Angewandte Chemie
Eine Zeitschrift der Gesellschaft Deutscher Chemiker

Supporting Information

69451 Weinheim, Germany

Alkyl Migration and a new tetramethylaluminate coordination mode: Unusual reactivity of organolanthanide imino-amido-pyridine complexes

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[**] Financial support from the Norwegian Research Council (Project No 171245/V30), the program Nanoscience@UiB, and the Fonds der Chemischen Industrie is gratefully acknowledged.

Experimental Details

General Procedures. All operations were performed with rigorous exclusion of air and water, using standard Schlenk, high-vacuum, and glovebox techniques (MBraun MBLab; <1 ppm O_2, <1 ppm H_2O). Hexane, THF, and toluene were purified by using Grubbs columns (MBraun SPS, solvent purification system) and stored in a glovebox. C_6D_6 was obtained from Aldrich, degassed, dried over Na for 24 h, and filtered. $AlMe_3$ was purchased from Aldrich and used as received. Homoleptic $Ln(AlMe_4)_3$ (Ln = La, Nd, Y)[24] and 2-{(2,6-*i*$Pr_2C_6H_3$)N=CMe}-6-{(2,6-*i*$Pr_2C_6H_3$)NHCMe$_2$}C_5H_3N] (H**L$_2$**)[4b] were synthesized according to the literature method. NMR spectra were recorded at 25 °C on a Bruker-BIOSPIN-AV500 (5 mm BBO, ^{1}H: 500.13 Hz; ^{13}C: 125.77 MHz), and a Bruker-BIOSPIN-AV600 (5 mm cryo probe, ^{1}H: 600.13 MHz; ^{13}C: 150.91 MHz). ^{1}H and ^{13}C shifts are referenced to internal solvent resonances and reported in *parts per million* relative to TMS. IR spectra were recorded on a *NICOLET Impact 410 FTIR* spectrometer as Nujol mulls sandwiched between CsI plates. Elemental analyses were performed on an *Elementar Vario EL III*.

General procedure for the synthesis of complexes 2a-2c

In a glovebox $Ln(AlMe_4)_3$ (**1**) was dissolved in 3 mL of toluene and added to a stirred solution of 2-{(2,6-*i*$Pr_2C_6H_3$)N=CMe}-6-{(2,6-*i*$Pr_2C_6H_3$)NHCMe$_2$}C_5H_3N] (H**L$_2$**) in 4 mL of toluene. The resulting mixture turned red immediately and instant gas formation was observed. The reaction mixture was stirred another 8 h at ambient temperature while the formation of a claret-red precipitate was observed. The product was separated by centrifugation, washed four times with 5 mL of hexane, and dried under vacuum to yield **2** as powdery claret-red solids.

2-{(2,6-*i*$Pr_2C_6H_3$)N=CMe}-6-{(2,6-*i*$Pr_2C_6H_3$)NCMe$_2$}C_5H_3N]La$(AlMe_4)_2$ (2a).
Following the procedure described above, $La(AlMe_4)_3$ (**1a**, 241 mg, 0.60 mmol) and H**L$_2$** (300 mg, 0.60 mmol) yielded **2a** as a powdery claret-red solid (303 mg, 0.37 mmol, 62%). ^{1}H NMR (600 MHz, C_6D_6, 25 °C): d = 7.18-7.10 (m, 6 H, ar), 7.04 (t, $^3J \cong 7.8$ Hz, 1 H, C_5H_3N-*p*-proton), 6.86 (d, $^3J \cong 7.8$ Hz, 1 H, C_5H_3N-*m*-proton), 6.85 (d, $^3J \cong 7.8$ Hz, 1 H, C_5H_3N-*m*-proton), 3.26 (sept, $^3J \cong 6.6$ Hz, 2 H, ar-CH), 2.62 (sept, $^3J \cong 6.6$ Hz, 2 H, ar-CH), 1.71 (s, 3 H, N=CCH_3), 1.39 (s, 6 H, NCCH_3), 1.30 (d, $^3J \cong 6.6$ Hz, 6 H, CH_3), 1.26 (d, $^3J \cong 6.6$ Hz, 6 H, CH_3), 1.00 (d, $^3J \cong 6.6$ Hz, 6 H, CH_3), 0.88 (d, $^3J \cong 6.6$ Hz, 6 H, CH_3), -0.25 (s br, 24 H, Al$(CH_3)_4$). ^{13}C NMR (126 MHz, C_6D_6, 25 °C): d = 175.1, 158.7, 149.4, 140.7, 139.1, 138.4, 125.5, 125.3, 124.9, 117.3, 69.9, 33.7, 29.1, 28.6, 28.1, 26.3,

26.1, 25.5, 25.1, 20.3, 3.1 (s br, $Al(CH_3)_4$). IR (nujol): 1582 (s, C=N), 1468 (vs, nujol), 1375 (vs, nujol), 1303 (s), 1261 (m), 1220 (w), 1214 (w), 1173 (s), 1095 (w), 1007 (w), 971 (w), 950 (w), 888 (w), 847 (w), 821 (w), 785 (m), 769 (m), 723 (vs), 593 (w), 578 (w), 516 cm^{-1} (w). Elemental analysis (%) calcd for $C_{42}H_{70}N_3Al_2La$ (809.910 g mol^{-1}): C 62.29; H 8.71; N 5.19; found: C 62.21; H 8.77; N 5.13.

2-{(2,6-*i*Pr$_2$C$_6$H$_3$)N=CMe}-6-{(2,6-*i*Pr$_2$C$_6$H$_3$)NCMe$_2$}C$_5$H$_3$N]Nd(AlMe$_4$)$_2$ (2b).

Following the procedure described above, $Nd(AlMe_4)_3$ (**1b**, 215 mg, 0.53 mmol) and H**L$_2$** (264 mg, 0.53 mmol) yielded **2b** as a powdery claret-red solid (225 mg, 0.28 mmol, 52%). ^{1}H NMR (600 MHz, C_6D_6, 25 °C): d = 13.83, 10.60, 6.30, 4.69, 2.10, 1.67, 1.38, 0.89. IR (nujol): 1588 (s, C=N), 1468 (vs, nujol), 1375 (vs, nujol), 1306 (s), 1267 (m), 1234 (w), 1207 (w), 1168 (s), 1102 (w), 1047 (w), 1008 (w), 971 (w), 953 (w), 892 (w), 859 (w), 826 (w), 793 (m), 771 (m), 721 (vs), 599 (w), 572 (w), 533 (w), 528 cm^{-1} (w). Elemental analysis (%) calcd for $C_{42}H_{70}N_3Al_2Nd$ (815.24 g mol^{-1}): C 61.88; H 8.65; N 5.15; found: C 61.38; H 8.72; N 5.01.

2-{(2,6-*i*Pr$_2$C$_6$H$_3$)N=CMe}-6-{(2,6-*i*Pr$_2$C$_6$H$_3$)NCMe$_2$}C$_5$H$_3$N]Y(AlMe$_4$)$_2$ (2c).

Following the procedure described above, $Y(AlMe_4)_3$ (**1c**, 121 mg, 0.35 mmol) and H**L$_2$** (172 mg, 0.35 mmol) yielded **2c** as a powdery claret-red solid (129 mg, 0.17 mmol, 49%). ^{1}H NMR (600 MHz, C_6D_6, 25 °C): d = 7.20-7.11 (m, 6 H, ar), 7.08 (d, $^3J \cong 7.8$ Hz, 1 H, C_5H_3N-*m*-proton), 7.01 (t, $^3J \cong 7.8$ Hz, 1 H, C_5H_3N-*p*-proton), 6.95 (d, $^3J \cong 7.8$ Hz, 1 H, C_5H_3N-*m*-proton), 3.46 (sept, $^3J \cong 6.6$ Hz, 2 H, ar-CH), 2.64 (sept, $^3J \cong 6.6$ Hz, 2 H, ar-CH), 1.74 (s, 3 H, N=CCH_3), 1.35 (s, 6 H, NCCH_3), 1.34 (d, $^3J \cong 6.6$ Hz, 6 H, CH_3), 1.28 (d, $^3J \cong 6.6$ Hz, 6 H, CH_3), 1.24 (d, $^3J \cong 6.6$ Hz, 6 H, CH_3), 0.92 (d, $^3J \cong 6.6$ Hz, 6 H, CH_3), -0.38 (s br, 24 H, $Al(CH_3)_4$). ^{13}C NMR (151 MHz, C_6D_6, 25 °C): d = 177.4, 150.7, 149.4, 141.1, 140.0, 139.2, 139.0, 127.8, 126.4, 124.3, 117.3, 70.7, 31.8, 29.1, 28.3, 27.1, 26.5, 24.9, 24.8, 23.8, 23.0, 3.3 (s br, $Al(CH_3)_4$). IR (nujol): 1582 (s, C=N), 1468 (vs, nujol), 1375 (vs, nujol), 1300 (s), 1284 (m), 1223 (w), 1207 (w), 1168 (s), 1107 (w), 1019 (w), 975 (w), 936 (w), 897 (w), 859 (w), 826 (w), 798 (m), 776 (m), 721 (vs), 688 (w), 588 (w), 528 cm^{-1} (w). Elemental analysis (%) calcd for $C_{42}H_{70}N_3Al_2Y$ (759.906 g mol^{-1}): C 66.39; H 9.28; N 5.53; found: C 66.08; H 9.28; N 5.31.

2,6-{(2,6-*i*Pr$_2$C$_6$H$_3$)NCMe$_2$}$_2$C$_5$H$_3$N]AlMe (3).

Following the procedure described for the synthesis of compounds **2**, the supernatant and the hexane washing solutions were combined and dried under vacuum yielding a red-orange powdery solid which was redissolved in hexane. Fractionate crystallization from hexane at -30 °C gave orange crystals of **3** in yields depending on the lanthanide metal size. (Ln = La 8%, Nd 10%, Y 10% calculated on $Ln(AlMe_4)_3$). ^{1}H NMR (600 MHz, C_6D_6, 25 °C): d = 7.22-7.20 (m, 6 H, ar), 7.13 (t, $^3J \cong 7.8$ Hz, 1 H, C_5H_3N-*p*-proton),

6.73 (d, $^{3}J \cong 7.8$ Hz, 2 H, C_5H_3N-*m*-proton), 3.65 (sept, $^{3}J \cong 6.6$ Hz, 4 H, ar-CH), 1.31 (d, $^{3}J \cong 6.6$ Hz, 12 H, CH_3), 1.29 (d, $^{3}J \cong 6.6$ Hz, 12 H, CH_3), 1.22 (s, 12 H, $NCCH_3$) -0.74 (s, 3 H, $AlCH_3$). ^{13}C NMR (151 MHz, C_6D_6, 25 °C): d = 168.3, 149.0, 145.6, 139.5, 124.8, 124.0, 117.3, 60.9, 31.0, 28.4, 26.3, 24.8. IR (nujol): 1592 (s), 1463 (vs, nujol), 1380 (vs, nujol), 1308 (s), 1266 (m), 1251 (m), 1235 (m), 1230 (m), 1204 (w), 1178 (s), 1137 (m), 1085 (m), 1049 (m), 987 (w), 935 (w), 904 (m), 821 (w), 811 (m), 769 (m), 738 (m), 697 (m), 650 (w), 614 (w), 567 (w), 526 cm^{-1} (w). Elemental analysis (%) calcd for $C_{36}H_{52}N_3Al$ (553.810 g mol^{-1}): C 78.08; H 9.46; N 7.59; found: C 77.70; H 9.09; N 7.35.

2-{(2,6-*i*Pr$_2$C$_6$H$_3$)NCMe$_2$}-6-{(2,6-*i*Pr$_2$C$_6$H$_3$)NHCMe$_2$}C$_5$H$_3$N]AlMe$_2$ (4).

Following the procedure described for the synthesis of compounds **2**, the supernatant and the hexane washing solutions were combined and dried under vacuum yielding a red-orange powdery solid which was redissolved in hexane. Fractionate crystallization from hexane at -30 °C gave light red crystals of **4** in yields depending on the lanthanide metal size. (Ln = La 30%, Nd 38%, Y 41% calculated on $Ln(AlMe_4)_3$). ^{1}H NMR (600 MHz, C_6D_6, 25 °C): d = 7.27-7.21 (m, 6 H, ar), 6.99 (t, $^{3}J \cong 7.8$ Hz, 1 H, C_5H_3N-*p*-proton), 6.87 (d, $^{3}J \cong 7.8$ Hz, 1 H, C_5H_3N-*m*-proton), 6.64 (d, $^{3}J \cong 7.8$ Hz, 1 H, C_5H_3N-*m*-proton), 4.54 (s, 1 H, N-H), 3.81 (sept, $^{3}J \cong 6.6$ Hz, 2 H, ar-CH), 2.75 (sept, $^{3}J \cong 6.6$ Hz, 2 H, ar-CH), 1.49 (s, 6 H, $NCCH_3$), 1.37 (s, 6 H, $NCCH_3$), 1.34 (d, $^{3}J \cong 6.6$ Hz, 12 H, CH_3), 1.09 (d, $^{3}J \cong 6.6$ Hz, 12 H, CH_3), -0.25 (s, 6 H, $Al(CH_3)_2$). ^{13}C NMR (151 MHz, C_6D_6, 25 °C): d = 175.6, 165.9, 150.7, 145.5, 144.0, 140.0, 139.4, 125.1, 124.2, 123.7, 119.3, 117.3, 62.5, 31.1, 30.3, 28.5, 28.4, 28.1, 26.9, 25.0, 24.6, 0.6 (s br, $Al(CH_3)_2$). IR (nujol): 3405 (m) (N-H), 1577 (s), 1463 (vs, nujol), 1380 (vs, nujol), 1313 (s), 1251 (m), 1220 (w), 1194 (w), 1142 (w), 1106 (w), 1049 (w), 1018 (w), 987 (w), 971 (w), 919 (w), 868 (w), 826 (w), 769 (m), 723 (vs), 661 (w), 614 (w), 583 cm^{-1} (w).Elemental analysis (%) calcd for $C_{37}H_{56}N_3Al$ (569.852 g mol^{-1}): C 77.94; H 9.31; N 7.37; found: C 77.69; H 9.09; N 7.41.

2,6-{(2,6-*i*Pr$_2$C$_6$H$_3$)NCMe$_2$}$_2$C$_5$H$_3$N]La(AlMe$_4$)(THF) (5).

To a stirred suspension of **2a** (126 mg, 0.16 mmol) in 3 mL of hexane 3 mL THF were added dropwise. The claret-red solid dissolved immediately accompanied by decolorization of the reaction mixture. After stirring for 4 h at ambient temperature the solvent was removed in vacuo to form a white solid which was washed three times with 2 mL of hexane and dried under vacuum to yield **5** as a powdery white solid (117 mg, 0.14 mmol, 90%). ^{1}H NMR (600 MHz, C_6D_6, 25 °C): d = 7.20-7.11 (m, 6 H, ar), 7.06 (t, $^3J \cong$ 7.8 Hz, 1 H, C_5H_3N-*p*-proton), 6.81 (d, $^3J \cong$ 7.8 Hz, 2 H, C_5H_3N-*m*-protons), 3.47 (sept, $^3J \cong$ 6.6 Hz, 4 H, ar-CH), 2.74 (m, 4 H, THF), 1.40 (s, 12 H, $NCCH_3$), 1.18 (d, $^3J \cong$ 6.6 Hz, 12 H, CH_3), 1.15 (d, $^3J \cong$ 6.6 Hz, 12 H, CH_3), 0.98 (m, 4 H, THF), -0.15 (s, 12 H, $Al(CH_3)_4$). ^{13}C NMR (151 MHz, C_6D_6, 25 °C): d = 174.3, 150.3, 141.3, 139.0, 125.6, 125.0, 117.8, 70.8 (THF), 69.1, 32.8, 31.9, 28.2, 28.0, 25.1, 23.0, 1.7 (s, $Al(CH_3)_4$). IR (nujol): 1572 (w), 1468 (vs, nujol), 1375 (vs, nujol), 1303 (s), 1256 (w), 1220 (w), 1194 (m), 1158 (m), 1126 (w), 1101 (w), 1044 (w), 1013 (w), 982 (w), 930 (w), 852 (m), 816 (w), 785 (m), 764 (m), 723 (vs), 692 (w), 583 (w), 562 (w), 536 (w), 516 cm^{-1} (w). Elemental analysis (%) calcd for $C_{43}H_{69}N_3OAlLa$ (809.930 g mol^{-1}): C 63.77; H 8.59; N 5.19; found: C 63.37; H 8.58; N 5.02.

2,6-{(2,6-*i*Pr$_2$C$_6$H$_3$)NCMe$_2$}$_2$C$_5$H$_3$N]La(AlMe$_4$) (6).

To a stirred solution of **5** (71 mg, 0.09 mmol) in 3 mL of toluene $AlMe_3$ (6 mg, 0.09 mmol) was added dropwise. After stirring the colorless reaction mixture for 4 h at ambient temperature the solvent was removed in vacuo to form a white solid which was washed three times with 2 mL of hexane and dried under vacuum to yield **6** as a powdery white solid (63 mg, 0.09 mmol, 98%). ^{1}H NMR (600 MHz, C_6D_6, 25 °C): d = 7.20-7.16 (m, 6 H, ar), 7.14 (t, $^3J \cong$ 7.8 Hz, 1 H, C_5H_3N-*p*-proton), 6.78 (d, $^3J \cong$ 7.8 Hz, 2 H, C_5H_3N-*m*-protons), 3.28 (sept, $^3J \cong$ 6.6 Hz, 4 H, ar-CH), 1.41 (s, 12 H, $NCCH_3$), 1.31 (d, $^3J \cong$ 6.6 Hz, 12 H, CH_3), 1.05 (d, $^3J \cong$ 6.6 Hz, 12 H, CH_3), -0.40 (s, 12 H, $Al(CH_3)_4$). ^{13}C NMR (151 MHz, C_6D_6, 25 °C): d = 175.1, 149.4, 141.5, 139.1, 126.1, 125.3, 117.3, 69.9, 33.7, 28.1, 26.3, 26.1, 2.83 (s, $Al(CH_3)_4$). IR (nujol): 1577 (w), 1468 (vs, nujol), 1375 (vs, nujol), 1303 (s), 1251 (w), 1240 (w), 1194 (w), 1168 (m), 1095 (w), 1044 (w), 997 (w), 971 (m), 852 (w), 816 (w), 790 (w), 764 (m), 723 (vs), 609 (w), 567 (w), 562 (w), 536 (w), 516 cm^{-1} (w). Elemental analysis (%) calcd for $C_{39}H_{61}N_3AlLa$ (737.824 g mol^{-1}): C 63.49; H 8.33; N 5.70; found: C 63.54; H 8.35; N 5.44.

[24] W. J. Evans, R. Anwander, J. W. Ziller, *Organometallics* **1995**, *14*, 1107.