A Two-Coordinate Manganese(0) Complex with an Unsupported Mn−Mg Bond: Allowing Access to Low Coordinate Homo- and Heterobimetallic Compounds

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Ⓢ Supporting Information

ABSTRACT: This study details the synthesis and characterization of an unprecedented two-coordinate, high-spin manganese(0) complex that incorporates an unsupported Mn−Mg bond, viz. $L^{†}MnMg(^{Mes}Nacnac)$ ($L^{†}$ = $-N(Ar^{†})(SiPr^{i}_{3})$, $Ar^{†}$ = $C_6H_2\{C(H)Ph_2\}_2Pr^{i}$-2,6,4; $^{Mes}Nacnac$ = $[(MesNCMe)_2CH]^{-}$; Mes = mesityl). This compound has been utilized as an "inorganic Grignard reagent" in the preparation of the first two-coordinate manganese(I) dimer, $L^{†}MnMnL^{*}$ (L^{*} = $-N(Ar^{*})(SiMe_3)$, Ar^{*} = $C_6H_2\{C(H)Ph_2\}_2Me$-2,6,4), and the related mixed valence, bis(amido)-hetereobimetallic complex, $Mn^{II}(\mu\text{-}L^{†})(\mu\text{-}L^{*})Cr^{0}$. It is also shown to act as a two-electron reducing agent in reactions with unsaturated substrates.

$\mathbf{M}$etal−metal bonded compounds have been intensively studied for many decades, not only due to their fundamental appeal but also because of the many applications they have found in areas such as small molecule activations, catalysis, enzyme mimicry, etc.[1] With respect to the d-block metals, the vast majority of efforts in this field have lain with the second- and third-row elements, though the development of highly reactive, and often open-shell, first-row metal−metal bonded complexes has been rapid in recent years.[1] Arguably, the most impressive advances here stem from the kinetic stabilization of low coordinate, carbonyl free, metal(I)−metal(I) bonded dimers using very bulky mono- and higher dentate ligands. Landmark compounds from this work include Carmona's zinc(I) dimer, $Cp^{*}ZnZnCp^{*}$ (Cp^{*} = $C_5Me_5^{-}$),[2] Power's quintuply bonded, terphenyl-coordinated chromium(I) dimer, Ar′CrCrAr′ (Ar′ = $C_6H_3Dip_2$-2,6, Dip = $C_6H_3Pr^{i}_2$-2,6),[3] Roesky's β-diketiminate chelated manganese(I) dimer, $(^{Dip}Nacnac)MnMn$-$(^{Dip}Nacnac)$ ($^{Dip}Nacnac$ = $[(DipNCMe)_2CH]^{-}$),[4] and a variety of systems with extremely short M^{I}−M^{I} (M = Cr,[5] Fe[6] or Co[7]) multiple bonds bridged by bulky amidinate, guanidinate, or reduced diazabutadiene ligands. Given the highly reactive nature of such compounds, it is not surprising that they are finding synthetic applications in a variety of areas.[5a,8]

In order to significantly enhance the reactivity scope of neutral first-row d-block metal−metal bonded systems, it would be a great advantage to be able to access representatives that exhibit their lowest possible metal coordination number, namely two. In this regard, while one diamagnetic terphenyl-zinc(I) example, Ar′ZnZnAr′, has been reported,[9] two-coordinate, open-shell metal(I) dimers remain unknown.[10] This paucity likely stems from a lack of suitably bulky monodentate ligands for the kinetic stabilization of such species. We have recently developed an extremely bulky class of monodentate amide ligand, e.g., $-N(Ar^{†})(SiPr^{i}_3)$ ($Ar^{†}$ = $C_6H_2\{C(H)Ph_2\}_2Pr^{i}$-2,6,4 ($L^{†}$),[11] which we have utilized in the preparation of a variety of very reactive one- and two-coordinate p-block metal(I) compounds.[12] It seemed reasonable that these amides might also prove their worth in the stabilization of novel low-valent/low-coordinate first-row d-block systems. To this end, here we report that the reduction of a bulky amido-manganese(II) halide with a magnesium(I) dimer yields an unprecedented two-coordinate, high-spin manganese(0) complex bearing an unsupported Mn−Mg bond. This has been utilized as an "inorganic Grignard reagent" to access the first two-coordinate manganese(I) dimer and a related mixed valence heterobimetallic (Mn^{II}/Cr^{0}) species, both of which incorporate two amides as their only ligands. The reactivity of the Mn−Mg bonded species toward several unsaturated substrates is also reported.

At the outset of this study the reaction of the dimeric manganese(II) bromide complex, $\{L^{†}Mn(THF)(\mu\text{-}Br)\}_2$ (see Supporting Information (SI)), with 1 equiv of the magnesium(I) dimer, $\{(^{Mes}Nacnac)Mg\}_2$ ($^{Mes}Nacnac$ = $[(MesNCMe)_2CH]^{-}$; Mes = mesityl),[13] was carried out with the expectation that the manganese(I) compound, $L^{†}MnMnL^{†}$, would be formed. Instead, the reaction returned the intensely royal blue colored manganese(0) compound, $L^{†}MnMg(^{Mes}Nacnac)$ **1**, and unreacted $\{L^{†}Mn(THF)(\mu\text{-}Br)\}_2$ in an ∼2:1 ratio. Repeating the reaction in a 1:2 ratio led to the complete consumption of $\{L^{†}Mn(THF)(\mu\text{-}Br)\}_2$ and afforded a good isolated yield of **1** (Scheme 1). Consequently, it is likely that the mechanism of these reactions involves the generation of the transient manganese(I) fragment, "$L^{†}Mn$", which, because of its high steric loading, is incapable of dimerizing (to give $L^{†}MnMnL^{†}$)

Scheme 1. Synthesis of Compounds 1−4[a]
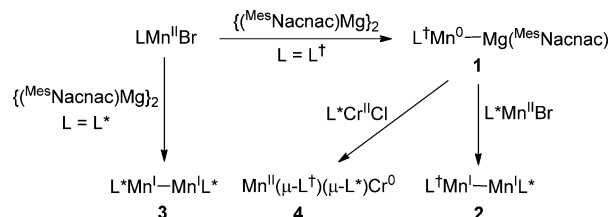
[a] The metal(II) halide precursor complexes are dimeric in the solid state.

and instead is further reduced by the magnesium(I) reagent, yielding **1**.

Compound **1** is of considerable fundamental interest for a number of reasons. First, while a handful of complexes containing d-block metal-Mg bonds have been reported,[14] none incorporate manganese, and all are higher coordinate closed-shell species. Furthermore, compound **1** is the first bimetallic system to contain two-coordinate manganese, formally in the zero oxidation state.[15] These novel features strongly suggested that **1** should exhibit potent reactivity, which was initially explored by examining its use as an "inorganic Grignard reagent" for the transfer of the L†Mn fragment. In this regard, its reaction with the amido-manganese(II) halide, {L*Mn(THF)-(μ-Br)}₂ (L* = -N(Ar*)(SiMe₃), Ar* = C₆H₂{C(H)Ph₂}₂Me-2,6,4), afforded a good yield of the unsymmetrically substituted manganese(I) dimer, L†MnMnL* **2**, as red-purple crystals (Scheme 1). The formation of **2**, in combination with the fact that **1** does not readily react with the bulkier precursor complex, {L†Mn(THF)(μ-Br)}₂, is consistent with our proposed mechanism for the generation of **1**. To add further weight to this, the reduction of the less bulky precursor, {L*Mn(THF)(μ-Br)}₂, with {(Mes Nacnac)Mg}₂ was carried out, and this proceeded directly to the symmetrical manganese(I) dimer, L*MnMnL* **3**, with no evidence for the formation of a Mn−Mg bonded species.

Low-valent heterobimetallic systems incorporating electronically distinct first-row d-block metals have proved valuable as reagents/catalysts in a variety of organic transformations.[1] It seemed reasonable that **1** could be used as a synthon to access novel examples of such systems incorporating one Mn center. To probe this possibility, the compound was reacted with the chromium(II) halide complex, {L*Cr(THF)(μ-Cl)}₂,[16] which yielded the mixed-valence bis(amido)-Mn^II/Cr⁰ compound, **4** (Scheme 1). Based on the chemistry described above, it is feasible that this reaction proceeds via a metal−metal bonded intermediate, L†Mn-CrL*, which undergoes an internal redox process to give **4**. This compound is an unprecedented example of a first-row d-block heterobimetallic complex, the coordination sphere of which encompasses only two amide ligands.[17] The formation of **4** implies that the synthesis of a variety of related systems should be achievable, especially given that groups 6−9 and group 12 metal(II) halide complexes incorporating bulky amide ligands (e.g., L* and L†) have recently been made available as potential precursors.[16]

Compounds **1−4** were crystallographically characterized, and the molecular structures of **1**, **2** and **4** are depicted in Figure 1. Compound **1** is monomeric and exhibits a nonlinear, two-coordinate Mn center (N−Mn−Mg = 160.85(9)°). Its unsupported Mn−Mg bond (2.8244(13) Å) is markedly longer than the handful of previously reported first-row d-block metal−
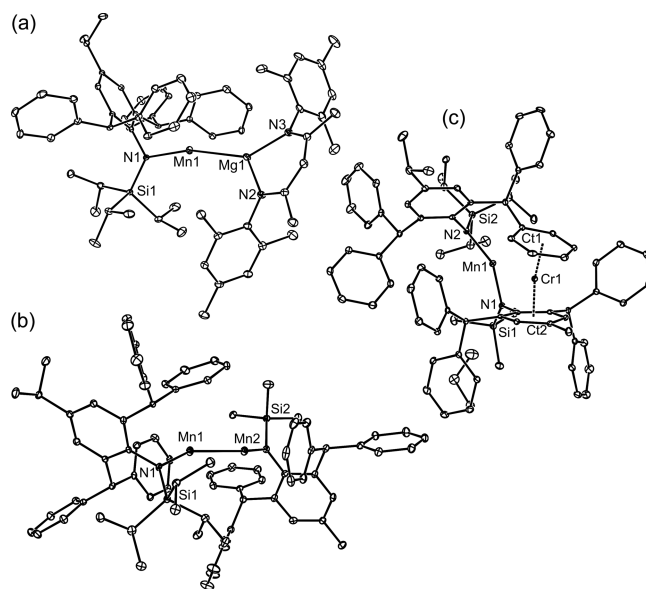

Figure 1. Thermal ellipsoid plots (20% probability surface) of (a) **1**, (b) **2**, and (c) **4**.

magnesium bonds (range: 2.481−2.633 Å),[14] all of which belong to higher-coordinate, closed-shell systems. It is, however, well within the sum of the covalent radii of Mg and high-spin Mn (3.02 Å).[18] Compounds **2** and **3** represent the first open-shell, two-coordinate d-block metal(I) dimers and do not exhibit any close interactions between their metal centers and the benzhydryl phenyl groups of their amide ligands (closest Mn⋯C_Ph = 2.970(3) Å **2**; 3.043(3) Å **3**, cf. 3.033 Å **1**). They have similar, mildly *trans*-bent structures (N−Mn−Mn = 153.05° (mean) **2**; 148.39(5)° **3**) and their Mn−Mn bonds (2.7431(7) Å **2**; 2.7224(6) Å **3**) are comparable to that in three-coordinate (Dip Nacnac)MnMn(Dip Nacnac) (2.721(1) Å).[4] The heterobimetallic system, **4**, possesses a two-coordinate, bis(amido)-Mn^II center (N−Mn−N = 140.00(9)°), while its Cr⁰ atom is η⁶-coordinated by the central phenyl ring of the L† ligand and a flanking phenyl group of the other amide, L* (centroid−Cr−centroid =164.42(6)°). Although the separation between the two metal centers (3.0443(6) Å) is close to the sum of the covalent radii for Cr and high-spin Mn (3.00 Å),[18] computational studies (*vide infra*) indicate a negligible metal−metal interaction.

All of **1−4** are paramagnetic and exhibit solution-state magnetic moments (Evans method: **1** 5.3 μ_B, **2** 3.4 μ_B (per Mn), **3** 3.4 μ_B (per Mn), **4** 5.5 μ_B) indicative of them containing high-spin Mn centers. So as to gain some insight into the nature of their metal−metal interactions, variable-temperature solid-state magnetic susceptibility measurements were carried out. Those for **1** (see Figure 2a) show it to exhibit a χ_M T value at 300 K of 4.14 cm³ mol⁻¹ K (μ_eff = 5.76 μ_B), which slowly decreases, in a Curie−Weiss fashion, to reach ∼3.9 cm³ mol⁻¹ K (μ_eff = 5.59 μ_B) at ∼6 K then, more rapidly due to zero-field splitting, reaching 3.0 cm³ mol⁻¹ K (μ_eff = 4.90 μ_B) at 2 K. Such data are suggestive of an isolated S = 5/2 ground state, as would be expected for a compound containing high-spin Mn⁰ ("4s²3d⁵"). The low-temperature (10 K) X-(9 GHz) and Q-(35 GHz) band EPR spectra of frozen solutions of **1** are largely consistent with this conclusion, in that their simulations yielded spin Hamiltonian parameters characterized by g = 2.004, S = 5/2, and anisotropic zero-field parameters of D = 0.1 cm⁻¹ (2850 MHz) and E = 0.04 cm⁻¹ (1250 MHz) (see SI).
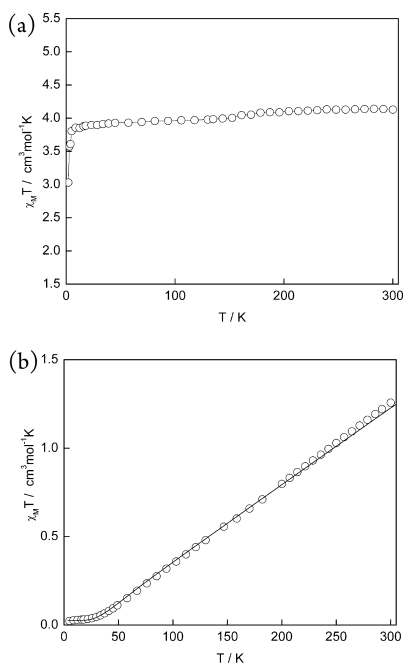
Figure 2. Plot of $\chi_M T$ vs T for (a) **1** and (b) **3** (per Mn center). The solid line in (a) is a guide to the eye, while that in (b) is the calculated best fit using the parameters in the text.

Figure 3. Representations of (a) the Mn−Mg σ-bonding orbital of $\mathbf{1^{Me}}$ and (b) the Mn−Mn σ-bonding orbital of **3**, derived from the CASSCF calculations.

The solid-state magnetic behavior of **4** is similar to that of **1** (see SI), again implying an isolated $S = 5/2$ ground state, though originating from high-spin Mn^{II} ($3d^5$) in this case. Quite different magnetic data were obtained for **3**, which exhibits an $\chi_M T$ value of 1.28 cm^3 mol^{-1} K per Mn center at 300 K ($\mu_{eff} = 3.20$ μ_B, the Curie temperature is significantly higher than 300 K). This decreases almost linearly down to ~50 K (reaching ~0.1 cm^3 mol^{-1} K), before plateauing at close to 0 cm^3 mol^{-1} K below that (Figure 2b). The corresponding χ_M vs T plot (see SI) is typical of an antiferromagnetic coupled system, the data for which were fitted to an $S = 5/2$ (per Mn) dimer model ($-2J\mathbf{S_1}\cdot\mathbf{S_2}$) using $g = 2.18$, $J = -47.5$ cm^{-1}. Theoretical calculations (*vide infra*) confirm an $S = 0$ coupled ground state for the compound. This magnetic profile is similar to those reported for the higher coordinate dimers, (^{Dip}Nacnac)MnMn(^{Dip}Nacnac)[4] and (Piso)-MnMn(Piso) (Piso = [(DipN)$_2$CBu^t]$^-$),[6] which were both shown to have Mn−Mn single bonds derived from the 4s electron at each antiferromagnetically coupled, high-spin Mn^I center.

In order to further examine the metal−metal bonding in the compounds reported here, calculations (CASSCF/CASPT2) were carried out to determine the ground-state electronic structures of a model of **1**, with its isopropyl substituents replaced with methyl groups (viz. $\mathbf{1^{Me}}$), and the full molecules of **3** and **4** (see SI for full details). Consistent with the magnetochemical studies on **1**, a sextet ground state was determined for $\mathbf{1^{Me}}$, arising from single occupation of its five, nonbonding Mn 3d orbitals. Moreover, the compound possesses a Mn−Mg single bond (effective bond order, EBO = 0.97), which largely originates from the 4s and 3s orbitals on Mn and Mg, respectively (Figure 3a). As manganese is more electronegative than magnesium (1.55 vs 1.31 on the Pauling scale),[19] the compound formally contains Mn^0 and Mg^{II} centers. However, this electronegativity difference is not great, and therefore, the Mn−Mg bond would not be expected to be heavily polarized and should have significant covalent character. Indeed, the LoProp atomic charges were
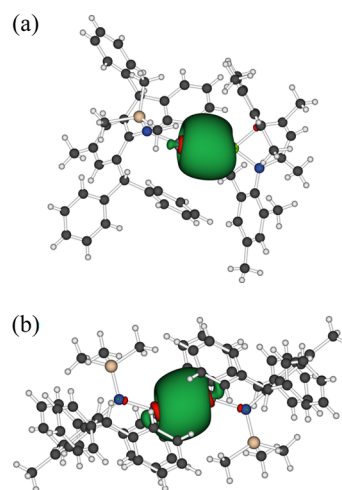
calculated to be similar and positive for both metals (Mn +0.69, Mg +0.83).[20] It is noteworthy that the calculations on $\mathbf{1^{Me}}$ also indicate that the intense blue color of **1** is not due to Mn d−d electronic transitions and more likely originates from charge-transfer excitations involving the ligands. Calculations on **3** revealed a comparable bonding picture to that reported for (Piso)MnMn(Piso).[7] That is, the low-energy states are highly multiconfigurational, with the singlet spin state being the ground state. In the ground state, the compound has a Mn−Mn single bond (EBO = 0.90, Figure 3b), and each high-spin Mn center encompasses five singly occupied 3d orbitals that are essentially nonbonding. Again in line with the experimental magneto-chemical studies, compound **4** was calculated to have a high-spin Mn^{II} center and a dominant sextet ground state. The calculations showed effectively no Mn^{II}−Cr^0 bonding in the compound.

In light of the reducing abilities displayed by **1** in its reactions with metal halide precursors, preliminary studies of its reactivity toward several unsaturated molecules were also carried out. First, while it reacts with dioxygen to give an intractable mixture of products, its treatment with stoichiometric or excess N$_2$O in THF afforded a good yield of the colorless μ-oxo-bridged manganese(II) complex, L†MnOMg(THF)(^{Mes}Nacnac) **5**.[21] Like **1**, this compound is high spin in solution ($\mu_{eff} = 5.9$ μ_B) and the solid state (see SI), and its molecular structure (Figure 4) shows it to have a two-coordinate Mn center (N−Mn−O 163.85(8)°), which is unprecedented for an oxo-manganese complex. Similarly, reaction of **1** with the carbodiimide, Pr^{i}NCNPr^i, led to a two-electron reduction of the substrate, and its insertion into the Mn−Mg bond of the bimetallic
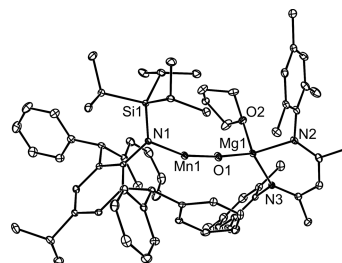

Figure 4. Thermal ellipsoid plot (20% probability surface) of **5**.

compound, giving a good yield of the high-spin ($\mu_{\text{eff}} = 5.1\ \mu_{\text{B}}$) magnesium manganesio-amidinate complex, $L^{\dagger}Mn\{\kappa^1\text{-}C,\kappa^2\text{-}N,N'\text{−}C(NPr^i)_2\}Mg(^{\text{Mes}}Nacnac)$ **6** (see SI for further details).[22] It is of note that this reactivity is broadly similar to that displayed by β-diketiminato magnesium(I) dimers, e.g., $(^{\text{Dip}}Nacnac)\text{-}MgMg(^{\text{Dip}}Nacnac)$,[13,23] which suggests that **1** may well prove of comparable utility to such compounds as a reducing agent in organic synthesis and small molecule activations.

In conclusion, a novel two-coordinate, high-spin manganese(0) complex, bearing an unsupported Mn−Mg bond, has been prepared, and its reactivity explored. Its versatility as an "inorganic Grignard reagent" in the preparation of bimetallic systems is evidenced by the synthesis of an unprecedented two-coordinate manganese(I) dimer and a mixed valence, bis-(amido)-heterobimetallic (Mn^{II}/Cr^0) complex. Moreover, preliminary reactivity studies suggest it will prove a powerful reducing agent in organic synthesis. We are currently investigating this possibility, in addition to developing the chemistry of other low-valent d-block metal−Mg bonded systems.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Synthesis details and characterizing data. This material is available free of charge via the Internet at http://pubs.acs.org

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

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