tr>
<tr>
<td>(\text{N}(1)-\text{Fe}(1)-\text{N}(4))</td>
<td>83.18(7)</td>
</tr>
<tr>
<td>(\text{N}(2)-\text{Fe}(1)-\text{N}(2))</td>
<td>152.10(7)</td>
</tr>
<tr>
<td>(\text{N}(3)-\text{Fe}(1)-\text{N}(4))</td>
<td>100.05(7)</td>
</tr>
</tbody>
</table>

\(^a\)Estimated standard deviations are given in parentheses.
Table S8. Selected Bond Lengths (Å) and Angles (deg) of [Mn$^{II}$$_2$(TPA)$_2$(OAc)$_2$(BPh$_4$)$_2$ (4)$^a$

<table>
<thead>
<tr>
<th>Bond Length/Angle</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mn(1)-O(1)</td>
<td>2.0753(13)</td>
</tr>
<tr>
<td>Mn(1)-O(2)*</td>
<td>2.1645(12)</td>
</tr>
<tr>
<td>Mn(1)-N(1)</td>
<td>2.3518(14)</td>
</tr>
<tr>
<td>Mn(1)-N(2)</td>
<td>2.2230(16)</td>
</tr>
<tr>
<td>Mn(1)-N(3)</td>
<td>2.3599(14)</td>
</tr>
<tr>
<td>Mn(1)-N(4)</td>
<td>2.2047(18)</td>
</tr>
<tr>
<td>Mn(1)-Mn(1)*</td>
<td>4.1955(4)</td>
</tr>
<tr>
<td>O(1)-Mn(1)-O(2)*</td>
<td>111.75(5)</td>
</tr>
<tr>
<td>O(1)-Mn(1)-N(1)</td>
<td>156.15(5)</td>
</tr>
<tr>
<td>O(1)-Mn(1)-N(2)</td>
<td>113.18(6)</td>
</tr>
<tr>
<td>O(1)-Mn(1)-N(3)</td>
<td>86.06(5)</td>
</tr>
<tr>
<td>O(1)-Mn(1)-N(4)</td>
<td>97.49(6)</td>
</tr>
<tr>
<td>O(2)*-Mn(1)-N(1)</td>
<td>161.77(5)</td>
</tr>
<tr>
<td>O(2)*-Mn(1)-N(2)</td>
<td>83.43(5)</td>
</tr>
<tr>
<td>O(2)*-Mn(1)-N(3)</td>
<td>76.13(5)</td>
</tr>
<tr>
<td>N(1)-Mn(1)-N(3)</td>
<td>73.37(5)</td>
</tr>
<tr>
<td>N(1)-Mn(1)-N(4)</td>
<td>74.39(5)</td>
</tr>
<tr>
<td>N(2)-Mn(1)-N(3)</td>
<td>81.33(5)</td>
</tr>
<tr>
<td>N(2)-Mn(1)-N(4)</td>
<td>149.18(5)</td>
</tr>
<tr>
<td>N(3)-Mn(1)-N(4)</td>
<td>98.56(5)</td>
</tr>
</tbody>
</table>

$^a$Estimated standard deviations are given in parentheses.
Figure S1. ORTEP drawing of [Ni^{II}(TPA)(OAc)(H_2O)]BPh_4 (1) showing 50% probability thermal-ellipsoids. Hydrogen atoms are omitted for clarity.
Figure S2. ORTEP drawing of [Co\textsuperscript{II}(TPA)(OAc)]BPh\textsubscript{4} (2) showing 50% probability thermal-ellipsoids. Hydrogen atoms are omitted for clarity.
Figure S3. ORTEP drawing of [Fe$^{II}_2$(TPA)$_2$(OAc)$_2$](BPh$_4$)$_2$ (3) showing 50% probability thermal-ellipsoids. Hydrogen atoms are omitted for clarity.
Figure S4. ORTEP drawing of [Mn$^{II}$$_2$(TPA)$_2$(OAc)$_2$](BPh$_4$)$_2$ (4) showing 50% probability thermal-ellipsoids. Hydrogen atoms are omitted for clarity.
Figure S5. $^1$H NMR spectrum of [Ni$^{II}$(TPA)(OAc)(H$_2$O)]BPh$_4$ (1) in CD$_2$Cl$_2$ at room temperature.