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Aluminum-Stabilized Low-Spin Iron(II) Hydrido Complexes of 1,4,7-Trimethyl-1,4,7-triazacyclononane

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Supporting Information

ABSTRACT: We investigated herein the reactions of $(Me_3tacn)FeCl_n$ (1a: n = 3, 1b: n = 2) with common aluminum hydride reagents and a bulky dihydridoaluminate $\{Li(ether)_2\}\{Al(OC_6H_3-2,6^{-t}Bu_2)\}(\mu-H)_2$, which yielded the diamagnetic hydrido complexes 2-4 containing Fe(II) and Al(III). In particular, the use of divalent 1b afforded excellent isolated yields. The structures of 2-4 were determined using spectroscopic and crystallographic analyses. The crystal structures showed distorted octahedral Fe centers and fairly short Fe-Al distances [2.19-2.24 Å]. The structures of cation



moiety 2 and neutral complex 4 were further probed using DFT calculations, which indicated a stable low-spin Fe(II) state and strongly electron-donating nature of the (Me₃tacn)FeH₃ fragment toward the Al(III) center.

INTRODUCTION

Dinuclear transition metal motifs are found as the active centers of a number of metalloenzymes,¹ wherein the transition metal centers are typically stabilized by the amino acid residues of polypeptides and siderophores. Successful models of hemeerythrin as an oxygen-storage metalloprotein have been described as O-bridged diiron frameworks supported by the facial nitrogen-based ligands 1,4,7-triazacyclononanes (tacn)² and hydrotris(pyrazolyl)borates (Tp).³

Despite these pioneering studies on the di-iron oxo complexes, little known are the corresponding hydrido forms having these ligand systems. Hitherto, the syntheses of the related dinuclear hydrido clusters of group 8 and 9 metals by Wieghardt,⁴ our group,⁵ Paneque, and Ruiz,⁶ respectively, have involved $[(Me_3tacn)_2Rh_2(H)_2(\mu-H)_2]^{2+}$, $[(Me_3tacn)_2M_2(\mu-H)_2]^{2+}$ $[H]_{3}^{+}$ (M = Fe, Ru), and $[(Tp^{Me_{2}})_{2}Ir_{2}(H)_{2}(\mu-H)(\mu-L)]$ (L = Cl, SC_4H_3). We became intrigued with their reactivity toward unactivated substrates, compared to other ligand systems of Cp, CO, and triphos. Additionally, the formation of heterobinuclear complexes implies anisotropic reactivity.⁷ For instance, a recent study from our laboratory has shown promising reactivity of the diruthenium hydride containing a (Me3tacn)Ru unit, { $(Me_3tacn)Ru$ } $(Cp*Ru)(\mu-H)_3$, with CO₂ (1 atm), leading to the formation of the $bis(\mu$ -formato) complex, whereas $(Cp*Ru)_2(\mu-H)_4$ exhibited no reactivity even at a much higher pressure of CO2.7b The development of useful starting (hydrido) complexes is crucial before the initiation of systematic reactivity studies. We report herein the reactions between Me3tacn-ligated iron(II) and -(III) chlorides and several hydride reagents and the structures of the iron(II) hydrido complexes.

RESULTS AND DISCUSSION

1. Reaction of $(Me_3tacn)FeCl_3$ (1a) and LiAlH₄. Primarily, we reinvestigated the reaction of $(Me_3tacn)FeCl_3$ (1a) with LiAlH₄ using Wieghardt's procedure (Scheme 1).⁴

Scheme 1



After counteranion exchange with NaBPh₄, a THF-soluble fraction was separated from the reaction mixture, and two signals in the hydrido region of the ¹H NMR spectrum (THF- d_8 , rt) were observed at δ –24.1 and –25.7 ppm with an integration ratio of 6:1 (56% and 9% NMR yields, respectively). The chemical shift of the former major resonance was close to that reported previously.⁴ The major component (2-BPh₄) was isolated as purple platelets by recrystallization from THF. The reddish-purple platelet crystals of the minor product 2'-BPh₄ were eventually obtained from a THF/toluene mixture. The preliminary X-ray analysis of the sample suggested that 2'-BPh₄ might be a monocation having two Fe–H₃–Al fragments,⁸ which was analogous to the structure of **3** (shown later). The

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Figure 1. ¹H NMR spectrum of 2-BPh₄ (THF- d_8). Asterisks denote solvent.

structure of **2**-BPh₄ was established using NMR and singlecrystal X-ray analyses. As reported previously, this material was highly air- and moisture-sensitive and immediately decolorized on exposure to air and moisture.⁴ Once purified, **2**-BPh₄ became decreasingly soluble in THF to a great extent. The ¹H NMR spectrum of the pure, diamagnetic **2**-BPh₄ clearly showed resonances of Me₃tacn and counteranion moieties as well as a single hydride resonance (Figure 1). The spectrum of **2**-BPh₄, however, showed two (Me₃tacn)Fe(H)₃ fragments over one counteranion based on the integration ratio of the tacn ligand, hydride, and borate.

Moreover, the X-ray analysis of 2-BPh_4 unequivocally demonstrated a structure with two iron fragments and one borate, in accordance with the ¹H NMR data. As shown in Figure 2, the crystal structure of 2-BPh_4 has a linear three-



Figure 2. Crystal structure of $[\{(Me_3tacn)Fe(\mu-H)_3\}_2AI]BPh_4$ (2-BPh₄) (cation structure of one of the two independent molecules). Hydrogen atoms in Me₃tacn ligands are omitted for clarity. Thermal ellipsoids are drawn at the 50% probability level. Selected bond distances (Å) and angles (deg): Fe1-Al1 2.1918(5), Fe1-N1 2.043(3), Fe1-N2 2.040(3), Fe1-N3 2.031(3); Fe1-Al1-Fe1 180.0; Fe2-Al2 2.1879(4), Fe2-N4 2.040(3), Fe2-N5 2.035(3), Fe2-N6 2.035(3); Fe2-Al2-Fe2 180.0.

metal-centered core, Fe–Al–Fe [Fe1–Al1–Fe1# = 180°]. In the solid-state structure, each of the two Me₃tacn-Fe fragments of 2-BPh₄ adopted $\delta\delta\delta$ and $\lambda\lambda\lambda$ tacn configuration, respectively. The Fe–Al distances [2.1918(5) and 2.1879(4) Å] were significantly shorter than the distances of known Fe-Al bonds.⁹ Fischer and co-workers reported FeAl₄ and FeAl₅ hydrido clusters, in which unsupported Fe-Al bonds [2.21-2.26 Å] were shorter than the hydride-bridged Fe-Al bonds [2.32-2.44 Å].^{9b} However, in the crystal structure of 2-BPh_4 three bridging hydride ligands were located between Fe and Al atoms in the difference Fourier map, and the hydride-bridged Fe-Al distance of 2-BPh₄ was shorter than those in the above examples as well as unsupported Fe-Al-bonded complexes.¹⁰ In addition, an ²⁷Al{¹H} NMR spectrum of 2-BPh₄ (THF-d₈, 60 °C) demonstrated the presence of the aluminum atom, whose resonance was observed at δ 97.9 ppm with a relatively smaller half-height width $(w_{1/2})$ of 79 Hz. The resultant ²⁷Al NMR parameters were reasonable for the highly symmetric aluminum hydrides.¹¹

In order to obtain insight into the Fe–H₃–Al structure, we performed DFT calculation of **2** at the B3LYP level of theory. The optimized structure of cation **2** (singlet state) and selected bond distances of the singlet and triplet states are shown in Figure 3 and Table 1, respectively. The geometrical parameters of the singlet state agreed with those obtained from the X-ray analysis, in particular, in terms of Fe–Al and Fe–N distances [2.222 and 2.059 Å, respectively]. However, the corresponding triplet state indicated a relatively low symmetrical structure of the two (Me₃tacn)Fe fragments. Subsequently, the calculation indicated that the triplet state of **2** was much higher in energy compared to the corresponding singlet state; that is, the free energy difference between the two states was estimated to be 17.9 kcal mol⁻¹ (Table S1).

Although the molecular orbitals of singlet-state 2 were somewhat complicated, six occupied high-lying HOMO to HOMO-5 and six unoccupied molecular orbitals LUMO+2, +3, +7, +8, +10, and +11 were found to have major



Figure 3. DFT-optimized structures of 2 (singlet state).

Table 1. Selected Bond Distances (Å) from DFT-Optimized and Experimentally Determined Structures of 2

| | DFT | | X-ray | | |
|-----------|---------------|---------------|------------------------|---|--|
| bond | singlet state | triplet state | 2-BPh ₄ | 2- ⁱ Bu ₂ AlCl ₂ | |
| Fe1-Al3 | 2.2220 | 2.2233 | 2.1918(5) 2.1879(4) | 2.1906(3) | |
| Fe2-Al3 | 2.2220 | 2.3178 | | | |
| Fe1-N(av) | 2.0590 | 2.0610 | 2.038 | 2.042 | |
| | | | 2.038 | | |
| Fe2-N(av) | 2.0590 | 2.1423 | | | |
| Fe1-H(av) | 1.6478 | 1.6454 | 1.44 | 1.55 | |
| | | | 1.56 | | |
| Fe2-H(av) | 1.6577 | 1.7487 | | | |

contributions from Fe-based d orbitals (Figure S1-1). Clear N-Fe-H bonding orbital interactions were found in fairly lowArticle

| lying HOMO-11, -12, -14, and -15 (Figure 4), whereas |
|---|
| occupied molecular orbitals were not clearly found, implying |
| the presence of either Al-H or Al-Fe bonding interaction. As |
| listed in Table 2, the NBO analysis indicated the presence of |

| | Table | 2. | NBO | Anal | ysis | of | 0 | ptimized 1 | 2 |
|--|-------|----|-----|------|------|----|---|------------|---|
|--|-------|----|-----|------|------|----|---|------------|---|

| | natural charge | bond | Wiberg index |
|----------------------|----------------|-------|---------------|
| Fe (av) | +0.0419 | Fe-H | 0.4726-0.4738 |
| Al | +1.0801 | Fe-N | 0.2518-0.2526 |
| N (av) | -0.4740 | Fe-Al | 0.2764 |
| μ -H (av) | -0.2210 | Al–H | 0.3662-0.3676 |
| Me ₃ tacn | +0.5811 | | |

positively charged Al (+1.08) and negatively charged N (-0.47) and H (-0.22) centers with a higher covalent bond order for Fe-H (0.47) than that for Fe-Al (0.28). The relatively small covalent bond indexes for Fe-H and Fe-N could be ascribed to contributions from Fe-H antibonding orbital interactions found in HOMO-35, -16, -10, and -9 and from Fe-N antibonding orbital interactions found in HOMO-13, -10, -9 to -7, and -6 (Figures S1, S2). Although the covalent bond index for each Al-H (0.37) is small, the sum of the bond indexes for the three Al-H (total 1.10) may indicate the presence of sufficient bonding interaction between the Al and the almost electrically neutral (Me₃tacn)FeH₃ moiety (total charge -0.040). Previous reports on crystallographically characterized transition metal-aluminum complexes with triply bridging hydrides are limited to Re– Al, W–Al, and Sc–Al hydrides.¹² The formal shortness ratios (FSRs)¹³ for the metal-aluminum distance in these complexes are in a range of 0.99-1.03. In contrast, 2-BPh₄ has a smaller



Figure 4. Molecular orbitals (HOMO-11, -12, -14, and -15) in 2 including N-Fe-H bonding interactions. Each orbital is drawn by a 0.04 contour value.

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FSR (0.91). This may be due to the presence of Fe and Me_3 tacn as the electron-rich late metal and ligand. Therefore, we concluded that the experimentally observed short Fe–Al distance resulted from the strong donating property of the polarized (Me_3 tacn)FeH₃ fragments toward the Al(III) center. Such a Fe₂AlH₆ core structure with any ligand systems has not been reported hitherto; rather experimental and theoretical studies on the structures of Fe₂BH₆, [{(R_3P)₃Fe}₂B(μ -H)₆]⁺ (R = Et, R₃ = triphos), have been reported.¹⁴ The bonding nature of D_{3d} -symmetric Fe₂BH₆ was interpreted as having direct Fe–B bonds and a hypervalent boron center.

2. Reactions of (Me₃tacn)FeCl₂ (1b) and Other Hydride Reagents. The structure and iron formal oxidation state of **2**-BPh₄ led us to examine the reactions of the corresponding Fe(II) chloride as a starting complex with other known hydride reagents. (Me₃tacn)FeCl₂ (**1b**), reported by Rauchfuss and his co-worker, is composed of a dinuclear cation and mononuclear anion [{Me₃tacn)Fe}₂(μ -Cl)₃][(Me₃tacn)FeCl₂] (described as "(Me₃tacn)FeCl₂" for simplicity).¹⁵ **1b** was suspended in THF and treated with 5 equiv of DIBAL-H at 25 °C to yield a purple solution (Scheme 2). After workup, a viscous solid was





obtained. The ¹H NMR spectrum in C_6D_6 showed that the product, having a characteristic hydride resonance at δ –24.0 ppm, resembled **2**-BPh₄ except for the resonances of the counteranion moiety. The recrystallization of the product from a THF/pentane mixture at ambient temperature yielded purple platelets, which allowed us to carry out single-crystal X-ray studies. The results of both X-ray and NMR studies were consistent with the formulation of **2**-^{*i*}Bu₂AlCl₂ (see CIF file). The *S*₆-symmetric cation was essentially the same as that in **2**-BPh₄. Cations **2** were reproducibly formed from **1b** with either DIBAL-H or LiAlH₄ with over 70% isolated yields, which were much higher and more selective than those from the trivalent iron chloride **1a** (Scheme 2).

A reaction of **1a** with DIBAL-H was also performed, yielding **2**-^{*i*}Bu₂AlCl₂ along with a minor product, which showed a hydride resonance at -25.1 ppm in the ¹H NMR spectrum (hydride integration ratio: **2**-^{*i*}Bu₂AlCl₂/the minor product = 3.2:1). The structure of the minor product was tentatively assigned to **2**'-^{*i*}Bu₂AlCl₂.

We also reacted **1b** with borohydride reagents such as LiBH₄, LiEt₃BH, and NaBH₄ under similar conditions; however, all attempts resulted in the formation of paramagnetic black solids. These materials were insoluble in THF, CH₃CN, and CH₂Cl₂ and reacted with protic solvents. This led to the evolution of gas; therefore, we did not characterize them any further. Next, we turned our attention to the use of another aluminum-based hydride reagent, NaAlH₂(OCH₂CH₂OMe)₂ (Red-Al). When 5 equiv of Red-Al was employed for **1b** in THF, the reaction proceeded at 25 °C and reached completion in 24 h, affording the diamagnetic purple product **3** (Scheme 3). **3** was soluble in



THF but insoluble in pentane, toluene, and ether. It was readily isolated as red-purple platelets after filtration and recrystallization from a THF/ether mixture (76% isolated yield based on **1b**). ¹H NMR and COSY spectra of **3** (THF- d_8) exhibited not only the characteristic resonances of Me₃tacn ligand protons (δ 2.95 and 2.93–3.06 ppm for Me and CH₂CH₂, respectively) and hydride (δ –25.6 ppm) but also proton signals of the 2-methoxyethoxy group in the typical magnetic field (δ 3.41 and 3.43–3.92 ppm for Me and CH₂CH₂, respectively). $T_{1 \text{ min}}$ for the hydride signal was measured [130(1) ms at 235 K]. The value indicates the absence of the nonclassical hydride nature of **3**.¹⁶

The X-ray analysis of **3** was performed, and the molecular structure is presented in Figure 5. The solid-state structure of **3**



Figure 5. Crystal structure of **3** (cation moiety only). Hydride ligands could not be located. All other hydrogen atoms are omitted for clarity. Thermal ellipsoids are drawn at the 50% probability level. Selected bond distances (Å) and angles (deg): Fe1–Al1 2.2450(17), Fe1–N1 2.064(5), Fe1–N2 2.072(5), Fe1–N3 2.044(5), Al1–O1 1.860(4), Al1–O3 1.891(4), Al1–O7 1.780(4); O1–Al1–O3 79.05(15), O3–Al1–O7 92.25(18), O1–Al1–O7 97.47(18).

showed two Fe–Al units linked by alkoxyl ligands on the Al atoms and one Na atom trapped by six alkoxide and ethereal oxygen atoms. The Fe–Al distance [Fe1-Al1 = 2.2450(17) Å] was comparable to that of **2**. The incorporation of the Na and Cl atoms into the molecule apparently decreased the solubility of the complex in organic solvents and resulted in a *syn* configuration of the Fe1-Al1-Al2-Fe2 core. We attempted to liberate the Na cation in the structure of **3** by addition of excess

crown ethers (15-crown-5 and 18-crown-6). However, NaCl elimination did not occur even at elevated temperatures.

Lithium and sodium aluminum dihydrides bearing bulky aryloxides were reported by Nöth and co-workers.¹⁷ We envisaged that the lithium hydridoaluminate $\{Li(OEt_2)_2\}\{Al-(ArO)_2\}(\mu-H)_2$ (Ar = C₆H₃-2,6^{-t}Bu₂) would serve as a hydride reagent to afford a neutral Fe–H₃–Al complex, into which a lithium salt (byproduct) would no longer be incorporated owing to the presence of the sterically congested Al(OAr)₂ moiety. The reaction of **1b** with 5 equiv of $\{Li(OEt_2)_2\}\{Al-(ArO)_2\}(\mu-H)_2$ in THF led to the formation of Fe–Al hydride **4** (Scheme 4). **4** was readily isolated by the filtration of





insoluble byproducts followed by the evaporation of THF solvent and successive removal of the remaining aluminum hydride reagent by simply rinsing the residue with ether and a small amount of toluene. This was because 4 was moderately soluble in THF but scarcely soluble in ether and toluene. The structure of 4 was established using spectroscopy and crystallography. The ¹H NMR spectrum recorded at 25 °C displayed a characteristic resonance at δ –25.20 ppm for the three hydrides, which were observed to be equivalent at the temperature. Consequently, the signals of two aryloxide ligands on aluminum as well as methyl proton signals of Me₃tacn on iron were also observed to be equivalent on the NMR time scale. The single crystals of 4, suitable for X-ray analysis, were grown by the slow diffusion of ether into the THF solution. The crystal structure of **4** is shown in Figure 6. The structure of the distorted octahedral iron hydride moiety and intermetal distance [Fe1-Al1 = 2.2137(4) Å] in 4 were essentially the same as those in the complexes 2 and 3. One exception was the pentacoordinated Al center, in which the four atoms Fe1, Al1, O1, and O2 share the same plane: summation of aluminum angles = 360.0° [O1-Al1-O2 = $96.05(5)^{\circ}$, O1-Al1-Fe1 = $134.42(4)^{\circ}$, O2-Al1-Fe1 = 129.54(4)°].

The DFT calculation of the neutral complex 4 (singlet state) was also carried out. As summarized in Table S5, the DFToptimized structure of 4 is in good agreement with the crystal structure in terms of Fe-Al, Fe-N, and Al-O distances and O-Al-O angle (within 3% error). The molecular orbital diagrams of 4, presented in Figure S2-1 and S2-2, are more comprehensive than those of 2. The Fe-based nonbonding orbitals were clearly found in the three molecular orbitals HOMO, HOMO-1, and HOMO-2. Fe-N and Fe-H bonding interactions were mainly observed in the low-lying HOMO-12 and -13, whereas the LUMO+5, +6, and +7 displayed antibonding orbital interactions of Fe-N, Fe-H, and Fe-Al (Figure S2-1). The NBO analysis of 4, summarized in Table S6, showed nearly identical bonding interactions in the (Me₃tacn)FeH₃Al moiety with those in cation 2 (natural charge in 4: Fe -0.0421, Al +1.7106, N_{av} -0.4857, and Me₃tacn +0.5131; Wiberg index in 4: Fe-Al 0.2164, Fe-H 0.4916-0.5950, Al-H 0.2214-0.3005).



Figure 6. Crystal structure of 4. Hydrogen atoms in Me_3 tacn, alkoxide ligands, and a crystallization THF solvent are omitted for clarity. Thermal ellipsoids are drawn at the 50% probability level. Selected bond distances (Å) and angles (deg): Fe1-Al1 2.2137(4), Fe1-N1 2.0622(12), Fe1-N2 2.0610(12), Fe1-N3 2.0439(12), Al1-O1 1.7444(10), Al1-O2 1.7817(10); N1-Fe1-N2 84.17(5), N2-Fe1-N3 84.48(5), N1-Fe1-N3 84.59(5), O1-Al1-O2 96.05(5).

3. Electronic Spectra of Fe(II) Hydrides. To verify the preference of the low-spin Fe(II) center, UV-vis spectra of diamagnetic 2-4 were recorded (Figure 7). The detected absorption bands in the spectra of 2-4 are listed in Table 3 for comparison with those of related low-spin Fe(II) complexes. In contrast to nearly colorless Fe(II) complexes Ib and $[{(Me_3tacn)Fe}_2(\mu-Cl)_3]BPh_4$, 14,18d 2-BPh₄ and 2-^{*i*}Bu₂AlCl₂, having common cationic structure, yielded almost identical absorptions in both the UV and visible-light regions. The spectra include four bands, two of which (2-BPh₄: 543 and 311 nm; 2-iBu₂AlCl₂: 537 and 328 nm) were assignable to typical spin-allowed d-d transitions of low-spin Fe(II) complexes.¹⁴ As mentioned above in the DFT results, owing to the large energy difference between the two spin states, there was no contribution from the high-spin Fe(II) electronic configuration to the spectra. These characteristic bands for low-spin Fe(II) states were also detected in the spectra of 3 and 4; however, the two extra bands corresponding to ~455 and ~390 nm detected in the spectra of 2 were not clearly observed for 3 and 4. Interestingly, the two common absorption bands of 2-4 (522– 543 and 310-360 nm) were significantly blue-shifted and had much higher molar extinction coefficients than those of previously reported low-spin Fe(II) (Table 3).

CONCLUSIONS

The synthesis of Al-capped $(Me_3tacn)FeH_3$ complexes 2–4 was accomplished through the reaction of 1 with aluminumbased hydride reagents under mild conditions, irrespective of the valency of the starting iron chlorides. On the other hand,



Figure 7. UV–vis spectra of 2-4 (0.24–1.70 mM in THF at 25 °C).

Table 3. Comparison of Electronic Transitions of Fe(II) Complexes

| complex | solvent | λ , nm (ε , L mol ⁻¹ cm ⁻¹) | ref |
|---|----------|---|--------------|
| $[Fe(tacn)_2]Br_2$ | H_2O | 601 (6), 387 (17), 288 (560) | 18b |
| $\begin{array}{c} [Fe(Me_3tacn) \\ (NCMe)_3] (OTf)_2 \end{array}$ | MeCN | 562 (23), 388 (43) | 18d |
| [Fe(Me ₃ tacn) (NCMe) ₃](BPh ₄) ₂ | MeCN | 577 (40), 384 (58) | 18d |
| $\begin{bmatrix} Fe(trans-diammac) \\ (PF_6)_2^a \end{bmatrix}$ | D_2O | 584 (100), 405 (140) | 18e |
| $ \begin{bmatrix} \operatorname{Fe}\{(\operatorname{NH}_2)_2 \operatorname{sar}\} \\ (\operatorname{OTf})_2^{\mathcal{B}} \end{bmatrix} $ | D_2O^c | 590 (14), 394 (15) | 18f |
| 2-BPh ₄ | THF | 543 (452), 457 (412), 388 (295), 311 $(1180)^d$ | this work |
| $2^{-i}Bu_2AlCl_2$ | THF | 53 7 (800), 454 (907), 391 (990), 328 (1810) ^d | this work |
| 3 | THF | 535 (716), 360 (878) ^d | this work |
| 4 | THF | 522 (208), 310 (827) ^{d} , 282 (4461) ^{e} | this work |
| | | | |

^{*a*}diammac = *exo*-6,13-diamino-6,13-dimethyl-1,4,8,11-tetraazatetradecane. ^{*b*}(NH₂)₂sar = 1,8-diamino-3,6,10,13,16,19-hexaazabicyclo[6.6.6]eicosane. ^{*c*}pH = 8.5. ^{*d*}Observed as a shoulder. ^{*e*}Assigned to an absorption of aryloxy group by comparison with the spectrum of $\{Li(OEt_2)_2\}$ {Al(ArO)₂)(μ -H)₂ (Ar = 2,6-di-*tert*-butylphenyl).

commonly used borohydrides, such as NaBH₄ and LiEt₃BH, yielded only insoluble unidentified materials. The X-ray analysis of **2**–4 clearly revealed significantly short Fe–Al distances (ca. 2.2 Å). The trihydride-bridged Fe–Al structures were probed using DFT calculations for **2** and **4**, which suggested a stable low-spin Fe(II) state and the presence of a strongly electron-donating property of the polarized $[(Me_3tacn)Fe(\mu-H)_3]$ and the Lewis acidic Al(III) center. The UV–vis spectra of **2**–4 included the characteristic absorption bands for low-spin Fe(II) species with a significant blue shift of the LF transitions. These spectroscopic features agreed with the diamagnetic nature, as revealed from the NMR and DFT analysis. Hagen reported the temperature-dependent spin-crossover behavior of $[(Me_3tacn)-FeL_3]^{2+}$ (L = acetonitrile and trifluoromethanesulfonate), where the subtle structural change, i.e., the type of L and N-

substituents (ⁱPr and ⁱBu) in the tacn ligand, dramatically altered the spin states.¹⁹ We conclude that the low-spin Fe(II) state in **2**–**4** was governed by the presence of the hydride ligands as σ -donors. Moreover, at the same time, the Al fragment played an important role in stabilizing the polarized [(Me₃tacn)Fe(μ -H)₃] fragment. So far, several bimetallic hydrides of Fe(II) and main group metals (e.g., B, Si, Sn) with other facial ligand systems, e.g., triphos, have been synthesized and structurally characterized.²⁰ The synthetic application of the Fe–H₃–Al species to other heterobimetallic hydrides is currently under investigation in our laboratory.

EXPERIMENTAL SECTION

General Procedures. All manipulations for air- and moisturesensitive compounds were carried out under an argon atmosphere using standard Schlenk techniques or in a glovebox filled with argon ($H_2O < 1$ ppm, $O_2 < 1$ ppm). Dehydrated solvents (toluene, pentane, ether, tetrahydrofuran, acetonitrile, methylene chloride, and methanol) were purchased from Kanto Chemical Co. Ltd. Deuterated solvents (benzene- d_{sv} tetrahydrofuran- d_{8v} and toluene- d_8) were purchased from Cambridge Isotope Laboratories, Inc. and Sigma-Aldrich Co. (Non)deuterated hydrocarbon and ethereal solvents were distilled from Na– K alloy and stored under an argon atmosphere. Other reagents and organic and inorganic chemicals were used as received.

Instrumentation. ¹H and ¹³C NMR spectra were recorded on Varian INOVA 400 and Varian 400-MR Fourier transform spectrometers. ¹H chemical shifts were referenced to the residual proton peaks of benzene- d_6 at δ 7.15 ppm or tetrahydrofuran- d_8 at δ 3.58 ppm vs tetramethylsilane at δ 0.00 ppm. NMR yields were estimated by integration changes based on integrations of 2,2,4,4tetramethylpentane as an internal standard. The central peak of a triplet for benzene- d_6 at δ 128.0 ppm or the central peak of a quintet for tetrahydrofuran- d_8 at δ 67.57 ppm vs tetramethylsilane δ 0.00 ppm was used as the ¹³C NMR internal reference. The peak for Al(NO₃)₃ (D₂O) was used as an ²⁷Al NMR external reference. UV-vis spectra were recorded on a Shimadzu UV-2550 spectrophotometer. Infrared spectra were recorded on a JASCO FT-IR 4200 type A spectrophotometer. Elemental analyses (C, H, and N) were recorded on a PerkinElmer 2400II. Single crystals suitable for X-ray analysis were coated with Paratone-N in a glovebox. Crystals of proper size were picked by using a nylon CryoLoop and quickly transferred in a low-temperature N2 stream to the goniometer head. The diffraction

Table 4. Crystallographic Data of 2-BPh₄, 2-^{*i*}Bu₂AlCl₂, 3, and 4

| complex | 2-BPh_4 | $2^{-i}Bu_2AlCl_2$ | 3 | 4 |
|--|---------------------------------|---------------------------------|---|---------------------------------|
| empirical formula | C42H68AlBFe2N6 | $C_{26}H_{66}Al_2Cl_2Fe_2N_6$ | C ₃₀ H ₇₆ Al ₂ ClFe ₂ N ₆ NaO ₈ | C41H74AlFeN3O3 |
| mol wt (g mol ⁻¹) | 800.47 | 699.41 | 873.07 | 739.86 |
| cryst habit | platelet | platelet | platelet | block |
| cryst syst | monoclinic | monoclinic | monoclinic | monoclinic |
| space group | $P2_1/a$ (#14) | C2/c (#15) | $P2_1/n$ (#14) | $P2_1/n$ (#14) |
| cryst color | red | red | red | red |
| cryst size (mm) | $0.15 \times 0.07 \times 0.05$ | $0.54 \times 0.13 \times 0.05$ | $0.39 \times 0.37 \times 0.10$ | $0.51\times0.28\times0.23$ |
| a (Å) | 16.0332(8) | 12.3874(7) | 15.5885(5) | 10.1258(2) |
| b (Å) | 15.8365(8) | 11.9798(7) | 17.5040(5) | 16.6997(4) |
| c (Å) | 17.3741(9) | 25.1828(15) | 16.9997(5) | 24.9425(6) |
| α (deg) | | | | |
| β (deg) | 100.921(2) | 92.973(2) | 97.035(3) | 90.111(1) |
| γ (deg) | | | | |
| V (Å ³) | 4331.6(4) | 3732.1(4) | 4603.6(2) | 4217.7(2) |
| Z value | 4 | 4 | 4 | 4 |
| measurement temp (°C) | -150 | -150 | -150 | -150 |
| $D_{\rm calc}({\rm g~cm^{-3}})$ | 1.237 | 1.245 | 1.261 | 1.165 |
| μ (Mo K α) (mm ⁻¹) | 0.725 | 0.992 | 0.781 | 0.417 |
| $2\theta_{\max}$ (deg) | 55 | 51 | 51 | 55 |
| reflns collected | 35 022 | 15 313 | 74 772 | 68 315 |
| indept reflns | 9849 ($R_{\rm int} = 0.0918$) | $3606 \ (R_{\rm int} = 0.0411)$ | 14417 ($R_{\rm int} = 0.0795$) | 9645 ($R_{\rm int} = 0.0324$) |
| reflns obsd (>2 σ) | 6177 | 3062 | 10 526 | 8491 |
| abs corr type | empirical | empirical | empirical | numerical |
| abs transmn | 0.6907 (min.) | 0.4513 (min.) | 0.5516 (min.) | 0.8258 (min.) |
| | 1.0000 (max.) | 1.0000 (max.) | 1.0000 (max.) | 1.0000 (max.) |
| $R_1 \ (I > 2\sigma(I))$ | 0.0509 | 0.0356 | 0.0822 | 0.0344 |
| R_1 (all data) | 0.1019 | 0.0403 | 0.1120 | 0.0401 |
| wR_2 (all data) | 0.1206 | 0.0865 | 0.2477 | 0.0935 |
| data/restraints/params | 9849/0/492 | 3429/0/193 | 14 417/0/462 | 9645/0/672 |
| goodness of fit on F^2 | 1.058 | 1.057 | 1.064 | 1.039 |
| largest diff peak | 0.688 | 0.849 | 1.92 | 0.761 |
| and hole (e Å ⁻³) | -0.842 | -0.318 | -1.90 | -0.628 |

data were collected on a R-AXIS RAPID diffractometer equipped with graphite-monochromated Mo K α radiation ($\lambda = 0.71069$ Å). Structures were solved by heavy-atom Patterson or direct methods and expanded using Fourier techniques. The non-hydrogen atoms were refined by full-matrix least-squares refinement in F^2 using the SHELXS-97 program.²¹ The twin refinement of complex **3** was performed with SHELXS using the data in HKLF5 format. Hydrogen atoms were located by difference Fourier maps and refined isotropically. Crystallographic data of **2**-BPh₄, **2**-^{*i*}Bu₂AlCl₂, **3**, and **4** are summarized in Table 4.

Synthesis of 2-BPh₄. To a suspension of 1b (0.106 mmol, 95 mg) in THF (6 mL) was added LiAlH₄ (2.03 mmol, 77 mg) at 25 °C under an argon atmosphere. After the mixture was stirred at this temperature for 1.5 h while the reaction system was closed, NaBPh₄ (0.16 mmol, 55 mg) was subsequently added under argon purge. After stirring for 24 h, the resulting purple suspension was filtered through glass frits and the insoluble salts were washed with THF (0.5 mL \times 2). Solvent was removed from the combined filtrates under reduced pressure, and then the residue was washed with ether to afford essentially pure 2-BPh₄ (102 mg, 80%). Storage of a concentrated THF solution of 2-BPh_4 at -30 °C afforded diffraction quality crystals. ¹H NMR (THF- d_{8} , rt): δ 7.26 (8H, m, Ph-H, ortho), 6.84 (8H, t, J = 6.8 Hz, Ph-H, meta), 6.69 (4H, t, J = 6.8 Hz, Ph-H, para), 2.95 (18H, s, NMe), 2.87 (24H, m, NCH₂), -24.1 (6H, s, μ -H) ppm. ¹³C{¹H} NMR (THF- d_8 , rt): δ 164.7 (q, J_{BC} = 49.1 Hz, Ph-ipso), 136.7 (Ph-ortho), 125.2 (Ph-meta), 121.4 (Ph-para), 60.2 (NCH₂), 59.3 (NCH₃) ppm. ²⁷Al{¹H} NMR (THF- d_8 , 60 °C): δ 97.9 ppm ($w_{1/2}$ = 79 Hz). IR (KBr, cm⁻¹): ν 2897 (m), 1655 (s), 1578 (s), 1457 (s), 1289 (m), 1078 (m), 1011 (s), 732 (s), 706 (s), 612 (s). Anal. Calcd for C42H68AlBFe2N6: C, 62.55; H, 8.50; N, 10.42. Found: C, 62.36; H, 9.00; N, 10.47.

Synthesis of 2-ⁱBu₂AlCl₂. To a suspension of 1b (0.0906 mmol, 81 mg) in THF (5 mL) was added a solution of DIBAL-H in toluene (0.9 mL, 1.5 M) at 25 °C under an argon atmosphere. After the mixture was stirred at this temperature for 12 h, the resulting purple suspension was filtered through glass frits, and the solvent was removed from the filtrates under reduced pressure. The residue was washed with pentane and ether to yield $2^{-i}Bu_2AlCl_2$ (69 mg, 73%). Single crystals of 3 were grown from THF/pentane at ambient temperature. ¹H NMR (benzene- d_6 , rt): δ 2.73 (18H, s, NMe), 2.70 (2H, m, AlCH₂CH), 2.41 (24H, m, NCH₂), 1.57 (12H, d, J = 6.6 Hz, CH₃), 0.85 (4H, d, J = 6.6 Hz, AlCH₂), -24.0 (6H, s, μ -H) ppm. COSY (benzene- d_{60} rt): 2.70/1.57, 0.85. ¹³C{¹H} NMR (benzene- d_{60} rt): δ 59.7 (NCH₂), 59.3 (NCH₃), 57.7 (AlCCH), 29.3 (AlCCCH₃), 27.4 (AlCH₂) ppm. HMQC ($^{13}C/^{1}H$, benzene- d_{6} , rt): δ 59.7/2.41; 59.3/2.73; 57.7/2.70; 29.3/1.57; 27.4/0.85. HMBC (¹³C/¹H, benzene d_{6} rt): δ 57.7/1.57, 0.85; 29.3/2.70; 27.4/2.70. IR (KBr, cm⁻¹): ν 2852 (m), 1655 (s), 1578 (s), 1450 (s), 1052 (m), 1010 (s), 785 (s), 745 (s), 687 (s), 670 (s). Anal. Calcd for C26H66Al2Cl2Fe2N6: C, 44.65; H, 9.51; N, 12.02. Found: C, 44.91; H, 9.91; N, 11.45.

Synthesis of 3. To a suspension of 1b (0.0906 mmol, 81 mg) in THF (5 mL) was added a solution of NaAlH₂(OCH₂CH₂OMe)₂ in toluene (3.6 M, 0.38 mL) at 25 °C under an argon atmosphere while the mixture immediately turned purple. After the mixture was stirred at this temperature for 12 h, the resulting purple suspension was filtered through glass frits, and the solvent was removed from the filtrates under reduced pressure. The residue was washed with toluene and ether to afford 3 (91 mg, 76%). Single crystals of 3 were grown from THF/ether at ambient temperature. ¹H NMR (THF-*d*₈, rt): δ 3.92 (4H, t, *J* = 5.6 Hz, OCH₂), 3.43 (4H, t, *J* = 5.6 Hz, OCH₂), 3.41 (6H, s,

OCH₃), 3.33 (6H, s, OCH₃), 3.06 (12H, m, NCH₂), 2.95 (18H, s, NMe), 2.93 (12H, m, NCH₂), -25.6 (6H, s, μ -H) ppm. COSY (THF- $d_{6^{\circ}}$ rt): 3.92/3.67; 3.79/3.43; 3.06/2.93. ¹³C{¹H} NMR (THF- $d_{8^{\circ}}$ rt): δ 78.1 (OCH₂), 74.4 (OCH₂), 61.0 (OCH₂), 60.3 (NCH₂), 60.0 (OCH₂), 59.6 (NCH₃), 58.7 (OCH₃), 58.3 (OCH₃) ppm. HMQC (¹³C/¹H, THF- $d_{8^{\circ}}$ rt): δ 78.1/3.43; 74.4/3.67; 61.0/3.79; 60.3/3.06, 2.93; 60.0/3.92; 59.6/2.95; 58.7/3.33; 58.3/3.41. HMBC (¹³C/¹H, THF- $d_{8^{\circ}}$ rt): δ 78.1/3.79; 74.4/3.92; 61.0/3.43; 60.3/3.06, 2.93; 60.0/3.67. IR (KBr, cm⁻¹): ν 2851 (s), 1655 (s), 1648 (s), 1638 (s), 1458 (s), 1119 (s), 1086 (s), 1014 (s), 835 (s), 763 (s), 603 (m). Anal. Calcd for C₃₀H₇₆Al₂ClFe₂N₆NaO₈: C, 41.27; H, 8.77; N, 9.63. Found: C, 41.70; H, 9.81; N, 9.64.

Synthesis of 4. In the glovebox, to a suspension of 1b (0.101 mmol, 90 mg) in THF (7 mL) was added {Li(OEt₂)₂}{Al(OC₆H₃- $2,6^{-t}Bu_2)_2$ (μ -H)₂ (1.56 mmol, 930 mg) at room temperature. The mixture was stirred for 15 h while the system was closed. Then, insoluble byproduct was filtered and solvent was evaporated from the filtrate. Washing the residue with ether and a small amount of toluene followed by dryness in vacuo gave 4 as a red-purple solid (190 mg, 94%). Single crystals were obtained from a THF solution by slow diffusion of ether. ¹H NMR (THF- d_8 , rt): δ 6.99 (4H, d, J = 7.6 Hz, Ar-H, meta), 6.42 (2H, t, J = 7.6 Hz, Ar-H, para), 2.69–2.59 (12H, m, NCH₂), 2.37 (9H, s, NMe), 1.59 (36H, s, ¹Bu), -25.20 (3H, s, μ -H) ppm. COSY (THF- d_8 , rt): 6.99/6.42. ¹³C{¹H} NMR (THF- d_8 , rt): δ 160.2 (Ar, ipso), 139.9 (Ar, ortho), 124.9 (Ar, meta), 116.2 (Ar, para), 60.1 (NCH₂), 58.7 (NCH₃), 36.3 (CMe₃), 33.3 (CMe₃) ppm. HMQC ($^{13}C/^{1}H$, THF- d_{8} , rt): δ 124.9/6.99; 116.2/6.42; 60.1/2.69-2.59; 58.7/2.37; 33.3/1.59. HMBC (¹³C/¹H, THF-d₈, rt): δ 160.2/ 6.99; 139.9/6.42; 36.3/6.99, 1.59. IR (KBr, cm⁻¹): ν 2950 (s), 1719 (m), 1638 (m), 1408 (s), 1245 (s), 1013 (s), 895 (s), 866 (s), 750 (s), 677 (s). Anal. Calcd for C₄₁H₇₄AlFeN₃O₃: C, 66.56; H, 10.08; N, 5.68. Found: C, 66.70; H, 10.65; N, 5.77.

Calculation Methods. All geometry optimizations, vibrational frequencies, and energy calculations were carried out using the density functional theory (DFT)²² at the B3LYP level^{23,24} with a mixed basis set in the Gaussian03 program.²⁵ The mixed basis set contained 3-21G²⁶ for the carbons and hydrogens of Me₃tacn and aryloxide ligands and the oxygens of aryloxide ligands, 6-31G for nitrogens of Me₃tacn and the hydrogens of the bridging ligands, and 6-31+G(d,p)²⁷⁻³¹ for irons and aluminum. Wiberg bond indexes^{32,33} were calculated using natural bond orbital (NBO) analysis.³⁴

ASSOCIATED CONTENT

S Supporting Information

X-ray crystallographic data for 2-4 in cif format. Cartesian coordinates of 2 and 4 from the computation. Diagrams of molecular orbitals of the singlet states of 2 and 4. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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