# **ORGANOMETALLICS**

# N,N,O-Tridentate Mixed Lithium–Magnesium and Lithium–Aluminum Complexes: Synthesis, Characterization, and Catalytic Activities

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**Supporting Information** 

**ABSTRACT:** The syntheses and crystal structures of a series of heterobimetallic Li/Mg and Li/Al complexes prepared from an N,N,O-tridentate ligand are described. The ligand HOC(CH<sub>2</sub>)<sub>3</sub>CH<sub>2</sub>N<sub>(We)</sub>-(W<sub>4</sub>)<sup>-</sup>, (W<sub>4</sub>)<sup>-</sup>, (W<sub>4</sub>)<sup>-</sup>

# INTRODUCTION

Various heterobimetallic complexes have beenreported in recent years because they contain at least two types of metal centers and consequently exhibit structures and reactivities differing from those of both of their homometallic precursors.<sup>1</sup> For example, the bimetallic base (TMEDA)Na(TMP)(CH<sub>2</sub>SiMe<sub>3</sub>)Zn(CH<sub>2</sub>Si-Me<sub>3</sub>) could deprotonate tetrahydrofuran under mild conditions without opening its heterocyclic  $(OC_4)$  ring.<sup>2</sup> The heterobimetallic complex [Na<sub>4</sub>Mg<sub>2</sub>(TMP)<sub>6</sub>(nBu)<sub>2</sub>] doubly deprotonated N,N-dialkylanilines and tert-butylbenzene selectively at the meta, meta' positions and did not follow the ortho-metalation principles.<sup>3</sup> Hevia recently reported [LiZnPh<sub>3</sub>(OBu<sub>2</sub>)<sub>2</sub>], which selectively arylated acridine at its C9 position in 95% yield, and the reaction time was significantly shorter than that using ZnPh<sub>2</sub> as an arylating reagent.<sup>4</sup> Our group previously reported the mixed-alkali-metal *tert*-butoxides  $[Li_4Na_2K_2(OtBu)_8(\mu-L)]_n$ showing symbiotic deprotonating ability, in comparison not only with that of individual Li, Na, or K tert-butoxides but also with binary mixtures of any two of these metal alkoxides.<sup>5</sup> Here, we continue to focus on developing heterobimetallic complexes, especially lithium-containing heterobimetallic complexes, and investigating their catalytic activities.

Lithium-containing heterobimetallic complexes have been of wide interest due to their unique synthetic properties, such as in deprotonation and metalation reactions using alkyls,<sup>6</sup> in selective

halogen-metal exchange reactions,<sup>7</sup> and as polymerization initiators.<sup>8</sup> Mulvey contributed a series of alkali amide magnesiates and lithium aluminates which were successfully utilized in metal-hydrogen exchange reactions of challenging weakly acidic aromatic substrates.<sup>9</sup> Wheatley and co-workers reported a novel polymeric species incorporating the lithiumnitrogen cluster cation  $(\text{Li}_4\text{Am}_3)^+ \cdot \{\text{Li}[(\mu-\text{Me})_2\text{Al}(\text{Me})^t\text{Bu}]_2\}^{-10}$ Subsequently, they synthesized the aluminum ate base <sup>i</sup>Bu<sub>3</sub>Al-(TMP)Li, which was developed for regio- and chemoselective direct generation of functionalized aromatic aluminum compounds.<sup>11</sup> The latter work showed that in fact the deprotonation was not performed by the aluminum ate base at all but instead by a trans-metal-trapping procedure.<sup>6b,12</sup> Recently, Xi's group reported lithium aluminate complexes containing the alumole (aluminacyclopentadienes) ring structure, which afforded a yield higher than of the alumole for reactions synthesizing thiophene compounds.<sup>13</sup>

In this work, five lithium-containing heterobimetallic complexes were synthesized by using the new N,N,O-tridentate ligand HOC(CH<sub>2</sub>)<sub>5</sub>CH<sub>2</sub>N(Me)CH<sub>2</sub>CH<sub>2</sub>NMe<sub>2</sub> (LH) or the complex [{LMgOC(CH<sub>2</sub>)<sub>5</sub>CH<sub>2</sub>N(Me)CH<sub>2</sub>CH<sub>2</sub>NMe<sub>2</sub>}] (1)

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as the initial reagent. The lithium alkylmagnesiate complexes display a 1:1 ratio of lithium to magnesium in  $[\{Bu_2Mg\{LiOC-(CH_2)_5CH_2N(Me)CH_2CH_2NMe_2\}_2]$  (2) and a 3:1 ratio in  $[\{BuMgOLi\{LiOC(CH_2)_5CH_2N(Me)CH_2CH_2NMe_2\}_2\}_2]$  (3), respectively. There is a polymeric structure of one-dimensional chains in the lithium aluminate complexes  $[\{-LiOC-(CH_2)_5CH_2N(Me)CH_2CH_2NMe_2\}Al(Me)(n-Bu)CH_3-\}_n]$ (4) and  $[\{-LiOC(CH_2)_5CH_2N(Me)CH_2CH_2NMe_2\}Al(n-Bu)_2CH_2-\}_n]$  (5), respectively. Complexes 1–5 were characterized by NMR spectroscopy, and single-crystal X-ray diffraction techniques and were tested as precatalysts for Meerwein– Ponndorf–Verley (MPV) reactions.

#### RESULTS AND DISCUSSION

**Synthesis and Characterization.** The syntheses of the N,N,O-tridentate ligand LH and complexes 1–5 presented here are shown in Schemes 1 and 2, respectively. Deprotonation of





TMEDA (TMEDA = N,N,N',N'-tetramethylethylenediamine) by 1.2 equiv of *n*-butyllithium in the *N*,*N*-dimethylaniline and anhydrous diethyl ether yielded the corresponding lithium salt. Then, the addition of lithium salt to cyclohexanone gave a pale yellow solution, which followed by acid hydrolysis gave LH in 42% yield. The structure of LH was characterized by <sup>1</sup>H and <sup>13</sup>C NMR and ESI-HRMS spectra.

Reaction of LH with  ${}^{n}Bu_{2}Mg$  in diethyl ether with the release of *n*-butane gave complex 1. Treatment of 1 with 2 equiv of  ${}^{n}BuLi$ afforded the simple lithium alkylmagnesiate 2. Accordingly, the treatment of complex 2 with degassed H<sub>2</sub>O (1.0 M solution in diethyl ether) gave the lithium alkylmagnesiate 3. Furthermore, LH was transferred readily to 2 via the sequential reaction of LH with an equivalent amount of  ${}^{n}BuLi$  and  ${}^{n}Bu_{2}Mg$  in diethyl ether



at 0 °C. Although two methods have been proved to be successful in the synthesis of complex **2**, the yield of method 1 is obviously higher (see the Experimental Section).

Treatment of LH with AlMe<sub>3</sub> in diethyl ether results in the facile evolution of CH4 and formation of a colorless solution. Reaction of this solution with an equivalent amount of "BuLi afforded the corresponding lithium aluminate 4 as colorless crystals in 92% yield. The sequential reaction of a solution of LH in diethyl ether with an equivalent amount of Me<sub>2</sub>AlCl and 2 equiv of "BuLi afforded the lithium aluminate 5. X-ray diffraction analysis indicated that complexes 4 and 5 crystallized in a polymeric structure of one-dimensional chains containing two monomeric fragments in the unit, respectively. Polymerization results from the intermolecular stabilization of lithium ion by Al-bonded methyl groups (mean Li-C 2.373, 2.428, and 2.337 Å, respectively). It is noteworthy that, using the similar synthetic procedure, treatment of a solution of LH with AlEt<sub>3</sub> or Et<sub>2</sub>AlCl instead of AlMe<sub>3</sub> or Me<sub>2</sub>AlCl did not give the expected products. This process presumably results from the electron-rich nature of these Me groups.

An ORTEP drawing of the molecular structure of complex 1 is shown in Figure 1. The Mg atom in 1 adopts a five-coordinate mode, where two monoanionic ligands are coordinated to the central magnesium atom by their O atom and N atom, forming an Mg1O1Mg2O3 planar core in the center of the dimeric structure. The rms (root mean square) deviation of the central Mg1O1Mg2O3 ring is 0.040 Å. The five-coordination around the Mg atom involves two N atoms and three O atoms from the different ligands. The planar Mg<sub>2</sub>O<sub>2</sub> core is flanked by the two adjacent five-membered chelate rings O-C-C-N-Mg and Mg-N-C-C-N, each of which shares an N-Mg bond. The Mg(1)-O(2) (1.876(3) Å) or Mg(2)-O(4) (1.7277(14) Å) bond is shorter than any of the other Mg–O bonds (Mg(1)-O(1) 2.005(3) Å, Mg(1)-O(3) 2.011(3) Å, Mg(2)-O(1)2.000(3) Å, Mg(2)-O(3) 2.016(3) Å), respectively, while the Mg-N bond (2.268-2.465 Å) is slightly longer than the previously reported Mg-N bond (2.1456-2.256 Å).14

The molecular structure of complex 2 is shown in Figure 2. Complex 2 adopts a dimeric structure, where two anionic alkoxy ligands bridge two Li atoms via oxygen atoms, generating an Mg101Mg202 planar core in the center of the molecule.





Figure 1. ORTEP diagram of 1 (at the 25% probability level). Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): Mg(1)-O(1) 2.005(3), Mg(1)-O(2) 1.876(3), Mg(1)-O(3)2.011(3), Mg(1)-N(1) 2.465(4), Mg(1)-N(2) 2.280(4), Mg(2)-O(1) 2.000(3), Mg(2)-O(3) 2.016(3), Mg(2)-O(4) 1.879(3), Mg(2)-N(5) 2.437(4), Mg(2)-N(6) 2.268(4); O(1)-Mg(1)-O(3) 80.00(13), O(1)-Mg(2)-O(3) 80.01(13), O(1)-Mg(2)-O(4) 114.00(15), O(3)-Mg(2)-O(4) 141.06(15), Mg(1)-O(1)-Mg(2)100.16(14), Mg(1) - O(3) - Mg(2) 99.44(14), O(1) - Mg(1) - O(2)132.16(15), O(1)-Mg(1)-N(1) 75.51(13), O(1)-Mg(1)-N(2)118.77(18), O(2)-Mg(1)-O(3) 114.64(15), O(2)-Mg(1)-N(1) 95.93(16), O(2)-Mg(1)-N(2) 103.77(17), O(3)-Mg(1)-N(1)149.03(16), O(3)-Mg(1)-N(2) 100.02(15), N(1)-Mg(1)-N(2)76.11(15), O(1)-Mg(2)-N(5) 153.43(15), O(1)-Mg(2)-N(6) 98.29(15), O(3)-Mg(2)-N(5) 76.60(13), O(3)-Mg(2)-N(6)108.46(15), O(3)-Mg(2)-O(4) 141.06(15), O(4)-Mg(2)-N(5)92.23(15), O(4)-Mg(2)-N(6) 105.18(16), N(5)-Mg(2)-N(6) 77.64(15).



Figure 2. ORTEP diagram of 2 (at the 25% probability level). Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): Mg(1)-O(1) 2.032(3), Mg(1)-O(2) 2.045(4), Mg(2)-O(1) 2.063(4), Mg(2)-O(2) 2.039(3), Li(1)-O(1) 1.955(9), Li(1)-N(1) 2.095(10), Li(1)-N(2) 2.235(10), Li(2)-O(2) 1.978(10), Li(2)-N(3) 2.103(9), Li(2)-N(4) 2.192(10); O(1)-Mg(1)-O(2) 85.99(14), O(1)-Mg(2)-O(2) 85.35(14), Mg(1)-O(1)-Mg(2) 93.69(14), Mg(1)-O(2)-Mg(2) 94.00(14), Li(1)-O(1)-Mg(1) 105.9(3), Li(1)-O(1)-Mg(2) 84.7(3), Li(2)-O(2)-Mg(1) 84.4(3), Li(2)-O(2)-Mg(2) 108.0(3), O(1)-Li(1)-N(1) 86.3(4), O(1)-Li(1)-N(2) 137.4(5), O(2)-Li(2)-N(3) 86.2(4), O(2)-Li(2)-N(4) 138.7(5).

The rms deviation of the central Mg1O1Mg2O2 ring is 0.066 Å. The four-coordinated Mg atom is surrounded by two O atoms from the ligand and two butyl-C atoms in a distorted-tetrahedral geometry in **2**. The Li atom adopts a three-coordinate mode in a distorted-pyramidal geometry. **2** also has two adjacent five-membered chelate rings, O-C-C-N-Mg and Mg-N-C-C-N, which is similar to those of **1**. The dihedral angle between the

plane Mg101Mg2O2 and O1N1Li1 or O2Li2N3 is 85.30 or 84.44°, respectively. The dihedral angle between the plane Mg101Mg2O2 and Li1N1N2 or Li2N3N4 is 56.55 or 59.19°, respectively.

X-ray diffraction analysis indicated that complex 3 crystallized as a centrosymmetric dimer with a planar O3Li3'O3'Li3 core, and its selected bond lengths and angles are given in Figure 3.



Figure 3. ORTEP diagram of 3 (at the 25% probability level). Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): Li(1)-O(1) 1.934(5), Li(1)-O(2) 1.925(5), Li(1)-N(1)2.191(5), Li(1)-N(2) 2.076(5), Li(2)-O(1) 1.927(5), Li(2)-O(2) 1.976(5), Li(2)-N(3) 2.188(5), Li(2)-N(4) 2.032(5), Li(3)-O(1) 1.867(5), Li(3)-O(3) 1.947(5), Li(3)-O(3)' 1.943(5), Mg(1)-O(2) 2.008(2), Mg(1)-O(3) 2.084(2); O(3)-Li(3)-O(3)' 98.9(2), Li(3)-O(3)-Li(3)' 81.1(2), O(1)-Li(1)-O(2) 98.0(2), O(1)-Li(1)-N(1) 87.0(2), O(1)-Li(1)-N(2) 129.8(3), O(2)-Li(1)-N(1) 155.1(3), O(2)-Li(1)-N(2) 106.8(2), N(1)-Li(1)-N(2) 87.78(19), O(2)-Li(1)-O(3) 80.97(18), O(1)-Li(1)-O(3) 83.54(17), O(1)-Li(2)-O(2) 96.6(2), O(1)-Li(2)-N(3) 149.2(3), O(1)-Li(2)-N(4)118.2(3), O(2)-Li(2)-N(3) 83.6(2), O(2)-Li(2)-N(4) 114.9(2), N(3)-Li(2)-N(4) 88.8(2), O(1)-Li(3)-O(3) 109.8(2), O(1)-Li(3)-O(3)' 148.4(3), O(3)-Li(3)-O(3)' 98.9(2), O(2)-Mg(1)-O(3) 96.04(8). Symmetry elements for 3: (') 1 - x, 1 - y, 1 - z.

The Mg atom is three-coordinated with two O atoms and the butyl-C atom in **3**. The three Li atoms exhibit different coordination environments with three-coordination for Li3 and four-coordination for Li1 or Li2. In complex **3**, the six-membered chelate ring Mg1O3Li3O1Li1O2 has a boat conformation, with the O3 and Li1 atoms occupying the apex positions, and the other ring, Mg1O3Li3O1Li2O2, has a chair conformation with the O1 and Mg1 atoms occupying the apex positions. The atoms of the four-membered ring Li1O1Li2O2 are not in the same plane; the dihedral angle between the plane Li1O1Li2 and Li2O2Li2 is  $21.96^{\circ}$ . The Mg(1)–O(2) (2.008(2) Å) and Mg(1)–O(3) bonds (2.084(2) Å) are slightly longer than the previously reported Mg–O bond (1.877–1.945 Å).<sup>15</sup> The Li–O bond distances are quite similar in **3**, ranging from 1.927 to 1.976 Å; except for the Li(3)–O(1) bond distance of 1.867(5) Å.

X-ray diffraction analysis indicated that complex 4 crystallized in a one-dimensional polymeric structure (Figure 4a). The fragments of two monomers are connected by a weak bond between the Li atom and the Al-bonded methyl carbon atom (mean Li(1)–C(17)' 2.373 Å) in the structural unit of 4 (Figure 4b). The Al atom is four-coordinated by the O atom from the LH ligand, two methyl-C atoms, and a butyl-C atom. The Al(1)– C(17) bond (2.002 Å) is slightly longer than the Al(1)–C(13) (1.997(4) Å) and Al(1)–C(18) bonds (1.991(4) Å), respectively.



Figure 4. (a) Polymeric chain structure of 4. (b) Structural unit of 4 (at the 25% probability level). Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): Al(1)-O(1) 1.805(2), Al(1)-C(13) 1.997(4), Al(1)-C(17) 2.002(3), Al(1)-C(18) 1.991(4), Li(1)-O(1) 1.876(6), Li(1)-N(1) 2.126(6), Li(1)-N(2) 2.119(6), Li(1)-C(17)' 2.373(6); Al(1)'-C(17)'-Li(1) 174.1(2), Al(1)-O(1)-Li(1) 117.5(2), O(1)-Li(1)-C(17)' 121.3(3), O(1)-Li(1)-N(1) 89.2(2), O(1)-Li(1)-N(2) 118.7(3), N(1)-Li(1)-C(17)' 110.5(3), N(2)-Li(1)-C(17)' 116.8(3), N(1)-Li(1)-N(2) 87.8(2), O(1)-Al(1)-C(13) 103.75(13), O(1)-Al(1)-C(17)' 108.17(13), O(1)-Al(1)-C(18) 115.03(14), C(13)-Al(1)-C(18) 109.57(16). Symmetry elements for 4: (') 1/2 - x, 1/2 + y, 1/2 - z.

This afforded the approximately tetrahedral aluminate fragment a charge which is offset by that on the metal lithium center. Several reports exist of Al/Li complexes containing an Al( $\mu$ -N)Li bond and incorporating with external Lewis bases in the solid state.<sup>16</sup> However, the structure of 4 represents a lithium aluminate incorporated with an Al( $\mu$ -O)Li bonding pattern in the absence of solvation by an external Lewis base. The molecular structure of complex 5 is similar to that of complex 4, except that the methyl group connected to the Al atom is substituted by a butyl group. The corresponding bond lengths and angles of 4 or 5 are given in Figures 4 and 5, respectively.

Catalysis by Complexes 1–5 of the MPV Reactions of Carbonyl Compounds. MPV reduction reactions, usually using a low-toxicity hydrogen donor and showing high chemoselectivity for selective synthesis of primary or secondary alcohols, have received widespread attention.<sup>17</sup> Various catalyst systems have been reported, such as transition-metal complexes, alkali-metal alkoxides,<sup>18</sup> aluminium alkoxides,<sup>19</sup> rare-earth-metal alkoxides,<sup>20</sup> metal oxides,<sup>21</sup> and other catalysts.<sup>22</sup> The most active systems are based on ruthenium complexes containing nitrogen-, oxygen-, and/or phosphorus-bearing ligands, which lead to the easy formation of catalytically active intermediate species. For example, Noyori's group reported the Ru(II) complex containing 1,2-diamino ligands for the MPV reaction of ketones with >99% yield.<sup>23</sup> Recently, our group reported that a monomeric bidentate N,O-aluminum complex exhibited good to excellent catalytic activity for MPV reactions.<sup>24</sup> Meanwhile, new and effective catalytic systems for MPV reactions should be developed for future industrial applications: in particular, the use of an earthabundant, inexpensive metal alternative to precious metals in



**Figure 5.** Structural unit of **5** (at the 25% probability level). Hydrogen atoms are omitted for clarity.. Selected bond lengths (Å) and angles (deg): Al(1)–O(1) 1.803(2), Al(1)–C(13) 2.010(3), Al(1)–C(14) 2.004(4), Al(1)–C(18) 1.998(3), Li(1)–O(1) 1.873(6), Li(1)–N(1) 2.125(6), Li(1)–N(2) 2.123(6), Li(1)–C(13)' 2.337(6), Al(1)'–C(13)' 2.010(3); Al(1)'-C(13)'–Li(1) 175.0(2), Al(1)–O(1)–Li(1) 115.9(2), O(1)–Li(1)–C(13)' 122.9(3), O(1)–Li(1)–N(1) 88.9(2), O(1)–Li(1)–N(2) 120.5(3), N(1)–Li(1)–C(13)' 109.0(3), N(2)–Li(1)–C(13)' 113.9(3), N(1)–Li(1)–N(2) 88.4(2), O(1)–Al(1)–C(13) 107.00(13), O(1)–Al(1)–C(14) 113.97(13), O(1)–Al(1)–C(18) 102.35(13), C(13)–Al(1)–C(14) 111.2(15), C(13)–Al(1)–C(18) 109.87(14), C(14)–Al(1)–C(18) 112.09(16). Symmetry elements for **5**: (') 1 – *x*, 1 – *y*, 1 – *z*.

transition-metal catalytic reactions. Although various heterobimetallic complexes have been synthesized and used for the catalytic reactions, heterobimetallic catalysts for MPV reactions have not been reported, as far as we know. Thus, to further explore the application of main-group-metal complexes, the catalytic behavior of lithium-containing heterobimetallic complexes bearing N,N,O-tridentate ligands in the MPV reaction was tested in this paper.

The initial study of the MPV reaction was carried out using benzaldehyde and dry isopropyl alcohol as a model substrate catalyzed by complexes 1-5, respectively, as shown in Table 1. First, the reduction reaction of benzaldehyde was carried out in toluene with 5 mol % of 1-5 under reflux conditions to afford the corresponding benzyl alcohol in moderate yields, and complex 2

Table 1. Catalysis by Complexes 1-5 of the MPV Reactions of Benzaldehyde<sup>*a*</sup>

	CH	+ Cat.	OH C	
entry	catalyst	amt of catalyst (mol %)	solvent	yield (%) <sup>b</sup>
1	1	5	toluene	52.7
2	2	5	toluene	87.6
3	3	5	toluene	81.4
4	4	5	toluene	54.6
5	5	5	toluene	43.5
6	1	5	none	61.8
7	2	5	none	93.8
8	3	5	none	90.2
9	4	5	none	73.0
10	5	5	none	64.3
11	2	5	none	94.4 <sup>c</sup>
12	2	10	none	94.8
13	2	15	none	95.2

"Conditions unless specified otherwise: reflux, 4 h. <sup>b</sup>Determined by <sup>1</sup>H NMR spectroscopy. <sup>c</sup>6 h. gave the highest yield (Table 1, entries 1-5). Further tests showed that the reduction of benzaldehyde by 2 under solventfree conditions also gave the highest yield (Table 1, entries 6–10). Encouragingly, complex 2 at 5 mol % loading under solvent-free conditions over 4 h afforded a 93.8% yield of benzaldehyde to benzyl alcohol (Table 1, entry 7). The yield increased slightly when the reaction time was prolonged to 6 h and catalyst loading increased to 10% or 15%, respectively (Table 1, entries 11–13). In any case, the catalytic activity was in the sequence 2 > 3 > 1under the tested conditions. This would be due to the synergistic effect of magnesium and lithium for 2 or 3, which used the Lewis acidity and electrophilicity of the metal center and increased the probability of attack at benzaldehyde.

Under the optimized reaction conditions, a variety of aldehyde and ketone substrates were examined for the MPV reaction using 2 as catalyst (Table 2). First, electronic effects were examined by

Table 2. Complex 2 Catalyzed MPV Reactions of Selected Carbonyl Compounds $^a$ 



<sup>*a*</sup>Conditions: reflux, 5 mol % catalyst, solvent free, 4 h. <sup>*b*</sup>Determined by <sup>1</sup>H NMR spectroscopy. <sup>*c*</sup>Determined by GC-MS.

employing 4-substituted benzaldehyde. As expected, aromatic aldehydes with an electron-donating group on the phenyl ring gave lower conversions to the corresponding alcohols (Table 2, entries 2 and 3) in comparison to that of benzaldehyde. Citronellal, a representative of the aliphatic aldehydes, could achieve 91.7% yield (Table 2, entry 4), and some challenging  $\alpha,\beta$ -unsaturated aldehydes were selectively reduced to the corresponding alcohols under the optimized conditions, such as cinnamaldehyde and citral (Table 2, entries 5 and 6). Generally, low-activity cyclohexanone and acetophenone were also reduced to the corresponding alcohols in our catalytic system with 81.7% and 62.4% yields, respectively (Table 2, entries 7 and 8).

## CONCLUSION

In summary, we have successfully synthesized the novel N,N,Otridentate homoleptic (Mg/Mg) complex 1 and four heteroleptic (Li/Mg or Li/Al) complexes 2-5 with the ligand HOC-(CH<sub>2</sub>)<sub>5</sub>CH<sub>2</sub>N(Me)CH<sub>2</sub>CH<sub>2</sub>NMe<sub>2</sub>. The molecular structures of 1-5 were characterized by elemental analysis, NMR spectroscopy, and X-ray crystallography. Furthermore, 1-5 were tested for their capability to catalyze MPV reactions. **2** showed the best catalytic activities toward this reaction, and a range of aldehydes and ketones was selectively transferred to the corresponding alcohols in good yields. Further study is focusing on the isolation of the reaction intermediates, which will be helpful in understanding the catalytic mechanism of heterobimetallic complexes in MPV reactions.

#### EXPERIMENTAL SECTION

General Procedures, Materials, and Instrumentation. All experiments were carried out under a purified dry nitrogen atmosphere by using standard Schlenk techniques. Solvents were dried with appropriate drying agents, degassed, and stored over a potassium mirror or activated molecular sieves (4 Å) prior to use. TMEDA, aldehydes, and ketones were sublimed, recrystallized, or distilled before use. AlMe<sub>3</sub> (hexane, 2.0 M solution), "BuLi (hexane, 2.5 M solution), MeLi (diethyl ether, 1.6 M solution), "Bu<sub>2</sub>Mg (heptane, 1 M solution), and Me<sub>2</sub>AlCl (heptane, 1.0 M solution) were used as purchased. Elemental analyses were performed on a Vario ELIII instrument. Melting points were determined on a STUART SMP10 melting point apparatus and are uncorrected. <sup>1</sup>H NMR (600 MHz) and <sup>13</sup>C NMR (150 MHz) spectra of the complexes were recorded on a Bruker AVANCE III HD 600 instrument and referenced internally to the residual solvent resonances (chemical shift data in  $\delta$ ). ESI-MS were recorded on a Thermo Scientific Q Exactive liquid chromatograph-tandem mass spectrometer.

Single-crystal X-ray diffraction data of compounds 1–5 were collected on a Bruker Smart Apex CCD diffractometer using monochromated Mo K $\alpha$  radiation ( $\lambda = 0.71073$  Å). A total of N reflections were collected by using the  $\omega$  scan mode. Corrections were applied for Lorentz and polarization effects as well as absorption using multiscans (SADABS).<sup>25</sup> Each structure was solved by direct methods and refined on  $F^2$  by full-matrix least squares (SHELX97)<sup>26</sup> using all unique data. All non-hydrogen atoms were refined with anisotropic displacement parameters, whereas the hydrogen atoms were constrained to parent sites, using a riding mode (SHELXTL).<sup>27</sup> Crystal data and refinement parameters for all crystalline complexes are given in the Supporting Information. CCDC files 1517600–1517603 and 1517605 contain crystallographic data for this paper.

Synthesis of HOC(CH<sub>2</sub>)<sub>5</sub>CH<sub>2</sub>N(Me)CH<sub>2</sub>CH<sub>2</sub>NMe<sub>2</sub> (LH). A dry 250 mL two-necked flask was filled with TMEDA (11.02 g, 73 mmol), 80 mL of anhydrous diethyl ether and 7.18 mL of N,N-dimethylaniline, and the solution was stirred under a nitrogen atmosphere. A 29.20 mL portion of 2.5 M of n-butyllithium in hexane was added at 0 °C. The solution was warmed to room temperature and refluxed for an additional 1 h. Cyclohexanone (7.54 mL, 73 mmol) was added dropwise to the reaction mixture at 0 °C and refluxed for 2 h. The solution was hydrolyzed with 50 mL of distilled water and then washed with aqueous 5% hydrochloric acid (5  $\times$  50 mL). The aqueous phases were combined and made alkaline with 10% sodium hydroxide aqueous solution. The aqueous phase was then extracted with dichloromethane  $(3 \times 20 \text{ mL})$ , and the organic phase was dried over anhydrous magnesium sulfate. The crude product was distilled under vacuum to afford s colorless oil at 78-81 °C. Then, the crude product was prepared according to the general procedure and purified by column chromatography (methanol/ dichloromethane 1/10) to give the product in 42% yield. <sup>1</sup>H NMR  $(CDCl_3, \delta/ppm)$ : 1.26–1.33 (m, 3H,  $C_5H_{10}$ ), 1.43–1.44 (m, 2H,  $C_5H_{10}$ ), 1.54–1.55 (m, 3H,  $C_5H_{10}$ ), 1.64–1.69 (m, 2H,  $C_5H_{10}$ ), 2.25 (s, 6H, NC<sub>2</sub>H<sub>6</sub>), 2.36 (s, 4H, NC<sub>2</sub>H<sub>4</sub>N), 2.40 (s, 3H, NCH<sub>3</sub>), 2.55–2.57 (t, 2H,  $C_5H_{10}CH_2$ ), 5.25 (br, 1H,  $C_5H_{10}OH$ ). <sup>13</sup>C NMR (CDCl<sub>3</sub>,  $\delta$ /ppm): 22.37, 26.17, 36.46, 45.06, 46.97, 57.38, 57.69, 66.58, 70.52. Anal. Calcd for C<sub>12</sub>H<sub>26</sub>N<sub>2</sub>O: C, 67.24; H, 12.23; N, 13.07. Found: C, 67.18; H, 11.28; N, 13.01. MS (m/z): HRMS (ESI): calcd for C<sub>12</sub>H<sub>26</sub>N<sub>2</sub>O ([M + H]<sup>+</sup>), 215.2123; found, 215.2119.

Synthesis of  $[[LM_{9}OC(CH_2)_5CH_2N(Me)CH_2CH_2NMe_2]_2]$  (1). A 2.0 mL portion of <sup>n</sup>Bu<sub>2</sub>Mg (heptane, 1 M solution) was added dropwise at -78 °C to a solution of LH (0.43 g, 2.0 mmol) in diethyl ether (10 mL). The reaction mixture was then warmed to room temperature and stirred for 2 h. Colorless crystals were obtained from diethyl ether at -5 °C. Yield: 0.34 g (76%). Mp: 134–136 °C. <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>,  $\delta$ /ppm): 1.18–1.21 (m, 8H, C<sub>5</sub>H<sub>10</sub>), 1.51–1.52 (m, 4H, C<sub>5</sub>H<sub>10</sub>), 1.65–1.66 (m, 3H, C<sub>5</sub>H<sub>10</sub>), 1.76–1.78 (m, 5H, C<sub>5</sub>H<sub>10</sub>), 1.96–2.04 (m, 13H, NC<sub>2</sub>H<sub>4</sub>N and N(CH<sub>3</sub>)<sub>3</sub>), 2.07–2.09 (m, 4H, NC<sub>2</sub>H<sub>4</sub>N), 2.18 (s, 3H, NCH<sub>3</sub>), 2.21 (s, 6H, NC<sub>2</sub>H<sub>6</sub>), 2.27–2.28 (t, 4H, (C<sub>5</sub>H<sub>10</sub>CH<sub>2</sub>)<sub>2</sub>). <sup>13</sup>C NMR (C<sub>6</sub>D<sub>6</sub>,  $\delta$ /ppm): 22.37, 26.70, 36.58, 36.63, 44.46, 47.16, 57.08, 57.58, 67.34, 69.90, 77.37. Anal. Calcd for C<sub>48</sub>H<sub>100</sub>Mg<sub>2</sub>N<sub>8</sub>O<sub>4</sub>: C, 63.92; H, 11.17; N, 12.42. Found: C, 63.89; H, 11.23; N, 12.36.

Synthesis of  $[\{Bu_2Mg\{LiOC(CH_2)_5CH_2N(Me)CH_2CH_2NMe_2\}\}_2]$ (2). Method 1. A 1.66 mL portion of *n*-butyllithium (hexane, 2.5 M solution) was added dropwise at 0 °C to a solution of complex 1 (0.45 g, 2.0 mmol) in diethyl ether (10 mL). The resulting mixture was then warmed to room temperature and stirred for 2 h. The reaction mixture was filtered and crystallized from diethyl ether at -10 °C to give colorless crystals of complex 2. Yield: 1.19 g (83%).

Method 2. To a stirred solution of LH (0.43 g, 2.0 mmol) in diethyl ether (10 mL) was added <sup>n</sup>BuLi (0.96 mL, 2.4 mmol) dropwise at 0 °C. The resulting mixture was slowly warmed to room temperature and stirred for an additional 2 h. Then "Bu<sub>2</sub>Mg (2.0 mL, 2.0 mmol) was added to the mixture at 0 °C. The mixture was warmed to room temperature and stirred for 2 h. The reaction mixture was filtered and crystallized from diethyl ether at -10 °C to give colorless crystals of complex 2. Yield: 0.81 g (57%). Mp: 128–130 °C. <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>,  $\delta$ /ppm): -0.94--0.90 (m, 1H, MgCH<sub>2</sub>), -0.83--0.79 (m, 1H, MgCH<sub>2</sub>), -0.94 to -0.90 (m, 1H, MgCH<sub>2</sub>), -0.17 to -0.09 (m, 2H, MgCH<sub>2</sub>), 0.84-0.86 (t, 3H, MgC<sub>3</sub>H<sub>6</sub>CH<sub>3</sub>), 1.11-1.15 (t, 3H, MgC<sub>3</sub>H<sub>6</sub>CH<sub>3</sub>), 1.20-1.23 (m, 6H, MgC3H6CH3 and MgCH2), 1.32-1.34 (t, 3H, MgC<sub>3</sub>H<sub>6</sub>CH<sub>3</sub>), 1.37-1.40 (m, 4H, NC<sub>2</sub>H<sub>4</sub>N), 1.51-1.59 (m, 8H, MgCH<sub>2</sub>C<sub>3</sub>H<sub>6</sub> and NC<sub>2</sub>H<sub>4</sub>N), 1.65-1.67 (m, 6H, MgCH<sub>2</sub> and MgCH<sub>2</sub>C<sub>3</sub>H<sub>6</sub>), 1.74-1.81 (m, 6H, MgCH<sub>2</sub> and C<sub>5</sub>H<sub>10</sub>), 1.85-1.93 (m, 10H, MgCH<sub>2</sub>C<sub>3</sub>H<sub>6</sub> and NC<sub>2</sub>H<sub>6</sub>), 2.06–2.12 (m, 13H, C<sub>5</sub>H<sub>10</sub>) NC<sub>2</sub>H<sub>6</sub> and NC<sub>2</sub>H<sub>4</sub>N), 2.14-2.22 (m, 10H, MgCH<sub>2</sub>C<sub>3</sub>H<sub>6</sub> and 2NCH<sub>3</sub>), 2.24-2.26 (m, 3H, NC<sub>2</sub>H<sub>6</sub>), 2.32-2.43 (m, 4H, NC<sub>2</sub>H<sub>4</sub>N), 2.50-2.67  $(m, 3H, 2C_5H_{10}CH_2), 2.80-2.83 (d, 1H, C_5H_{10}CH_2).$ <sup>13</sup>C NMR  $(C_6D_{64})$ δ/ppm): 12.14, 13.05, 13.61, 14.29, 14.36, 23.98, 24.15, 24.81, 25.43, 32.82, 32.98, 33.19, 34.73, 38.54, 43.17, 45.58, 55.19, 58.15, 63.29, 71.94. <sup>7</sup>Li NMR (C<sub>6</sub>D<sub>6</sub>,  $\delta$ /ppm): 1.13. Anal. Calcd for C<sub>40</sub>H<sub>86</sub>Li<sub>2</sub>Mg<sub>2</sub>N<sub>4</sub>O<sub>2</sub>: C, 66.95; H, 12.08; N, 7.81. Found: C, 66.87; H, 12.15; N, 7.78.

Synthesis of [{BuMgOLi{LiOC(CH<sub>2</sub>)<sub>5</sub>CH<sub>2</sub>N(Me)-

CH<sub>2</sub>CH<sub>2</sub>MMe<sub>2</sub>}<sub>2</sub>] (3). To a stirred solution of LH (0.43 g, 2.0 mmol) in diethyl ether (10 mL) was added "BuLi (0.96 mL, 2.4 mmol) dropwise at 0 °C. The resulting mixture was slowly warmed to room temperature and stirred for an additional 2 h. "Bu<sub>2</sub>Mg (2.0 mL, 2.0 mmol) was added to the mixture at 0 °C. The mixture was warmed to room temperature and stirred for 2 h. Then, degassed H2O (2.0 mL, 1.0 M solution in diethyl ether) was added dropwise at 0 °C to the mixture. The reaction mixture was filtered and crystallized from diethyl ether at -10 °C to give colorless crystals of complex 3. Yield: 0.66 g (61%). Mp: 121-124 °C. <sup>1</sup>H NMR ( $C_6 D_{6t} \delta/ppm$ ): -0.73 (m, 4H, MgCH<sub>2</sub>), 0.81-0.83 (t, 6H, CH<sub>3</sub>), 1.18–1.21 (m, 10H, C<sub>5</sub>H<sub>10</sub>), 1.46–1.50 (m, 8H, C<sub>5</sub>H<sub>10</sub>), 1.50– 1.58 (m, 8H, MgCH<sub>2</sub>C<sub>2</sub>H<sub>4</sub>), 1.59–1.65 (m, 6H, C<sub>5</sub>H<sub>10</sub>), 1.71–1.73 (m, 8H,  $C_5H_{10}$ ), 1.92–1.96 (m, 8H,  $C_5H_{10}$ ), 2.00 (s, 24H, 2NC<sub>2</sub>H<sub>6</sub>), 2.08-2.10 (m, 8H, NC<sub>2</sub>H<sub>4</sub>N), 2.18 (s, 8H, 2C<sub>5</sub>H<sub>10</sub>CH<sub>2</sub>), 2.21 (s, 12H, 2NCH<sub>3</sub>), 2.28–2.32 (m, 8H, NC<sub>2</sub>H<sub>4</sub>N). <sup>13</sup>C NMR ( $C_6D_6$ ,  $\delta$ /ppm): 8.12, 13.59, 22.28, 24.78, 26.60, 36.53, 44.41, 47.03, 57.02, 57.49, 67.29, 69.93. <sup>7</sup>Li NMR (C<sub>6</sub>D<sub>6</sub>, δ/ppm): 1.00, 1.23, 1.54. Anal. Calcd for C<sub>56</sub>H<sub>118</sub>Li<sub>6</sub>Mg<sub>2</sub>N<sub>8</sub>O<sub>6</sub>: C, 61.72; H, 10.91; N, 10.28. Found: C, 61.58; H, 10.95; N, 10.24.

Synthesis of  $[\{-LiOC(CH_2)_5CH_2N(Me)CH_2CH_2NMe_2\}Al(Me)(n-Bu)CH_3-]_n]$  (4). To a stirred solution of LH (0.23 g, 1.1 mmol) in diethyl ether (10 mL) was added 0.55 mL of AlMe<sub>3</sub> (hexane, 2.0 M solution) dropwise at 0 °C. The resulting mixture was slowly warmed to room temperature and stirred for an additional 2 h. Then "BuLi (0.44 mL, 1.1 mmol) was added to the mixture at 0 °C. The mixture was warmed to room temperature and stirred for 2 h. The reaction mixture was filtered and crystallized from diethyl ether/hexane to give colorless crystals of complex 4. Yield: 0.34 g (92%). Mp: 154–157 °C. <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>,  $\delta$ /ppm): -0.51 (s, 2H, AlCH<sub>3</sub>Li), -0.48 (s, 3H, AlCH<sub>3</sub>),

−0.43 (s, H, AlCH<sub>3</sub>Li) 0.26−0.29 (m, 2H, AlCH<sub>2</sub>CH<sub>2</sub>), 1.19−1.21 (m, 5H, AlC<sub>3</sub>H<sub>6</sub>CH<sub>3</sub> and C<sub>5</sub>H<sub>10</sub>), 1.30−1.34 (m, 1H, C<sub>5</sub>H<sub>10</sub>), 1.48−1.51 (m, 2H, C<sub>3</sub>H<sub>10</sub> and NC<sub>2</sub>H<sub>4</sub>N), 1.62−1.65 (m, 1H, NC<sub>2</sub>H<sub>6</sub>), 1.72−1.81 (m, 6H, C<sub>5</sub>H<sub>10</sub>, AlCH<sub>2</sub>C<sub>2</sub>H<sub>4</sub> and NC<sub>2</sub>H<sub>6</sub>), 1.82−1.85 (m, 2H, NC<sub>2</sub>H<sub>4</sub>N), 1.86−1.92 (m, 10H, AlCH<sub>2</sub>C<sub>2</sub>H<sub>4</sub>, NC<sub>2</sub>H<sub>6</sub>), NCH<sub>3</sub> and C<sub>5</sub>H<sub>10</sub>CH<sub>2</sub>), 1.96−2.02 (m, 3H, NC<sub>2</sub>H<sub>6</sub> and NC<sub>2</sub>H<sub>4</sub>N), 2.36−2.38 (m, 1H, C<sub>5</sub>H<sub>10</sub>CH<sub>2</sub>). <sup>13</sup>C NMR (C<sub>6</sub>D<sub>6</sub>, δ/ppm): −6.70, −6.30, 14.49, 15.05, 23.95, 24.10, 25.98, 29.96, 30.51, 38.43, 41.71, 46.16, 56.80, 56.96, 64.90, 72.36. <sup>7</sup>Li NMR (C<sub>6</sub>D<sub>6</sub>, δ/ppm): 0.97. <sup>27</sup>Al NMR (C<sub>6</sub>D<sub>6</sub>, δ/ppm): 153.53. Anal. Calcd for C<sub>18</sub>H<sub>39</sub>AlLiN<sub>2</sub>O: C, 64.84; H, 11.79; N, 8.40. Found: C, 64.63; H, 11.71; N, 8.29.

Synthesis of [{-LiOC(CH<sub>2</sub>)<sub>5</sub>CH<sub>2</sub>N(Me)CH<sub>2</sub>CH<sub>2</sub>NMe<sub>2</sub>}Al(*n*-Bu)<sub>2</sub>CH<sub>2</sub>-]<sub>n</sub>] (5). A 2.1 mL portion of Me<sub>2</sub>AlCl (heptane, 1.0 M solution) was added dropwise at 0 °C to a solution of LH (0.44 g, 2.1 mmol) in diethyl ether (10 mL). The reaction mixture was then warmed to room temperature and stirred for 2 h. Then "BuLi (1.7 mL, 4.2 mmol) was added to the mixture at 0 °C. The mixture was warmed to room temperature and stirred for 2 h. Colorless crystals were obtained from diethyl ether/hexane at -5 °C. Yield: 0.66 g (84%). Mp: 107-110 °C. <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>, δ/ppm): -0.62 (s, 2H, AlCH<sub>3</sub>Li), 0.10-0.14 (m, 1H, AlCH<sub>2</sub>CH<sub>2</sub>), 0.19-0.24 (m, 3H, AlCH<sub>2</sub>CH<sub>2</sub>), 1.17-1.25 (m, 7H, AlC<sub>3</sub>H<sub>6</sub>CH<sub>3</sub> and C<sub>5</sub>H<sub>10</sub>), 1.29–1.36 (m, 2H, C<sub>5</sub>H<sub>10</sub>), 1.51–1.54 (m, 2H, C<sub>5</sub>H<sub>10</sub> and NC<sub>2</sub>H<sub>4</sub>N), 1.58-1.60 (m, 1H, NC<sub>2</sub>H<sub>6</sub>), 1.67-1.74 (m, 7H,  $C_5H_{10}$ , AlCH<sub>2</sub>C<sub>2</sub>H<sub>4</sub> and NC<sub>2</sub>H<sub>6</sub>), 1.85–1.88 (m, 11H, AlCH<sub>2</sub>C<sub>2</sub>H<sub>4</sub>, NC2H6, NCH3 and NC2H4N), 1.90-2.02 (m, 8H, NC2H6, NCH3,  $NC_{2}H_{4}N$  and  $C_{5}H_{10}CH_{2}$ , 2.34–2.37 (m, 1H,  $C_{5}H_{10}CH_{2}$ ). <sup>13</sup>C NMR (C<sub>6</sub>D<sub>6</sub>, δ/ppm): -8.42, 13.61, 14.19, 14.41, 23.84, 23.91, 25.92, 29.92, 30.02, 30.42, 30.47, 38.74, 41.99, 45.64, 56.68, 56.69, 65.22, 71.99. <sup>7</sup>Li NMR ( $C_6D_{6\prime} \delta/ppm$ ): 0.85. <sup>27</sup>Al NMR ( $C_6D_{6\prime} \delta/ppm$ ): 149.67. Anal. Calcd for C21H45AlLiN2O: C, 67.17; H, 12.08; N, 7.46. Found: C, 67.03; H, 12.14; N, 7.38.

**General Procedure for the MPV Reaction.** Complex 2 is used as an example of the typical reaction procedure. A 50 mL Schlenk flask was charged with complex 2 (0.2 mmol), and the carbonyl compound (4.0 mmol) was added, followed by the addition of isopropyl alcohol (0.37 mL, 4.8 mmol). The reaction mixture was then refluxed for 4 h, and the yield was determined by <sup>1</sup>H NMR spectroscopic studies on the basis of the integration of methylene and the CHO region of the benzyl group.

# ASSOCIATED CONTENT

#### **Supporting Information**

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.organomet.6b00921.

Crystallographic details and ESI-HRMS and NMR spectra (PDF)

Crystallographic data (CIF)

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#### Notes

The authors declare no competing financial interest.

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