

# Coordination of alane and aluminum alkyls to the N-donor atom of side chain functionalized cyclopentadienyl iron and nickel complexes; structure of $\{[(C_5H_5)(C_5H_4CH_2NMe_2)]Fe\}_2AlH_3$

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## Abstract

The synthesis of iron and nickel complexes with interaction of alane and trialkylaluminum compounds to the amino group is described. Treatment of [2-(*N,N*-dimethylamino)methyl] ferrocene  $[(C_5H_5)(C_5H_4CH_2NMe_2)]Fe$  (**1**) with trimethylaminealane ( $H_3AlNMe_3$ ), leads to the formation of the iron alane complex  $\{[(C_5H_5)(C_5H_4CH_2NMe_2)]Fe\}_2AlH_3$  (**2**), with a five-coordinated aluminum center. The structure of **2** has been determined by single-crystal X-ray diffraction. The reaction of  $FeCl_2$  with two equivalents of  $\{(C_5H_4CH_2CH_2NMe_2)Li\}$  leads to the formation of  $[(C_5H_4CH_2CH_2NMe_2)_2Fe]$  (**3**). Complex **3** reacts quantitatively with two equivalents of trimethylaluminum to the compound  $[(C_5H_4CH_2CH_2NMe_2)_2Fe](AlMe_3)_2$  (**4**). Addition of trimethylaluminum or triethylaluminum to the nickel complex  $[(C_5H_4CH_2CH_2NMe_2)_2Ni]Ni$  (**5**) give the paramagnetic nickel aluminum compounds  $[(C_5H_4CH_2CH_2NMe_2)_2Ni](AlMe_3)_2$  (**6a**) and  $[(C_5H_4CH_2CH_2NMe_2)_2Ni](AlEt_3)_2$  (**6b**), respectively. These compounds were characterized by  $^1H$ ,  $^{13}C$  and  $^{27}Al$  NMR, elemental analysis and mass spectroscopy. Studies to deposit intermetallic thin films using these compounds as bimetallic single source precursors revealed that aluminum was deposited, only. © 1997 Elsevier Science S.A.

**Keywords:** Organo-nickel and iron complexes; Dative amine aluminum bonds; [2-(*N,N*-dimethylamino)ethyl]cyclopentadienyl ligand ( $Cp^N$ ); Paramagnetic NMR; MOCVD

## 1. Introduction

The application of (organo-) aluminum compounds as precursors for metal organic chemical vapor deposition (MOCVD) of aluminum containing thin films for microelectronics [1] has been one of the driving forces for the recently renewed interest in the chemistry of alane and its derivatives [2–4]. We were attracted to this chemistry, since it was recognized that compounds which contain transition metal and aluminum in the same molecular unit may serve as ‘single source precursors’ to deposit *mixed-metal* thin films [5,6]. However, transition metal aluminum compounds substituted with carbonyl ligands were not generally suitable for obtaining pure films. Carbonyl ligands may cause problems by forming isocarbonyl structures (M–CO–Al), which eventually leads to CO dissociation and, thus, the contamination of the film with C and O. The Al–C bond is

also not the ideal choice, especially in the case of trimethylaluminum, because inefficient Al–C bond cleavage (absence of the  $\beta$ -hydrogen elimination pathway) causes hydrocarbon impurities [5,6]. Carbonyl group free transition metal alane complexes appear to be good candidates for obtaining purer films. But only few ‘all hydrocarbon’ compounds with direct transition metal aluminum bonds have been described so far [5,6]. Compounds in which M and Al are linked together by an ancillary Lewis base function rather than by M–Al bonds, have been proposed to be potentially interesting for their relationship to materials and solid state chemistry, e.g., MOCVD of intermetallic films [7]. We were interested to further explore this latter strategy and investigated some ferrocene and nickelocene complexes supplemented by N-donor functionalized ligands and their chemistry with aluminum derivatives, e.g., with  $H_3AlNMe_3$ . It should be mentioned, that cyclopentadienyl systems functionalized with Lewis bases, in particular the [2-(*N,N*-dimethylamino)ethyl] cyclopentadienyl

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ligand, have attracted general interest, because this ligand can reversibly protect a vacant coordination site at a metal center for subsequent reactions [8–12]. We report here the synthesis and characterization of new heterobimetallic complexes formed by the interaction of the N-donor functionalized cyclopentadienyl iron or nickel complexes by the amine atom with alane or alkyl aluminum derivatives.

## 2. Results and discussion

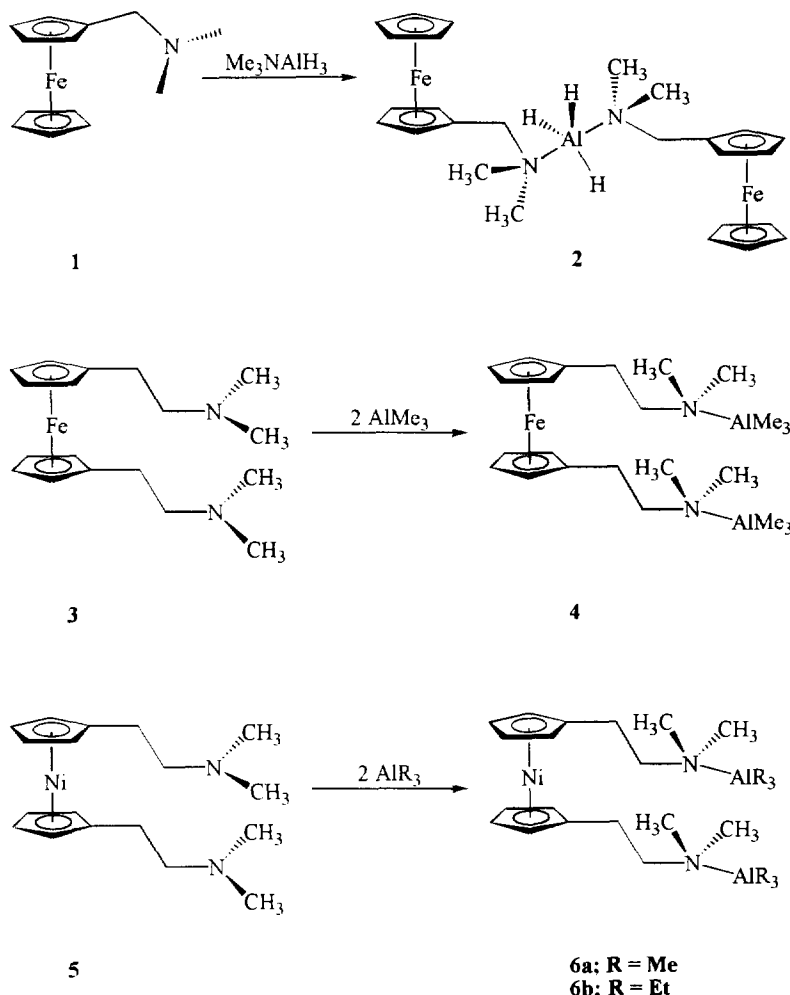
### 2.1. Synthesis and properties

The amino group of [2-(*N,N*-dimethylamino)methyl]ferrocene (**1**) reacts as a strong donor rapidly with 0.5 equivalents of the alane adduct ( $\text{H}_3\text{AlNMe}_3$ ) at  $-30^\circ\text{C}$  to replace trimethylamine and forming quantitatively the ferrocene alane complex  $\{[(\text{C}_5\text{H}_5)(\text{C}_5\text{H}_4\text{CH}_2\text{NMe}_2)]\text{Fe}\}_2\text{AlH}_3$  (**2**) with a five-coordinated aluminum center (Scheme 1). The corresponding 1:1 adduct, using 1.0 equivalents of the alane, could not be obtained in a pure form. Compound **2**

sublimes under moderate conditions ( $10^{-3}$  Torr,  $90^\circ\text{C}$ ). As seen in Scheme 1, the ferrocene complex  $\text{Cp}_2^{\text{N}}\text{Fe}$  (**3**) is obtained as a yellow distillable oil ( $90^\circ\text{C}$ ,  $10^{-3}$  Torr, dynamic vacuum) in very good yield (90%) by treatment of  $\text{FeCl}_2$  in THF with  $\text{Cp}^{\text{N}}\text{Li}$  (prepared in situ from  $\text{Cp}^{\text{N}}\text{H}$  and *n*-BuLi). Reaction of **3** with two equivalents of trimethylaluminum yields the bimetallic iron aluminum complex **4** as a four-coordinate aluminum species (yellow crystals). Analogously to **4**, treatment of the nickelocene complex  $\text{Cp}_2^{\text{N}}\text{Ni}$  (**5**) [9] with trialkylaluminum ( $\text{AlR}_3$ ) leads to the formation of trialkylaluminum iron compounds **6a**, ( $\text{R} = \text{Me}$ ), and **6b**, ( $\text{R} = \text{Et}$ ), respectively (Scheme 1). Complex **6a** is obtained as green crystals, in contrast to **6b**, which is available as a green oil. The mixed metal aluminum compounds (**2–6b**) are extremely air and moisture sensitive.

### 2.2. Spectroscopic characterization

The  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra of **2** (see Section 4) are similar to the known bimetallic compounds of the aluminum adduct and [(dimethylamino)methyl]ferrocene



Scheme 1.

[7]. The chemical shifts of **2** are in good agreement with the reference compounds. The proton resonance of the  $\text{NMe}_2$  group is a singlet and is shifted upfield in comparison to the free ligand. The  $\text{CH}_2$  protons also resonates as a singlet and are shifted downfield to that of the free ligand. The protons of the substituted cyclopentadienyl ring are well resolved and appear as pseudotriplets. This pattern is consistent with an  $\text{AA}'\text{BB}'$  spin system. The  $^{27}\text{Al}$  NMR shift of **2** (109 ppm) is within the range of five-coordinated organo-aluminum compounds [2]. The IR spectra in THF solution present a broad band at  $1717\text{ cm}^{-1}$ , which is assigned to the terminal  $\nu(\text{Al}-\text{H})$  vibration. This value is very similar to those for related base stabilized five-coordinated aluminum hydride species [2]. The mass spectra (CI = chemical ionization, positive ions) of **2** do not show the molecular peak. The [(dimethylamino)methyl]ferrocene fragment is the base peak. The cleavage of the Lewis base aluminum bond is the predominant fragmentation process. Similar results were obtained by Kumar et al. [7] with trimethylaluminum adducts of [(dimethylamino)methyl]ferrocene. The  $^1\text{H}$  and  $^{13}\text{C}$  NMR data for **3** are similar to those reported for the corresponding tetramethyl substituted derivative  $[\text{Cp}_2^*\text{N} \text{Fe}]$  ( $\text{Cp}^*\text{N} = [2-(N,N\text{-dimethylamino)ethyl]-2,3,4,5\text{-tetramethylcyclopentadienyl}]$ ) [13]. In the  $^1\text{H}$  NMR spectra of **3** two multiplets are obtained for the two methylene groups. The NMR spectroscopic data for **4** are comparable to those for {trimethylaluminum}[(dimethylamino)methyl]ferrocene [7]. The  $^{27}\text{Al}$  NMR resonance of **4** (178 ppm) was observed in the range of a four-coordi-

nated organo-aluminum compound [14]. The paramagnetic NMR of the heterobimetallic compounds **6a–b** and  $[\text{Cp}_2^*\text{Ni}]$  (**5**) [9] can be recorded easily. Due to the excellent solubility of **6a** and **6b**, no special equipment is needed as described elsewhere [15]. As expected, the linewidth of the signals decreases with increasing distance of the corresponding nuclei from the paramagnetic center. The  $^1\text{H}$  and  $^{13}\text{C}$  NMR shift for the [(2- $N,N$ -dimethylamino)ethyl] group of these compounds are almost similar to those of complex **5**, and other known nickelocene complexes,  $[\text{MeCp}]_2\text{Ni}$  [16],  $[\text{EtMe}_4\text{Cp}]_2\text{Ni}$  [17] and  $[\text{EtCp}]_2\text{Ni}$  [18]. The  $^{27}\text{Al}$  NMR resonances of **6a** and **6b** (196 and 206 ppm) were observed within the usual range of four-coordinated organo-aluminum compounds [14].

### 2.3. Structure of compound **2**

The molecular structure of **2** in the solid state was determined by X-ray single crystal diffraction (Fig. 1) and confirms the expected trigonal bipyramidal coordination of the Al center by three equatorial hydride ligands and two apical amine ligands [19]. The angle  $\text{N}(1)-\text{Al}-\text{N}(2)$  with  $178.18(9)^\circ$  and the  $\text{Al}-\text{N}$  donor-acceptor bonds of 2.168(2) and 2.178(2) Å compare well with other bis(donor)adducts of alane, e.g., 2.18(1) Å in  $\text{H}_3\text{Al}(\text{NMe}_3)_2$  [20] and 2.187(4), 2.188(4) Å in  $\text{H}_3\text{Al}(\text{1,3,5-trimethylhexahydro-1,3,5-triazine})_2$  [2]. These bond lengths are typically longer than those in tetra-coordinated amino alane species, e.g., 2.063(8) for  $\text{H}_3\text{AlNMe}_3$  [21]. All hydrogen atom positions were

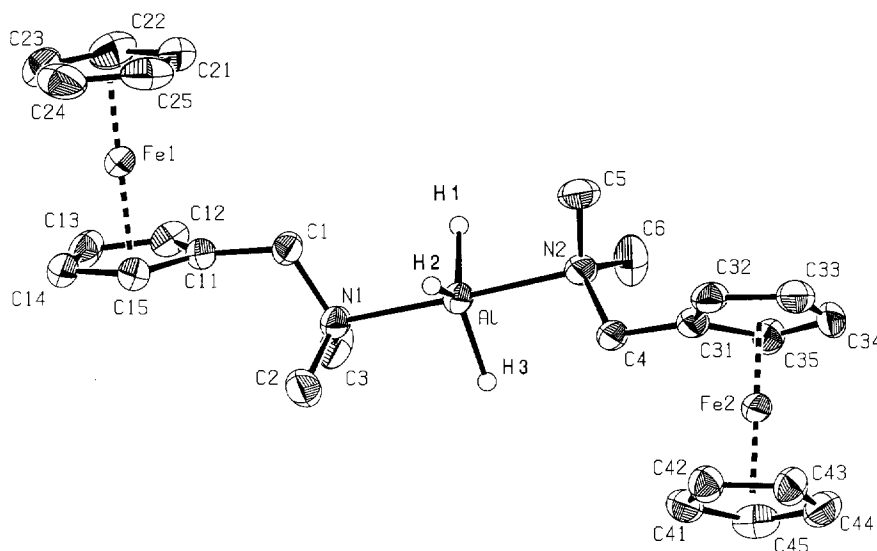


Fig. 1. The molecular structure of **2** in the solid state (ORTEP drawing, the thermal ellipsoids are represented at a 50% probability level). Selected bond distances [Å] and angles  $^\circ$ :  $\text{Al}-\text{N}1$  2.168(2),  $\text{Al}-\text{N}2$  2.178(2),  $\text{Al}-\text{H}1$  1.53(3),  $\text{Al}-\text{H}2$  1.62(3),  $\text{Al}-\text{H}3$  1.57(3),  $\text{N}1-\text{C}1$  1.495(4),  $\text{N}1-\text{C}2$  1.473(5),  $\text{N}1-\text{C}3$  1.474(4),  $\text{N}2-\text{C}4$  1.494(3),  $\text{N}2-\text{C}5$  1.470(5),  $\text{N}2-\text{C}6$  1.472(5),  $\text{N}1-\text{Al}-\text{N}2$  178.18(9),  $\text{H}1-\text{Al}-\text{H}2$  119.2(18),  $\text{H}1-\text{H}3$  120.7(17),  $\text{H}2-\text{Al}-\text{H}3$  120.0(18),  $\text{N}1-\text{Al}-\text{H}1$  88.9(10),  $\text{N}1-\text{Al}-\text{H}2$  92.5(13),  $\text{N}1-\text{Al}-\text{H}3$  91.7(103),  $\text{N}2-\text{Al}-\text{H}1$  89.4(10),  $\text{N}2-\text{Al}-\text{H}2$  88.0(13),  $\text{N}2-\text{Al}-\text{H}3$  89.9(13),  $\text{Al}-\text{N}1-\text{C}1$  108.55(17),  $\text{Al}-\text{N}1-\text{C}2$  108.67(18),  $\text{Al}-\text{N}1-\text{C}3$  108.71(19),  $\text{Al}-\text{N}2-\text{C}4$  108.91(17),  $\text{Al}-\text{N}2-\text{C}6$  107.72(18),  $\text{Al}-\text{N}2-\text{C}5$  109.1(2).

found in the Fourier difference map calculated from the model containing all non-hydrogen atoms. The hydrogen positions were refined with individual isotropic temperature parameters. The Al–H bond lengths of 153–162 pm are within the expected range. In summary, the structural features of **2** are quite normal.

#### 2.4. MOCVD experiments

MOCVD experiments were conducted using an isothermal horizontal hot wall tube reactor described elsewhere equipped with a quadrupole mass spectrometer for in situ analysis of the exhaust gases [22]. Compound **2** was sublimed at 80°C,  $10^{-4}$  Torr, through the hot zone of the reactor kept at temperatures between 200–500°C in vacuo ( $10^{-4}$  Torr) without the use of carrier gases (typical deposition time: 3 h).

It is quite likely that the compound decomposes in the gas phase upon heating in vacuo (sublimation) into two fragments,  $\{(C_5H_5)[C_5H_4CH_2NMe_2(AlH_3)]\}Fe$  and  $\{(C_5H_5)[C_5H_4CH_2NMe_2]Fe$  as it is the case for  $H_3Al(NMe_3)_2$  [20]. Compound **2** was however recovered unchanged by preparative sublimation. This is understandable, because upon work-up of the obtained re-sublimate, which is supposed to be a mixture of the two molecular fragments above, the stable bis-adduct of alane will certainly be formed again in solution. The mass spectra (CI) of **2** only showed the fragment  $\{(C_5H_5)[C_5H_4CH_2NMe_2]Fe$  as the base peak. No Fe/Al fragments were detected.

The obtained metallic coatings (0.1–0.5  $\mu m$ , by profilometry) on borosilicate glass substrates were examined by SEM–EDX showing the presence of aluminum only (> 95%; confirmed by AAS after dissolution of the film; only traces of iron were detected). The ferrocene part of the precursor molecule collected quantitatively in the cold trap. A mass balance (by AAS) of the condensables and the obtained coatings showed, that no Al was found in the cold trap and the ratio of Fe (in the cold trap) to Al (thin film on the substrates and the reactor walls) was about 2:1.

Similar observations were made for the alkyl congener **4**. However, in this case, significant amounts of Al collected in the cold trap also. Due to the chemical instability of **6a–b** under the conditions of volatilization ( $10^{-3}$  Torr, 90°C) good quality metallic films could not be grown from these compounds. The analysis of the obtained coatings again revealed the absence of the transition metal component.

### 3. Conclusions

It was shown that ferrocene and nickelocene complexes with N-donor functionalized ligands react with alane or alkylaluminum compounds, to form bimetallic

donor acceptor complexes of various M/Al stoichiometries. The single crystal X-ray study of **2** and  $^{27}Al$ -NMR spectroscopy proves the presence of a five-coordinated aluminum species in the solid state as well as in solution.

The results of MOCVD experiments suggest that such metallocene aluminum Lewis-base/acid adducts are of limited use as single molecule precursors for mixed metal alloy thin films at typical low temperature deposition conditions. This is understandable, because metallocenes are thermally very robust. The weakest bond, namely the Al–N donor/acceptor bond, will be cleaved first, thus leading to an independent ‘fate’ of the two metal moieties of the precursor during the decomposition on the substrate surface as well as in the gas phase. Even the  $AlH_3$  moiety, as it is present in the case of complex **2**, does not change the situation. The expectation, that a hydrogen transfer from the aluminum to the transition metal or the Cp ring during the decomposition may occur and may assist the Fe–Cp cleavage was not fulfilled.

We thus conclude that a strong direct M–Al interaction [23] is still the best concept for single source precursors of transition metal aluminide thin films superior to the adduct type precursors described herein as well as in Ref. [7]. In any case, the ligand surroundings of the two metals in question have to be designed in a way that the typical activation energies for the metal–ligand splitting processes match.

### 4. Experimental

All manipulations were undertaken with standard Schlenk and glove box techniques under inert gas atmosphere (purified  $N_2$ ) using carefully dried (< 2 ppm  $H_2O$ ) oxygen-free solvents. All samples for NMR spectra were contained in vacuum-sealed NMR tubes. JEOL JNM-GX400 and JNM-GX270 spectrometers and usual data collection parameters were used for  $^1H$ ,  $^{13}C$ , and  $^{27}Al$  NMR spectroscopy of the diamagnetic compounds **2–4**.  $^1H$ ,  $^{13}C$ ,  $^{27}Al$  NMR spectra were referenced to internal solvent and corrected to TMS, for  $^{27}Al$  relative to 1 M  $[Al(H_2O)_6(NO_3)_3]$  [24]. All  $J$  values are reported in Hz (Hertz). The NMR spectra of a saturated solution of paramagnetic **6a** and **6b** in  $C_6D_6$  were recorded on a BRUKER MSL 300 NMR spectrometer operating in the low power mode and equipped with a conventional 5 mm  $^1H/^{13}C$  dual probehead. Measurement frequencies of 300 ( $^1H$ ) and 75.5 ( $^{13}C$ ) MHz were applied. A dead time delay of 10  $\mu s$  and a pulse repetition time of 200 ms were integrated within the single pulse sequence. The linewidths  $\nu_{1/2}$  at half height of the signals were obtained by the deconvolution routine of the BRUKER WINNMR program. The paramagnetic  $^{27}Al$  NMR spectra of a saturated solution

of **6a** and **6b** in  $C_6D_6$  were recorded on a BRUKER MSL 300 NMR spectrometer operating in the low power mode and equipped with a conventional 10 mm multinuclear probehead. A measurement frequency of 78.2 MHz, a dead time delay of 10  $\mu$ s, a (non-optimized) pulse width of 10  $\mu$ s, a pulse delay of 500 ms, and a single pulse sequence were applied. The linewidths  $\nu_{1/2}$  at half height of the signals were obtained by the deconvolution routine of the BRUKER WINNMR program. A dilute solution of 1 M  $[Al(H_2O)_6(NO_3)_3]$  with  $\delta = 0$  was used as an external chemical shift standard [24]. A  $^{27}Al$  NMR background signal at 67 ppm ( $\nu_{1/2} = 4.3$  kHz), due to the 5 mm glass NMR tube, was visible in all the spectra, but did not overlap with signals of the samples, as careful subtraction studies showed. Mass spectra were recorded with a Finnigan MAT90 instrument;  $m/z$  values are reported for  $^{27}Al$ ,  $^{56}Fe$ , and  $^{59}Ni$ , normal isotope distribution observed. The starting compounds were prepared as described in the literature. Abbreviations are as follows:  $Cp^N = \eta^5-C_5H_4CH_2CH_2NMe_2$ ,  $Me = CH_3$ ,  $Et = CH_2CH_3$ . Elemental analysis were provided by the Microanalytic Laboratory of the Technical University at Munich.

#### 4.1. Synthesis

##### 4.1.1. Bis{2-(*N,N*-dimethylamino)methylferrocene} (trihydrido)aluminum (2)

The pentane solution (20 ml) of  $Me_3NAIH_3$  (0.178 g, 2 mmol) was added at  $-30^\circ C$  to a stirred pentane solution (30 ml) of  $[(C_5H_5)(C_5H_4CH_2NMe_2)Fe]$  (**1**) (0.486 g, 2 mmol). During the addition, the formation of a yellow precipitate was observed. The resulting mixture was allowed to warm to room temperature and stirred for 2 h. After evaporation of the solvent, the residue was washed three times with 10 ml of pentane and dried in vacuo. The crude product was purified by crystallization from ether/pentane at  $-30^\circ C$ . Yield: 0.475 g (92%).

**2**: yellow crystals.  $^1H$  NMR (399.78 MHz,  $C_6D_6$ ,  $25^\circ C$ ):  $\delta = 2.21$  (s, 12H,  $NCH_3$ ); 3.63 (s, 4H,  $CH_2$ ); 3.88 (s, 10H,  $C_5H_5$ ); 3.91 (t,  $^1J_{H-H} = 1.8$  Hz, 4H,  $C_5H_4$ ).  $^{13}C\{^1H\}$  NMR (100.5 MHz,  $C_6D_6$ ,  $25^\circ C$ ):  $\delta = 43.6$  ( $NCH_3$ ); 57.9 ( $CH_2$ ); 68.3 ( $C_5H_4$ ); 68.8 ( $C_5H_5$ ); 68.9 ( $C_5H_4$ ); 70.9 ( $C_{ipso}$  of  $C_5H_4$ ).  $^{27}Al\{^1H\}$  NMR (78.2 MHz,  $C_6D_6$ ,  $25^\circ C$ ):  $\delta = 109.1$  ( $AlH_3$ ). IR (THF): 1714, 1720  $cm^{-1}$  ( $\nu(Al-H)$ ). MS(Cl):  $m/z$  (%) = 243 (100) [ $(M^+ - \{(C_5H_5)(C_5H_4CH_2NMe_2)AlH_3\}Fe)$ ]; 199 (16) [ $\{(C_5H_5)(C_5H_4CH_2NMe_2)Fe\}^+ - NMe_2$ ]. Anal. calcd. for  $C_{26}H_{37}N_2AlFe_2$  (516.14): C, 60.45; H, 7.22; N, 5.43; Al, 5.23. Found: C, 60.23; H, 7.30; N, 5.52; Al, 4.9.

##### 4.1.2. Bis{2-(*N,N*-dimethylamino)ethylcyclopentadienyl}iron(II) (3)

A THF suspension of  $FeCl_2$  (1.27 g, 10 mmol) was added at  $-78^\circ C$  to a stirred solution (THF/hexane) of

$[Cp^N Li]$  (20 mmol) [obtained from reaction of 1.6 M *n*-BuLi (12.5 ml, 20 mmol) with  $C_5H_5CH_2CH_2NMe_2$  (2.74 g, 20 mmol)]. The resulting mixture was allowed to warm to room temperature, and stirred for 2 h. After evaporation of the solvent, the residue was extracted with toluene and the crude product was purified by flask to flask distillation ( $90^\circ C$ ,  $10^{-3}$  Torr). Yield: 2.95 g (90%).

**3**: yellow oil.  $^1H$  NMR (399.78 MHz,  $C_6D_6$ ,  $25^\circ C$ ):  $\delta = 2.11$  (s, 6H,  $NCH_3$ ); 2.37 (m, 2H,  $NCH_2CH_2$ ); 2.46 (m, 2H,  $NCH_2CH_2$ ); 3.92–3.94 (2  $\times$  m, 2  $\times$  2H,  $C_5H_4$ ).  $^{13}C\{^1H\}$  NMR (100.5 MHz,  $C_6D_6$ ,  $25^\circ C$ ):  $\delta = 28.2$  ( $NCH_2CH_2$ ); 45.6 ( $NCH_3$ ); 61.5 ( $NCH_2CH_2$ ); 68.1–69.1 ( $C_5H_4$ ); 87.3 ( $C_{ipso}$  of  $C_5H_4$ ). MS(Cl):  $m/z$  (%) = 328 (100) [ $M^+$ ]; 270 (3) [ $M^+ - CH_2NMe_2$ ]. Anal. calcd. for  $C_{18}H_{28}N_2Fe$  (328.48): C, 65.85; H, 8.59; N, 8.53. Found: C, 65.68; H, 8.81; N, 8.79.

##### 4.1.3. Bis{2-(*N,N*-dimethylaminoethyl)cyclopentadienyl}(trimethylaluminum)-iron(II) (4)

The pentane solution (10 ml) of trimethylaluminum (0.180 g, 2.5 mmol) was added at  $-30^\circ C$  to a stirred pentane solution (30 ml) of **3** (0.328 g, 1 mmol). The resulting mixture was allowed to warm up to room temperature and stirred for 5 h. The crude product was purified by crystallisation at  $-30^\circ C$ . Yield: 0.449 g (95%).

**4**: yellow crystals.  $^1H$  NMR (399.78 MHz,  $C_6D_6$ ,  $25^\circ C$ ):  $\delta = -0.41$  (s, 9H,  $AlCH_3$ ); 1.85 (s, 6H  $NCH_3$ ); 2.38 (m, 2H,  $NCH_2CH_2CH_2$ ); 2.50 (m, 2H,  $NCH_2CH_2$ ); 3.85–3.93 (2  $\times$  m, 2  $\times$  2H,  $C_5H_4$ ).  $^{13}C\{^1H\}$  NMR (100.5 MHz,  $C_6D_6$ ,  $25^\circ C$ ):  $\delta = -8.5$  ( $AlCH_3$ ); 23.5 ( $NCH_2CH_2$ ); 43.9 ( $NCH_3$ ); 60.4 ( $NCH_2CH_2$ ); 68.6–68.9 ( $C_5H_4$ ); 85.0 ( $C_{ipso}$  of  $C_5H_4$ ).  $^{27}Al\{^1H\}$  NMR (78.2 MHz,  $C_6D_6$ ,  $25^\circ C$ ):  $\delta = 178.0$  ( $AlMe_3$ ). Anal. calcd. for  $C_{18}H_{31}N_2AlFe_2$  (472.45): C, 61.01; H, 9.81; N, 5.72; Al, 11.42. Found: C, 60.85; H, 9.94; N, 5.80; Al, 11.4.

##### 4.1.4. Bis{2-(*N,N*-(dimethylaminoethyl)cyclopentadienyl}(trimethylaluminum)nickel(II) (6a) and Bis{2-(*N,N*-(dimethylaminoethyl)cyclopentadienyl}(triethylaluminum)nickel(II) (6b)

The pentane solution (10 ml) of trimethylaluminum (0.180 g, 2.5 mmol) was added at  $-30^\circ C$  to a stirred pentane solution (30 ml) of  $(Cp^N)_2Ni$  (**5**) (0.330 g, 1 mmol). The resulting mixture was allowed to warm up to room temperature and stirred for 2 h. After evaporation of the solvent, the crude product was extracted with pentane and purified by crystallisation at  $-30^\circ C$ . Yield: 0.403 g (85%). **6b** was prepared analogously from 0.330 g (1 mmol) of **5** and triethylaluminum (0.287 g, 2.5 mmol). Yield: 0.492 g (88%).

**6a**: green crystals.  $^1H$  NMR (300 MHz,  $C_6D_6$ ,  $25^\circ C$ ):  $\delta \{ \nu_{1/2} [Hz] \} = -248.7 \{1500\}$  (4H,  $C_5H_4$ ); 0.47 {40} (9H,  $Al(CH_3)_3$ ); 0.68 {59} (2H,  $H_\beta$ ,  $NCH_2CH_2$ ); 4.24 {40} (6H,  $NCH_3$ ); 175.4 {480} (2H,  $H_\alpha$ ,  $N(CH_2CH_2)$ ).

$^{13}\text{C}$  NMR (75.5 MHz,  $\text{C}_6\text{D}_6$ , 25°C):  $\delta$   $\{\nu_{1/2}$  [kHz] = -568.8 {0.47} ( $\text{C}_\alpha$   $\text{NCH}_2\text{CH}_2$ ); -3.4 {0.21} ( $\text{Al}(\text{CH}_3)_3$ ); 56.8 {0.13} ( $\text{NCH}_3$ ); 822.6 {0.72} ( $\text{C}_\beta$ ,  $\text{NCH}_2\text{CH}_2$ ); 1398 {4–5} ( $\text{C}_5\text{H}_4$ ); 1530 {4–5} ( $\text{C}_5\text{H}_4$ ).  $^{27}\text{Al}$  NMR ( $\text{C}_6\text{D}_6$ , 25°C):  $\delta$   $\{\nu_{1/2}$  [kHz] = 196 {5.0} ( $\text{Al}(\text{CH}_3)_3$ ). MS(CI):  $m/z$  (%) = 474 (not detected) [ $\text{M}^+$ ], 388 (7) [ $(\text{Cp}^{\text{N}})_2\text{Ni}_2^+$ ], 330 (100) [ $(\text{M}^+-2(\text{AlMe}_3))$ ], 136 (2) [ $\text{Cp}^{\text{N}+}$ ]. Anal. calcd. for  $\text{C}_{24}\text{H}_{46}\text{N}_2\text{Al}_2\text{Ni}$  (474.2): C, 60.65; H, 9.76; N, 5.89; Al, 11.35, Ni, 12.35. Found: C, 60.31; H, 9.41; N, 5.65; Al, 11.50, Ni, 12.00.

**6b**: green oil.  $^1\text{H}$  NMR (300 Mhz,  $\text{C}_6\text{D}_6$ , 25°C):  $\delta$   $\{\nu_{1/2}$  [Hz] = -253.6 {1700} ( $\text{H}_b$  and  $\text{H}_c$ ,  $\text{C}_5\text{H}_4$ ); 1.05 {35} (6H,  $\text{Al}(\text{CH}_2\text{CH}_3)_3$ ); 1.63 {59} (2H,  $\text{H}_\beta$   $\text{NCH}_2\text{CH}_2$ ); 2.24 {40} (9H,  $\text{Al}(\text{CH}_2\text{CH}_3)_3$ ); 4.32 {40} (6H  $\text{NCH}_3$ ); 180.4 {540} (2H,  $\text{H}_\alpha$ ,  $\text{NCH}_2\text{CH}_2$ ).  $^{13}\text{C}$  NMR (75.5 MHz  $\text{C}_6\text{D}_6$ , 25°C):  $\delta$   $\{\nu_{1/2}$  [kHz] = -578.9 {0.42} ( $\text{C}_\alpha$ ,  $\text{NCH}_2\text{CH}_2$ ); 2.8 12 {0.17} ( $\text{Al}(\text{CH}_2\text{CH}_3)_3$ ); 13.3 {0.18} ( $\text{Al}(\text{CH}_2\text{CH}_3)_3$ ); 56.7 {0.17} ( $\text{NCH}_3$ ); 823.5 {0.85} ( $\text{C}_\beta$ ,  $\text{NCH}_2\text{CH}_2$ ); 1411 {4–5} ( $\text{C}_5\text{H}_4$ ); 1558 {4–5} ( $\text{C}_5\text{H}_4$ ).  $^{27}\text{Al}$  NMR ( $\text{C}_6\text{D}_6$ , 25°C):  $\delta$   $\{\nu_{1/2}$  [kHz] = 206 {6.6} ( $\text{Al}(\text{CH}_2\text{CH}_3)_3$ ). MS(CI):  $m/z$  (%) = 559 (2) [ $\text{M}^+$ ]; 388 (7) [ $(\text{Cp}^{\text{N}})_2\text{Ni}_2^+$ ]; 330 (100) [ $(\text{M}^+-2(\text{AlEt}_3))$ ]; 136 (3) [ $\text{Cp}^{\text{N}+}$ ]. Anal. calcd. for  $\text{C}_{30}\text{H}_{58}\text{N}_2\text{Al}_2\text{Ni}$  (559.48): C, 64.40; H, 10.44; N, 5.00; Al, 9.64, Ni, 10.49. Found: C, 63.26; H, 10.08; N, 4.91; Al, 10.1, Ni, 11.49.

#### 4.2. X-ray single crystal structure determination of 2

Crystals of the compound **2** have been obtained by slow solvent diffusion from pentane/toluene mixtures at -30°C. Preliminary examination and data collection were carried out on an IPDS (Stoe & Cie) diffractometer. The compound crystallizes in the orthorhombic space group  $P2_12_12_1$  (Nr. 19). The final cell constants of  $a = 11.1360(10)$  Å,  $b = 12.6860(10)$  Å,  $c = 17.9260(10)$  Å,  $\alpha = 90^\circ$ ,  $\beta = 90^\circ$ ,  $\gamma = 90^\circ$ ,  $V = 2532.4(3)$  Å<sup>3</sup>;  $Z = 4$ , Mo  $K_\alpha$  radiation  $\mu = 12.0$  cm<sup>-1</sup>. The data collection was performed at 273 K. A total number of 27244 reflections were collected, 4276 unique reflections, 4022 observed with  $I > 2.0 \sigma(I)$ . The last cycles of the refinement showed a shift/error = 0.00,  $R = 0.0267$ ,  $wR = 0.0633$ ,  $S = 1.04$ , and a residual electron density of (min/max) -0.22/0.21 eÅ<sup>-3</sup>. Supplementary material including full crystallographic and experimental data, hydrogen positional parameters, thermal parameters, interatomic distances, and bond angles may be obtained from the Fachinformationzentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information, D-76344 Eggenstein-Leopoldshafen 2 (Germany), on quoting the depository

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