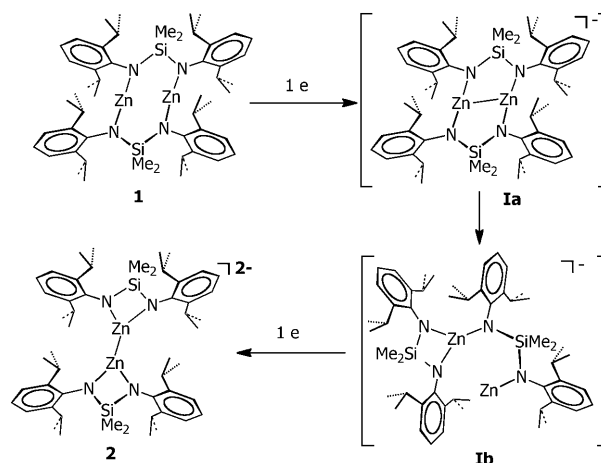


Theory-Guided Experiments on the Mechanistic Elucidation of the Reduction of Dinuclear Zinc, Manganese, and Cadmium Complexes**

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Since the recognition of the first $\text{Zn}^{\text{I}}\text{--Zn}^{\text{I}}$ bond in the dinuclear sandwich decamethyldizincocene $[(\eta^5\text{-C}_5\text{Me}_5)\text{Zn--Zn}(\eta^5\text{-C}_5\text{Me}_5)]$,^[1] the chemistry of Zn--Zn -bonded species has grown so rapidly that many complexes of the type LZn--ZnL have been characterized and studied.^[2] Regardless of the denticity of the supporting ligands L , they all coordinate to Zn in a terminally chelating mode.^[2] However, formation of these dinuclear compounds has not been mechanistically examined. We recently described the characterization of dinuclear $\text{Zn}^{\text{I}}\text{--Zn}^{\text{I}}$ -bonded species $[(\kappa^2\text{-Me}_2\text{Si}(\text{NDipp})_2)_2\text{Zn--Zn}(\kappa^2\text{-Me}_2\text{Si}(\text{NDipp})_2)]^{2-}$ (**2**) ($\text{Dipp} = 2,6\text{-iPr}_2\text{C}_6\text{H}_3$) from KC_8 reduction of dinuclear zinc complex $[\text{Zn}_2(\mu\text{-}\kappa^2\text{-Me}_2\text{Si}(\text{NDipp})_2)_2]$ (**1**), whereby the coordination mode of the diamido ligands dramatically changes from bridging to chelating.^[2] We thus became interested in the structural preference and the formation mechanism of $\text{Zn}^{\text{I}}\text{--Zn}^{\text{I}}$ -bonded complexes. Elaborate calculations were performed to understand the reduction of **1**, and a plausible mechanism was then proposed (Scheme 1). On two-electron reduction of **1**, two intermediates, **Ia** and **Ib**, are generated, and the energy difference between them is only 0.3 kcal mol^{-1} .^[2] The $\text{Zn}^{\text{II}}\text{--Zn}^{\text{I}}$ -bonded mixed-valent intermediate **Ia** is produced by one-electron reduction of **1**, and subsequently undergoes a dramatic structural rearrangement to give **Ib**, in which one three-coordinate and one one-coordinate Zn atoms are proposed. The exact valence of the Zn atoms in **Ib** is still not clear.



Scheme 1. Calculated mechanism of transformation of **1** into **2**.

Although the application of quantum chemical methods (ab initio molecular orbital and density functional theory) to elucidate reaction mechanisms has been very successful,^[3] most of the time it is difficult to prove the theoretically developed reaction mechanisms by experiments. This is indeed the case for the transformation from **1** to **2**. Attempts to probe both intermediates **Ia** and **Ib** failed. To this end, we turned our attention from zinc to manganese and cadmium, because they not only show structural similarity in the reported $\text{M}^{\text{I}}\text{--M}^{\text{I}}$ -bonded dinuclear complexes $[(\kappa^2\text{-Nacnac})\text{M--M}(\kappa^2\text{-Nacnac})]$ ($\text{M} = \text{Zn}$,^[20] Mn ,^[4] $\text{Nacnac} = \text{HC}[\text{C}(\text{Me})\text{NDipp}]_2$) and $[\text{Ar}'\text{M--MAR}']$ ($\text{M} = \text{Zn}$,^[21] Cd ,^[5] $\text{Ar}' = 2,6\text{-(2,6-iPr}_2\text{C}_6\text{H}_3)_2\text{C}_6\text{H}_3$), but also feature an identical M--M σ -bonding scheme. Herein we report structural transformations on reduction of dinuclear manganese and cadmium complexes $[\text{Mn}_2(\mu\text{-}\kappa^2\text{-Me}_2\text{Si}(\text{NDipp})_2)_2]$ (**3**) and $[\text{Cd}_2(\mu\text{-}\kappa^2\text{-Me}_2\text{Si}(\text{NDipp})_2)_2]$ (**4**). Characterization of the products supports the computed mechanism shown in Scheme 1.

As shown in Scheme 2, reactions of the dilithiated diamido ligand and 1 equiv of anhydrous MnCl_2 and CdCl_2 in diethyl ether and THF, respectively, yielded the corresponding dimeric compounds **3** and **4** in good yields. The dinuclear nature of **3** and **4** was deciphered by single-crystal X-ray crystallography,^[6] and their molecular structures are provided in Figures S1 and S2 of the Supporting Information. Complex **3** is essentially composed of two Mn_2Si four-membered rings, which are brought together by two Mn--N bonds, and consequently exhibit a boat conformation with two manganese atoms at the stern and two Si atoms at the bow. Each Mn atom is embraced by three nitrogen atoms and adopts a distorted T-shaped geometry. The central Mn_2N_2

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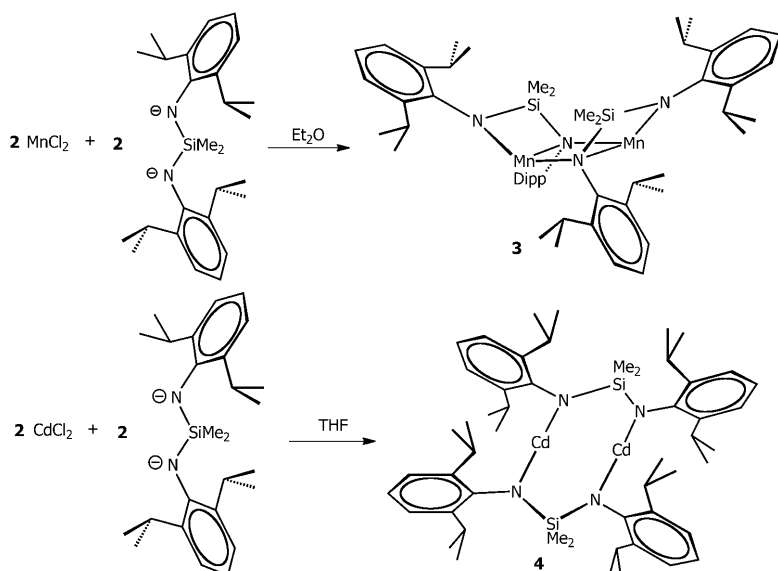
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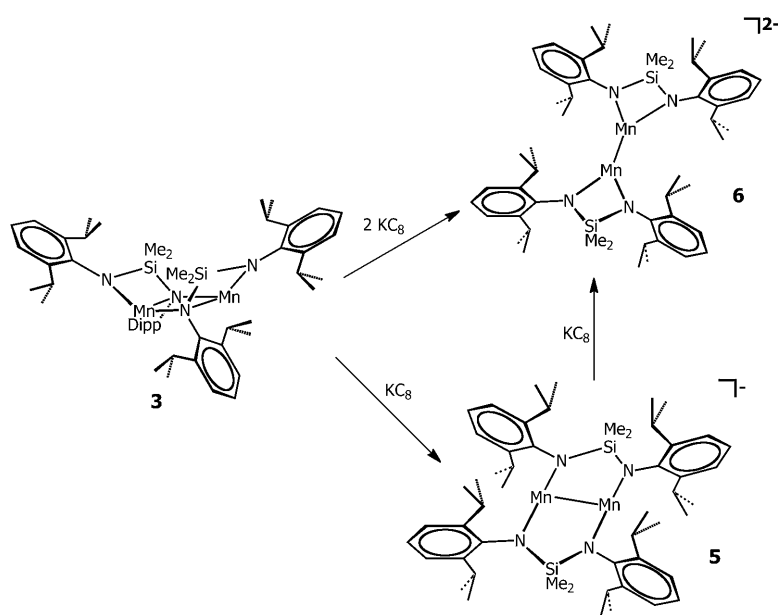
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Supporting information for this article (experimental details for the synthesis and characterization of complexes **3–7**) is available on the WWW under <http://dx.doi.org/10.1002/anie.201102296>.



Scheme 2.



Scheme 3.

four-membered ring adopts a nonplanar conformation, with a dihedral angle of 11.0° . Presumably, this arrangement is a consequence of strain between the sterically encumbered Dipp substituents. A similar bonding mode was also observed in complexes $[M_2\{\kappa^2\text{-N}(\text{Dipp})(\text{CH}_2)_3(\text{Dipp})\text{N}\}_2]$ ($M = \text{Mn}, \text{Fe}$, and Zn).^[7]

The $\text{Mn}\cdots\text{Mn}$ distance of $2.7746(11)$ Å in **3** is significantly longer than that of 2.69 Å in $[M_2\{\kappa^2\text{-N}(\text{Dipp})(\text{CH}_2)_3\text{-}(\text{Dipp})\text{N}\}_2]$ ^[7] but shorter than those of $[Mn_2\{N(\text{SiMe}_3)_2\}_4]$ ($2.811(1)$ Å at 140 K^[8a] and $2.841(1)$ at room temperature^[8b]). Solid-state magnetic data of **3** are shown in Figure S3 of the Supporting Information. Variation of χ_m and μ_{eff} with temperature indicates antiferromagnetic coupling between two

manganese centers. The μ_{eff} value of $4.88 \mu_B$ at 300 K is significantly lower than the spin-only value ($S = 5/2$ for dinuclear manganese species).

Complex **4**, on the other hand, is essentially isostructural with complex **1**,^[2] whereby two metal atoms are spanned by two bidentate diamido ligands, and the $\text{Cd}\cdots\text{Cd}$ distance of $3.042(1)$ Å indicates no bonding interaction between the two cadmium atoms.

Both **3** and **4** show interesting reduction chemistry. Whereas **2** is the only isolable product from the reduction of **1**, the reduction of complex **3** is slightly more complicated. As shown in Scheme 3, treatment of **3** with 1 equiv of KC_8 in the presence of 18-crown-6 in THF afforded orange mixed-valent $\text{Mn}^{\text{II}}\text{-Mn}^{\text{I}}$ complex $[(\text{thf})_2\text{-K}\subset 18\text{-crown-6}][Mn_2[\mu\text{-}\kappa^2\text{-Me}_2\text{Si}(\text{NDipp})_2]_2]$ ($[(\text{thf})_2\text{K}\subset 18\text{-crown-6}][\textbf{5}]$). Subsequent reduction of $[(\text{thf})_2\text{K}\subset 18\text{-crown-6}][\textbf{5}]$ gave purple $\text{Mn}^{\text{I}}\text{-Mn}^{\text{I}}$ species $[(\text{thf})_2\text{K}\subset 18\text{-crown-6}]_2[Mn\{\kappa^2\text{-Me}_2\text{Si}(\text{NDipp})_2\}_2]$ ($[(\text{thf})_2\text{K}\subset 18\text{-crown-6}]_2[\textbf{6}]$). Alternatively, dianionic complex **6** can be prepared directly from **3** by two-electron reduction. For crystallographic experiments, two more complexes containing dianionic fragment **6** were prepared by KC_8 reduction of **3** in neat toluene and in THF in the presence of 222-cryptand to give $[\text{K}_2\subset \textbf{6}]$ and $[\text{K}\subset 222\text{-cryptand}]_2[\textbf{6}]$, respectively.

The solid-state molecular structure of anionic **5** was determined by single crystal X-ray crystallography (Figure 1).^[6] The structure of **5** is close to that of calculated intermediate **1a**; both feature two bidentate diamido ligands spanning an $\text{M}^{\text{II}}\text{-M}^{\text{I}}$ ($M = \text{Mn}, \text{Zn}$) bond. In contrast to the planar Mo_2N_4 core in quadruply bonded dimolybdenum complex $[\text{Mo}_2\{\mu\text{-}\kappa^2\text{-Me}_2\text{Si}(\text{NDipp})_2\}_2]$,^[9] in which two bidentate diamido ligands also span the Mo-Mo bond, the core structure of **5** displays a puckered conformation with an N1-Mn1-Mn2-N2 dihedral angle of 24.3° . Each Mn atom is ligated by two nitrogen donors of the ligands and one adjacent Mn atom, and thus adopts a T-shaped geometry. Although **5** is a mixed-valent ($\text{Mn}^{\text{II}}\text{Mn}^{\text{I}}$) species, the two Mn atoms are essentially indistinguishable, because the structure has

local C_i symmetry. Characterization of **5** therefore supports the accuracy of the calculated intermediate **1a** for the reduction of **1**.

Surprisingly, the X-ray structure of dianionic complex **6** in both $[\text{K}\subset 222\text{-cryptand}]_2[\textbf{6}]$ and $[\text{K}_2\subset \textbf{6}]$ (Figure 2) is dramatically different from that of **5**, but similar to that of **2**. In both compounds, each Mn atom is terminally chelated by two bidentate diamido ligands, and the two resultant MnN_2Si four-membered rings are brought together by the Mn-Mn bond. In **6**, each Mn atom is three-coordinate with respect to the diamido ligand and the neighboring Mn atom, and adopts a trigonal-planar geometry with a sum of the bond angles at each Mn center of 360° . Noteworthy, the two MnN_2Si four-

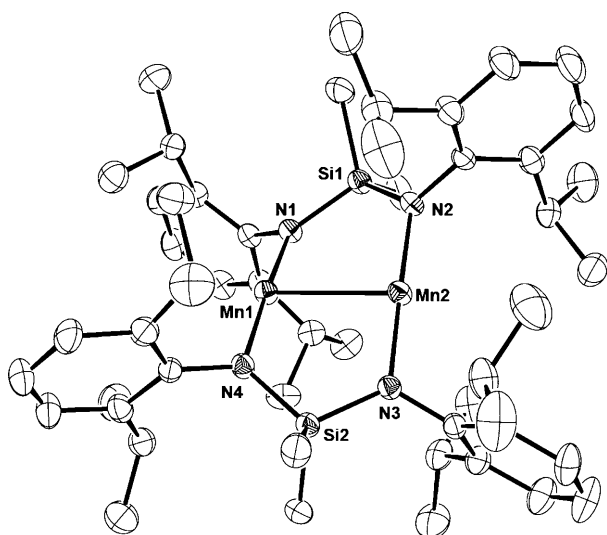


Figure 1. Molecular structure of **5** with thermal ellipsoids at 35 % probability. Selected bond lengths [Å] and angles [°]: Mn1–Mn2 2.6848(8), Mn1–N1 1.934(3), Mn1–N4 1.940(3), Mn2–N2 1.941(3), Mn2–N3 1.937(3); N1–Mn1–N4 173.99(13), N2–Mn2–N3 177.09(13), N1–Mn1–Mn2 88.56(9), N4–Mn1–Mn2 91.26(9), N3–Mn2–Mn1 89.52(9), N2–Mn2–Mn1 91.14(9).

membered rings are coplanar in both complexes regardless of the encapsulated potassium ions. This array is in sharp contrast with that of $[(\kappa^2\text{-Nacnac})\text{Mn}-\text{Mn}(\kappa^2\text{-Nacnac})]$, in which two $\text{C}_3\text{N}_2\text{Mn}$ six-membered rings are orthogonal to each other.^[4]

Not only do monoanionic **5** and dianionic **6** exhibit different structures, but they have very different metrics according to XRD analysis. The average Mn–N bond lengths are 1.939 (**5**), 2.054 ($[\text{K}_2\text{C6}]$), and 2.089 Å ($[\text{K}(\text{C}222\text{-cryptand})_2\text{6}]$). The significantly short Mn–N bond lengths in **5** suggest significant π -bonding interactions between manganese atoms and four nitrogen donors. For a dinuclear complex, the metal–metal distance is usually the most interesting metric parameter. The Mn–Mn bond length of 2.6851(9) Å in **5** is much shorter than those in $[\text{K}(\text{C}222\text{-cryptand})_2\text{6}]$ (2.7871(8) Å) and $[\text{K}_2\text{C6}]$ (2.7464(13) Å). Interestingly, the Mn–Mn bond length is strongly dependent on the ancillary ligands. For example, the Mn–Mn bond lengths in univalent dimanganese species are 2.721(1) Å in $[(\kappa^2\text{-Nacnac})\text{Mn}-\text{Mn}(\kappa^2\text{-Nacnac})]$ ^[4] and 2.6745(5) Å in $[\text{Mn}_2(\mu\text{-S}_2)(\text{CO})_6(\mu\text{-CO})]$.^[10] In addition, the Mn–Mn bond length in zero-valent dimanganese carbonyl complex $[\text{Mn}_2(\text{CO})_{10}]$ is 2.9042(8) Å.^[11] Nevertheless, all of these values are shorter than those of diatomic Mn_2 (3.4 Å, estimated in rare-gas matrix) and Mn_2^+ (3.06 Å, estimated in MgO matrix).^[12] Roesky et al. have shown that the $\text{Mn}^{\text{I}}\text{-Mn}^{\text{I}}$ bond in $[(\kappa^2\text{-Nacnac})\text{Mn}-\text{Mn}(\kappa^2\text{-Nacnac})]$ ^[4] is formed by overlap of a pair of 4s orbitals. Accordingly, a similar bonding scheme is also proposed for the Mn–Mn bonds in **5** and **6**, but the formal Mn–Mn bond order is 0.5 in **5** and 1 in **6**. The shorter Mn–Mn bond length in **5** is presumably due to the bridging ligands, while **6** bears two chelating ligands.

It is noteworthy that the two ZnN_2Si four-membered rings in the reported dinuclear $\text{Zn}^{\text{I}}\text{-Zn}^{\text{I}}$ -bonded complex $[\text{Zn}\{\kappa^2\text{-}$

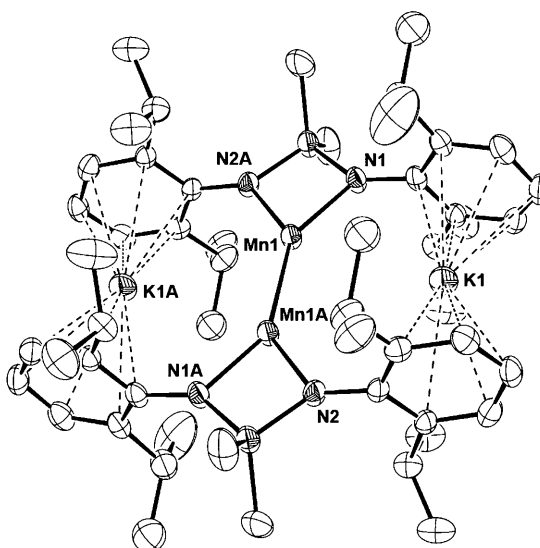
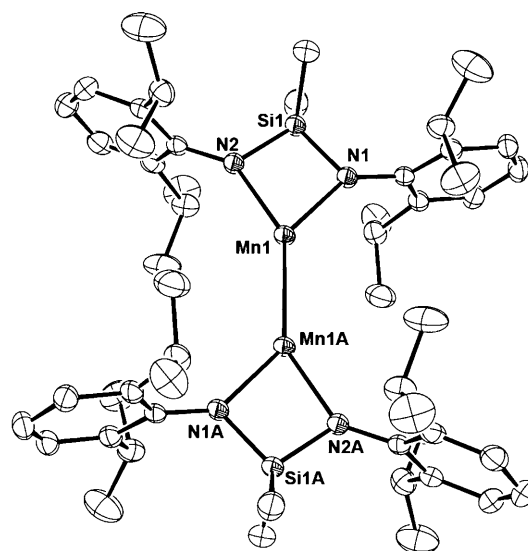
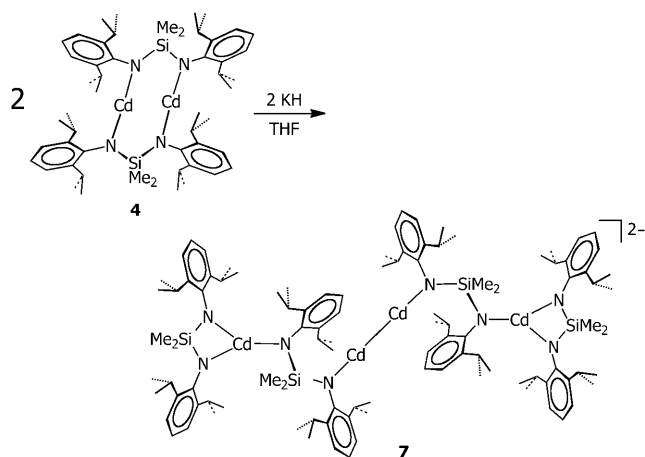


Figure 2. Molecular structures of **6** in $[\text{K}(\text{C}222\text{-cryptand})_2\text{6}]$ (top) and $[\text{K}_2\text{C6}]$ (bottom) with thermal ellipsoids at 35 % probability. Selected bond lengths [Å] and angles [°]: $[\text{K}(\text{C}222\text{-cryptand})_2\text{6}]$: Mn1–Mn1A 2.7871(8), Mn1–N1 2.078(3), Mn1–N2 2.100(2); N1–Mn1–N2 76.44(10), N1–Mn1–Mn1A–N2A 11.69(10). $[\text{K}_2\text{C6}]$: Mn1–Mn1A 2.7464(13), Mn1–N1 2.065(4), Mn1–N2 2.044(4), Mn1...K1 3.8731(14); N1–Mn1–N2 76.74(15), N1–Mn1–Mn1A–N2 4.02(12).

$\text{Me}_2\text{Si}(\text{NDipp})_2]$ ₂²⁻ (**2**)^[2j] are not coplanar and display a dihedral angle of 50.6°. The Zn–Zn σ -bonding character was further corroborated by characterization of $\text{K}_2\text{C2}$, in which each potassium atom is sandwiched by two adjacent phenyl rings of Dipp groups, and consequently the dihedral angle of the two N_2SiZn four-membered rings is reduced to 10.8°. The steady Zn–Zn distances of 2.3695(17) and 2.3634(11) Å in these two complexes, independent of rotation about the Zn–Zn axis, indeed signify σ bonding between the two Zn atoms. On the other hand, in light of the Mn–Mn σ -bonding scheme in $[(\kappa^2\text{-Nacnac})\text{Mn}-\text{Mn}(\kappa^2\text{-Nacnac})]$,^[4] both $[\text{K}_2\text{C6}]$ and $[\text{K}(\text{C}222\text{-cryptand})_2\text{6}]$ should also have a Mn–Mn σ bond on the basis of equivalent Mn–Mn distances. However, the

parallel arrangement of two MnN_2Si four-membered rings in both $[\text{K}\subset 222\text{-cryptand}]_2[\mathbf{6}]$ and $[\text{K}_2\subset \mathbf{6}]$ suggests strong anti-ferromagnetic coupling between two Mn centers. This is indeed the case. The temperature dependence of the magnetic susceptibility of mixed-valent dimanganese $\text{Mn}^{\text{II}}\text{Mn}^{\text{I}}$ species $[(\text{thf})_2\text{K}\subset 18\text{-crown-6}][\mathbf{5}]$ and univalent $\text{Mn}^{\text{I}}\text{--Mn}^{\text{I}}$ complex $[\text{K}_2\subset \mathbf{6}]$ in the temperature range of 2–300 K is shown in Figures S4 and S5 of the Supporting Information, respectively. The room-temperature effective magnetic moments μ_{eff} of $[(\text{thf})_2\text{K}\subset 18\text{-crown-6}][\mathbf{5}]$ and $[\text{K}_2\subset \mathbf{6}]$ are 6.10 and 4.84 μ_{B} , respectively. These values are smaller than that expected for two noninteracting univalent manganese centers ($\mu_{\text{eff}} = 9.8 \mu_{\text{B}}$ for ^7S and $\mu_{\text{eff}} = 6.9 \mu_{\text{B}}$ for ^5D states).

To isolate the **5**-analogous dicadmium complex, reduction of **4** by 1 equiv of potassium hydride in the presence of 18-crown-6 was also carried out in THF. To our surprise, a diamagnetic tetranuclear mixed-valent complex formulated as $[(\text{thf})_2\text{K}\subset 18\text{-crown-6}]_2[(\kappa^2\text{-Me}_2\text{Si}(\text{NDipp})_2)\text{Cd}\{\mu\text{-Me}_2\text{Si}(\text{NDipp})_2\}\text{Cd}]_2$ ($[(\text{thf})_2\text{K}\subset 18\text{-crown-6}]_2[\mathbf{7}]$) was obtained from the reaction (Scheme 4). Two signals at $\delta = 436.0$ and



Scheme 4.

420.3 ppm were observed in the ^{113}Cd NMR spectrum. In contrast to the high stability of the only structurally characterized $\text{Cd}^{\text{I}}\text{--Cd}^{\text{I}}$ -bonded dimeric species $[\text{Ar}^{\text{I}}\text{Cd}^{\text{I}}\text{--Cd}^{\text{I}}\text{Ar}^{\text{I}}]$ ($\text{Ar}^{\text{I}} = 2,6\text{-}(2,6\text{-iPr}_2\text{C}_6\text{H}_3)_2\text{C}_6\text{H}_3$), $[(\text{thf})_2\text{K}\subset 18\text{-crown-6}]_2[\mathbf{7}]$ is thermally unstable in organic solvents. On dissolution in THF at room temperature, it quickly decomposes to cadmium metal, free ligands, and unidentified cadmium complexes over 12 h. X-ray diffraction analysis of **7** (Figure 3) indicates that it is a dimeric complex in which two monomers $\{(\kappa^2\text{-Me}_2\text{Si}(\text{NDipp})_2)\text{Cd}(\mu\text{-Me}_2\text{Si}(\text{NDipp})_2)\text{Cd}\}$, containing one one-coordinate and one three-coordinate Cd atoms, are linked through a $\text{Cd}^{\text{I}}\text{--Cd}^{\text{I}}$ bond. The structure of this monomer is identical to that of calculated dizinc intermediate **1b** in Scheme 1. It is therefore clear that the one-coordinate zinc atom in **1b** is univalent, and the three-coordinate zinc atom is divalent. The Cd1--Cd1A bond length of 2.6103(9) Å is shorter than that in $\text{Ar}^{\text{I}}\text{Cd}^{\text{I}}\text{--Cd}^{\text{I}}\text{Ar}^{\text{I}}$ (2.6257(5) Å),^[5] in which both cadmium atoms are also mono-coordinate with respect to the aryl ligand. Presumably, owing to the smaller size of Mn

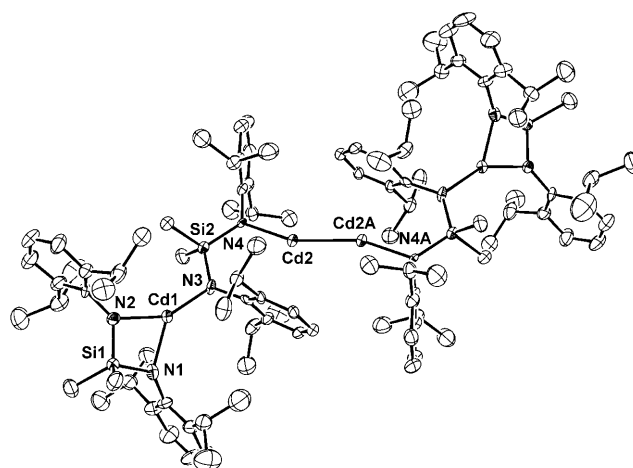


Figure 3. Molecular structure of **7** with thermal ellipsoids at 35% probability. Selected bond lengths [Å] and angles [°]: Cd1--Cd1A 2.6103(9), Cd1--N1 2.103(5), Cd2--N2 2.111(5), Cd2--N3 2.183(6), Cd2--N4 2.169(5); N1--Cd1--Cd1A 158.24(15), N2--Cd2--N3 139.54(19), N2--Cd2--N4 147.7(2), N3--Cd2--N4 72.3(2).

and Zn atoms, the **7**-analogous dimanganese and dizinc complexes have not yet been observed.

In summary, we have demonstrated the synthesis and characterization of two remarkable Mn–Mn-bonded dimanganese complexes, **5** and **6**, and one tetracadmium complex **7** featuring a $\text{Cd}^{\text{I}}\text{--Cd}^{\text{I}}$ bond. Collectively, characterization of these complexes is consistent with the proposed intermediates in the computed mechanism for the transformation of dizinc complex **1** on reduction, and this mechanism is applicable to the reduction of dimanganese complex **3** and dicadmium complex **4**. Although the recently reported dinuclear complexes LM–ML ($\text{M} = \text{Zn},^{[2]} \text{Mn},^{[4]} \text{Cd}^{[5]}$) can be stabilized by various ligands with different denticity, the mechanism described herein sheds light on their formation. Reactivity studies on **5–7** are currently underway.

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