ORGANOMETALLICS

Article

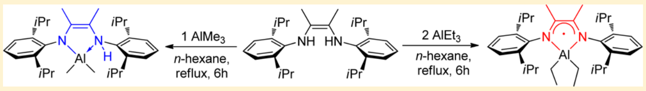
pubs.acs.org/Organometallics

Synthesis and Reactions of a Redox-Active α-Diimine Aluminum Complex

Jianfeng Li, Kun Zhang, Hanmin Huang, Ao Yu, Hongfan Hu, Haiyan Cui, and Chunming Cui*

State Key Laboratory of Elemento-Organic Chemistry, Nankai University, Tianjin 300071, People's Republic of China

Supporting Information

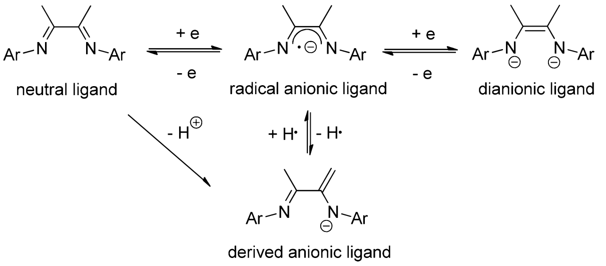


ABSTRACT: The reaction of the ene-diamine LH_2 (L = $[ArNC(Me)C(Me)NAr]^{2-}$, Ar = 2,6-iPr$_2C_6H_3$) with $AlMe_3$ and $AlEt_3$ yielded the aluminum dimethyl complex $(LH)AlMe_2$ (**1**) and the radical $(L^{\bullet})AlEt_2$ (**2**; $L^{\bullet}$ = $[ArNC(Me)C(Me)NAr]^{\bullet-}$), respectively. Treatment of **2** with O_2 and TEMPO (2,2,6,6-tetramethylpiperidin-1-oxyl) led to hydrogen abstraction from the methyl group at the ligand backbone to give the diamagnetic species $(L^*)AlEt_2$ (**3**; L^* = $[ArN{=}C(Me)C(CH_2)NAr]^{-}$) and $(L^*)Al(TEMPO)(Et)$ (**4**). In contrast, the reaction of **2** with iodine resulted in the iodination of the Al−C bonds and yielded the radical $(L^{\bullet})AlI_2$ (**5**). Reaction of **2** with BCl_3 led to electron transfer between the α-diimine radicals with the formation of the aluminum cation $[(L^0)AlCl_2]^+[AlCl_4]^-$ (**6**; L^0 = $ArN{=}C(Me)(Me)C{=}NAr$) and the diazaborole LBCl (**7**). The structures of compounds **2**, **3**, and **7** have been determined by X-ray single-crystal diffraction, and the paramagnetic species **2** has been characterized by EPR measurements.

INTRODUCTION

The introduction of noninnocent ligands into metal complexes has attracted intense interest in the past decade, as the cooperation of a metal ion and the ligand offers a unique opportunity to modify the reactivity of the corresponding complexes.[1,2] Main-group-element complexes based on ligands containing α-diimine moieties, such as 1,4-diazabutadiene,[3] bis(imino)acenaphthene,[4] iminopyridine[5] and bipyridine,[6] are typical representatives. The α-diimine backbone can undergo one- or two-electron reduction to form the corresponding radical anion and dianionic ene-diamide ligand (Chart 1),[5b,7,8] which allows the generally redox-inactive main-group ions to access multiple redox states.[4b,5a]

Chart 1. Chemical Conversions of Noninnocent α-Diimine Ligands



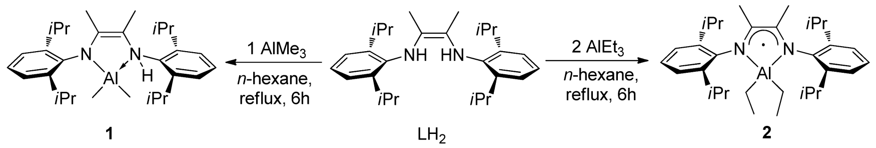
Main-group-element complexes supported by a radical anionic α-diimine ligand, in general, can be prepared by two different routes: (i) reduction of the adducts formed by neutral α-diimines with main-group precursors via a single-electron transfer process[3g] or reduction with main-group metals and low-valent main-group halides such as Li, Ba, Al, GaI, InCl, and $GeCl_2$[3c−f,4a] and (ii) salt elimination reactions of alkali-metal salts of radical anionic α-diimines with main-group metal halides.[3h,4,5b−d] The formation of a paramagnetic aluminum complex by the transmetalation of a redox-active ligand from a transition-metal complex has also been reported.[5e] Herein we report on the direct generation of the α-diimine diethylaluminum radical **2** by the reaction of triethylaluminum with an ene-diamine (Scheme 1). Moreover, the radical **2** can be involved in electron-transfer reactions, as demonstrated by its reactions with dioxygen, TEMPO (2,2,6,6-tetramethylpiperidin-1-oxyl), and BCl_3.[9]

RESULTS AND DISCUSSION

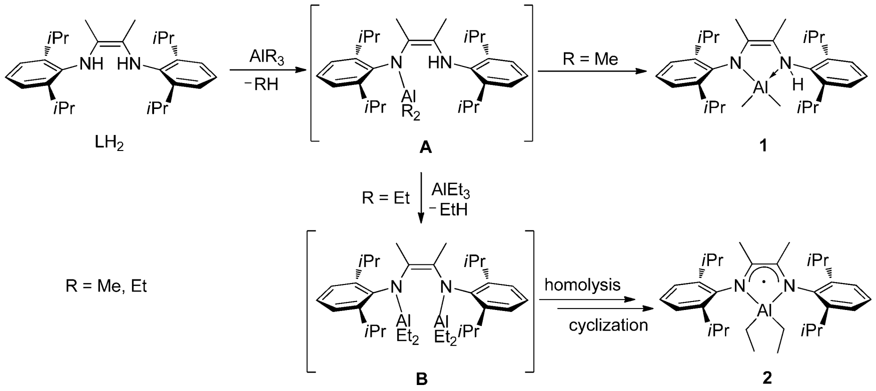
The reactions of the ene-diamine LH_2 (L = $[ArNC(Me)C(Me)NAr]^{2-}$, Ar = 2,6-iPr$_2C_6H_3$) with the three different aluminum alkyls $AlMe_3$, $AlEt_3$, and Al(iBu)$_3$ have been investigated for the preparation of the desired aluminum compounds. Reaction of $AlMe_3$ with 1 equiv of LH_2 in refluxing n-hexane yielded the neutral compound $(LH)AlMe_2$ (**1**) as orange crystals in good yield (Scheme 1). However, similar reactions with $AlEt_3$ and Al(iBu)$_3$ resulted in oily mixtures, from which a product could not be isolated and characterized. Reaction of LH_2 with 2 equiv of $AlMe_3$ also yielded **1** as the sole isolable product under different conditions. In contrast, reaction of LH_2 with 2 equiv of $AlEt_3$ in refluxing n-hexane afforded air- and moisture-sensitive red crystals of the radical $(L^{\bullet})AlEt_2$ (**2**; $L^{\bullet}$ = $[ArNC(Me)C(Me)NAr]^{\bullet-}$) in high yield (82%) with the formation of aluminum powder.[10] A similar reaction with 2 equiv of Al(iBu)$_3$ led to the formation of a complicated mixture. Attempts to isolate a single product from the mixture were unsuccessful to date. These results indicated

Received: September 28, 2012

Scheme 1. Synthesis of Complexes 1 and 2



Scheme 2. Proposed Synthetic Pathways of 1 and 2



that the steric factors of aluminum trialkyls have substantial effects on the reactions.

Since no products can be isolated for the reaction of LH_2 with 1 equiv of $AlEt_3$, we proposed that the initial product $(LH)AlEt_2$ (Scheme 2, **A**) as formed in the reaction of $AlMe_3$ cannot form the same cyclic structure as **1**, due to the steric effects of ethyl groups in comparison to small methyl groups in **1**, and thus another free NH group in $(LH)AlEt_2$ can easily react with an excess of $AlEt_3$ to give the dimetallic intermediate **B** (Scheme 2).[11] This dimetallic species subsequently underwent the homolytic cleavage of one of the Al—N bonds to give the radical **2**.[12] The reaction of $AlEt_3$ with the same amount of isocyanide ligands in $Ir_2(CNR)_4(dmpm)$ (R = 2,6-$Me_2C_6H_3$, dmpm = $Me_2PCH_2PMe_2$) has been reported to yield the radical complex $Ir_2[C_2(NR)_2AlEt_2](CNR)_2(dmpm)_2$.[13] The failure to give the similar radical species in the reaction of $AlMe_3$ may be attributed to the stable five-membered-ring structure of **1**. Indeed, reaction of **1** with $AlMe_3$ in refluxing *n*-hexane and even in hot toluene for several hours only led to the recovery of a significant amount of **1**.

The structure of **1** was identified by ^1H and ^{13}C NMR and IR spectroscopy and elemental analysis. In the ^1H NMR spectrum, the two methyl groups bonded to the aluminum atom show two singlets at δ −0.51 and −0.29 ppm and the remaining proton on one of the nitrogen atoms resonates at δ 6.01 ppm, which is shifted to low field in comparison to the free amine due to the nitrogen coordination to the aluminum atom. The paramagnetic compound **2** has been characterized by EPR spectroscopy in toluene. Figure 1 shows the EPR spectrum of **2** and the corresponding simulated spectrum. The signals of the EPR spectrum are well resolved except those at the ends of the spectrum, which are probably due to the fact that the resonances at low and high field are beyond the detection limit of the instrument. The ^{27}Al and ^{14}N nuclei in **2** feature large hyperfine coupling constants in comparison to those in $(Ar\text{-}BIAN^\bullet)AlEt_2$[4c] (Ar-BIAN = 1,2-bis[(2,6-diisopropylphenyl)imino]acenaphthene) and $[ArNC(H)C(H)NAr^\bullet]AlI_2$[3d] (Ar = 2,6-$iPr_2C_6H_3$) (Table 1). These differences suggested that the unpaired electron in **2** distributes more electron density to the central five-membered ring atoms than those in $(Ar\text{-}BIAN^\bullet)AlEt_2$ and $[ArNC(H)C(H)NAr^\bullet]AlI_2$, since the two reported complexes have a naphthalene unit or two electronegative iodine atoms, which can share electron density of the unpaired electron via delocalization to the large aromatic ring and the iodine atoms, respectively.

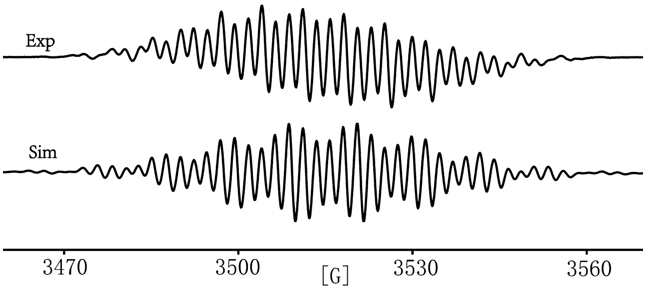


Figure 1. Experimental (in toluene at 298 K) and simulated EPR spectra of **2**.

Table 1. Isotropic *g* and Hyperfine Coupling Constants (mT) for 2, $(Ar\text{-}BIAN^\bullet)AlR_2$ (R = Me, Et, *i*Bu),[4c] and $[ArNC(H)C(H)NAr^\bullet]AlI_2$,[3d] Obtained from Computer Simulations of the Corresponding EPR Spectra[a]

		hyperfine coupling			
complex	g_{iso}	^{27}Al	$^{14}N^b$	^1H	^{127}I
2	2.0029	1.17	0.94	0.25^c	
$(Ar\text{-}BIAN^\bullet)AlMe_2$	2.0031	0.60	0.46	$0.14^d/0.10^e$	
$(Ar\text{-}BIAN^\bullet)AlEt_2$	2.0033	0.62	0.46	$0.14^d/0.10^e$	
$(Ar\text{-}BIAN^\bullet)Al\textit{i}Bu_2$	2.0032	0.61	0.46	$0.14^d/0.10^e$	
$[ArNC(H)C(H)NAr^\bullet]AlI_2$	2.0038	0.285	0.67	0.59^f	0.04

[a] Ar = 2,6-$iPr_2C_6H_3$. [b] ^{14}N refers to two equivalent nitrogen nuclei. [c] Refers to six equivalent ^1H nuclei in two equivalent methyl groups of ligand $L^\bullet$. [d] Refers to two equivalent ^1H nuclei in ortho positions of the naphthalene system (relative to the diimine fragment). [e] Refers to two equivalent ^1H nuclei in para positions of the naphthalene system (relative to the diimine fragment). [f] Refers to two equivalent imine ^1H nuclei.

The structure of **2** in Figure 2 shows that the aluminum atom is four-coordinate, being bound to the radical anionic ligand in an η^2 fashion. The aluminum atom in **2** can be best described as having a distorted-tetrahedral geometry due to the small N1−Al1−N2 angle (85.28(8)°). This angle is very close to that observed in (Ar-BIAN$^•$)AlEt$_2$ (85.31(12)°).[4c] The average Al−C bond length of 1.981(3) Å in **2** is only slightly longer than that observed in (Ar-BIAN$^•$)AlEt$_2$ (average 1.962(4) Å); the average Al−N bond length of 1.925(2) Å in **2** is slightly shorter than those reported for (Ar-BIAN$^•$)AlEt$_2$ (average 1.957(3) Å). The bond lengths in the NCCN fragment of the ene-diamine ligand (C−C = 1.391(3) Å, C−N = 1.383(3) Å (average)) lie between those of double and single bonds reported for free ene-diamines (C−C = 1.339(2) Å, C−N = 1.431(2) Å (average))[14] and free α-diimines (C−C = 1.498(3) Å, C−N = 1.279(3) Å (average)),[15] indicating the delocalized five-membered-ring framework.

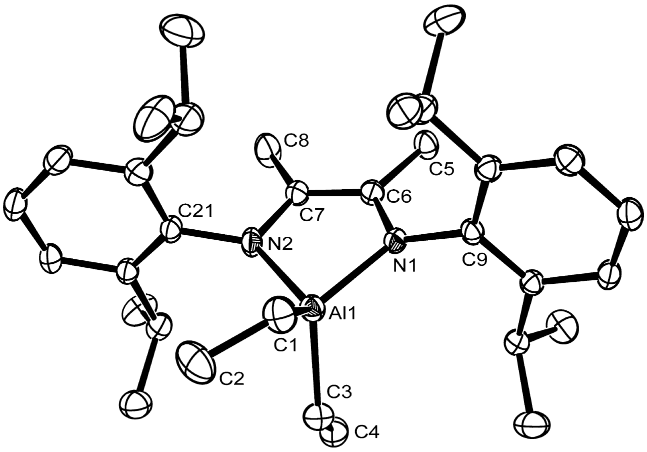
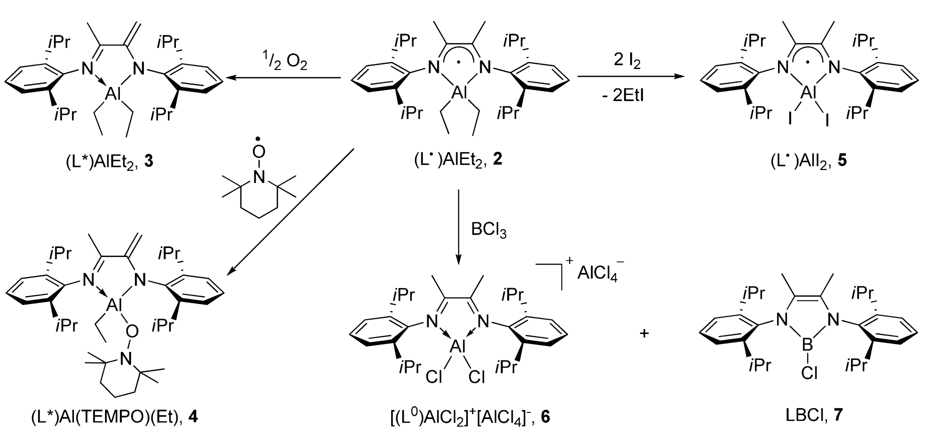


Figure 2. ORTEP representation of the X-ray structure of **2**. Hydrogen atoms and disordered atom C29′ have been omitted for clarity. Thermal ellipsoids are drawn at the 30% probability level. Selected bond lengths (Å) and angles (deg): Al1−N1 = 1.914(2), Al1−N2 = 1.935(2), Al1−C1 = 1.963(3), Al1−C3 = 1.999(3), N1−C6 = 1.375(3), N2−C7 = 1.390(3), C5−C6 = 1.503(3), C6−C7 = 1.391(3), C7−C8 = 1.488(3); N1−Al1−N2 = 85.28(8), C1−Al1−C3 = 107.68(12).

The reactions of **2** with dioxygen[16] and the oxyl radical TEMPO (2,2,6,6-tetramethylpiperidin-1-oxyl)[4e,17] were investigated. When a red solution of **2** in *n*-hexane was exposed to $^1/_2$ equiv of dioxygen at −78 °C, the solution immediately turned light yellow. The compound (L*)AEt$_2$ (**3**; L* = [ArN=C(Me)C(CH$_2$)NAr]$^-$) was isolated in 34% yield after a standard workup. In addition, small amounts of aluminum metal and 3,3′,5,5′-tetraisopropyl-1,1′-biphenyl-4,4′-diamine were isolated. Obviously, **3** was formed by the abstraction of a hydrogen radical from one of the methyl groups on the ligand backbone in **2**.[18] It is quite possible that the radical species **2** initially couples with dioxygen to form a peroxyl radical, which is highly reactive and rapidly abstracts the hydrogen atom from the rest of **2** in the reaction system to yield **3** and a hydroperoxide. The peroxide may degrade to aluminum metal and some organic fragments, including the isolated compound 3,3′,5,5′-tetraisopropyl-1,1′-biphenyl-4,4′-diamine. The reactions of **2** with 1 equiv or more of dioxygen led to the formation of an oily mixture containing a number of species which could not be identified to date. These experiments support the abstraction of hydrogen by the initially formed peroxyl radical intermediate rather than by dioxygen itself. The mechanism is further supported by the reaction of **2** with TEMPO. The reaction of **2** with TEMPO in toluene from −78 °C to room temperature afforded the compound (L*)Al(TEMPO)(Et) (**4**) (Scheme 3). It appears that the TEMPO radical acted as a radical trap reagent to abstract hydrogen radical from one of the methyl groups on the ligand backbone in **2** to generate TEMPOH and **3** followed by the ethane elimination reaction of TEMPOH with **3**. In order to prove the last step of the reaction, the reaction of TEMPOH with **3** was performed. As expected, this reaction indeed yielded **4**, as indicated by NMR analysis.

The structure of **3** has been confirmed by X-ray single-crystal diffraction and is shown in Figure 3. The Al1−N1 bond length of 1.874(2) Å is significantly shorter than Al1−N2 (1.966(2) Å). In addition, the N2−C15 bond length of 1.295(3) Å and the C13−C14 bond length of 1.335(4) Å are indicative of N=C and C=C double bonds. These parameters suggest a monoanionic ligand framework featuring an exocyclic C=C double bond. The ^{1}H NMR spectrum of **3** shows two singlets at δ 4.03 and 4.46 ppm, attributed to exocyclic C*H*$_2$ resonances. In ^{13}C NMR spectrum, the two singlets at δ 94.03 and 141.58 ppm can be assigned to the carbon atoms of the exocyclic CH$_2$ and imine carbon in the ring. Compound **4** was characterized by ^{1}H and ^{13}C NMR, IR, and mass spectroscopy and elemental analysis. Consistent with the ^{1}H NMR and ^{13}C NMR spectroscopic data of **3**, those of **4** show two singlets (δ 4.14

Scheme 3. Reactivity of 2



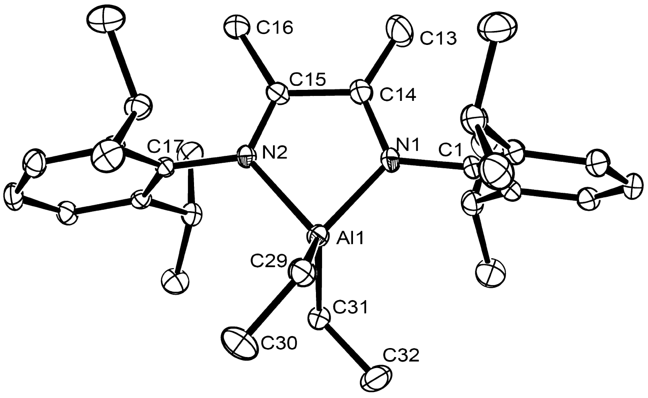


Figure 3. ORTEP representation of the X-ray structure of **3**. Hydrogen atoms have been omitted for clarity. Thermal ellipsoids are drawn at the 30% probability level. Selected bond lengths (Å) and angles (deg): Al1−N1 = 1.874(2), Al1−N2 = 1.966(2), Al1−C29 = 1.965(3), Al1−C31 = 1.956(3), N1−C14 = 1.381(3), N2−C15 = 1.295(3), C13−C14 = 1.335(4), C14−C15 = 1.485(3), C15−C16 = 1.489(4); N1−Al1−N2 = 83.64(9), C29−Al1−C31 = 112.43(12).

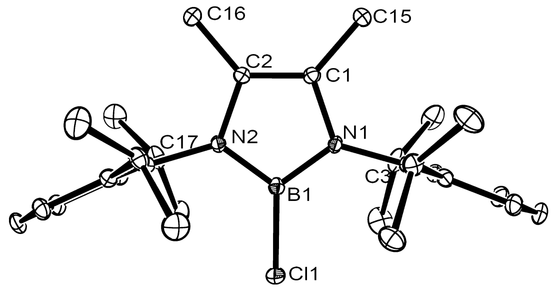


Figure 4. ORTEP representation of the X-ray structure of **7**. Hydrogen atoms have been omitted for clarity. Thermal ellipsoids are drawn at the 30% probability level. Selected bond lengths (Å) and angles (deg): B1−N1 = 1.4096(15), B1−N2 = 1.4105(16), B1−Cl1 = 1.7739(14), N1−C1 = 1.4256(14), N2−C2 = 1.4229(14), C1−C2 = 1.3515(16), C1−C15 = 1.4924(16), C2−C16 = 1.4904(16); N1−B1−N2 = 107.35(10), N1−B1−Cl1 = 126.73(10), N2−B1−Cl1 = 125.93(9).

(C═C*H*H), 4.49 (C═CH*H*) ppm) in the proton NMR and two singlets (δ 95.27 (C═CH_2), 142.95 (*C*═CH_2) ppm) in the ^{13}C NMR spectrum. These data indicated that the ligands in **3** and **4** have the same coordination mode.

Reaction of **2** with iodine yielded the aluminum diiodide $(L^\bullet)AlI_2$ (**5**). It has been reported that reactions of aluminum dimethyl and diethyl complexes with iodine provided an efficient and facile route to the corresponding aluminum diiodides.[19] The mechanism for this reaction has not been well established. It is quite possible that the alkyl anion arising from the highly polarized Al−C bond initially attacks iodine to form an alkyl iodide followed by the combination of the aluminum cation with the iodide ion. In the reaction of **2** with iodine, the delocalized radical is not involved in the reaction and only acts as a spectator ligand. The paramagnetic species **5** was characterized by EPR (Figure 1S in the Supporting Information), IR, and mass spectroscopy and elemental analysis. The similar paramagnetic diiodide $[ArNC(H)C(H)NAr^\bullet]AlI_2$ was prepared by the reaction of the corresponding α-diimine with AlI_3 in the presence of aluminum powder in toluene.[3g] Reaction of **2** with 1 equiv of BCl_3 in *n*-hexane yielded the neutral α-diimine-stabilized cationic aluminum dichloride $[(L^0)AlCl_2]^+[AlCl_4]^-$ (**6**; L^0 = ArN═C(Me)(Me)C═NAr) and the diazaborole LBCl (**7**). Compounds **6** and **7** were characterized by ^{1}H and ^{13}C NMR, IR, and mass spectroscopy and elemental analysis. The structure of **7** was determined by an X-ray single-crystal analysis (Figure 4). Compound **7** features the ene-diamide ligand, as indicated by the planar and delocalized BN_2C_2 five-membered ring and the three-coordinate boron atom with a planar geometry. These structural features are similar to those reported for the diazaboroles [ArNC(R)C(R)NAr]BCl (R = H, Cl, Ph).[3e,20] The formation of **6** and **7** apparently resulted from the electron transfer between the ligand in the different molecules. The mechanism for the reaction has yet to be investigated. However, it is possible that transmetalation of the radical anionic ligand from aluminum to boron may take place during the reaction. The driving force for the electron transfer reaction can be attributed to the high stability of the aromatic diazaborole ring.

■ CONCLUSION

The paramagnetic aluminum diethyl compound **2** has been prepared in a one-step reaction of the diamine ligand LH_2 with triethylaluminum. The variation of aluminum alkyls did not yield similar paramagnetic species, indicating that the reaction is sensitive to the steric factors of aluminum alkyls. The radical **2** could be converted to a diamagnetic species in the presence of peroxyl and oxyl radicals via the abstraction of a hydrogen atom from **2**. The electron transfer from ligand to ligand in the different coordination environments may also take place, as indicated by the reaction of **2** with BCl_3. The delocalized radical ligand in **2** can also act as a spectator ligand in the reaction of **2** with iodine. The results demonstrated that the anionic radical α-diimine ligand in **2** not only participates in electron transfer reactions but also acts as a spectator ligand.

■ EXPERIMENTAL SECTION

All manipulations involving air- and moisture-sensitive compounds were carried out under an atmosphere of dry argon by using modified Schlenk-line and glovebox techniques. Elemental analyses were carried out using an Elementar Vario EL analyzer. The ^{1}H, ^{11}B, and ^{13}C NMR spectroscopic data were recorded on a Bruker AV400 spectrometer. Infrared spectra were recorded on a Bio-Rad FTS 6000 spectrophotometer. An EPR spectrum was recorded on a Bruker EMX-6/1 spectrometer. Computer simulation was performed using the WINEPR SimFoniA Bruker software.[21] The solvents (THF, toluene, *n*-hexane, and diethyl ether) were freshly distilled from sodium and degassed prior to use. The ene-diamine[14] and TEMPOH[22] were synthesized according to the published procedures. Other chemicals were of analytical grade and were used as received.

Synthesis of (LH)AlMe$_2$ (1). A solution of $AlMe_3$ (5 mL, 1 M in toluene) in *n*-hexane (10 mL) was added to a solution of LH_2 (2.03 g, 5 mmol) in *n*-hexane (40 mL). Then the mixture was refluxed for 6 h. The resulting orange solution was concentrated to 5 mL. Storage at −35 °C overnight afforded orange crystals of **1** (1.55 g, 67%). Mp: 210−212 °C. Anal. Calcd for $C_{30}H_{47}AlN_2$ (462.69): C, 77.88; H, 10.24; N, 6.05. Found: C, 77.35; H, 10.73; N, 5.99. ^{1}H NMR (C_6D_6, 400 MHz, 25 °C): δ −0.51 (s, 3H, Al*Me*), −0.29 (s, 3H, Al*Me*), 1.02 (d, *J* = 6.5 Hz, 3H, CH*Me*$_2$), 1.09 (d, *J* = 6.7 Hz, 3H, CH*Me*$_2$), 1.17 (d, *J* = 6.5 Hz, 3H, CH*Me*$_2$), 1.27 (d, *J* = 6.8 Hz, 3H, CH*Me*$_2$), 1.31 (d, *J* = 6.8 Hz, 3H, CH*Me*$_2$), 1.37 (d, *J* = 6.7 Hz, 3H, CH*Me*$_2$), 1.41 (s, 6H, C*Me*), 1.42 (d, *J* = 6.1 Hz, 6H, CH*Me*$_2$), 2.83 (sept, *J* = 6.7 Hz, 1H, C*H*Me$_2$), 3.61 (sept, *J* = 6.6 Hz, 1H, C*H*Me$_2$), 3.69 (sept, *J* = 6.8 Hz, 1H, C*H*Me$_2$), 3.93 (sept, *J* = 6.8 Hz, 1H, C*H*Me$_2$), 6.01 (s, 1H, N*H*), 6.91−7.23 (m, 6H, Ar-*H*). ^{13}C NMR (C_6D_6, 100 MHz, 25 °C): δ −9.65 (Al*Me*), −6.09 (Al*Me*), 14.56 (C*Me*), 23.59, 24.95, 25.57, 26.47, 27.73 (CH*Me*$_2$), 28.37, 28.85 (*C*HMe$_2$), 101.53 (CN), 124.03, 124.29, 125.87, 126.19, 126.85, 135.40, 140.62, 141.38, 142.87, 147.74, 148.55 (Ar-*C*). EI-MS: *m*/*z* (%) 462.4 (25).

Synthesis of ($L^•$)AlEt$_2$ (2). A solution of $AlEt_3$ (1.14 g, 10 mmol) in *n*-hexane (10 mL) was added to a solution of LH_2 (2.03 g, 5 mmol) in *n*-hexane (40 mL). Then the mixture was refluxed for 6 h. After filtration the red solution was concentrated to 5 mL. Storage at −35 °C overnight afforded red crystals of **2** (2.01 g, 82%). Mp: 124−126 °C. Anal. Calcd for $C_{32}H_{50}AlN_2$ (489.72): C, 78.48; H, 10.29; N, 5.72. Found: C, 77.91; H, 10.30; N, 5.65. EPR (25 °C, toluene): $g = 2.0029$, $A_{Al} = 1.17$ mT, $A_N = 0.94$ mT (2N), $A_H = 0.25$ mT (6H). IR (cm^{-1}): $\tilde{\nu}$ 685 (m), 762 (m), 766 (m), 935 (m), 1024 (m), 1100 (m), 1117 (m), 1182 (m), 1216 (w), 1259 (m), 1324 (m), 1362 (m), 1382 (m), 1430 (m), 1463 (m), 1588 (m), 1641 (m), 1705 (w), 2722 (w), 2868 (m), 2961 (s), 3062 (m). EI-MS: *m*/*z* (%) 489.1 (16).

Synthesis of (L*)AlEt$_2$ (3). Dry O_2 gas (22.4 mL, 1 mmol) was injected by syringe into a solution of **2** (980 mg, 2 mmol) in *n*-hexane (20 mL) at −78 °C. The mixture was stirred and warmed to room temperature. After filtration the yellow solution was concentrated to 3 mL. Storage at −35 °C overnight afforded yellow crystals of **3** (0. 33 g, 34%). Mp: 122−124 °C. Anal. Calcd for $C_{32}H_{49}AlN_2$ (488. 71): C, 78.64; H, 10.11; N, 5.73. Found: C, 78.37; H, 10.19; N, 5.41. ^{1}H NMR (C_6D_6, 400 MHz, 25 °C): δ 0.31 (q, *J* = 9.1 Hz, 4H, AlC*H*$_2$), 0.87 (d, *J* = 6.7 Hz, 6H, CH*Me*$_2$), 1.16 (t, *J* = 9.1 Hz, 6H, AlCH$_2$*Me*), 1.28 (d, *J* = 6.8 Hz, 6H, CH*Me*$_2$), 1.32 (d, *J* = 6.8 Hz, 6H, CH*Me*$_2$), 1.43 (d, *J* = 6.8 Hz, 6H, CH*Me*$_2$), 1.64 (s, 3H, C*Me*), 2.98 (sept, *J* = 6.7 Hz, 2H, C*H*Me$_2$), 3.60 (sept, *J* = 6.9 Hz, 2H, C*H*Me$_2$), 4.03 (s, 1H, CC*H*H), 4.46 (s, 1H, CCH*H*), 7.02−7.27 (m, 6H, Ar-*H*). ^{13}C NMR (C_6D_6, 100 MHz, 25 °C): δ 0.24 (Al*C*H$_2$), 9.55 (AlCH$_2$*Me*), 17.55 (C*Me*), 23.89, 24.73, 24.89, 26.17 (CH*Me*$_2$), 28.37, 28.56 (*C*HMe$_2$), 94.03 (C*C*H$_2$), 124.43, 124.74, 126.09, 138.71, 141.44, 146.79, 153.12 (Ar-*C*), 141.58 (*C*CH$_2$), 181.24 (*C*=N). IR (cm^{-1}): $\tilde{\nu}$ 442 (m), 561 (m), 566 (m), 623 (m), 642 (s), 744 (m), 795 (s), 978 (m), 1026 (m), 1105 (m), 1183 (m), 1217 (m), 1255 (m), 1318 (m), 1349 (m), 1438 (m), 1464 (m), 1564 (m), 1580 (s), 2864 (s), 2968 (s). EI-MS: *m*/*z* (%) 488.2 (31).

Synthesis of (L*)Al(TEMPO)(Et) (4). A solution of TEMPO (156 mg, 1 mmol) in toluene (10 mL) was added to **2** (490 mg, 1 mmol) in toluene at −78 °C. The mixture was warmed to room temperature and stirred continuously for 8 h. All volatile materials were removed under vacuum. The yellow residue was extracted with 10 mL of *n*-hexane, and the yellow filtrate was concentrated. Storage at −35 °C overnight afforded yellow crystals of **4** (0.41 g, 67%). Mp: 198−200 °C. Anal. Calcd for $C_{39}H_{62}AlN_3O$ (615.91): C, 76.05; H, 10.15; N, 6.82. Found: C, 75.89; H, 10.58; N, 5.98. ^{1}H NMR (C_6D_6, 400 MHz, 25 °C): δ 0.54 (q, *J* = 7.9 Hz, 2H, AlC*H*$_2$), 0.65 (s, 3H, TEMPO-*Me*), 078 (s, 3H, TEMPO-*Me*), 0.94 (d, *J* = 6.4 Hz, 3H, CH*Me*$_2$), 0.96 (d, *J* = 6.4 Hz, 3H, CH*Me*$_2$), 1.02 (s, 6H, TEMPO-*Me*), 1.29 (d, *J* = 7.0 Hz, 3H, CH*Me*$_2$), 1.30 (m, 4H, TEMPO-C*H*$_2$), 1.32 (d, *J* = 7.0 Hz, 3H, CH*Me*$_2$), 1.40 (d, *J* = 6.8 Hz, 3H, CH*Me*$_2$), 1.43 (m, 2H, TEMPO-C*H*$_2$), 1.45 (d, *J* = 6.9 Hz, 3H, CH*Me*$_2$), 1.54 (t, *J* = 7.9 Hz, 3H, AlCH$_2$*Me*), 1.55 (d, *J* = 6.8 Hz, 6H, CH*Me*$_2$), 1.62 (d, *J* = 6.9 Hz, 3H, CH*Me*$_2$), 1.66 (s, 3H, C*Me*), 2.93 (sept, *J* = 6.7 Hz, 1H, C*H*Me$_2$), 3.33 (sept, *J* = 6.7 Hz, 1H, C*H*Me$_2$), 3.49 (sept, *J* = 6.9 Hz, 1H, C*H*Me$_2$), 3.80 (sept, *J* = 6.9 Hz, 1H, C*H*Me$_2$), 4.14 (s, 1H, CC*H*H), 4.49 (s, 1H, CCH*H*), 7.01−7.36 (m, 6H, Ar-*H*). ^{13}C NMR (C_6D_6, 100 MHz, 25 °C): δ 2.34 (Al*C*H$_2$), 10.15 (AlCH$_2$*Me*), 17.76, 17.83 (TEMPO-*Me*), 19.59 (C*Me*), 23.89 (TEMPO-*C*H$_2$), 24.39, 24.40 (TEMPO-*Me*), 24.53, 24.89, 24.95, 26.23, 26.42, 28.07, 28.15, 28.76 (CH*Me*$_2$), 29.07, 30.23, 32.62, 32.36 (*C*HMe$_2$), 40.58, 40.48 (TEMPO-*C*H$_2$), 58.97, 58.77 (TEMPO-*C*Me$_2$), 95.27 (C*C*H$_2$), 123,86, 124.49, 124.69, 124.75, 126.09, 139.93, 141.27, 141.90, 146.55, 147.05, 152.46 (Ar-*C*), 142.95 (*C*CH$_2$), 181.19 (*C*=N). IR (cm^{-1}): $\tilde{\nu}$ 441 (m), 495 (w), 745 (m), 797 (s), 869 (m), 1027 (m), 1098 (m), 1182 (w), 1214 (m), 1259 (m), 1318 (m), 1352 (m), 1437 (m), 1461 (m), 1563 (m), 1606 (m), 2865 (m), 2964 (s), 3058 (w). EI-MS: *m*/*z* (%) 615.4 (29).

Conversion of 3 to 4. In an NMR tube, a mixture of **3** (24 mg, 0.05 mol) and TEMPOH (8 mg, 0.05 mol) was added to C_6D_6 (0.6 mL), and then the NMR tube was shaken carefully. After the NMR tube stood at room temperature for 2 h, it was identified by NMR spectroscopy. The corresponding ^{1}H NMR was consistent with that of **4**.

Synthesis of ($L^•$)AlI$_2$ (5). A solution of I_2 (508 mg, 2 mmol) in toluene (10 mL) was added to a solution of **2** (490 mg, 1 mmol) in toluene (20 mL) at 0 °C. The mixture was warmed to room temperature and stirred continuously for 8 h. The red solution was concentrated to 3 mL. Storage at −35 °C overnight afforded orange-red crystals of **5** (0.58 g, 84%). Mp: 265−268 °C. Anal. Calcd for $C_{28}H_{40}AlI_2N_2$ (685.42): C, 48.92; H, 6.16; N, 4.08. Found: C, 48.97; H, 6.57; N, 4.32. IR (cm^{-1}): $\tilde{\nu}$ 422 (w), 684 (m), 729 (m), 761 (m), 804 (m), 840 (m), 900 (w), 940 (m), 972 (m), 1101 (m), 1179 (w), 1259 (m), 1302 (w), 1327 (w), 1364 (m), 1487 (m), 1499 (w), 1640 (m), 2869 (s), 2963 (s). EI-MS: *m*/*z* (%) 685.3 (27).

Synthesis of [(L^0)AlCl$_2$]$^+$[AlCl$_4$]$^-$ (6) and LBCl (7). BCl_3 (1 mL, 1 M in *n*-hexane) was added to **2** (490 mg, 1 mmol) in ether at −78 °C. The mixture was warmed to room temperature and stirred continuously for 8 h. All volatile materials were removed under vacuum. The yellow residue was extracted with 10 mL of *n*-hexane to give a colorless filtrate and a yellow solid. The colorless filtrate was concentrated and stored at −35 °C overnight to afford colorless crystals of **7** (108 mg, 24% based on BCl_3 consumed). The yellow solid was extracted with 10 mL of diethyl ether, and the yellow filtrate was concentrated. Storage at −35 °C overnight afforded orange crystals of **6** (0.17 g, 47% based on Al). Data for **6** are as follows. Mp: 143−145 °C. Anal. Calcd for $C_{31}H_{48}Al_2Cl_6N_2$ (715.41): C, 52.04; H, 6.76; N, 3.92. Found: C, 52.36; H, 7.19; N, 4.06. ^{1}H NMR (C_6D_6, 400 MHz, 25 °C): δ 1.05 (d, *J* = 6.7 Hz, 12H, CH*Me*$_2$), 1.20 (d, *J* = 6.7 Hz, 12H, CH*Me*$_2$), 2.39 (s, 6H, C*Me*), 3.25 (sept, *J* = 7.0 Hz, 4H, C*H*Me$_2$), 7.00−7.10 (m, 6H, Ar-*H*). ^{13}C NMR (C_6D_6, 100 MHz, 25 °C): δ 15.53 (C*Me*), 22.88, 23.63 (CH*Me*$_2$), 29.21 (*C*HMe$_2$), 124.61, 129.80, 135.77, 139.69 (Ar-C), 171.63 (CN). IR (cm^{-1}): $\tilde{\nu}$ 403 (w), 528 (w), 683 (m), 763 (m), 802 (m), 936 (w), 1021 (m), 1097 (m), 1181 (w), 1260 (m), 1325 (w), 1363 (m), 1414 (m), 1434 (m), 1464 (m), 1507 (m), 1541 (m), 1590 (m), 1639 (m), 1726 (w), 2871 (m), 2929 (s), 2961 (s). EI-MS: *m*/*z* (%) 501.2 (10) [**6** − [AlCl$_4$]$^-$]. Data for **7** are as follows. Mp: 121−123 °C. Anal. Calcd for $C_{28}H_{40}BClN_2$ (450.88): C, 74.58; H, 8.94; N, 6.21. Found: C, 73.97; H, 7.57; N, 5.32. ^{1}H NMR (C_6D_6, 400 MHz, 25 °C): δ 1.19 (d, *J* = 6.9 Hz, 12H, CH*Me*$_2$), 1.31 (d, *J* = 6.8 Hz, 12H, CH*Me*$_2$), 1.65 (s, 6H, C*Me*), 3.11 (sept, *J* = 6.8 Hz, 4H, C*H*Me$_2$), 7.17−7.23 (m, 6H, Ar-*H*). ^{13}C NMR (C_6D_6, 100 MHz, 25 °C): δ 10.76 (C*Me*), 23.51, 24.78 (CH*Me*$_2$), 28.84 (*C*HMe$_2$), 119.89 (CN), 123.80, 135.43, 147.06 (Ar-C). ^{11}B NMR (C_6D_6, 128 MHz, 25 °C): δ 21.08. IR (cm^{-1}): $\tilde{\nu}$ 444 (m), 517 (w), 531 (w), 588 (w), 620 (w), 646 (w), 679 (w), 741 (m), 757 (w), 786 (w), 817 (w), 938 (m), 1057 (w), 1106 (w), 1178 (w), 1255 (w), 1281 (s), 1316 (s), 1387 (s), 1468 (s), 1587 (w), 1927 (w), 2867 (m), 2960 (s), 3069 (w). EI-MS: *m*/*z* (%) 450.1 (56).

X-ray Structural Determination. All intensity data were collected with a Bruker SMART CCD diffractometer, using graphite-monochromated Mo Kα radiation (λ = 0.710 73 Å). The structures were resolved by direct methods and refined by full-matrix least squares on F^2.[23] Hydrogen atoms were considered in calculated positions. All non-hydrogen atoms were refined anisotropically. The ORTEP-3 program was utilized to draw the molecules.[24] Crystal data and data collection details are collected in Table 1S in the Supporting Information. Crystals of **2**, **3**, and **7** suitable for X-ray diffraction were obtained from *n*-hexane at −35 °C.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

CIF files and a table giving crystal data and data collection details for compounds **2**, **3**, and **7** and a figure giving the experimental EPR spectrum of **5**. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: cmcui@nankai.edu.cn.

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This work was supported by the National Natural Science Foundation of China and 973 program (Grant No. 2012CB821600).

■ REFERENCES

(1) d-block metal complexes: (a) Yamada, H.; Siems, W. F.; Koike, T.; Hurst, J. K. *J. Am. Chem. Soc.* **2004**, *126*, 9786. (b) Chirik, P. J.; Wieghardt, K. *Science* **2010**, *327*, 794. (c) Sylvester, K. T.; Chirik, P. J. *J. Am. Chem. Soc.* **2009**, *131*, 8772. (d) Blackmore, K. J.; Sly, M. B.; Haneline, M. R.; Ziller, J. W.; Heyduk, A. F. *Inorg. Chem.* **2008**, *47*, 10522. (e) Dzik, W. I.; van der Vlugt, J. I.; Reek, J. N. H.; de Bruin, B. *Angew. Chem., Int. Ed.* **2011**, *50*, 3356. (f) Zhu, D.; Thapa, I.; Korobkov, I.; Gambarotta, S.; Budzelaar, P. H. M. *Inorg. Chem.* **2011**, *50*, 9879. (g) Chen, Z.; Chen, C.; Weinberg, D. R.; Kang, P.; Concepcion, J. J.; Harrison, D. P.; Brookhart, M. S.; Meyer, T. J. *Chem. Commun.* **2011**, *47*, 12607. (h) Bachmann, J.; Nocera, D. G. *Inorg. Chem.* **2005**, *44*, 6930. (i) Blackmore, K. J.; Lal, N.; Ziller, J. W.; Heyduk, A. F. *J. Am. Chem. Soc.* **2008**, *130*, 2728. (j) Haneline, M. R.; Heyduk, A. F. *J. Am. Chem. Soc.* **2006**, *128*, 8410. (k) Zarkesh, R. A.; Ziller, J. W.; Heyduk, A. F. *Angew. Chem., Int. Ed.* **2008**, *47*, 4715. (l) Bachmann, J.; Nocera, D. G. *J. Am. Chem. Soc.* **2004**, *126*, 2829.

(2) f-block metal complexes: (a) Fedushkin, I. L.; Maslova, O. V.; Baranov, E. V.; Shavyrin, A. S. *Inorg. Chem.* **2009**, *48*, 2355. (b) Fedushkin, I. L.; Maslova, O. V.; Hummert, M.; Schumann, H. *Inorg. Chem.* **2010**, *49*, 2901. (c) Fedushkin, I. L.; Maslova, O. V.; Lukoyanov, A. N.; Fukin, G. K. *C. R. Chimie* **2010**, *13*, 584. (d) Lyaskovskyy, V.; de Bruin, B. *ACS Catal.* **2012**, *2*, 270. (e) Diaconescu, P. L.; Arnold, P. L.; Baker, T. A.; Mindiola, D. J.; Cummins, C. C. *J. Am. Chem. Soc.* **2000**, *122*, 6108. (f) Kraft, S. J.; Fanwick, P. E.; Bart, S. C. *Inorg. Chem.* **2010**, *49*, 1103. (g) Lam, O. P.; Heinemann, F. W.; Meyer, K. *Angew. Chem., Int. Ed.* **2011**, *50*, 5965. (h) Lam, O. P.; Anthon, C.; Heinemann, F. W.; O'Connor, J. M.; Meyer, K. *J. Am. Chem. Soc.* **2008**, *130*, 6567.

(3) For selected examples, see: (a) Cloke, F. G. N.; Dalby, C. I.; Henderson, M. J.; Hitchcock, P. B.; Kennard, C. H. L.; Lamb, R. L.; Raston, C. L. *J. Chem. Soc., Chem. Commun.* **1990**, 1394. (b) Cloke, F. G. N.; Dalby, C. I.; Daff, J.; Green, J. *J. Chem. Soc., Dalton Trans.* **1991**, 181. (c) Baker, R. J.; Farley, R. D.; Jones, C.; Kloth, M.; Murphy, D. M. *Dalton Trans.* **2002**, 1196. (d) Baker, R. J.; Farley, R. D.; Jones, C.; Kloth, M.; Murphy, D. M. *Dalton Trans.* **2002**, 3844. (e) Hinchliffe, A.; Mair, F. S.; McInnes, E. J. L.; Pritchard, R. G.; Warren, J. E. *Dalton Trans.* **2008**, 222. (f) Panda, T. K.; Kaneko, H.; Michel, O.; Pal, K.; Tsurugi, H.; Törnroos, K. W.; Anwander, R.; Mashima, K. *Organometallics* **2012**, *31*, 3178. (g) Bailey, P. J.; Dick, C. M.; Fabre, S.; Parsons, S.; Yellowlees, L. J. *Dalton Trans.* **2006**, 1602. (h) Liu, Y.; Zhao, Y.; Yang, X.-J.; Li, S.; Gao, J.; Yang, P.; Xia, Y.; Wu, B. *Organometallics* **2011**, *30*, 1599.

(4) For selected examples, see: (a) Fedushkin, I. L.; Khvoinova, N. M.; Baurin, A. Y.; Fukin, G. K.; Cherkasov, V. K.; Bubnov, M. P. *Inorg. Chem.* **2004**, *43*, 7807. (b) Fedushkin, I. L.; Skatova, A. A.; Hummert, M.; Schumann, H. *Eur. J. Inorg. Chem.* **2005**, 1601. (c) Schumann, H.; Hummert, M.; Lukoyanov, A. N.; Fedushkin, I. L. *Organometallics* **2005**, *24*, 3891. (d) Fedushkin, I. L.; Morozov, A. G.; Hummert, M.; Schumann, H. *Eur. J. Inorg. Chem.* **2008**, 1584. (e) Fedushkin, I. L.; Morozov, A. G.; Chudakova, V. A.; Fukin, G. K.; Cherkasov, V. K. *Eur. J. Inorg. Chem.* **2009**, 4995.

(5) (a) Myers, T. W.; Berben, L. A. *J. Am. Chem. Soc.* **2011**, *133*, 11865. (b) Myers, T. W.; Kazem, N.; Stoll, S.; Britt, R. D.; Shanmugam, M.; Berben, L. A. *J. Am. Chem. Soc.* **2011**, *133*, 8662. (c) Myers, T. W.; Berben, L. A. *Inorg. Chem.* **2012**, *51*, 1480. (d) Kowolik, K.; Shanmugam, M.; Myers, T. W.; Cates, C. D.; Berben, L. A. *Dalton Trans.* **2012**, 7969. (e) Scott, J.; Gambarotta, S.; Korobkov, I.; Knijnenburg, Q.; de Bruin, B.; Budzelaar, P. H. M. *J. Am. Chem. Soc.* **2005**, *127*, 17204.

(6) (a) Herzog, S.; Geisler, K.; Praekel, H. *Angew. Chem., Int. Ed. Engl.* **1963**, *2*, 47. (b) Köster, R.; Benedikt, G.; Schrötter, H. W. *Angew. Chem., Int. Ed. Engl.* **1964**, *3*, 514. (c) Lehmkuhl, H.; Fuchs, G.; Köster, R. *Tetrahedron Lett.* **1965**, *29*, 2511. (d) Kaim, W. *J. Organomet. Chem.* **1980**, *201*, C5. (e) Kaim, W. *Chem. Ber.* **1981**, *114*, 3789. (f) Kaim, W. *Z. Naturforsch.* **1982**, *37B*, 783. (g) Flamini, A.; Poli, N. *Inorg. Chim. Acta* **1988**, *150*, 149.

(7) (a) Kaim, W. *Inorg. Chem.* **2011**, *50*, 9752. (b) Fedushkin, I. L.; Skatova, A. A.; Chudakova, V. A.; Fukin, G. K. *Angew. Chem., Int. Ed.* **2003**, *42*, 3294.

(8) (a) Bhadbhade, M.; Clentsmith, G. K. B.; Field, L. D. *Organometallics* **2010**, *29*, 6509. (b) Trifonov, A. A.; Fedorova, E. A.; Fukin, G. K.; Druzhkov, N. O.; Bochkarev, M. N. *Angew. Chem., Int. Ed.* **2004**, *43*, 5045. (c) Cavallo, L.; Macchioni, A.; Zuccaccia, C.; Zuccaccia, D.; Orabona, I.; Ruffo, F. *Organometallics* **2004**, *23*, 2137.

(9) Uhl, W.; Layh, M. Formal Oxidation State +II: Metal-Metal Bonded Versus Mononuclear Derivatives. In *The Group 13 Metals Aluminium, Gallium, Indium and Thallium: Chemical Patterns and Pecularities*; Wile: Oxford, U.K., 2011; p 246.

(10) Scott, J.; Gambarotta, S.; Korobkov, I.; Knijnenburg, Q.; de Bruin, B.; Budzelaar, P. H. *J. Am. Chem. Soc.* **2005**, *127*, 17204.

(11) Lukoyanov, A. N.; Fedushkin, I. L.; Schumann, H.; Hummert, M. *Z. Anorg. Allg. Chem.* **2006**, *632*, 1471.

(12) (a) Dubois, L. H.; Zegarski, B. R.; Kao, C. T.; Nuzzo, R. G. *Surf. Sci.* **1990**, *236*, 77. (b) Nakajima, T.; Nakatomi, M.; Yamashita, K. *Mol. Phys.* **2003**, *101*, 267.

(13) Wu, J.; Fanwick, P. E.; Kubiak, C. P. *J. Am. Chem. Soc.* **1988**, *110*, 1319.

(14) Gans-Eichler, T.; Gudat, D.; Nättinen, K.; Nieger, M. *Chem. Eur. J.* **2006**, *12*, 1162.

(15) Cope-Eatough, E. K.; Mair, F. S.; Pritchard, R. G.; Warren, J. E.; Woods, R. J. *Polyhedron* **2003**, *22*, 1447.

(16) (a) Kumar, S. S.; Singh, S.; Roeksy, H. W.; Magull, J. *Inorg. Chem.* **2005**, *44*, 1199. (b) Li, X.; Song, H.; Duan, L.; Cui, C.; Roesky, H. W. *Inorg. Chem.* **2006**, *45*, 1912. (c) Myers, T. W.; Berben, L. A. *J. Am. Chem. Soc.* **2011**, *133*, 11865. (d) Gallo, E.; Solari, E.; Re, N.; Floriani, C.; Chiesi-Villa, A.; Rizzoli, C. *J. Am. Chem. Soc.* **1997**, *119*, 5144. (e) Stanciu, C.; Jones, M. E.; Fanwick, P. E.; Abu-Omar, M. M. *J. Am. Chem. Soc.* **2007**, *129*, 12400.

(17) (a) Lippert, C. A.; Hardcastle, K. I.; Soper, J. D. *Inorg. Chem.* **2011**, *50*, 9864. (b) Lippert, C. A.; Soper, J. D. *Inorg. Chem.* **2010**, *49*, 3682.

(18) Tsurugi, H.; Saito, T.; Tanahashi, H.; Arnold, J.; Mashima, K. *J. Am. Chem. Soc.* **2011**, *133*, 18673.

(19) For selected references, see: (a) Cui, C.; Roesky, H. W.; Noltemeyer, M.; Lappert, M. F.; Schmidt, H. G.; Hao, H. J. *Organometallics* **1999**, *18*, 2256. (b) Cui, C.; Roesky, H. W.; Schmidt, H. G.; Noltemeyer, M.; Hao, H. J.; Cimpoesu, F. *Angew. Chem., Int. Ed.* **2000**, *39*, 4274. (c) Wright, R. J.; Philips, A. D.; Power, P. P. *J. Am. Chem. Soc.* **2003**, *125*, 10784. (d) Li, X.; Chen, X.; Song, H.; Cui, C. *Organometallics* **2007**, *26*, 1039.

(20) (a) Weber, L.; Förster, J.; Stammler, H.-G.; Neumann, B. *Eur. J. Inorg. Chem.* **2006**, 5048. (b) Tian, D.; Jiang, J.; Hu, H.; Zhang, J.; Cui, C. *J. Am. Chem. Soc.* **2012**, *134*, 14666.

(21) *WINEPR SimFoniA Version 1.25*; Bruker Analytische Messtechnik GmbH, 1996.

(22) McGrath, A. J.; Garrett, G. E.; Valgimigli, L.; Pratt, D. A. *J. Am. Chem. Soc.* **2010**, *132*, 16759.

(23) Sheldrich, G. M. *Acta Crystallogr.* **2008**, *A64*, 112.

(24) Farrugia, L. J. *J. Appl. Crystallogr.* **1997**, *30*, 837.