Synthesis and Reactivity of Manganese Complexes Bearing Anionic PNP- and PCP-Type Pincer Ligands toward Nitrogen Fixation

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Abstract: A series of manganese complexes bearing an anionic pyrrole-based PNP-type pincer ligand and an anionic benzene-based PCP-type pincer ligand is synthesized and characterized. The reactivity of these complexes toward ammonia formation and silylamine formation from dinitrogen under mild conditions is evaluated to produce only stoichiometric amounts of ammonia and silylamine, probably because the manganese pincer complexes are unstable under reducing conditions.

Keywords: manganese; nitrogen fixation; pincer ligand

1. Introduction

The production of ammonia from dinitrogen in the air, known as nitrogen fixation, has been an essential chemical process in industry and biology. The industrial nitrogen fixation, known as the Haber–Bosch process, requires harsh reaction conditions and dihydrogen derived from fossil fuels [1]. The development of new systems capable of fixing dinitrogen into ammonia efficiently under mild reaction conditions has remained a challenging goal.

Transition-metal catalyzed nitrogen fixation under mild reaction conditions has gained much attention in the last two decades [2–11]. Reduction of dinitrogen into ammonia [12–25] or its equivalents, such as hydrazine [26], silylamines [27–44], and borylamines [45], catalyzed by well-defined transition-metal complexes was found by several research groups. We have found that transition-metal complexes bearing anionic pincer ligands worked as highly active catalysts for nitrogen fixation. Recently, we have succeeded in the development of iron-, cobalt-, and vanadium-catalyzed formation of ammonia and hydrazine from dinitrogen under mild reaction conditions using the corresponding dinitrogen complexes bearing an anionic pyrrole-based PNP-type ligand as catalysts [46–48]. The PNP ligand was originally developed by groups of Gade, Mani, and Tonzetich [49–51]. More recently, we have reported that iron-dinitrogen complexes supported by a benzene-based PCP-type pincer ligand, one of the classical pincer ligands [52], exhibited a high catalytic activity for reduction of dinitrogen into ammonia and hydrazine [53]. In addition, a rhodium-dinitrogen complex supported by the same PNP-type ligand and an iridium-dinitrogen complex bearing the same benzene-based PCP-type ligand have been found to work as effective catalysts for the formation of silylamine from dinitrogen under mild reaction conditions [54,55].

Based on these backgrounds, we have focused on the development of manganese-catalyzed nitrogen fixation under mild reaction conditions. Manganese is the third most abundant transition-metal on the earth. However, successful examples of manganese-catalyzed nitrogen fixation under mild conditions are limited to the silylamine formation from dinitrogen [35,39]. Herein, we have prepared a series of manganese complexes bearing the anionic pyrrole-based PNP-type pincer ligand and the anionic benzene-based PCP-type pincer ligand to investigate their reactivity for the ammonia and silylamine formation under mild reaction conditions.
2. Result and Discussion

2.1. Synthesis and Characterization of Manganese Complexes

The reaction of [MnCl₂(thf)₂] (thf = tetrahydrofuran) with Li-PNP (PNP = 2,5-bis(di-tert-butylphosphinomethyl)pyrrolide) in the presence pyridine in THF at room temperature for 18 h gave a Mn(II) complex bearing the PNP-type pincer ligand [Mn(PNP)Cl(pyridine)] (1) in 48% yield (Scheme 1). The structure of 1 was confirmed by X-ray analysis, and an ORTEP drawing of 1 is shown in Figure 1. Table 1 presents selected bond lengths and angles of 1. Complex 1 has a distorted square pyramidal geometry, where pyridine and chloride ligands are coordinated to the cobalt center supported by the PNP ligand. Complex 1 was paramagnetic with an effective solution magnetic moment of 5.8 ± 0.5 µB at room temperature by Evans’ method, in agreement with the theoretical value of \( S = \frac{5}{2} \) state (5.9 µB). This result indicates that the manganese center of 1 is assigned as a d⁵ high-spin state.

![Scheme 1. Synthesis of 1.](image)

![Figure 1. ORTEP drawings of 1 (left), 2 (middle), and 3 (right). Thermal ellipsoids are shown at the 50% probability level. Hydrogen atoms are omitted for clarity.](image)

| Bond | Length (Å) | Angle (deg) |
|------|------------|-------------|
| Mn(1)–P(1) | 2.7189(8) | Mn(1)–P(2) | 2.7275(7) |
| Mn(1)–N(1) | 2.127(2) | Mn(1)–N(2) | 2.188(2) |
| Mn(1)–Cl(1) | 2.3716(10) |
| P(1)–Mn(1)–P(2) | 147.46(3) | N(1)–Mn(1)–N(2) | 107.34(8) |
| P(1)–Mn(1)–P(2) | 152.86(6) |

We attempted to prepare the corresponding manganese-dinitrogen complex by reduction of 1 with 1.1 equiv of KC₈ in THF at room temperature under 1 atm N₂ atmosphere (Scheme 2). However, no dinitrogen-coordinated species was observed by the IR spectrum. Instead, the recrystallization of the reaction mixture afforded a Mn(II) complex bearing the
two PNP ligands [Mn(PNP)_2] in 21% yield, which was previously reported by Tonzetich and coworkers [56].

Scheme 2. Reduction of 1.

The reaction of [Mn(N(SiMe_3)_2)_2](thf)_2 with H-PNP afforded a Mn(II)-amide complex bearing the PNP-type ligand [Mn(PNP)(N(SiMe_3)_2)] (2) in 75% yield (Scheme 3). An ORTEP drawing of 2 is shown in Figure 1, and bond lengths and angles of 2 are listed in Table 2. Complex 2 has a four-coordinated manganese center with a distorted tetrahedral structure. The Mn–P lengths of 2 (ca. 2.76 Å) are slightly longer than those of 1 (ca. 2.72 Å), while the P–Mn–P angle of 2 (132°) is smaller than that of 1 (147°). These structural differences between 1 and 2 may derive from the different coordination geometry around the cobalt centers. Complex 2 displayed a room-temperature magnetic moment of 6.0 ± 0.6 µB in solution, which indicates an S = 5/2 high-spin Mn(II) state.

Scheme 3. Synthesis of 2.

Table 2. Selected Bond Lengths (Å) and Angles (deg) for 2.

|                  | Mn(1)–P(1)  | Mn(1)–P(2)  | Mn(1)–N(1)  | Mn(1)–N(2)  | P(1)–Mn(1)–P(2) | N(1)–Mn(1)–N(2) |
|------------------|-------------|-------------|-------------|-------------|-----------------|-----------------|
|                  | 2.7618(8)   | 2.7539(7)   | 2.0549(18)  | 2.0215(19)  | 132.94(2)       | 139.15(6)       |

The reaction of [MnBr_2(thf)_2] with Li-PCP (PCP = 2,6-bis(di-tert-butylphosphinomethyl)phenyl), which was generated in situ from Br-PCP with n-butyllithium, in the presence of 1,2-dibromoethane as an oxidant in THF at room temperature for 4 h gave a Mn(III) complex bearing the PCP-type ligand [Mn(PCP)Br_2] (3) in 44% yield (Scheme 4). X-ray analysis revealed the molecular structure of 3, and an ORTEP drawing and selected metric parameters are shown in Figure 1 and Table 3, respectively. The manganese center of 3 has a distorted square pyramidal geometry with two bromide ligands and the PCP ligand. One of the bromide ligands occupies the trans position to the C atom of the PCP ligand to make an equatorial plane, and the other is in the axial position. Shorter Mn–P bonds (ca. 2.49 Å) of 3 compared to those of 1 and 2 (2.72–2.76 Å) can be attributable to the six-membered backbone of the PCP ligand. The solution magnetic moment of 3 was 4.3 ± 0.4 µB at room temperature. Because this value is close to the theoretical value for an S = 2 high-spin Mn(III) state, 3 may have a high-spin Mn(III) oxidation state. Complex 3 displayed a room-temperature magnetic moment of 4.3 ± 0.4 µB at room temperature.
state (4.9 $\mu_B$), 3 is assignable as an $S = 2$ state. Reported Mn(III)-aryl complexes exhibited effective magnetic moments between 4.8–5.3 $\mu_B$ [57–59].

![Scheme 4. Synthesis of 3.](image)

**Table 3.** Selected Bond Lengths (Å) and Angles (deg) for 3.

| Bond/Angle | Length (Å)     | Angle (deg) |
|------------|----------------|-------------|
| Mn(1)–P(1) | 2.4792(17)     |             |
| Mn(1)–P(2) | 2.4865(17)     |             |
| Mn(1)–Br(1)| 2.5208(9)      |             |
| Mn(1)–Br(2)| 2.4513(9)      |             |
| Mn(1)–C(1) | 2.071(5)       |             |
| P(1)–Mn(1)–P(2) | 144.70(6) |            |
| C(1)–Mn(1)–Br(1) | 163.25(14) |             |

2.2. Reactivity for Nitrogen Fixation

2.2.1. Attempted Catalytic Ammonia Formation Using 1–3 as Catalysts

We investigated the catalytic reduction of dinitrogen into ammonia or hydrazine using the synthesized manganese complexes 1–3 as catalysts under the conditions previously applied for our group [46–48], which were initially reported by Peters [19]. Typical results are shown in Table 4. The reaction of an atmospheric pressure of dinitrogen with 40 equiv of KC$_8$ as a reductant and 38 equiv of [H(OEt)$_2$]BArF$_4$ (Ar$^F$ = 3,5-(CF$_3$)$_2$C$_6$H$_3$) as a proton source in the presence of a catalytic amount of 1 in Et$_2$O was conducted at $-78$ °C for 1 h. As a result, neither ammonia nor hydrazine was obtained, while 7.8 equiv of dihydrogen based on the Mn atom were formed as a product (Table 4, entry 1). The use of 2 as a catalyst afforded 1.4 equiv of ammonia and 7.5 equiv of dihydrogen under the same reaction conditions (Table 4, entry 2), where 1 equiv of ammonia is considered to be derived from the N(SiMe$_3$)$_2$ ligand in 2. We also attempted catalytic ammonia formation using complex 3 as a catalyst; however, no formation of ammonia nor hydrazine was observed. (Table 4, entry 3). These results indicate that the newly synthesized manganese complexes bearing the anionic PNP-type or PCP-type ligands did not work as catalysts for catalytic ammonia or hydrazine formation from dinitrogen.
Table 4. Attempted catalytic reduction of dinitrogen into ammonia or hydrazine using 1–3 at −78 °C <sup>a</sup>.

| Entry | Cat. | NH<sub>3</sub> (equiv) <sup>b</sup> | NH<sub>2</sub>NH<sub>2</sub> (equiv) <sup>b</sup> | H<sub>2</sub> (equiv) <sup>b</sup> |
|-------|------|-------------------------------|---------------------------------|------------------|
| 1     | 1    | 0                             | 0                               | 7.8              |
| 2     | 2    | 1.4                           | 0                               | 7.5              |
| 3     | 3    | 0                             | 0                               | 7.0              |

<sup>a</sup> A mixture of cat. (1 equiv), KC<sub>8</sub> (40 equiv) and [H(OEt<sub>2</sub>)<sub>2</sub>][BArF<sub>4</sub>] (38 equiv) was stirred in Et<sub>2</sub>O at −78 °C for 1 h under 1 atm of dinitrogen. Silylamine was quantified as ammonia after acid hydrolysis of the reaction mixture.

<sup>b</sup> Based on the manganese atom in the catalyst.

2.2.2. Attempted Catalytic Silylamine Formation Using 1–3 as Catalysts

We then tested 1–3 for their potential as catalysts for the formation of silylamine (N(SiMe<sub>3</sub>)<sub>3</sub>), which is easily converted to ammonia upon hydrolysis. Hence silylamine formation is regarded as an alternative nitrogen fixation process [8]. Typical results are shown in Table 5. The reaction of an atmospheric pressure of dinitrogen with 600 equiv of Na as a reductant and 600 equiv of Me<sub>3</sub>SiCl as a silylating reagent in the presence of 1 as a catalyst in THF was performed at room temperature for 20 h, followed by hydrolysis of the reaction mixture to convert silylamine to ammonia for quantification. This reaction afforded only 0.4 equiv of ammonia based on the Mn atom in the catalyst (Table 5, entry 1). When KC<sub>8</sub> was used as a reductant in place of Na, 1.4 equiv of ammonia were obtained based on the Mn atom in the catalyst (Table 5, entry 2). The catalytic activity of 2 toward silylamine formation was also investigated in the same reaction conditions to give less than 2 equiv of ammonia (Table 5, entries 3 and 4). The use of 3 as a catalyst in the presence of Na or KC<sub>8</sub> as a reductant afforded 2.5 or 2.2 equiv of ammonia based on the Mn atom in the catalyst, respectively, which are regarded as superstoichiometric amounts (Table 5, entries 5 and 6). These results suggest that these manganese complexes did not work as catalysts for silylamine formation under the current conditions.

Table 5. Attempted catalytic reduction of dinitrogen into silylamine using 1–3 at rt <sup>a</sup>.

| Entry | Cat. | Reductant | NH<sub>3</sub> (equiv) <sup>b</sup> |
|-------|------|-----------|-------------------------------|
| 1     | 1    | Na        | 0.4                           |
| 2     | 1    | KC<sub>8</sub> | 1.5                           |
| 3     | 2    | Na        | 0.8                           |
| 4     | 2    | KC<sub>8</sub> | 1.4                           |
| 5     | 3    | Na        | 2.5                           |
| 6     | 3    | KC<sub>8</sub> | 2.2                           |

<sup>a</sup> A mixture of cat. (1 equiv), KC<sub>8</sub> (600 equiv), and Me<sub>3</sub>SiCl (600 equiv) was stirred in THF at room temperature for 20 h under 1 atm of dinitrogen. Silylamine was quantified as ammonia after acid hydrolysis of the reaction mixture.

<sup>b</sup> Based on the manganese atom in the catalyst.

3. Materials and Methods

3.1. General Methods

<sup>1</sup>H NMR (400 MHz), <sup>13</sup>C<sup>1</sup>H NMR (100 MHz), and <sup>31</sup>P<sup>1</sup>H NMR (162 MHz) spectra were recorded on a JEOL ECS-400 spectrometer (Tokyo, Japan) or a JEOL ECZ-400S spectrometer in a suitable solvent, and spectra were referenced to residual solvent (<sup>1</sup>H, etc.).
13C([1]H)) or external standard (31P([1]H): H3PO4). IR spectra were recorded on a JASCO FT/IR 4100 Fourier Transform infrared spectrometer (JASCO, Tokyo, Japan) or a Shimadzu IR Spirit spectrometer (Shimadzu, Kyoto, Japan). UV-vis absorption spectra were recorded on a Shimadzu UV-1850. Magnetic susceptibility was measured in C6D6 using the Evans method. Elemental analyses were performed at the Microanalytical Center of The University of Tokyo.

All manipulations were carried out under an atmosphere of nitrogen or argon by using standard Schlenk techniques or glovebox techniques, unless otherwise stated. Solvents were dried by general methods and degassed before use. Me3SiCl was distilled prior to use. Li-PNP [47], H-PNP [60–62], [MnCl2(thf)2] [63], [MnBr2(thf)2] [64], [Mn[Ni(SiMe3)2](thf)2] [65], [H(OEt2)2]BARF4 [20,66], and KC8 [67] were prepared according to the literature methods. All the other reagents were commercially available (reagent grade from TCI (Tokyo, Japan), FUJIFILM Wako Pure Chemical (Osaka, Japan), and Sigma-Aldrich (St. Louis, MO, USA)) and used as received.

3.2. Synthesis

3.2.1. Preparation of PCP–Br

A mixture of 2-bromo-1,3-bis(bromomethyl)benzene (2.61 g, 7.61 mmol) and 1Bu2PH (2.94 g, 20.1 mmol) in acetone (55 mL) was stirred at reflux temperature for 2 h. The mixture was cooled to room temperature, and then the solvent was removed in vacuo. The residue was washed with Et2O (8 mL, 3 times). NaOAc (5.0 g), Et2O (20 mL), and water (15 mL) were added to the white residue. The product was extracted by Et2O (15 mL, 3 times). The combined extracts were dried over anhydrous MgSO4, and then the mixture was filtered.

The filtrate was evaporated to dryness to afford Br-PCP as a white solid (2.83 g, 5.98 mmol, 79%). 1H NMR (C6D6): δ 7.68 (d, J = 7.6 Hz, 2H), 7.04 (t, J = 7.6 Hz, 1H), 3.11 (s, 4H), 1.10 (d, J = 10.8 Hz, 36H). 13C([1]H) NMR (C6D6): δ 141.9 (d, J = 13.4 Hz), 130.0 (d, J = 19.1 Hz), 128.5, 126.5, 32.0 (d, J = 23.9 Hz), 29.8 (d, J = 14.3 Hz), 29.7 (d, J = 24.8 Hz). 31P([1]H) NMR (C6D6): δ 34.1 (s). Anal. Calcd. for C28H28BrP: C, 60.88; H, 9.15. Found: C, 60.88, H, 9.03.

3.2.2. Preparation of 1

To a solution of Li-PNP (195 mg, 0.501 mmol) in THF (10 mL), pyridine (82 µL, 1.02 mmol) and [MnCl2(thf)2] (134 mg, 0.496 mmol) were added at room temperature. The reaction mixture was stirred at room temperature for 18 h, and the solvent was removed in vacuo. Et2O (10 mL) was added to the brown residue. The suspension was filtered through Celite, and the filter cake was washed with Et2O (3 mL, 4 times). The combined filtrate was concentrated into 5 mL. The resultant mixture was kept at −30 ◦C to give a yellow solid, which was collected by filtration, washed with a small amount of cold pentane, and dried in vacuo to afford 1 as a yellow solid (132 mg, 0.239 mmol, 48%). Single crystals of 1 suitable for X-ray crystallography were obtained as yellow crystals from Et2O at −30 ◦C. Magnetic susceptibility: µeff = 5.8 ± 0.5 µB in C6D6 at 298 K. Anal. Calcd. for C27H47ClN2P2Mn: C, 58.75; H, 8.58; N, 5.07. Found: C, 58.74; H, 8.57; N, 5.23.

3.2.3. Preparation of 2

To a solution of [Mn[Ni(SiMe3)2](thf)2] (97.7 mg, 0.188 mmol) in THF (2 mL), a solution of H-PNP (68.3 mg, 0.178 mmol) in THF (2 mL) was added dropwise at room temperature. The reaction mixture was stirred at room temperature for 14 h, and then the solvent was removed in vacuo. Pentane (2 mL) was added to the pale-yellow residue. The suspension was filtered through Celite, and the filter cake was washed with pentane. The combined filtrate was concentrated into 1 mL. The resultant mixture was kept at −30 ◦C to give a pale orange solid, which was collected by decantation, washed with a small amount of cold pentane, and dried in vacuo to afford 2 as a pale orange solid (80.0 mg, 0.134 mmol, 75%). Single crystals of 2 suitable for X-ray crystallography were obtained as yellow crystals from pentane at −30 ◦C. Magnetic susceptibility: µeff = 6.0 ± 0.6 µB in C6D6 at 298 K. Anal. Calcd. for C28H60Si2N2P2Mn: C, 56.25; H, 10.12; N, 4.69. Found: C, 56.40; H, 10.20; N, 4.72.
3.2.4. Preparation of 3

To a solution of Br-PCP (142 mg, 0.300 mmol) in THF (5 mL), \(^{n}\)BuLi (1.55 M in hexane, 195 µL, 0.302 mmol) was added at room temperature. The reaction mixture was stirred at room temperature for 1 min, then [MnBr\(_2\)(thf)] (107 mg, 0.298 mmol) and 1,2-dibromoethane (31 µL, 0.36 mmol) in THF (5 mL) were added to the mixture. The reaction mixture was stirred at room temperature for 4 h, and then the solvent was removed in vacuo. Benzene (5 mL) was added to the reddish-brown residue. The suspension was filtered through Celite, and the filter cake was washed with benzene (1 mL, 4 times). The combined filtrate was concentrated into 3 mL. Slow addition of hexane (12 mL) to the mixture afforded red crystals suitable for X-ray crystallography of 3, which were collected by decantation and dried in vacuo to give 3 (0.5 C\(_6\)H\(_6\) as a red crystalline solid (81.1 mg, 0.133 mmol, 44%). Magnetic susceptibility: \(\mu_{\text{eff}} = 4.3 \pm 0.4 \mu_B\) in C\(_6\)D\(_6\) at 298 K. Anal. Calcd. for C\(_{27}\)H\(_{46}\)Br\(_2\)P\(_2\)Mn (3·0.5 C\(_6\)H\(_6\)): C, 50.10; H, 7.16. Found: C, 50.77; H, 7.04.

3.3. Reactivity for Nitrogen Fixation

3.3.1. Attempted Catalytic Ammonia Formation Using 1–3 as Catalysts

A typical experimental procedure for reduction of dinitrogen to ammonia or hydrazine using 1 is described below. In a 50 mL Schlenk flask, 1 (5.2 mg, 10.0 µmol), KC\(_8\) (54.1 mg, 0.400 mmol) and [H(OEt\(_2\)]\(_2\)BAr\(_{\text{F}}^\text{F}\) (385 mg, 0.380 mmol) were placed. After the mixture was cooled to –78 °C, cold Et\(_2\)O (5 mL) was added to the mixture. After the mixture was stirred at –78 °C for 1 h, the mixture was warmed to room temperature and further stirred at room temperature for 20 min. The amount of dihydrogen evolved in the reaction was determined by gas chromatography (GC) analyses. The reaction mixture was evaporated under reduced pressure, and the distillate was trapped in a dilute H\(_2\)SO\(_4\) solution (0.5 M, 10 mL). Aqueous solution of potassium hydroxide (30 wt%, 5 mL) was added to the residue, and the mixture was distilled into the same dilute H\(_2\)SO\(_4\) solution (0.5 M, 10 mL). The amount of NH\(_3\) present in H\(_2\)SO\(_4\) solution was determined by the indophenol method [68]. The amount of NH\(_2\)NH\(_2\) present in H\(_2\)SO\(_4\) solution was determined by the \(p\)-(dimethylamino)benzaldehyde method [69].

3.3.2. Attempted Catalytic Silylamine Formation Using 1–3 as Catalysts

A typical experimental procedure for reduction of dinitrogen to silylamine using 1 is described below. In a 50 mL Schlenk flask, 1 (2.4 mg, 5.0 µmol) and K\(_8\)C (406 mg, 3.00 mmol) were placed. After Et\(_2\)O (6 mL) and Me\(_2\)SiCl (380 µL, 3.00 mmol) were added to the mixture in the Schlenk, the mixture was stirred at room temperature for 1 min, then \([\text{MnBr}_2(\text{thf})_2]\) (0.5 C\(_6\)H\(_6\)) was added to the mixture, and the mixture was distilled into another dilute H\(_2\)SO\(_4\) solution (0.5 M, 10 mL). The amount of ammonia was determined by the indophenol method [68].

3.4. X-ray Diffraction

Crystallographic data of 1–3 are summarized in Table 6. Diffraction data for 1–3 were collected for the 2θ range of 4° to 55° at –100 °C (for 1 and 2) or –180 °C (for 3) on a Rigaku R-AXIS RAPID imaging plate area detector (Rigaku, Tokyo, Japan) with multi-layer mirror monochromated Mo-K\(_\alpha\) (\(\lambda = 0.71075 \text{ Å}\)) radiation with VariMax optics. Intensity data were corrected for Lorentz and polarization effects and for empirical absorptions (ABSCOR [70] for 1–3), while structure solutions and refinements were performed by using the CrystalStructure package [71]. The positions of non-hydrogen atoms were determined by direct methods (SHELXT version 2014/5 [72] for 1 and 3; SHELXS version 2013/1 [73] for 2) and subsequent Fourier syntheses (SHELXL [74] version 2016/6) and were refined on \(F^2\) using all unique reflections by full-matrix least-squares with anisotropic thermal parameters. All the hydrogen atoms were placed at the calculated positions with fixed isotropic parameters. Crystal of 1 and 3 contains an inverted structure as a disorder, which was solved as merohedral twins. Crystal of 2 contains heavy disorders among a
tert-butyl group, which were solved as disorders in a ratio of 0.52:0.48 for C(21A)–C(22A) and C(21B)–C(22B). All the hydrogen atoms attached to these carbon atoms could not be located, causing checkCIF/PLATON report Alert level B (PLAT043_ALERT_1_B Calculated and Reported Mol. Weight Differ by 6.06).

Table 6. X-ray crystallographic data for 1–3.

| Compound | 1   | 2   | 3   |
|----------|-----|-----|-----|
| chemical formula | \(\text{C}_2\text{H}_3\text{ClMnN}_2\text{P}_2\) | \(\text{C}_2\text{H}_6\text{MnN}_2\text{P}_2\text{Si}_2\) | \(\text{C}_2\text{H}_3\text{Br}_2\text{MnP}_2\) |
| CCDC number | 2149812 | 2149810 | 2149811 |
| dimensions of crystals, mm\(^3\) | \(0.500 \times 0.300 \times 0.200\) | \(0.300 \times 0.300 \times 0.300\) | \(0.150 \times 0.050 \times 0.050\) |
| crystal color, habit | orange, block | colorless, chunk | red, block |
| crystal system | orthorhombic | monoclinic | orthorhombic |
| space group | Pna\(_2\) \(#33\) | P2\(_1\)/n \(#14\) | Pna\(_2\) \(#33\) |
| \(a\), Å | 19.9909(11) | 10.6261(3) | 12.2701(4) |
| \(b\), Å | 19.141(2) | 24.7389(7) | 15.6675(5) |
| \(c\), Å | 7.849(3) | 14.0062(4) | 14.2993(4) |
| \(\alpha\), deg | 90 | 90 | 90 |
| \(\beta\), deg | 90 | 107.034(8) | 90 |
| \(\gamma\), deg | 90 | 90 | 90 |
| \(V\), Å\(^3\) | 3300.4(10) | 3520.4(2) | 2748.92(15) |
| Z | 4 | 4 | 4 |
| \(\rho\) \(_\text{calcld.}\), g cm\(^{-3}\) | 1.221 | 1.128 | 1.470 |
| \(F(000)\) | 1180.00 | 1300.00 | 1248.00 |
| \(\mu\), cm\(^{-1}\) | 5.519 | 5.518 | 35.217 |
| trans. factors range | 0.647–0.878 | 0.728–0.847 | 0.528–0.839 |
| no. reflections measured | 28090 | 33691 | 25377 |
| no. unique reflections | 6867 | 8055 | 5991 |
| no. parameters refined | 0.0398 | 0.0457 | 0.0835 |
| \(R_1 (I > 2\sigma(I))\) | 0.0322 | 0.0396 | 0.0386 |
| \(wR_2\) \((\text{all data})\) | 0.0865 | 0.0863 | 0.0652 |
| GOF | 1.042 | 1.005 | 0.975 |
| max diff peak/hole, e Å\(^{-3}\) | 0.30/−0.16 | 0.47/−0.34 | 0.73/−0.35 |

\(^a\) \(R_1 = \Sigma||F_o||−||F_c||/\Sigma||F_o||\). \(^b\) \(wR_2 = \sqrt{\sum w(F_o^2−F_c^2)^2}/\sum w(F_o^2)^2\)\(^{1/2}\). \(^c\) \(\text{GOF} = \sqrt{\sum w(F_o^2−F_c^2)^2}/(N_0−N\text{params})\)\(^{1/2}\).

4. Conclusions

In the current work, three manganese complexes bearing anionic PNP- and PCP-type pincer ligands were synthesized and fully characterized. Their catalytic activities for nitrogen fixation, such as ammonia and silylamine formation, were extensively studied. As a result, unfortunately, these manganese complexes did not promote the catalytic formation of ammonia or silylamine from nitrogen gas under mild reaction conditions. These results are in contrast to the previous results that vanadium, iron, cobalt, rhodium, and iridium complexes bearing the identical anionic pincer ligands worked as catalysts for ammonia formation or silylamine formation under mild reaction conditions [46–48,54,55]. Currently, we consider that the manganese pincer complexes are unstable under reducing conditions to cause catalyst decomposition. We hope the present result will help researchers to design nitrogen fixation systems using transition-metal complexes as catalysts.

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