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Reactivity of Permethylated Magnesium Complexes toward β-Diimines

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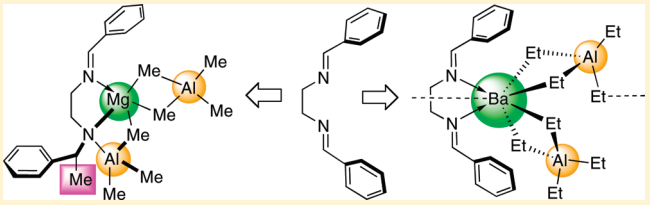
Supporting Information

ABSTRACT: The peralkylated magnesium complex $Mg(AlMe_4)_2$ reacts with bis-*N*,*N*′-diimine PhCH=NCH_2CH_2N=CHPh to yield the compound $[PhCH(Me)NCH_2CH_2N{=}CHPh]Mg(AlMe_4)(AlMe_3)$, via an alkyl migration. Such a 1,2-addition of the Mg−CH_3 moiety to the unsaturated N=C imino group is also observed for $[MgMe_2]$, affording dimagnesium complex $[\{PhCH(Me)NCH_2CH_2N{=}CHPh\}Mg(Me)]_2$. In contrast, treatment of PhCH=NCH_2CH_2N=CHPh with $AlMe_3$ gives the donor-adduct $[PhCH{=}NCH_2CH_2N{=}CHPh][(AlMe_3)_2]$. Based on these distinct reactivities a plausible reaction mechanism for the formation of $[PhCH(Me)NCH_2CH_2N{=}CHPh]Mg(AlMe_4)(AlMe_3)$ is proposed. Donor-adduct formation is also observed when the perethylated barium aluminate $[Ba(AlEt_4)_2]_n$ is reacted with a β-diimine, affording the complex $[Ba(AlEt_4)_2(PhC{=}NCH_2CH_2N{=}CPh)]_n$. The scope of this reaction behavior was further investigated by reacting $Mg(AlMe_4)_2$, $AlMe_3$, and $[MgMe_2]$ with β-diimines bearing substituted phenyl rings. Neither the *ortho*-methyl- nor the meta-*tert*-butyl-disubstituted proligands show any reaction with $[MgMe_2]$, while adducts $[(C_6H_3Me_2\text{-}2,6)CH{=}NCH_2CH_2N{=}CH(C_6H_3Me_2\text{-}2,6)][(AlMe_3)_2]$ and $[(C_6H_3tBu_2\text{-}3,5)CH{=}NCH_2CH_2N{=}CH(C_6H_3tBu_2\text{-}3,5)][(AlMe_3)_2]$ are the prevalent reaction products when $Mg(AlMe_4)_2$ and $AlMe_3$ are employed.



INTRODUCTION

Ever since their discovery in 1900 by Victor Grignard, organomagnesium halide compounds of the type RMgX have emerged as one of the most eminent metalorganic reagents in organic and organometallic synthesis.[1] Such "Grignard reagents" are still accessed by the original protocol, reacting organic halides RX with elemental magnesium in ethereal solvents.[2] Elucidation of the "Schlenk equilibrium" 2 RMgX ↔ R_2Mg + MgX_2[3] and the X-ray structure analyses of solvent- and alkali metal salt-free homoleptic dialkyl derivatives such as $Mg(2,4,6\text{-}tBu_3C_6H_2)_2$,[4] $Mg[C(SiMe_3)_3]_2$,[5] $Mg[CH(SiMe_3)_2]_2$,[6] and $(MgtBu_2)_2$[7] mark further milestones in organomagnesium chemistry. Moreover, heteroleptic Lewis-acidic magnesium alkyl complexes were found as promising catalysts for several polymerization reactions.[8−10]

The reactivity of magnesium dialkyls toward diimines nicely features distinct reaction pathways dependent on the steric bulk of the alkyl ligands and the functional groups integrated into the diimine backbone. In addition to simple chelate coordination of the diimine (**A**, Chart 1), single electron transfer (SET, **B**, Chart 1) and alkyl transfer products (selective C-alkylation (**C**, Chart 1) or N-alkylation (**D**, Chart 1)) were observed.[11−15] The latter alkylation capability and concomitant alkyl migration to iminic proligands (complexes **C** and **D**, Chart 1) have also been observed for other Lewis-acid main group and transition metal alkyl compounds (e.g., $AlMe_3$, $ZnMe_2$) and are currently exploited for the in situ generation of new monoanionic imino−amido ancillary ligands.[16−19]

We are particularly interested in the reactivity of peralkylated heterobimetallic complexes comprising metal tetraalkylaluminates and tetraalkylgallates.[20,21] Although the permethylated complex $Mg(AlMe_4)_2$ was described more than 50 years ago,[22,23] reports on its reactivity are scarce.[23] We anticipated that $Mg(AlMe_4)_2$ could be an ideal candidate for evaluating any distinct alkylating capability of Mg−CH_3 versus Al−CH_3 moieties. Moreover, β-diimines, recently shown to be prone to imine alkylation, were selected as target molecules.[19e] Herein, we report on alkyl migrations in the systems $Mg(AlMe_4)_2$/PhCH=NCH_2CH_2N=CHPh and $MgMe_2$/PhCH=NCH_2CH_2N=CHPh, yielding heteroleptic magnesium methyl complexes supported by an imino−amido ligand. In contrast simple adduct formation is found for the reactions of $AlMe_3$/PhCH=NCH_2CH_2N=CHPh and $[Ba(AlEt_4)_2]_n$/PhCH=NCH_2CH_2N=CHPh.

RESULTS AND DISCUSSION

The reaction of $Mg(AlMe_4)_2$ with N^1,N^2-bis(phenylmethylene)-1,2-diiminoethane **1a** in toluene at ambient temperature gave the bimetallic $MgAl_2$ complex **2**, which could be crystallized

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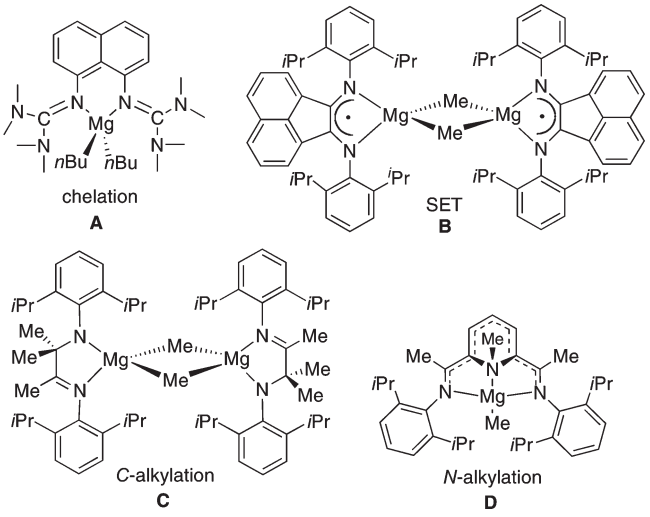
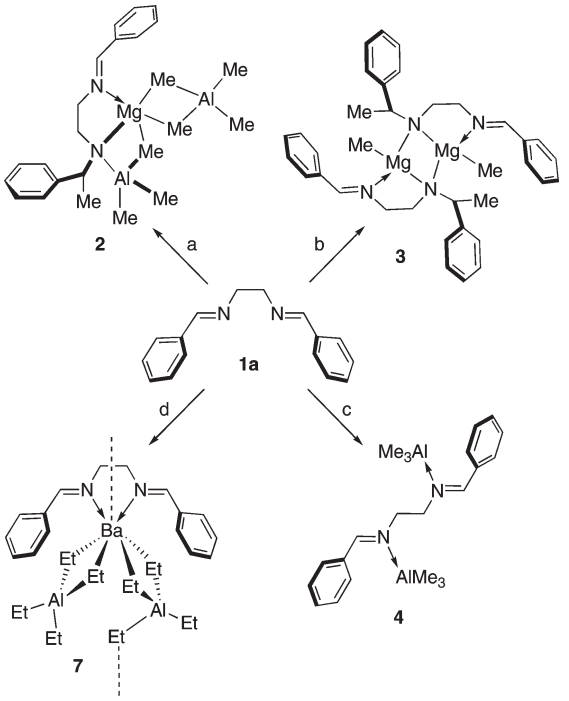
Chart 1. Reactivity of Magnesium Dialkyls toward Diimines



Scheme 1. Distinct Reaction Pathways between β-Diimine 1a and Group 2 and 13 Metal Alkyls[a]



[a] (a) $Mg(AlMe_4)_2$, toluene, rt, 16 h; (b) $MgMe_2$, toluene, rt, 16 h; (c) 2 equiv of $AlMe_3$, toluene, rt, 16 h; (d) $[Ba(AlEt_4)_2]_n$, toluene rt, 16 h.

from a saturated toluene solution at −40 °C in almost 50% yield (Scheme 1, reaction a). The ambient-temperature ^{1}H NMR spectrum of complex **2** in C_6D_6 displayed a resonance at δ 7.21 attributable to an imine group (*HC*═N). Mutually coupled methine and methyl proton resonances were observed at δ 4.30 and 1.83 ($^3J_{HH}$ = 7.1 Hz), respectively, while one broad resonance at δ −0.32 could be assigned to aluminum/magnesium-bonded methyl groups.

A variable-temperature (VT) ^{1}H NMR spectroscopic study in toluene-d_8 shed further light on the latter methyl coordination

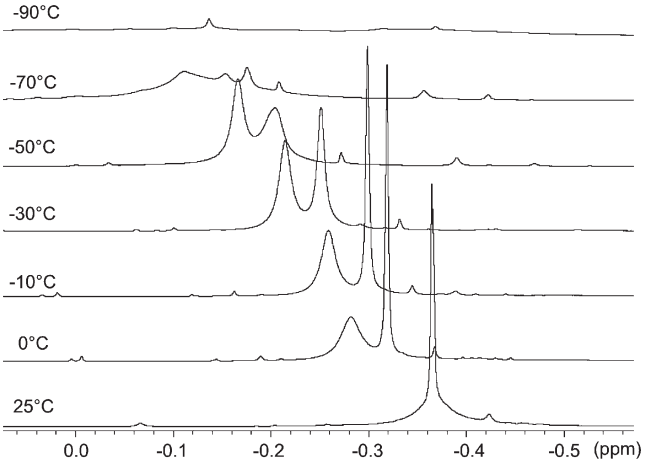


Figure 1. VT ^{1}H NMR spectra (500.13 MHz, d_8-toluene) of compound **2**, in the region of metal-bonded CH_3 protons.

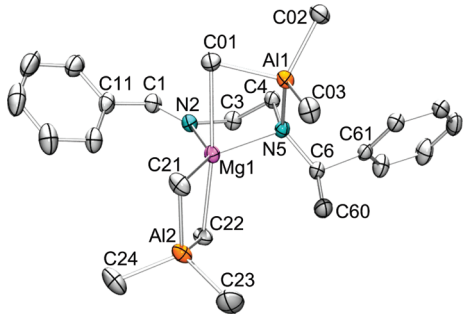


Figure 2. Molecular structure of [PhCH(Me)NCH_2CH_2N═CHPh]$Mg(AlMe_4)(AlMe_3)$ (**2**). Hydrogen atoms are omitted for clarity. Atoms are represented by atomic displacement ellipsoids at the 50% level.

Table 1. Selected Bond Distances and Angles for [PhCH(Me)NCH_2CH_2N═CHPh]$Mg(AlMe_4)(AlMe_3)$ (2)

bond distances [Å]		angles [deg]	
Mg1−N2	2.125(2)	C11−C1−N2	123.2(2)
Mg1−N5	2.122(1)	C1−N2−C3	118.8(2)
Al1−N5	1.954(1)	C4−N5−C6	109.9(1)
Mg1−C01	2.550(2)	N5−C6−C60	110.9(1)
Mg1−C21	2.265(2)	N5−C6−C61	114.7(1)
Mg1−C22	2.422(2)	C01−Mg1−C21	88.01(7)
C1−N2	1.274(2)	C01−Mg1−C22	172.85(7)
C1−C11	1.469(2)	C21−Mg1−C22	91.80(7)
N2−C3	1.474(2)	N2−Mg1−N5	86.63(5)
C3−C4	1.524(2)	N2−Mg1−C21	40.06(7)
C4−N5	1.494(2)	N5−Mg1−C21	131.71(7)
N5−C6	1.487(2)	N2−Mg1−C01	88.73(6)
C6−C60	1.522(2)	N5−Mg1−C01	80.00(6)
C6−C61	1.519(2)		

(Figure 1). At 0 °C the methyl resonance had decoalesced into a set of two signals in accordance with the presence of $Al(CH_3)_3$

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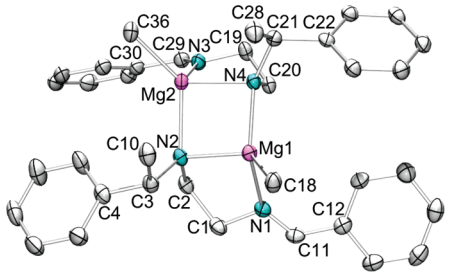

Figure 3. Molecular structure of [{PhCH(Me)NCH_2CH_2N=CHPh}Mg(Me)]$_2$ (**3**). Hydrogen atoms are omitted for clarity. Atoms are represented by atomic displacement ellipsoids at the 50% level.

"adduct" and $Al(CH_3)_4$ aluminate moieties. Upon further cooling to −70 °C, these signals significantly broadened simultaneously, adopting an overlapping four-peak pattern, pointing to a limited mobility of terminal and bridging Al−CH_3 methyl groups. Similar decoalescence phenomena have been observed previously for alkylated LnAl heterobimetallic complexes.[24]

The molecular structure of **2** was unequivocally revealed by an X-ray crystallographic study (Figure 2, Table 1). In the solid state the coordination geometry around the magnesium atom is best described as distorted trigonal bipyramidal. The three equatorial postions are occupied by the N atoms of a chelating amido−imino ligand and one methyl group of an η^2-coordinated $[AlMe_4]^-$ anion. The second methyl group of this aluminate moiety and another methyl group of the N(amido)-coordinated $AlMe_3$ are located in the apical positions. Formation of a four-membered ring as for the latter Mg(μ-CH_3)(μ-NR_2)$AlMe_2$ entity has been identified as a common structural motif in LnAl heterobimetallic amide complexes.[25] Apparently, one of the imine moieties in **1a** was selectively methylated to form this monoanionic amido−imino ligand.[19f] The bridging Mg−C(methyl) bond distances are in the order aluminate (equatorial, 2.265(2) Å) < aluminate (apical, 2.422(2) Å) < $AlMe_3$ (apical, 2.550(2) Å) and longer than in four-coordinate homoleptic Mg($AlMe_4$)$_2$ (av Mg−C, 2.208 Å).[26] The Mg−N2(imino) and Mg−N5(amido) bond lengths of 2.125(2) and 2.122(1) Å, respectively, are almost identical, matching the average Mg−N donor bond distance of 2.192 Å in four-coordinate (Me_3Si)$_2$Mg(TMEDA) (TMEDA = tetramethylethyldiamine).[27] Furthermore, the C1−N2 and C6−N5 bond distances of 1.274(2) and 1.488(1) Å, respectively, clearly evidence the presence of imino and amido moieties.

Previously, the occurrence of a donor-induced aluminate cleavage was reported when Mg($AlEt_4$)$_2$ and Mg($AlMe_4$)$_2$ were treated with 2 equiv of donor (OEt_2/THF), forming $AlEt_3$-(OEt_2)/$AlMe_3$(THF) and mixed alkyl-magnesium species EtMg($AlEt_4$) and MeMg($AlMe_4$), respectively.[23] It is noteworthy that exposure of a stirred solution of **2** in toluene to 1 equiv of diethyl ether at ambient temperature for 6 h did not give the respective $AlMe_3$-cleaved product (as evidenced by the relative signal intensities in the NMR spectrum). In order to further investigate the dual reactivity of Mg($AlMe_4$)$_2$, that is, imino alkylation and $AlMe_3$−imino adduct formation, we independently examined the reactions of $MgMe_2$ and $AlMe_3$ with β-diimine **1a**. Treatment of **1a** with $MgMe_2$ in toluene afforded a dark orange solution containing heteroleptic magnesium complex **3**, bearing the same monoanionic amido−imino ligand as complex **2** (Scheme 1, reaction b, upon stirring for 16 h at ambient temperature). Correspondingly, the ^{1}H NMR spectrum of **3** in C_6D_6 shows one

Table 2. Selected Bond Distances and Angles for [{PhCH(Me)NCH_2CH_2N=CHPh}Mg(Me)]$_2$ (3)

bond distances [Å]		angles [deg]	
Mg1−N1	2.201(1)	Mg1−N2−Mg2	88.11(5)
Mg1−N2	2.175(1)	Mg1−N4−Mg2	89.13(5)
Mg1−N4	2.084(1)	C18−Mg1−N1	106.45(6)
Mg1−C18	2.146(2)	C18−Mg1−N2	125.23(6)
Mg2−N2	2.102(1)	C1−N1−C11	115.6(1)
Mg2−N3	2.221(1)	C2−N2−C3	110.8(1)
Mg2−N4	2.155(1)	N2−C3−C10	109.4(1)
Mg2−C36	2.175(2)	C36−Mg2−N3	112.01(6)
N1−C1	1.481(2)	C36−Mg2−N4	127.61(6)
N1−C11	1.276(2)	C19−N3−C29	115.4(1)
N2−C2	1.475(2)	C20−N4−C21	110.8(1)
N2−C3	1.471(2)		
C3−C10	1.526(2)		
N3−C29	1.278(2)		
N3−C19	1.479(2)		
N4−C20	1.475(2)		
N4−C21	1.484(2)		
C21−C28	1.524(2)		

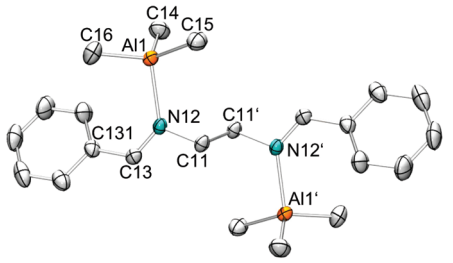

Figure 4. Molecular structure of [PhCH=NCH_2CH_2N=CHPh][($AlMe_3$)$_2$] (**4**). Hydrogen atoms are omitted for clarity. Atoms are represented by atomic displacement ellipsoids at the 50% level. Selected bond lengths (Å) and angles (deg) for **4**: Al1−N12 2.062(3), N12−C11 1.475(4), N12−C13 1.283(4), C13−C131 1.458(5); Al1−N12−C11 114.7(2), Al1−N12−C13 129.4(2), C11−N12−C13 115.3(3), N12−C11−C11′ 109.1(3), N12−C13−C131 126.7(3).

quartet and one doublet resonance at δ 4.30 and 2.25, respectively, for the NC*H*(CH_3)Ph moiety, giving clear evidence of a methyl group migration to the unsaturated N=C imino double bond. Also, a magnesium-bonded methyl group was revealed by singlet signals at δ_H −0.42 and δ_C −11.5. Single crystals of **3** suitable for X-ray diffraction analysis were obtained from a concentrated toluene solution at −40 °C. As shown in Figure 3, complex **3** forms a nitrogen(amido)-bridged dimer in the solid state. The shortest Mg−N distances are 2.084(1) and 2.102(1) Å and are observed for the amido nitrogen atoms, which engage in a chelate bonding with the other Mg center (Table 2). The terminal Mg1−C18 and Mg2−C36 bond distances of 2.146(2) and 2.175(2) Å, respectively, are longer than those in sterically less encumbered [(THF)MgMe(μ-Me)]$_2$ (Mg−$C_{terminal}$ = 2.121(2) Å).[23]

In contrast, treatment of ligand **1a** with 2 equiv of $AlMe_3$ in a stirred toluene solution at ambient temperature for 16 h yielded after crystallization at −40 °C the corresponding $AlMe_3$−diimino adduct **4**. The ^{1}H NMR spectrum of **4** in

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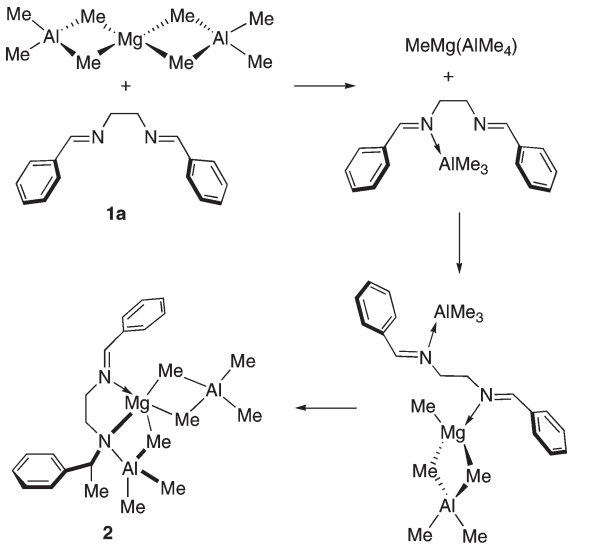
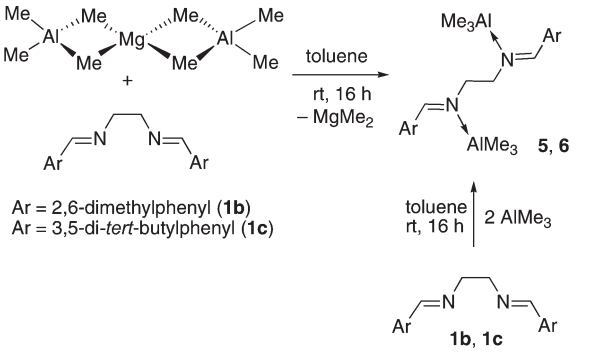
Scheme 2. Proposed Mechanism of Formation of Complex [PhCH(Me)NCH$_2$CH$_2$N=CHPh]Mg(AlMe$_4$)(AlMe$_3$) (2)



Scheme 3. Reactivity of β-Diimines 1b and 1c toward Mg(AlMe$_4$)$_2$ and AlMe$_3$



C_6D_6 showed a single resonance (δ 8.28, relative intensity of 2) for the imino protons (*H*C=N) of the ligand backbone, suggesting a highly symmetric and/or fluxional structure. The methylene and the aluminum-bonded methyl protons display a relative intensity of 4:18, indicating adduct formation of each imino nitrogen with one $AlMe_3$ group (Scheme 1, reaction c). The solid-state structure of **4** was elucidated by single-crystal X-ray diffraction (Figure 4). The Al−N bond distance of 2.062(3) Å is comparable to those found in similar adduct complexes,[25,28] while the N−C imino bond distance of 1.283(4) Å is clearly indicative of a C=N double bond.

Given this distinct reactivity of [$MgMe_2$] and Al_2Me_6 toward **1a**—methylation is observed only for $MgMe_2$—we propose the following reaction mechanism for the formation of compound **2** (Scheme 2). First, donor-induced cleavage of Mg(AlMe$_4$)$_2$ by one of the imino donor moieties of β-diimine **1a** proceeds to give heteroleptic MeMg(AlMe$_4$) and (diimine)$AlMe_3$. Subsequent coordination of the second imino nitrogen atom to the magnesium atom and methyl migration onto the C=N bond—1,2-addition of the Mg−CH_3 moiety to the aluminum-free C=N group—results in the $MgAl_2$ bimetallic complex **2**. It should also

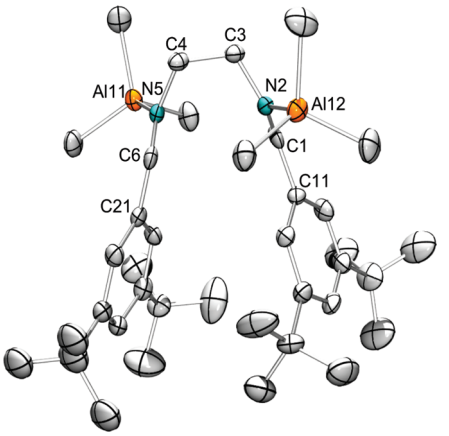


Figure 5. Molecular structure of [(C$_6$H$_3$*t*Bu$_2$-3,5)CH=NCH$_2$CH$_2$N=CH(C$_6$H$_3$*t*Bu$_2$-3,5)][(AlMe$_3$)$_2$] (**6**). Hydrogen atoms are omitted for clarity. Atoms are represented by atomic displacement ellipsoids at the 50% level. Co-crystallized toluene (one molecule per unit cell) is not shown.

be noted that the reaction of **3** with 2 equiv of $AlMe_3$ does not simply form complex **2** as indicated by NMR spectroscopy.

In order to further examine the scope of this reaction behavior, phenyl-substituted β-diimines **1b** and **1c** were reacted with homoleptic Mg(AlMe$_4$)$_2$ (Scheme 3). Interestingly, in toluene solution only the formation of $AlMe_3$−diimino complexes **5** and **6** was observed, consistent with the NMR data. Even heating a mixture of Mg(AlMe$_4$)$_2$ and **1c** for a prolonged time in a pressure tube did not lead to any significant alkylation. The molecular composition of compound **6** could be confirmed by X-ray diffraction analysis (Figure 5), although the limited quality of the crystals precludes a detailed discussion of metrical parameters. Not surprisingly, compounds **5** and **6** are also obtained by adding $AlMe_3$ directly to a toluene solution of the β-diimines **1b** and **1c**, respectively, at ambient temperature (Scheme 3) or upon heating in a pressure tube. Moreover, neither the *ortho*-methyl-disubstituted proligand **1b** nor the meta-*tert*-butyl-disubstituted ligand **1c** showed any reaction with [$MgMe_2$]. We assume that it is mainly the steric hindrance of the proligand[29] and/or conformational (im)mobility of the mono-$AlMe_3$-coordinated intermediates that cause the different reaction behavior. The different conformations of the diimine ligand are nicely featured by the bis($AlMe_3$) adducts **4** and **6** (Figures 4 and 5).

The enhanced alkylating power of the Mg−CH_3 moiety was further corroborated by examining the corresponding reaction of perethylated barium aluminate, [Ba(AlEt$_4$)$_2$]$_n$, with 1 equiv of proligand **1a** (Scheme 1, reaction d). The absence of any imine alkylation was suggested by an NMR spectroscopic investigation of the crystalline product **7** (65%), obtained by cooling the reaction mixture to −40 °C, and of the mother liquor. The ^{1}H NMR spectrum of **7** in C_6D_6 displays a triplet and a quartet at 1.49 and 0.10 ppm, respectively, with a relative integral ratio of 3:2, assignable to the $AlEt_4$ groups. An additional peak at δ 7.71 is attributed to the N=CH protons of the donor ligand. The formation of donor-adduct [Ba(AlEt$_4$)$_2$(PhC=NCH$_2$CH$_2$N=CPh)]$_n$ (**7**) was unequivocally proven by an X-ray structure analysis (Figure 6, Table 3), revealing that the three-dimensional network structure of [Ba(AlEt$_4$)$_2$]$_n$ has been disrupted to an infinite chain structure via chelate formation with the hard β-diimine.

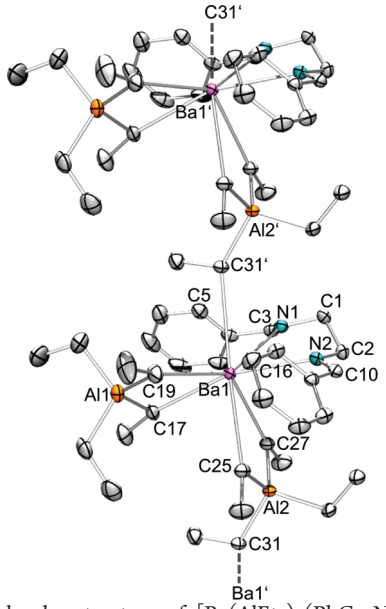


Figure 6. Molecular structure of $[Ba(AlEt_4)_2(PhC{=}NCH_2CH_2N{=}CPh)]_n$ (7). Hydrogen atoms are omitted for clarity. Atoms are represented by atomic displacement ellipsoids at the 50% level.

Table 3. Selected Bond Distances and Angles for $[Ba(AlEt_4)_2(PhC{=}NCH_2CH_2N{=}CPh)]_n$ (7)

bond distances [Å]		angles [deg]	
Ba1−N1	2.893(1)	N1−Ba1−N2	59.46(3)
Ba1−N2	2.848(1)	C17−Ba1−C19	67.99(4)
Ba1−C17	3.002(1)	C25−Ba1−C27	64.55(3)
Ba1−C19	3.072(1)	N1−Ba1−C19	149.47(4)
Ba1−C25	3.140(1)	N2−Ba1−C27	82.21(3)
Ba1−C27	3.188(1)	C17−Ba1−C27	78.92(4)
Ba1−C31′	3.281(1)	C25−Ba1−C31′	143.82(3)
Ba1···Al1	3.6469(4)	C27−Ba1−C31′	146.64(3)
Ba1····Al2	3.8016(4)	N2−Ba1−C17	161.05(4)
Ba1···C5	3.613(1)	N2−Ba1−C19	126.44(4)
Ba1···C15	3.572(1)	N1−Ba1−C17	115.72(3)
N1−C1	1.464(2)	Ba1−N1−C3	116.76(8)
N1−C3	1.275(2)	Ba1−N2−C10	123.71(8)
N2−C2	1.472(2)	C1−N1−C3	118.4(1)
N2−C10	1.276(2)	C2−N2−C10	117.0(1)

The seven-coordinate barium center is further surrounded by two tetraethylaluminate groups, one showing a "terminal" η^2-coordination, while the second bridges two barium centers in a μ_2-η^2:η^1 mode. The Ba−C bond distances of the terminal unit average 3.037 Å and are considerably shorter than those found for the interconnecting one (3.140(1)−3.281(1) Å), which shows the longest distance for the η^1-bonded ethyl group. For comparison, the Ba−C bond distances of the μ_3-η^1:η^1:η^1-bonded alkylaluminate ligands in homoleptic $[Ba(AlEt_4)_2]_n$ average 3.125 Å.[21h] While the μ_2-η^2:η^1 alkylaluminate coordination mode has been observed for Ln(III)−$AlMe_4$ complexes,[30] the intricate solid-state structure of $[M(AlEt_4)_2]_n$ (M = Sm, Eu, Yb, Ca) revealed μ_2-η^3:η^1-interconnecting ethylaluminate moieties.[23,31] Polymeric lithium tetraethylaluminate shows $[Li(AlEt_4)]_n$ units, which are aligned in linear chains via μ_2-η^2:η^2 alkylaluminate coordination.[32] Moreover, the β-diimine ligands in **7** twist such that one of the *ortho*-carbon ring atoms of each phenyl group seems to make contact with the barium metal center (Ba···C 3.572 and 3.613 Å), formally increasing the coordination number to 9. The Ba−N bond distances in **7** average 2.871 Å and are significantly longer than the Ba−N(pyrazolyl) bond lengths of 2.808 Å in eight-coordinate complex Tp′BaI(Hpz) (Tp′ = tris{3-methoxy-1, 1-dimethylpyrazolyl}hydroborate).[33]

As suggested by elemental analysis and NMR spectroscopic investigations, similar adduct formation occurs between $[Ba(AlEt_4)_2]_n$ and *tert*-butyl-disubstituted proligand **1c**; however,

Table 4. Crystallographic Data for 2, 3, 4, 6, and 7

	2	3	4
chemical formula	$C_{24}H_{40}Al_2MgN_2$	$C_{36}H_{44}Mg_2N_4$	$C_{22}H_{34}Al_2N_2$
M_r	434.85	581.37	380.47
cryst syst	monoclinic	triclinic	triclinic
space group	$P2_1/c$	$P\bar{1}$	$P\bar{1}$
a/Å	8.8863(8)	8.9465(4)	6.8629(18)
b/Å	18.9418(11)	10.0006(4)	7.7586(19)
c/Å	15.8136(12)	19.4059(8)	11.250(3)
α/deg	90.00	79.3630(10)	102.16(2)
β/deg	99.651(7)	82.6500(10)	91.06(2)
γ/deg	90.00	73.6380(10)	90.75(2)
V/Å^3	2624.1(3)	1631.99(12)	585.4(3)
Z	4	2	1
F(000)	944	624	206
T/K	173(2)	103(2)	173(2)
ρ_{calcd}/g cm^{-3}	1.101	1.183	1.079
μ/mm^{-1}	0.147	0.104	0.132
R_1(obsd)[a]	0.0516	0.0368	0.0575
wR_2(all)[b]	0.1046	0.0992	0.1382
S[c]	1.208	1.028	1.222

	6	7
chemical formula	$C_{45}H_{76}Al_2N_2$	$C_{32}H_{56}Al_2BaN_2$
M_r	699.04	660.09
cryst syst	monoclinic	triclinic
space group	$C2/c$	$P\bar{1}$
a/Å	37.826(4)	8.5950(2)
b/Å	11.3329(11)	11.4426(3)
c/Å	24.359(2)	18.5980(5)
α/deg	90.00	87.5142(2)
β/deg	112.235(9)	89.4389(3)
γ/deg	90.00	76.8646(3)
V/Å^3	9665.7(16)	1179.57(8)
Z	8	2
F(000)	3087	688
T/K	173(2)	123(2)
ρ_{calcd}/g cm^{-3}	0.961	1.232
μ/mm^{-1}	0.088	1.186
R_1(obsd)[a]	0.1489	0.0204
wR_2(all)[b]	0.3116	0.0542
S[c]	1.598	1.099

[a] $R_1 = \Sigma(||F_o| - |F_c||)/\Sigma|F_o|$, $F_o > 4\sigma(F_o)$. [b] $wR_2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$. [c] $S = [\Sigma w(F_o^2 - F_c^2)^2/(n_o - n_p)]^{1/2}$.

As suggested by elemental analysis and NMR spectroscopic investigations, similar adduct formation occurs between $[Ba(AlEt_4)_2]_n$ and *tert*-butyl-disubstituted proligand **1c**; however,

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donor-adduct $Ba(AlEt_4)_2[(C_6H_3tBu_2\text{-}3,5)CH{=}NCH_2CH_2N{=}CH\text{-}(C_6H_3tBu_2\text{-}3,5)]$ (**8**) did not produce single crystals suitable for an X-ray diffraction analysis. As proposed in Scheme 2, the key step of the diimine ligand alkylation for group 2 metal aluminate complexes is probably the donor-induced tetraalkylaluminate cleavage to generate a metal−alkyl−aluminate intermediate. Apparently, the large ionic size and moderate Lewis acidity of the barium(II) center, that is, its lower hardness compared to the small Mg^{2+}, impede the separation of triethylaluminum by the diimine ligand, resulting in the formation of simple donor-adducts **7** and **8**. This is in line with the reactivity of complexes $[M(AlEt_4)_2]_n$ (M = Sm, Eu, Yb, Ca) toward hard Lewis bases with HSAB interactions and tetraalkylaluminate ion separation prevailing over donor-induced tetraalkylaluminate cleavage.[23,31]

CONCLUSION

The distinct reactivity of $[MgMe_2]$ and Al_2Me_6 toward $PhC{=}NCH_2CH_2N{=}CPh$, affording $[\{PhCH(Me)NCH_2CH_2N{=}CHPh\}Mg(Me)]_2$ and $[PhCH{=}NCH_2CH_2N{=}CHPh]\text{-}[(AlMe_3)_2]$, respectively, clearly documents the enhanced alkylating power of Mg−CH_3 moieties. The formation of the same imino−amido ligand $[PhCH(Me)NCH_2CH_2N{=}CHPh]$ from the reaction of $Mg(AlMe_4)_2$ with a β-diimine suggests a donor(imino)-induced tetramethylaluminate cleavage and formation of $[(AlMe_4)Mg{-}Me]$ as the initiating step. Alkyl substitution of the phenyl rings of the β-diimine proligands crucially affects the alkylating capability of such $Mg(AlMe_4)_2$-derived Mg−CH_3 moieties, resulting predominantly in donor-adducts of type $[\beta\text{-diimine}][(AlMe_3)_2]$. Alkyl migration onto the imino functionality is also not prominent for the peralkylated compound $[Ba(AlEt_4)_2]_n$, featuring the highly electropositive barium center: the β-diimine partially disrupts the network structure of $[Ba(AlEt_4)_2]_n$, forming adducts $[(\beta\text{-diimine})Ba(AlEt_4)_2]_n$ exclusively. The infinite chain structure of $[Ba(AlEt_4)_2(PhC{=}NCH_2CH_2N{=}CPh)]_n$ features $\mu_2\text{-}\eta^2{:}\eta^1$-bridging alkylaluminate ligands as the lead structural motif. Ongoing studies in our laboratories are aimed at a deeper understanding of the reactivity of metal alkylaluminates toward unsaturated organic molecules.

EXPERIMENTAL SECTION

General Remarks. Materials and Methods. All reactions involving air- and moisture-sensitive organometallic compounds were performed under a dry argon atmosphere using standard Schlenk and glovebox techniques (MBraun MB250B; < 1 ppm O_2, < 1 ppm H_2O). Hexane, thf, and toluene were purified using Grubbs columns (MBraun SPS, solvent purification system). Deuterated solvents were dried over Na/K. All solvents were stored inside a glovebox. Complexes $[MgMe_2]$,[34] $Mg(AlMe_4)_2$,[22] and $[Ba(AlEt_4)_2]_n$[21h] as well as the proligand **1a**[35] were synthesized according to the literature. NMR spectra were recorded on a Varian UNITY INOVA-300, a Bruker-AVII-400, and a Bruker-BIOSPIN-AV500. ^1H and ^{13}C NMR chemical shifts were referenced to internal solvent resonances reported in parts per million relative to TMS. Infrared spectra were recorded on a Thermo Scientific Nicolet6700 FTIR spectrometer as Nujol mulls sandwiched between CsI plates. High-resolution mass spectra were recorded on a JEOL JMS-700. Elemental analyses were performed on an Elementar Vario MICRO.

$(C_6H_3Me_2\text{-}2,6)CH{=}NCH_2CH_2N{=}CH(C_6H_3Me_2\text{-}2,6)$ (1b). To a mixture of 2,6-dimethylbenzaldehyde (0.75 mL, 2.00×10^{-2} mol) in H_2O (20 mL) was added ethylenediamine (0.67 mL, 1.00×10^{-2} mol) at ambient temperature. The mixture was allowed to warm to 50 °C and stirred overnight. A white solid was isolated by filtration, washed with water, and dried in vacuo to give **1b** (93%). IR (Nujol cm^{-1}): 1695 w, 1641 s, 1590 w, 1278 w, 1210 w, 1189 w, 1166 m, 1093 w, 1046 w, 1025 m, 1004 m, 964 m, 915 w, 887 w, 857 w, 770 s, 737 w. ^1H NMR (300 MHz, C_6D_6, 35 °C): δ 8.45 (s, 2H, N=C*H*), 6.9−7.0 (m, 2H, *p-Ar*), 6.9 (m, 4H, *m-Ar*), 3.90 (s, 4H, NCH_2CH_2N), 2.33 (s, 12H, $ArCH_3$). ^{13}C NMR (75 MHz, C_6D_6, 35 °C): δ 161.8 (*C*=N), 137.9 (*Ar*), 134.2 (*Ar*), 129.0 (*Ar*), 128.9 (*Ar*), 63.6 (NCH_2CH_2N), 20.9 ($ArCH_3$). HRMS (EI): *m/z* calcd for $C_{20}H_{24}N_2$ 292.1939, found 292.1931.

$(C_6H_3tBu_2\text{-}3,5)CH{=}NCH_2CH_2N{=}CH(C_6H_3tBu_2\text{-}3,5)$ (1c). To a solution of 3,5-di-*tert*-butylbenzaldehyde (1.47 g, 0.67×10^{-2} mol) in ethanol (15 mL) was added ethylenediamine (0.23 mL, 0.33×10^{-2} mol) at ambient temperature. The mixture was stirred overnight. After all volatiles had been removed under reduced pressure, the resulting residue was washed with water to give **1c** (94% yield) as a white powder upon drying in vacuo. IR (Nujol cm^{-1}): 1641 s, 1592 m, 1288 w, 1269 w, 1246 m, 1210 m, 1168 w, 1018 m, 962 m, 894 w, 875 m 770 w. ^1H NMR (300 MHz, C_6D_6, 35 °C): δ 8.20 (s, 2H, N=C*H*), 7.77 (d, ^4J = 1.7 Hz, 4H, *o-Ar*), 7.54 (t, ^4J = 1.7 Hz, 2H, *p-Ar*), 4.03 (s, 4H, NCH_2CH_2N), 1.25 (s, 36H, $ArC(CH_3)_3$). ^{13}C NMR (75 MHz, C_6D_6, 35 °C): δ 163.0 (*C*=N), 151.2 (*Ar*), 136.9 (*Ar*), 124.7 (*Ar*), 123.1 (*Ar*), 62.4 (NCH_2CH_2N), 31.5 ($ArCH_3$). HRMS (EI): *m/z* calcd for $C_{32}H_{48}N_2$ 460.3817, found 460.3823.

$[PhCH(Me)NCH_2CH_2N{=}CHPh]Mg(AlMe_4)(AlMe_3)$ (2). A solution of **1a** (119 mg, 0.50 mmol) in toluene was added to a stirred solution of $Mg(AlMe_4)_2$ (100 mg, 0.50 mmol) in toluene at ambient temperature. The reaction mixture was allowed to stir for 16 h. The suspension was centrifuged and filtrated, and the remaining solution concentrated. Cooling the solution to −40 °C yielded **2** (49%, 0.25 mmol) as colorless crystals suitable for X-ray diffraction analysis. IR (Nujol cm^{-1}): 1641 s, 1595 w, 1578 w, 1491 w, 1311 w, 1215 s, 1175 m, 1130 w, 1100 m, 1074 m, 1025 m, 973 w, 919 w, 894 m, 751 m, 644 w, 590 m, 562 w, 505 w, 484 w. ^1H NMR (400 MHz, C_6D_6, 25 °C): δ 7.54 (d, ^3J = 7.2 Hz, 2H, *o-Ph*), 7.33 (m, 2H, *m-Ph*), 7.26 (m, 2H, *o-Ph*), 7.24 (s, 2H, *m-Ph*), 7.21 (s, 1H, N=C*H*Ph), 7.19 (m, 2H, *p-Ph*), 4.30 (q, ^3J = 7.1 Hz, 1H, NC*H*PhCH$_3$), 3.34 (m, 2H, NCH_2CH_2N), 2.67 (m, 2H, NCH_2CH_2), 1.83 (d, ^3J = 7.1 Hz, 3H, NCHPhC*H*$_3$), −0.32 (b, 21H, $AlCH_3$). ^{13}C NMR (100 MHz, C_6D_6, 25 °C): δ 168.8 (*C*=N), 144.5 (*ipso-Ph*), 133.6 (*Ph*), 129.8 (*Ph*), 128.7 (*Ph*), 128.6 (*Ph*), 61.4 (CH), 59.8 (CH_2), 47.3 (CH_2), 22.5 (CH_3), −4.6 ($Al(CH_3)_3$), −6.8 ($Al(CH_3)_4$). Anal. Calcd for $C_{24}H_{38}Al_2MgN_2$ (432.84): C, 66.60; H, 8.85; N, 6.47. Found: C, 66.20; H, 9.09; N, 6.37.

$[\{PhCH(Me)NCH_2CH_2N{=}CHPh\}Mg(Me)]_2$ (3). To a stirred suspension of $MgMe_2$ (25 mg, 0.46 mmol) in 5 mL of toluene was added a solution of **1a** (109 mg, 46 mmol) in toluene at ambient temperature. The reaction mixture was allowed to stir for 16 h while its color turned to orange. The suspension was centrifuged and the remaining solution filtrated and subsequently concentrated under reduced pressure. Cooling to −40 °C yielded single crystals of compound **3** (70%, 0.32 mmol) suitable for X-ray diffraction analysis. IR (Nujol cm^{-1}): 1634 s, 1578 w, 1337 w, 1309 w, 1292 w, 1274 w, 1217 w, 1105 m, 1079 w, 1042 m, 1025 w, 976 w, 890 m, 833 w, 779 w, 756 s, 728 w, 630 m, 587 m, 557 s, 515 s. ^1H NMR (400 MHz, C_6D_6, 25 °C): δ 7.86 (dd, ^3J = 7.7 Hz, ^4J = 1.2 Hz, 2H, *o-Ph*), 7.39 (dd, ^3J = 7.4 Hz, ^4J = 7.7 Hz, 2H, *m-Ph*), 7.33 (d, ^4J = 1.2 Hz, 1H, N=C*H*Ph), 7.32 (m, 2H, *o-Ph*), 7.23 (dd, ^3J = 7.4 Hz, ^4J = 1.2 Hz, 1H, *p-Ph*), 7.01 (m, 2H, *m-Ph*), 4.30 (q, ^3J = 6.7 Hz, 1H, NC*H*PhCH$_3$), 3.78 (m, 2H, NCH_2CH_2N), 2.67 (ddd, ^2J = 14.0 Hz, ^3J = 2.7, 2.9 Hz, 2H, NCH_2CH_2N), 2.50 (ddd, ^2J = 12.9 Hz, ^3J = 2.5, 2.7 Hz, 3H, NCHPhC*H*$_3$), −0.42 (s, 3H, $MgCH_3$). ^{13}C NMR (100 MHz, C_6D_6, 25 °C): δ 165.5 (*C*=N), 149.5 (*ipso-Ar*), 133.2 (*ipso-Ar*), 132.4 (*Ar*), 129.2 (*Ar*), 128.7 (*Ar*), 128.6 (*Ar*), 126.6 (*Ar*), 60.7 (CH), 60.5 (CH_2), 50.7 (CH_2), 26.1 (CH_3), −11.5 ($MgCH_3$). Anal. Calcd for $C_{36}H_{44}Mg_2N_4$ (581.37): C, 74.37; H, 7.63; N, 9.64. Found: C, 73.74; H, 7.17; N, 9.61.

General Procedure for the Synthesis of $AlMe_3$−Diimino Adducts. To a stirred solution of **1** dissolved in toluene were added

2 equiv of $AlMe_3$. After being stirred for 16 h at ambient temperature the mixture was filtrated and the remaining solution concentrated under reduced pressure. Cooling to −40 °C afforded single crystals suitable for X-ray diffraction analysis.

[PhCH═NCH$_2$CH$_2$N═CHPh][(AlMe$_3$)$_2$] (4). Following the procedure described above, **1a** (100 mg, 0.42 mmol) and $AlMe_3$ (61 mg, 0.85 mmol) yielded **4** as colorless crystals (35%; 0.15 mmol). IR (Nujol cm^{-1}): 1616 s, 1234 s, 1016 m, 981 m, 756 m, 627 w, 569 w, 514 w, 484 w, 416 w. ^{1}H NMR (400 MHz, C_6D_6, 25 °C): δ 7.94 (s, 2H, N═C*H*), 7.55 (d, ^3J = 7.1 Hz, 4H, *Ph*), 7.27 (s, 2H, *Ph*), 6.93 (m, 6H, *Ph*), 3.89 (s, 4H, NCH_2CH_2N), −0.27 (s, 18H, Al(CH_3)$_3$). ^{13}C NMR (100 MHz, C_6D_6, 25 °C): δ 176.7 (*C*═N), 133.8 (*Ph*), 131.5 (*Ph*), 131.2 (*Ph*), 128.5 (*Ph*), 128.3 (*Ph*), 127.8 (*Ph*), 61.7 (CH$_2$), −5.0 (Al(CH_3)$_3$). Anal. Calcd for $C_{22}H_{34}Al_2N_2$ (380.48): C, 69.45; H, 9.01; N, 7.36. Found: C, 69.51; H, 9.04; N, 7.37.

[(C$_6$H$_3$Me$_2$-2,6)CH═NCH$_2$CH$_2$N═CH(C$_6$H$_3$Me$_2$-2,6)][(AlMe$_3$)$_2$] (5). Following the procedure described above, **1b** (100 mg, 0.34 mmol) and $AlMe_3$ (49 mg, 0.69 mmol) yielded **5** as colorless crystals (15%; 0.02 mmol). IR (Nujol cm^{-1}): 1637 s, 1595 w, 1297 w, 1253 m, 1173 m, 1030 w, 1011 w, 836 w, 786 m, 630 w. ^{1}H NMR (400 MHz, C_6D_6, 25 °C): δ 8.28 (s, 2H, N═C*H*), 6.95 (t, ^3J = 7.7 Hz, 2H, *p*-Ar*H*), 6.72 (d, ^3J = 7.7 Hz, 4H, *m*-Ar*H*), 4.04 (s, 4H, NCH_2CH_2N), 1.92 (s, 12H, CH_3), −0.62 (s, 18H, Al(CH_3)$_3$). ^{13}C NMR (100 MHz, C_6D_6, 25 °C): δ 178.9 (*C*═N), 135.1 (*Ar*), 132.5 (*Ar*), 130.6 (*Ar*), 127.9 (*Ar*), 59.4 (NCH_2CH_2N), 19.8 (CH_3), −6.9 (Al(CH_3)$_3$). Anal. Calcd for $C_{26}H_{42}Al_2N_2$ (436.59): C, 71.53; H, 9.70; N, 6.42. Found: C, 71.15; H, 8.90; N, 6.54.

[(C$_6$H$_3$*t*Bu$_2$-3,5)CH═NCH$_2$CH$_2$N═CH(C$_6$H$_3$*t*Bu$_2$-3,5)][(AlMe$_3$)$_2$] (6). Following the procedure described above, **1c** (50 mg; 0.11 mmol) and $AlMe_3$ (16 mg, 0.22 mmol) yielded **6** as colorless crystals (55%; 0.06 mmol). IR (Nujol cm^{-1}): 1655 w, 1618 m, 1595 m, 1374 s, 1360 s, 1243 m, 1196 w, 1185 w, 1053 w, 887 w, 873 w, 630 w. ^{1}H NMR (400 MHz, C_6D_6, 25 °C): δ 7.95 (s, 2H, N═C*H*), 7.47 (s, 2H, *p*-Ar*H*), 7.44 (s, 4H, *o*-Ar*H*), 3.86 (s, 4H, NCH_2CH_2N), 1.11 (s, 36H, C(CH_3)$_3$), 0.35 (s, 18H, Al(CH_3)$_3$). ^{13}C NMR (100 MHz, C_6D_6, 25 °C): δ 177.9 (br, C═N), 151.4 (*Ar*), 128.7 (br, *Ar*), 126.4 (br, *Ar*), 61.2 (br, NCH_2CH_2N), 35.0 (*C*(CH$_3$)$_3$), 31.3 (C(*C*H$_3$)$_3$), −5.7 (br, Al(CH_3)$_3$). Anal. Calcd for $C_{38}H_{66}Al_2N_2$ (604.91): C, 75.45; H, 11.00; N, 4.63. Found: C, 75.54; H, 11.08; N, 4.65.

[Ba(AlEt$_4$)$_2$(PhC═NCH$_2$CH$_2$N═CPh)]$_n$ (7). To a stirred solution of **1a** (60 mg, 0.25 mmol) in 5 mL of toluene was added 1 equiv of [Ba(AlEt$_4$)$_2$]$_n$ (115 mg, 0.25 mmol) at ambient temperature. After being stirred for 16 h the orange solution was filtrated and its volume reduced under vacuum. Cooling the solution to −40 °C yielded **7** as single crystals suitable for X-ray diffraction analysis (65%, 0.16 mmol). IR (Nujol cm^{-1}): 1639 m, 1576 w, 1336 w, 1306 w, 1224 vw, 1171 m, 1114 vw, 1098 vw, 1072 w, 1037 w, 976 m, 932 m, 845 w, 747 m, 718 m, 702 w, 641 w, 590 m, 534 w, 501 vw. ^{1}H NMR (400 MHz, C_6D_6, 25 °C): δ 7.71 (br, 2H, C*H*═N), 7.35 (br, 4H, *Ph*), 7.27 (br, 2H, *Ph*), 7.22 (m, 2H, *Ph*), 3.19 (s, 4H, NCH_2CH_2N), 1.49 (t, ^3J = 7.7 Hz, 24H, AlCH$_2$CH_3), 0.10 (q, ^3J = 7.7 Hz, 16H, AlCH_2CH$_3$). ^{13}C NMR (100 MHz, C_6D_6, 25 °C): δ 169.5 (*C*═N), 134.8 (*Ph*), 133.3 (*Ph*), 130.4 (*Ar*), 127.5 (*Ar*), 61.7 (NCH_2CH_2N), 11.8 (AlCH$_2$CH_3), 7.2 (AlCH_2CH$_3$). Anal. Calcd for $C_{32}H_{56}Al_2BaN_2$ (660.09): C, 58.23; H, 8.55; N, 4.24. Found: C, 58.30; H, 8.40; N, 4.07.

Ba(AlEt$_4$)$_2$[(C$_6$H$_3$*t*Bu$_2$-3,5)CH═NCH$_2$CH$_2$N═CH(C$_6$H$_3$*t*Bu$_2$-3,5)] (8). To a stirred solution of **1c** (105 mg, 0.21 mmol) in 5 mL of toluene was added 1 equiv of [Ba(AlEt$_4$)$_2$]$_n$ (100 mg, 0.22 mmol) at ambient temperature. After being stirred for 16 h the orange solution was filtrated and its volume reduced under vacuum. Cooling the solution to −40 °C yielded **8** as a crystalline precipitate (65%, 0.14 mmol). IR (Nujol cm^{-1}): 1635 m, 1596 m, 1248 w, 1223 w, 1197 w, 1097 w, 985 m, 897 w, 719 m. ^{1}H NMR (400 MHz, C_6D_6, 25 °C): δ 7.91 (s, 2H, *p*-*Ph*), 7.78 (s, 2H, N═C*H*Ph), 7.48 (s, 4H, *o*-*Ph*), 3.44 (s, 4H, NCH_2CH_2N), 1.49 (t, ^3J = 7.7 Hz, AlCH$_2$CH_3), 1.45 (s, 36H, C(CH_3)$_3$), 0.06 (q, ^3J = 7.7 Hz, 16H, AlCH_2CH$_3$). ^{13}C NMR (100 MHz, C_6D_6, 25 °C): δ 171.8 (*C*═N), 152.9 (*Ar*), 134.2 (*Ar*), 128.2 (*Ar*), 122.9 (*Ar*), 62.5 (NCH_2CH_2N), 35.2 (*C*(CH$_3$)$_3$), 31.2 (C(*C*H$_3$)$_3$), 12.01 (AlCH$_2$CH$_3$), 7.2 (br, AlCH_2CH$_3$). Anal. Calcd for $C_{48}H_{88}Al_2BaN_2$ (884.52): C, 65.18; H, 10.03; N, 3.17. Found: C, 65.38; H, 9.338; N, 3.08.

Crystallographic Data Collection and Refinement. Crystals of **2**, **3**, **4**, **6**, and **7** were grown by standard techniques from saturated solutions using toluene at −40 °C. Suitable single crystals of **2**, **3**, **4**, **6**, and **7** were selected in a glovebox and coated with Paratone-N oil (Hampton Research), fixed in a nylon loop (**3**, **7**) or on a glass fiber (**2**, **4**, **6**). Data collection for **3** and **7** was done on a Bruker SMART 2K CCD diffractometer using graphite-monochromated Mo K_α radiation (λ = 0.71073 Å) performing 182° ω-scans in four orthogonal φ positions. Raw data were collected using the program SMART[36] and integrated and reduced with the program SAINT.[37] Corrections for absorption effects were applied using SHELXTL and/or SADABS.[38] Data collection for **2**, **4**, and **6** was done on a STOE-IPDS II system. The structure was solved by direct methods using WinGX suite of programs including SHELXS and SHELXL for structure solution and refinement.[39] Further details of the refinement and crystallographic data are listed in Table 4 and in CIF files.

■ ASSOCIATED CONTENT

Supporting Information. CIF files giving full crystallographic data for complexes **2**, **3**, **4**, **6**, and **7**. This material is available free of charge via the Internet at http://pubs.acs.org. Crystallographic data have also been deposited at the Cambridge Crystallographic Data Centre under CCDC reference numbers 818906−818909 and 821801 and can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif.

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■ REFERENCES

(1) (a) Grignard, V. *C. R. Acad. Sci.* **1900**, *130*, 1322–1324. (b) Grignard, V. *Ann. Chim.* **1901**, *24*, 433–490. (c) Seyferth, D. *Organometallics* **2009**, *28*, 1598–1605.

(2) (a) Bickelhaupt, F. *J. Organomet. Chem.* **1994**, *475*, 1–14. (b) Westerhausen, M. *Angew. Chem., Int. Ed.* **2001**, *40*, 2975–2977. (c) Westerhausen, M.; Gärtner, M.; Fischer, R.; Langer, J.; Yu, L.; Reiher, M. *Chem.—Eur. J.* **2007**, *13*, 6292–6306.

(3) Schlenk, W.; Schlenk, W., Jr. *Chem. Ber.* **1929**, *62*, 920–924.

(4) Wehmschulte, R. J.; Power, P. P. *Organometallics* **1995**, *14*, 3264–3267.

(5) Al-Juaid, S. S.; Eaborn., C.; Hitchcock, P. B.; McGeary, C. A.; Smith, J. D. *Chem. Commun.* **1989**, 273–274.

(6) Hitchcock, P. B.; Howard, J. A. K.; Lappert, M. F.; Leung, W. P.; Mason, S. A. *Chem. Commun.* **1990**, 847–849.

(7) Starowieyski, K. B.; Lewinski, J.; Wozniak, R.; Lipkowski, J.; Chrost, A. *Organometallics* **2003**, *22*, 2458–2463.

(8) Sarazin, Y.; Schormann, M.; Bochmann, M. *Organometallics* **2004**, *23*, 3296–3302.

(9) Wang, Z.-X.; Qi, C.-Y. *Organometallics* **2007**, *26*, 2243–2251.
(10) Sánchez-Barba, L. J.; Garcés, A.; Fajardo, M.; Alonso-Moreno, C.; Fernández-Baeza, J.; Otero, A.; Antinolo, A.; Tejeda, J.; Lara-Sánchez, A.; López-Solera, M. *Organometallics* **2007**, *26*, 6403–6411.
(11) Goebel, W. D.; Hencer, L.; Oliver, J. P. *Organometallics* **1983**, *2*, 746–750.
(12) Bailey, P. J.; Coxall, R. A.; Dick, C. M.; Fabre, S.; Henderson, L. C.; Herber, C.; Liddle, S. T.; Loroño-Gonzàlez, D.; Parkin, A.; Parsons, S. *Chem.—Eur. J.* **2003**, *9*, 4820–4828.
(13) Reinmuth, M.; Wild, U.; Rudolf, D.; Kaifer, E.; Enders, M.; Wadepohl, H.; Himmel, H.-J. *Eur. J. Inorg. Chem.* **2009**, 4795–4808.
(14) (a) Bailey, P. J.; Dick, C. M.; Fabre, S.; Parsons, S.; Yellowlees, L. J. *Dalton Trans.* **2006**, 1602–1610. (b) Bailey, P. J.; Dick, C. M.; Fabre, S.; Parsons, S.; Yellowlees, L. J. *Chem. Commun.* **2005**, 4563–4565.
(15) Blackmore, I. J.; Gibson, V. C.; Hitchcock, P. B.; Rees, C. W.; Williams, D. J.; White, A. J. P. *J. Am. Chem. Soc.* **2005**, *127*, 6012–6020.
(16) For $AlMe_3$-promoted alkyl migrations, see, for example: (a) Lechler, R.; Hausen, H.-D.; Weidlein, J. *J. Organomet. Chem.* **1989**, *359*, 1–12. (b) Gibson, V. C.; Redshaw, C.; White, A. J. P.; Williams, D. J. *J. Organomet. Chem.* **1998**, *550*, 453–456. (c) Walfort, B.; Leedham., A. P.; Russell, C. A.; Stalke, D. *Inorg. Chem.* **2001**, *40*, 5668–5674. (d) Cortright, S. B.; Coalter, J. N., III; Pink, M.; Johnston, J. N. *Organometallics* **2004**, *23*, 5885–5888. (e) Chivers, T.; Copsey, M. C.; Parvez, M. *Chem. Commun.* **2004**, 2818–2819. (f) Knijnenburg, Q.; Smits, J. M. M.; Budzelaar, P. H. M. *Organometallics* **2006**, *25*, 1036–1046. (g) Gibson, V. C.; Redshaw, C.; Solan, G. A.; White, A. J. P.; Williams, D. J. *Organometallics* **2007**, *26*, 5119–5123. (h) Olson, J. A.; Boyd, R.; Quail, J. W.; Foley, S. R. *Organometallics* **2008**, *27*, 5333–5338.
(17) For $ZnMe_2$-promoted alkyl migrations, see, for example:(a) Braun, U.; Böck, B.; Nöth, H.; Schwab, I.; Schwartz, M.; Weber, S.; Wietelmann, U. *Eur. J. Inorg. Chem.* **2004**, 3612–3628. (b) Blackmore, I. J.; Gibson, V. C.; Hitchcock, P. B.; Rees, C. W.; Williams, D. J.; White, A. J. P. *J. Am. Chem. Soc.* **2005**, *127*, 6012–6020. (c) Fedushkin, I. L.; Tishkina, A. N.; Fukin, G. K.; Hummert, M.; Schumann, H. *Eur. J. Inorg. Chem.* **2008**, 483–489.
(18) For group 3-promoted alkyl migrations, see, for example: (a) Zimmermann, M.; Törnroos, K. W.; Anwander, R. *Angew. Chem., Int. Ed.* **2007**, *46*, 3126–3130. (b) Kaneko, H.; Tsurugi, H.; Panda, T. K.; Mashima, K. *Organometallics* **2010**, *29*, 3463–3466.
(19) For group 4 metal-promoted diimine alkylation, see: (a) Mashima, K.; Ohnishi, R.; Yamagata, T.; Tsurugi, H. *Chem. Lett.* **2007**, *36*, 1420–1421.(b) Murray, R. E. U.S. Patent 6,096,676 (Union Carbide Corp.), 2000. (c) De Waele, P.; Jazdzewski, B. A.; Klosin, J.; Murray, R. E.; Theriault, C. N.; Vosejpka, P. C.; Petersen, J. L. *Organometallics* **2007**, *26*, 3896–3899. (d) Tsurugi, H.; Ohnishi, R.; Kaneko, H.; Panda, T. K.; Mashima, K. *Organometallics* **2009**, *28*, 680–687. (e) Tsurugi, H.; Yamamoto, K.; Mashima, K. *J. Am. Chem. Soc.* **2011**, *133*, 732–735.
(20) For review articles, see: (a) Fischbach, A.; Anwander, R. *Adv. Polym. Sci.* **2006**, *204*, 155–281. (b) Zimmermann, M.; Anwander, R. *Chem. Rev.* **2010**, *110*, 6194–6259.
(21) For recent examples, see: (a) Zimmermann, M.; Frøystein, N. Å.; Fischbach., A.; Sirsch, P.; Dietrich, H. M.; Törnroos, K. W.; Herdtweck, E.; Anwander, R. *Chem.—Eur. J.* **2007**, *13*, 8784–8800. (b) Litlabø, R.; Zimmermann, M.; Saliu, K.; Takats, J.; Törnroos, K. W.; Anwander, R. *Angew. Chem., Int. Ed.* **2008**, *47*, 9560–9564. (c) Dietrich, H. M.; Ziller, J. W.; Anwander, R.; Evans, W. J. *Organometallics* **2009**, *28*, 1173–1179. (d) Zimmermann, M.; Litlabø, R.; Törnroos, K. W.; Anwander, R. *Organometallics* **2009**, *28*, 6646–6649. (e) Dietrich, H. M.; Törnroos, K. W.; Herdtweck, E.; Anwander, R. *Organometallics* **2009**, *28*, 6739–6749. (f) Dietrich, H. M.; Törnroos, K. W.; Herdtweck, E.; Anwander, R. *Dalton Trans.* **2010**, *39*, 5783–5785. (g) Occhipinti, G.; Meermann, C.; Dietrich, H. M.; Litlabø, R.; Auras, F.; Törnroos, K. W.; Maichle-Mössmer, C.; Jensen, V. R.; Anwander, R. *J. Am. Chem. Soc.* **2011**, *133*, 6323–6337. (h) Michel, O.; Törnroos, K. W.; Maichle-Mössmer, C.; Anwander, R. *Chem.—Eur. J.* **2011**, *17*, 4964–4967.
(22) Atwood, J. L.; Stucky, G. D. *J. Am. Chem. Soc.* **1969**, *91*, 2538–2543.
(23) (a) Ziegler, K.; Holzkamp, E. *Liebigs Ann. Chem.* **1957**, *605*, 93–97. (b) Michel, O.; Meermann, C.; Törnroos, K. W.; Anwander, R. *Organometallics* **2009**, *28*, 4783–4790.
(24) (a) Fischbach, A.; Herdtweck, E.; Anwander, R.; Eicherling, G.; Scherer, W. *Organometallics* **2003**, *22*, 499–509. (b) Fischbach, A.; Perdih, F.; Herdtweck, E.; Anwander, R. *Organometallics* **2006**, *25*, 1626–1642. (c) Dietrich, H. M.; Törnroos, K. W.; Herdtweck, E.; Anwander, R. *Organometallics* **2009**, *28*, 6739–6749.
(25) For examples, see: (a) Zimmermann, M.; Törnroos, K. W.; Anwander, R. *Organometallics* **2006**, *25*, 3593–3598. (b) Zimmermann, M.; Estler, F.; Herdtweck, E.; Törnroos, K. W.; Anwander, R. *Organometallics* **2007**, *26*, 6029–6041.
(26) For bonding parameters in Mg—Al amido—alkyl complexes, see: (a) Her, T.-Y.; Chang, C.-C.; Liu, L.-K. *Inorg. Chem.* **1992**, *31*, 2291–2294. (b) Her, T.-Y.; Chang, C.-C.; Lee, G.-H.; Peng, S.-M.; Wang, Y. *Inorg. Chem.* **1994**, *33*, 99–104.
(27) Goebel, D. W.; Hencher, J. L., Jr.; Oliver, J. P. *Organometallics* **1983**, *2*, 746–750.
(28) Thomas, F.; Bauer, T.; Schulz, S.; Nieger, M. *Z. Anorg. Allg. Chem.* **2003**, *629*, 2018–2027.
(29) Tsurugi, H.; Yamagata, T.; Tani, K.; Mashima, K. *Chem. Lett.* **2003**, *32*, 756–757.
(30) For μ-η^1:η^2-[$AlMe_4$] coordination mode, see: (a) Dietrich, H. M.; Schuster, O.; Törnroos, K. W.; Anwander, R. *Angew. Chem., Int. Ed.* **2006**, *45*, 4858–4863. (b) Zimmermann, M.; Volbeda, J.; Törnroos, K. W.; Anwander, R. *C. R. Chim.* **2010**, *13*, 651–660.
(31) (a) Klimpel, M. G.; Anwander, R.; Tafipolsky, M.; Scherer, W. *Organometallics* **2001**, *20*, 3983–3992. (b) Sommerfeldt, H.-M.; Meermann, C.; Schrems, M. G.; Törnroos, K. W.; Frøystein, N. A.; Miller, R. J.; Scheidt, E.-W.; Scherer, W.; Anwander, R. *Dalton Trans.* **2008**, 1899–1907.
(32) Gerteis, R. L.; Dickerson, R. E.; Brown, T. L. *Inorg. Chem.* **1964**, *3*, 872–875.
(33) Chisholm, M. H.; Gallucci, J. C.; Yaman, G. *Dalton Trans.* **2009**, 368–374.
(34) Saheki, Y.; Sasada, K.; Satoh, N.; Kawaichi, N.; Negoro, K. *Chem. Lett.* **1987**, *16*, 2299–2300.
(35) Simion, A.; Simion, C.; Kanda, T.; Nagashima, S.; Mitoma, Y.; Yamada, T.; Mimura, K.; Tahiro, M. *J. Chem. Soc., Perkin Trans. 1* **2001**, 2071–2078.
(36) *SMART* v. 5.054; Bruker AXS Inc.: Madison, WI, 1999.
(37) *SAINT* v. 6.45a; Bruker AXS Inc.: Madison, WI, 2003.
(38) (a) *SHELXTL* v. 6.14; Bruker AXS Inc.: Madison, WI, 2003. (b) Sheldrix, G. M. *SADABS* v. 2008/1; University of Göttingen: Germany, 2006.
(39) (a) *X-AREA 1.26*; Stoe & Cie GmbH: Darmstadt, Germany, 2004. (b) Farrugia, F. *J. Appl. Crystallogr.* **1999**, *32*, 837–838.(c) Sheldrick, G. M. *SHELXS 97, Program for the Solution of Crystal Structures*; Göttingen, Germany, 1997. (d) *X-RED 1.26, Data Reduction for STAD4 and IPDS*; Stoe & Cie: Darmstadt, 1996. (e) *X-SHAPE 2.05, Crystal Optimization for Absorption Correction*; Stoe & Cie: Darmstadt, Germany, 1996.