Inorg. Chem. **1996,** *35,* 5435−5444

Utility of Arylamido Ligands in Yttrium and Lanthanide Chemistry[1]

William J. Evans,* Mohammad A. Ansari, and Joseph W. Ziller

Department of Chemistry, University of California, Irvine, California 92697-2025

Saeed I. Khan

Department of Chemistry and Biochemistry, University of California, Los Angeles, California 90024

Received November 22, 1995[⊗]

The reactivity of KNHAr reagents (Ar = C_6H_5, $C_6H_3Me_2$-2,6, $C_6H_3{}^iPr_2$-2,6) with lanthanide and yttrium trichlorides has been investigated. With the larger metals Nd and Sm and the smaller 2,6-dimethyl-substituted ligand, the bimetallic dianionic complexes $[K(THF)_6]_2[Ln(\mu\text{-}NHC_6H_3Me_2\text{-}2,6)(NHC_6H_3Me_2\text{-}2,6)_3]_2$ (Ln: Sm, **1a**; Nd, **1b**) are isolated as the potassium salts. Under the same reaction conditions YCl_3 forms a bimetallic anion which retains chloride: $[K(DME)_2(THF)_3][Y_2(\mu\text{-}NHC_6H_3Me_2\text{-}2,6)_2(\mu\text{-}Cl)(NHC_6H_3Me_2\text{-}2,6)_4(THF)_2]$, **2**. With the larger 2,6-diisopropyl ligands, neutral complexes are isolated in both solvated monometallic and unsolvated bimetallic forms. With Nd, a distorted octahedral trisolvate, $Nd(NHC_6H_3{}^iPr_2\text{-}2,6)_3(THF)_3$, **3**, was obtained, whereas with Yb and Y the trigonal bipyramidal disolvates, $Ln(NHC_6H_3{}^iPr_2\text{-}2,6)_3(THF)_2$ (Ln: Yb, **4a**; Y, **4b**), were isolated. THF-free complexes of the $NHC_6H_3{}^iPr_2$-2,6 ligand are available by reacting the amine $NH_2C_6H_3{}^iPr_2$-2,6 with $Ln[N(SiMe_3)_2]_3$ complexes. By this route, the dimers $[Ln(\mu\text{-}NHC_6H_3{}^iPr_2\text{-}2,6)(NHC_6H_3{}^iPr_2\text{-}2,6)_2]_2$ (Ln: Yb, **5a**; Y, **5b**) were isolated. The reaction of the unsubstituted arylamido salt $KNHC_6H_5$ with $NdCl_3$ produced an insoluble material which was characterized as $[Nd(NHC_6H_5)_3(KCl)_3]$, **6**. **6** reacted with Al_2Me_6 in hexanes and produced a heteroleptic mixed-metal complex $\{[Me_2Al(\mu\text{-}Me_2)]_2Nd(\mu_3\text{-}NC_6H_5)(\mu\text{-}Me)AlMe\}_2$, **7**, and the trimeric aluminum arylamido complex $[Me_2Al(\mu\text{-}NHC_6H_5)]_3$, **8**. The solvent of crystallization and relevant crystallographic data for the compounds identified by X-ray analysis follow: **1a,** THF, 156 K, $P2_1/n$, $a = 12.985(2)$ Å, $b = 27.122(5)$ Å, $c = 17.935(3)$ Å, $\beta = 100.19(1)°$, $V = 6216(1)$ Å^3, $Z = 2$, 6148 reflections ($I > 3\sigma(I)$), $R_F = 7.1\%$; **1b,** THF, 156 K, $P2_1$/n, $a = 12.998(2)$ Å, $b = 27.058(3)$ Å, $c = 17.962(2)$ Å, $\beta = 99.74(1)°$, $V = 6225(1)$ Å^3, $Z = 2$; **2,** DME/hexanes, $P2_1/n$, $a = 23.335(2)$ Å, $b = 12.649(1)$ Å, $c = 27.175(3)$ Å, $\beta = 96.36(1)°$, $V = 7971(1)$ Å^3, $Z = 4$, 2788 reflections ($I > 3\sigma(I)$), $R_F = 9.5\%$; **3**, THF, $P2_1$, $a = 12.898(1)$ Å, $b = 16.945(1)$ Å, $c = 13.290(1)$ Å, $\beta = 118.64(2)°$, $V = 2549.3(3)$ Å^3, $Z = 2$, 3414 reflections ($I > 3\sigma(I)$), $R_F = 4.3\%$; **4a**, hexanes, $P2_1$, $a = 9.718(2)$ Å, $b = 19.119(3)$ Å, $c = 12.640(2)$ Å, $\beta = 112.08(1)°$, $V = 2176.3(6)$ Å^3, $Z = 2$, 2933 reflections ($I > 3\sigma(I)$), $R_F = 4.3\%$; **4b**, hexanes, 158 K, $a = 9.729(2)$ Å, $b = 19.095(5)$ Å, $c = 12.744(1)$ Å, $\beta = 112.11(1)°$, $V = 2193.4(6)$ Å^3; **5b**, hot toluene, 158 K, $P2_1$, $a = 19.218(9)$ Å, $b = 9.375(3)$ Å, $c = 19.820(5)$ Å, $\beta = 110.25(2)°$, $V = 3350(2)$Å^3, $Z = 2$, 1718 reflections ($I > 2\sigma$ (I)), R1 = 9.7%; **7**, hexanes, 156 K, $P\bar{1}$, $a = 9.618(3)$ Å, $b = 12.738(4)$ Å, $c = 9.608(3)$ Å, $\alpha = 99.32(1)°$, $\beta = 108.87(1)°$, $\gamma = 94.23(1)°$, $V = 1089.1(6)$ Å^3, $Z = 2$, 2976 reflections ($I > 3\sigma(I)$), $R_F = 3.9\%$; **8**, hexanes, 156 K, $Pcab$, $a = 23.510(5)$ Å, $b = 25.462(5)$ Å, $c = 8.668(2)$ Å, $V = 5188(1)$ Å^3, $Z = 8$, 1386 reflections ($I > 3\sigma(I)$), $R_F = 5.7\%$.

Introduction

The organometallic chemistry of yttrium and the lanthanide metals has been overwhelmingly dominated by complexes containing cyclopentadienyl groups as the ancillary ligands which solubilize and stabilize these compounds.[2] Although the cyclopentadienyl complexes have an extensive chemistry, a more diverse selection of ancillary stabilizing ligand environments is desirable.[3] To date, the largest effort to develop coligands alternative to cyclopentadienyl ligands has involved alkyloxide and aryloxide ligands, and a broad new chemistry is developing with these ligands.[3−16]

In contrast to the major effort on OR ligands, relatively little effort has been devoted to the related NR_2 complexes.[17] Although the chemistry of delocalized polydentate ligands containing nitrogen such as polypyrazolylborates,[18] benzamidinates,[19] and pyrazoles[20] is being developed, the yttrium and

---

[⊗] Abstract published in *Advance ACS Abstracts,* August 1, 1996.

(1) Reported in part at the 209th National Meeting of the American Chemical Society, Anaheim, CA, 1995; abstract 215.

(2) (a) Marks, T. J.; Ernst, R. D In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon Press: Oxford, U.K., 1982; Chapter 21. (b) Evans, W. J. *Polyhedron* **1987**, *6*, 803−835. (c) Schaverien, C. J.; *Adv. Organomet. Chem.* **1994**, *36*, 283−362. (d) Meesemarktscheffel, J. A.; Esser, L.; Schumann, H. *Chem. Rev.* **1995**, *95*, 865−986.

(3) Evans, W. J. *New J. Chem.* **1995**, *19*, 525−533.

(4) Only some reviews and leading references[5−16] are given here: (a) Mehrotra, R. C.; Singh, A.; Tripathi, U. M. *Chem. Rev.* **1991**, *91*, 1287−1303. (b) Caulton, K. G.; Hubert-Pfalzgraf, L. G. *Chem. Rev.* **1990**, *90*, 969−995. (c) Hubert-Pfalzgraf, L. G. *New J. Chem.* **1995**, *19*, 727−750.

(5) Bradley, D. C.; Chudzynska, H.; Hursthouse, M. B.; Motevalli, M. *Polyhedron* **1994**, *10*, 7−14.

(6) Lappert, M. F.; Singh, A.; Smith, R. G. *Inorg. Synth.* **1990**, *27*, 164−168.

(7) Coan, P. S.; McGeary, M. J.; Lobkovsky, E. B.; Caulton, K. G. *Inorg. Chem.* **1991**, *30*, 3570−3572.

(8) (a) Clark, D. L.; Gordon, J. C.; Huffman, J. C.; Vincent-Hollis, R. L.; Watkins, J. G.; Zwick, B. D. *Inorg. Chem.* **1994**, *33*, 5903−5911. (b) Barnhart, D. M.; Clark, D. L.; Gordon, J. C.; Huffman, J. C.; Vincent, R. L.; Watkins, J. G.; Zwick, B. D. *Inorg. Chem.* **1994**, *32*, 3487−3497.

(9) Schaverien, C. J. *Organometallics* **1994**, *13*, 69−82.

(10) (a) Heeres, H. J.; Maters, M.; Teuben, J. H.; Helgessen, G.; Jagner, S. *Organometallics* **1992**, *11*, 350. (b) Hermann, W. A.; Anwander, R.; Scherer, W. *Chem. Ber.* **1993**, *126,* 1533−1539.

(11) Deacon, G. B.; Gatehouse, B. M.; Shen, Q.; Ward, G. N. *Polyhedron* **1993**, *12,* 1289−1294.

(12) Andersen, R. A.; Templeton, D. H.; Zalkin, A. *Inorg. Chem.* **1978**, *17*, 1962−1964.

S0020-1669(95)01499-6 CCC: $12.00

lanthanide chemistry of complexes of simple amido ligands is limited primarily to a single popular amido ligand, namely $N(SiMe_3)_2$.[21] A few reports are available on N^iPr_2 complexes,[22] and recently some mixed-metal NMe_2 compounds solubilized by $AlMe_3$ and $GaMe_3$ moieties were reported, e.g. $[La(NMe_2)_3(GaMe_3)_3]$.[23] Most other lanthanide chemistry involving simple NR_2 groups involves complexes which have cyclopentadienyl ligands as the ancillary ligands. Crystallographically characterized examples of cyclopentadienyl complexes are known with ligands such as NHPh,[24] NPhNHPh,[24] N_2H_2,[24,25] N_2H_3,[25] N_2Ph_2,[26,27] NH_2,[28] NPh_2,[29] N_3,[30a] and NHMe.[30b] We are aware of no examples of crystallographically characterized arylamido lanthanide or yttrium complexes, which is somewhat surprising considering the extensive use of the aryloxide analogs with these metals.[31] Relatively few types of amido ligands have been described for the actinides as well,[32] although examples of arylamido complexes of uranium are known.[32l,m]

We have investigated the utility of arylamide ligands with yttrium and the lanthanide complexes as well as their use in making mixed-metal organometallic complexes involving aluminum. We report here the synthetic and structural variations observed to date as well as a methane elimination reaction which gives an unusual mixed-metal Nd−Al complex.

Experimental Section

The chemistry described below was performed under nitrogen with rigorous exclusion of air and water by using Schlenk, vacuum-line, and glovebox techniques. Solvents were purified as previously described.[33] NMR spectra were recorded using a General Electric QE 300 spectrometer at 25 °C. Elemental analyses were determined on a Carlo Erba EA 108 instrument or performed by the Analytische Laboratorien, Gummersbach, Germany. Aniline, 2,6-dimethylaniline, and 2,6-diisopropylaniline (Aldrich) were dried over molecular sieves and distilled before use. The lanthanide and yttrium compounds reported below decompose without melting at temperatures around 200 °C.

$KNHC_6H_5$. In the glovebox, $NH_2C_6H_5$ (1.00 g, 10.7 mmol) was added dropwise to a stirred suspension of KH (430 mg, 10.7 mmol) in 25 mL of THF in a 100 mL round-bottom flask. After 10 h of stirring, the mixture was centrifuged and the supernatant was evaporated to dryness to yield $KNHC_6H_5$ (1.20 g, 90%) as a white powder. ^1H NMR (THF-d_8): δ 6.49 (t, 2H, C_6H_5), 5.96 (d, 1H, C_6H_5), 5.55 (t, 2H, C_6H_5), 3.26 (s, 1H, NH).

$KNHC_6H_3Me_2$-2,6. According to the above procedure, $KNHC_6H_3Me_2$-2,6 (2.87 g, 95%) was prepared from $NH_2C_6H_3Me_2$-2,6 (2.42 g, 20.0 mmol) and KH (0.802 g, 20.0 mmol) in 25 mL of THF. ^1H NMR (THF-d_8): δ 6.54 (d, 2H, $C_6H_3Me_2$), 5.63 (t, 1H, $C_6H_3Me_2$), 3.19 (d, 1H, NH), 2.10 (s, 6H, $C_6H_3Me_2$).

$KNHC_6H_3{}^iPr_2$-2,6. According to the above procedure, $KNHC_6H_3{}^iPr_2$-2,6 (3.560 g, 85%) was prepared from $NH_2C_6H_3{}^iPr_2$-2,6 (3.546 g, 20.0 mol) and KH (0.802 g, 20.0 mmol) in 25 mL of THF. ^1H NMR (THF-d_8): δ 6.73 (d, 2H, $C_6H_3{}^iPr_2$), 6.09 (t, 1H, $C_6H_3{}^iPr_2$), 2.13 (s, 1H, NH), 3.08 (q, 2H, $C_6H_3{}^iPr_2$), 1.17 (d, 12H, $C_6H_3{}^iPr_2$).

$[K(THF)_6]_2[Sm(\mu\text{-}NHC_6H_3Me_2\text{-}2,6)(NHC_6H_3Me_2\text{-}2,6)_3]_2$, 1a. $KNHC_6H_3Me_2$-2,6 (640 mg, 4.0 mmol) dissolved in 8 mL of THF was added to a suspension of $SmCl_3$ (256 mg, 1.0 mmol) in THF (10 mL). The resulting mixture was stirred for 18 h and centrifuged. The insolubles were discarded, and the volume of the supernatant was reduced to half on a rotary evaporator and then cooled to −35 °C. After 2 days, a few pale green crystals of **1a** precipitated. More crystals of **1a** were isolated when the solution was layered with small amounts of hexanes (total yield: 650 mg, 60%). Anal. Calcd for $C_{112}H_{176}N_8O_{12}Sm_2K_2$: C, 60.99; H, 8.04; N, 5.08; Sm, 13.63; K, 3.54. Calcd for the disolvate $C_{72}H_{96}N_8O_2Sm_2K_2$: C, 58.25; H, 6.51; N, 7.55; Sm, 20.25; K 5.26. Found: C, 58.29; H, 6.06; N, 7.69; Sm, 20.65; K, 5.15. IR (Nujol): 1601 m, 1473 s, 1396 s, 1293 m, 1216 w, 1100 w, 1062 w, 985 w, 908 w, 856 m, 754 m, 702 w cm^{-1}. ^1H NMR (THF-d_8): δ 8.12 (s, 4H, NH), 6.41 (d, 8H, $C_6H_3Me_2$), 6.04 (t, 4H, $C_6H_3Me_2$), 0.71 (s, 24H, $C_6H_3Me_2$). ^{13}C NMR (THF-d_8): δ 157.8, 128.1, 118.8, 109.7 ($C_6H_3Me_2$), 20.5 ($C_6H_3Me_2$).

$[K(THF)_6]_2[Nd(\mu\text{-}NHC_6H_3Me_2\text{-}2,6)(NHC_6H_3Me_2\text{-}2,6)_3]_2$, 1b. Reaction of $NdCl_3$ with $KNHC_6H_3Me_2$-2,6 as described above for **1a** formed **1b** as blue crystals (780 mg, 70%). X-ray crystallography showed that **1b** was isomorphous with **1a**. Anal. Calcd for $C_{112}H_{176}N_8O_{12}Nd_2K_2$: Nd, 13.15. Found: Nd, 14.6. ^1H NMR (THF-d_8): δ 7.02 (br, $\Delta\nu = 30$ Hz, $C_6H_3Me_2$), 4.96 (br, $\Delta\nu = 20$ Hz, $C_6H_3Me_2$), 4.08 (br, $\Delta\nu = 20$ Hz), −3.77 (br, $\Delta\nu = 50$ Hz, $C_6H_3Me_2$).

---

(13) Sen, A.; Stecher, H. A.; Rheingold, A. *Inorg. Chem.* **1992**, *31*, 473−479.

(14) Schumann, H.; Kociok-Köhn, G.; Loebel, J. *Z. Anorg. Chem.* **1990**, *581*, 69−81.

(15) (a) Evans, W. J.; Ansari, M. A.; Khan, S. I. *Organometallics* **1995**, *14*, 558−560. (b) Evans, W. J.; Anwander, R.; Berlekamp, U. H.; Ziller, J. W. *Inorg. Chem.* **1995**, *34*, 3583−3588.

(16) Edelmann, F. T.; Steiner, A.; Stalke, D.; Gilje, J. W.; Jagner, S.; Hakansson, M. *Polyhedron* **1994**, *13*, 539−546.

(17) Lappert, M. F.; Power, P. P.; Sanger, A. R.; Srivastava, R. C. *Metal and Metalloid Amides*; Wiley: New York, 1980; Chapter 8.

(18) (a) Santos, I.; Marques, N. *New J. Chem.* **1995**, *19*, 551−571. (b) Zhang, X.; McDonald, R.; Takats, J. *New J. Chem.* **1995**, *19*, 573−585.

(19) Edelmann, F. T. *Coord. Chem. Rev.* **1994**, *137*, 403−481.

(20) Schumann, H.; Winterfeld, J.; Hemling, H.; Kuhn, N. *Chem. Ber.* **1993**, *126*, 2657−2659.

(21) (a) Bradley, D. C.; Ghotra, J. S.; Hart, F. A. *J. Chem. Soc., Dalton Trans.* **1973**, 1021−1923. (b) Ghotra, J. S.; Hurthouse, M. B.; Welch, A. J. *J. Chem. Soc., Chem. Commun.* **1973**, 669−670.

(22) (a) Bradley, D. C.; Ghotra, J. S.; Hart, F. A. *Inorg. Nucl. Chem. Lett.* **1990**, *12*, 735−737. (b) Aspinall, H. C.; Tillotson, M. R. *Polyhedron* **1994**, *13*, 3229−3234. (c) Aspinall, H.; Moore, S. R.; Smith, A. K. *J. Chem. Soc., Dalton Trans.* **1993**, 993−996. (d) Evans, W. J.; Anwander, R.; Ziller, J. W.; Khan, S. I. *Inorg. Chem.* **1995**, *34*, 5927−5930.

(23) Evans, W. J.; Anwander, R.; Doedens, R. A.; Ziller, J. W. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 1641−1644.

(24) (a) Evans, W. J.; Kociok-Köhn, G.; Leong, V. S.; Ziller, J. W. *Inorg.Chem.* **1992**, *31*, 3592−3600. (b) Evans, W. J.; Kociok-Köhn, G.; Ziller, J. W. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 1081−1082.

(25) Wang, K.; Stevens, E. D.; Nolan, S. P. *Organometallics* **1992**, *11*, 1011−1013.

(26) Evans, W. J.; Drummond, D. K.; Chamberlain, L. R.; Doedens, R. J.; Bott, S. G.; Zhang, H.; Atwood, J. L. *J. Am. Chem. Soc.* **1988**, *110*, 4983−4994.

(27) Trifonov, A. A.; Bochkarev, M. N.; Schumann, H.; Loebel, J. *Angew. Chem., Int. Ed. Engl.* **1991**, *9*, 1149−1151.

(28) (a) Hammel, A.; Weidlein, J. *J. Organomet. Chem.* **1990**, *388*, 75−87. (b) Gagne, M. R.; Stern, C. L.; Marks, T. J. *J. Am. Chem. Soc.* **1992**, *114*, 275−294.

(29) (a) Schumann, H.; Palamidis, E.; Loebel, J. *J. Organomet. Chem.* **1990**, *390*, 45−52. (b) Guan, J.; Jin, S., Lin, Y.; Shen, Q. *Organometallics* **1992**, *11*, 2483. (c) Mao, L.; Qi, S.; Jin, S. *Polyhedron* **1994**, *13*, 1023−1025.

(30) (a) Schumann, H.; Janiak, C.; Pickardt, J. *J. Organomet. Chem.* **1988**, *349*, 117−122. (b) Gagné, M. R.; Stern, C. L.; Marks, T. J. *J. Am. Chem. Soc.* **1992**, *114*, 275−294.

(31) Even sulfur analogs of the aryloxide ligands have been reported: Cetinkaya, B.; Hitchcock, P. B.; Lappert, M. F.; Smith, R. G. *J. Chem. Soc., Chem. Commun.* **1992**, 932−934.

(32) (a) Hitchcock, P. B.; Lappert, M. F.; Singh, A.; Taylor, R. G.; Brown, D. *J. Chem. Soc., Chem. Commun.* **1983**, 561−563. (b) Brennan, J. G.; Andersen, R. A. *J. Am. Chem. Soc.* **1985**, *107*, 514−516. (c) Cramer, R. E.; Engelhardt, U.; Higa, K. T.; Gilje, J. W. *Organometallics*, **1987**, *6*, 41−45. (d) Arney, D. S. J.; Burns, C. J.; Smith, D. C. *J. Am. Chem. Soc.* **1992**, *114*, 10068−10069. (e) Burns, C. J.; Smith, D. C.; Huffman, J. C.; Sattelberger, A. P. *J. Am. Chem. Soc.* **1990**, *112*, 3237−3239. (f) Reynolds, J. G.; Zalkin, A.; Templeton, D. H.; Edelstein, N. M. *Inorg. Chem.* **1977**, *16*, 1090−1096. (g) Arney, D. S. J.; Burns, C. J. *J. Am. Chem. Soc.* **1993**, *115*, 9840−9841. (h) Reynolds, J. G.; Zalkin, A.; Templeton, D. H.; Edelstein, N. M.; Templeton, L. K. *Inorg. Chem.* **1976**, *15*, 2498−2502. (i) Zalkin, A.; Brennan, J. G.; Andersen, R. A. *Acta Crystallogr.* **1988**, *C44*, 1553. (j) Cramer, R. E.; Panchanatheswaran, K.; Gilje, J. W. *J. Am. Chem. Soc.* **1984,** *106*, 1853−1855. (k) Cramer, R. E.; Edelmann, F.; Mori, A. L.; Roth, S.; Gilje, J. W.; Tatsumi, K.; Nakamura, A. *Organometallics* **1988**, *7*, 841−849. (l) Nelson, J. E.; Clark, D. L.; Burns, C. L.; Sattelberger, A. P. *Inorg. Chem.* **1992**, *31*, 1973−1976. (m) Stewart, J. L.; Andersen, R. A. *New J. Chem.* **1995**, *19*, 587−595.

(33) Evans, W. J.; Chamberlain, L. R.; Ulibarri, T. A.; Ziller, J. W. *J. Am. Chem. Soc.* **1988**, *110*, 6423−6432.

[K(DME)$_2$(THF)$_3$][Y$_2$(μ-NHC$_6$H$_3$Me$_2$-2,6)$_2$(μ-Cl)(NHC$_6$H$_3$Me$_2$-2,6)$_4$(THF)$_2$], 2. In the glovebox, YCl$_3$ (196 mg, 1.0 mmol) and KNHC$_6$H$_3$Me$_2$-2,6 (478 mg, 3.0 mmol) were stirred overnight in THF (10 mL) to form a cloudy solution, which was centrifuged to remove insoluble material. Removal of solvent from the supernatant by rotary evaporation gave 620 mg of an off-white solid. Recrystallization from DME/THF/hexanes gave crystals of **2** suitable for X-ray diffraction. Anal. Calcd for C$_{76}$H$_{124}$N$_6$O$_9$ClKY$_2$: C, 60.12; H, 8.23; N, 5.53; Y, 11.71. Found: C, 60.04; H, 7.89; N, 5.50; Y, 12.1. IR (Nujol): 2923 s, 2384 m, 2352 w, 1601 s, 1473 s, 1396 s, 1349 s, 1293 m, 1216 w, 1113 m, 1062 w, 1023 w, 998 w, 921 w, 856 w, 754 w, 741 w, 702 w, 690 w cm^{-1}. ^{1}H NMR (THF-d_8): δ 6.57 (br, 12H, $\Delta\nu$ = 35 Hz, NHC$_6$*H*$_3$Me$_2$), 6.02 (br, 6H, $\Delta\nu$ = 80 Hz, NHC$_6$*H*$_3$Me$_2$), 4.46 (br, 6H, $\Delta\nu$ = 40 Hz, N*H*C$_6$H$_3$Me$_2$), 3.39 (s, 8H, CH$_3$OC*H*$_2$C*H*$_2$OCH$_3$), 3.23 (s, 12H, C*H*$_3$OCH$_2$CH$_2$OC*H*$_3$), 2.03 (b, 36H, $\Delta\nu$ = 130 Hz, NHC$_6$H$_3$*Me*$_2$). ^{13}C NMR (THF-d_8): δ 153.4, 126.5, 124.5, 119.2 (*C*$_6$H$_3$-Me$_2$), 69.9 (C$_6$H$_3$*Me*$_2$), 57.2 (C$_6$H$_3$*Me*$_2$). ^{1}H NMR of the product recrystallized from THF (THF-d_8): δ 6.66 (br, 12H, $\Delta\nu$ = 18 Hz, NHC$_6$*H*$_3$Me$_2$), 6.11 (br, 6H, $\Delta\nu$ = 30 Hz, NHC$_6$*H*$_3$Me$_2$), 4.55 (br, 6H, $\Delta\nu$ = 26 Hz, N*H*C$_6$H$_3$Me$_2$), 2.12 (br, 36H, $\Delta\nu$ = 20 Hz, NHC$_6$H$_3$*Me*$_2$). ^{13}C NMR (THF-d_8): δ 127.6, 127.50, 127.19 (*C*$_6$H$_3$Me$_2$), 19.9 (C$_6$H$_3$*Me*$_2$).

Nd(NHC$_6$H$_3{}^i$Pr$_2$-2,6)$_3$(THF)$_3$, 3. NdCl$_3$ (126 mg, 0.5 mmol) was stirred with KNHC$_6$H$_3{}^i$Pr$_2$-2,6 (323 mg, 1.5 mmol) in THF (10 mL) for 3 days. The mixture was centrifuged, and the supernatant was layered with hexanes to produce **3** as pale blue crystals (220 mg, 50%). Anal. Calcd for C$_{48}$H$_{78}$N$_3$O$_3$Nd: C, 65.04; H, 8.11; N, 4.74; Nd, 16.27. Found: C, 64.64; H, 8.27; N, 5.01; Nd, 16.3. IR (Nujol): 1640 w, 1601 m, 1473 s, 1396 s, 1280 s, 1165 w, 1126 w, 1080 w, 933 w, 895 w, 856 m, 754 m, 702 w cm^{-1}. ^{1}H NMR (THF-d_8): δ 11.58 (s, C$_6$*H*$_3{}^i$Pr$_2$), 8.01 (s, C$_6$*H*$_3{}^i$Pr$_2$), 3.42 (br, $\Delta\nu$ = 40 Hz), 1.23 (s, C$_6$H$_3$(CH*Me*$_2$)$_2$), $-$3.48 (br, $\Delta\nu$ = 270 Hz). ^{1}H NMR (C$_6$D$_6$): δ 10.71 (s, C$_6$*H*$_3{}^i$Pr$_2$), 6.31 (s, C$_6$*H*$_3{}^i$Pr$_2$), 2.64 (br, $\Delta\nu$ = 60 Hz), 0.41 (s, C$_6$H$_3$(CH*Me*$_2$)$_2$), $-$6.66 (br, $\Delta\nu$ = 120 Hz).

Yb(NHC$_6$H$_3{}^i$Pr$_2$-2,6)$_3$(THF)$_2$, 4a. Addition of a THF solution of KNHC$_6$H$_3{}^i$Pr$_2$-2,6 (626 mg, 3.0 mmol) to a THF suspension of YbCl$_3$ (280 mg, 1.0 mmol) caused an immediate reaction, and the solution turned pink. Removal of solvent after stirring the mixture for 3 h and extraction with hexanes gave a pink solution from which large block-shaped diffraction-quality crystals of **4a** (470 mg, 55%) were obtained after several hours at ambient temperature. Anal. Calcd for C$_{44}$H$_{70}$N$_3$O$_2$Yb: Yb, 20.45. Found: Yb, 19.7. IR (Nujol): 1620 s, 1595 m, 1465 s, 1440 w 1385 w, 1360 w, 1260 s, 1115 m, 1145 w, 1120 w, 925 w, 990 w, 850 w, 790 w, 750 m cm^{-1}.

Y(NHC$_6$H$_3{}^i$Pr$_2$-2,6)$_3$(THF)$_2$, 4b. **4b** (580 mg, 75%) was obtained as colorless crystals by following the procedure reported for **4a**. Anal. Calcd for C$_{44}$H$_{70}$N$_3$O$_2$Y: Y, 11.43. Found: Y, 12.8. IR (Nujol): 1620 s, 1560 m, 1540 w, 1525 w, 1460 s, 1435 s, 1390 m, 1370 s, 1060 w, 1050 w, 785 s, 745 s cm^{-1}. ^{1}H NMR (THF-d_8): δ 7.13 (d, 6H, C$_6$*H*$_3{}^i$Pr$_2$), 6.83 (t, 3H, C$_6$*H*$_3$-^{i}Pr$_2$), 4.60 (s, 3H, N*H*), 3.10 (m, 6H, C$_6$H$_3$-(*CH*Me$_2$)$_2$), 1.33 (d, 36H, C$_6$H$_3$(C*H*Me$_2$)$_2$). ^{1}H NMR (C$_6$D$_6$): δ 7.11 (d, 6H, C$_6$*H*$_3$(CHMe$_2$)$_2$), 6.79 (t, 3H, C$_6$*H*$_3$(CHMe$_2$)$_2$), 4.60 (s, 3H, N*H*), 3.79 (m, 8H, THF), 3.12 (m, 6H, C$_6$H$_3$(*CH*Me$_2$)$_2$), 1.33 (d, 36H, C$_6$H$_3$-(CH*Me*$_2$)$_2$), 1.06 (m, 8H, THF). **4b** is isomorphous with compound **4a** with cell constants of a = 9.729(2) Å, b = 19.095(5) Å, c = 12.744(1) Å, β = 112.11(1)°, and V = 2193.4(6) Å^3.

[Yb(μ-NHC$_6$H$_3{}^i$Pr$_2$-2,6)(NHC$_6$H$_3{}^i$Pr$_2$-2,6)$_2$]$_2$, 5a. 2,6-Diisopropylaniline (532 mg, 3.0 mmol) was added to a solution of Yb[N(SiMe$_3$)$_2$]$_3$ (653 mg, 1.0 mmol) in 10 mL of toluene, and the mixture was heated at 90 °C while being stirred for 30 min. As the solution cooled to ambient temperature, blue crystalline **5a** (610 mg, 87%) precipitated and then was washed with hexanes and dried on a rotary evaporator. Anal. Calcd for C$_{72}$H$_{108}$N$_6$Yb$_2$: Yb, 24.65. Found: Yb, 25.5. IR (Nujol): 1619 s, 1589 m, 1461 s, 1376 s, 1303 w, 1218w, 1168 w, 1149 w, 1110 w, 1076 w, 1052 w, 1037 w, 921 w, 883 w, 844 m, 765 s, 806 w, 744 s, 625 w cm^{-1}. NMR data are not available because **5a** is virtually insoluble in noncoordinating solvents.

[Y(μ-NHC$_6$H$_3{}^i$Pr$_2$-2,6)(NHC$_6$H$_3{}^i$Pr$_2$-2,6)$_2$]$_2$, 5b. 2,6-Diisopropylaniline (532 mg, 3.0 mmol) was reacted with a solution of Y[N(SiMe$_3$)$_2$]$_3$ (570 mg, 1.0 mmol) in 10 mL of toluene as reported above to produce yellow crystalline **5b** (520 mg, 84%). Anal. Calcd for C$_{72}$H$_{108}$N$_6$Y$_2$: Y, 14.39; C, 69.94; H, 8.81; N, 6.80. Found: Y, 14.50; C, 69.68; H, 8.92; N, 6.87. IR (Nujol): 1622 s, 1590 w, 1460 s, 1440 s, 1385 w, 1365 w, 1350 w, 1120 w, 1060 w, 1050 w, 935 w, 790 w, 750 m cm^{-1}. **5b** is insufficiently soluble in noncoordinating solvents to provide NMR data. The spectrum of a solution of **5b** in THF-d_8 is identical to **4b**.

[Nd(NHC$_6$H$_5$)$_3$(KCl)$_3$], 6. When KNHPh (131 mg, 1.0 mmol) was added to a THF (10 mL) suspension of NdCl$_3$ (83 mg, 0.33 mmol), the color lightened to pale blue and precipitate formed. The reaction was stirred for 18 h. The mixture was evaporated to dryness, washed twice with hexanes, and dried under high vacuum (10^{-5} Torr) for 24 h. The resulting blue solid (210 mg, 98%) had an elemental analysis consistent with the components of the reaction, i.e. [Nd(NHC$_6$H$_5$)$_3$-(KCl)$_3$]. Anal. Calcd for C$_{18}$H$_{18}$N$_3$Cl$_3$K$_3$Nd: C, 33.56; H, 2.82; N, 6.52. Found: C, 34.59; H, 3.16; N, 6.28.

[(Me$_4$Al)$_2$Nd(μ_3-NC$_6$H$_5$)(μ-Me)AlMe$_2$]$_2$, 7, and [Me$_2$Al(μ-NH-C$_6$H$_5$)]$_3$, 8. Al$_2$Me$_6$ (0.2 mL, 1.0 mmol) was added to a slurry of **6** (210 mg, 1.0 mmol) in hexanes (10 mL). A dark blue solution resulted which contained some precipitate. The mixture was stirred overnight and centrifuged to remove a small amount of solid. After several days at ambient temperature in a closed vial in the glovebox, some colorless and some pale blue crystals precipitated (150 mg). Crystals of blue **7** and colorless **8** suitable for X-ray and elemental analyses were taken from this mixture. Anal. Calcd for **7**, C$_{32}$H$_{70}$N$_2$Al$_6$Nd$_2$: C, 41.18; H, 7.56; N, 3.00. Found: C, 41.66; H, 7.29; N, 3.33. IR (Nujol): 1596 m, 1488 s, 1465 s, 1376 m, 1349 m, 1322 w, 1187 m, 1106 w, 1076 m, 1018 m, 952 w, 921 w, 867 w, 802 w, 759 w, 686 w cm^{-1}. The Al$_2$Me$_6$ free sample is insoluble in noncoordinating sovents and changes color from blue to green in THF. ^{1}H NMR (THF-d_8): δ 7.20 (m), 0.09 (s), $-$0.78 (s).

[Me$_2$Al(μ-NHC$_6$H$_5$)]$_3$, 8. IR (Nujol): 1614 m, 1479 s, 1389 m, 1376 w, 1210 s, 1094 w, 1045 w, 966 m cm^{-1}. ^{1}H NMR (C$_6$D$_6$): δ 7.01 (d, 6H, NHC$_6$*H*$_5$), 6.83 (d, 6H, NHC$_6$*H*$_5$), 6.70 (s, 3H, NHC$_6$*H*$_5$), 3.21 (d, 3H, N*H*C$_6$H$_5$), $-$0.2, $-$0.30, $-$0.44, $-$0.71, $-$0.85 (AlMe$_2$). The mass spectrum was found to be identical to that reported earlier.[34]

General Aspects of X-ray Data Collection and Structure Determination and Refinement. Except in the case of **5b**, the following general procedures were followed. Crystals were coated with Paratone oil, mounted on the tip of a glass fiber, and transferred to the nitrogen cold stream of a modified four-circle Picker diffractometer[35] equipped with a monochromatized Mo X-ray source. Accurate cell dimensions and the crystal orientation matrix were determined by a least-squares fit of the setting angles. Intensity data were collected by the θ-2θ method. Three intense reflections were monitored after every 97 reflections collected and showed no significant variations. Data were corrected for Lorentz and polarization effects, and an empirical absorption correction based on φ scans was applied. Summaries of crystallographic data are provided in Tables 1 and 2. The structures were solved by the Patterson or direct methods using SHELX86[36] and expanded using Fourier techniques. Anomalous dispersion corrections were applied to all non-hydrogen atoms.

[K(THF)$_6$]$_2$[Sm(μ-NHC$_6$H$_3$Me$_2$-2,6)(NHC$_6$H$_3$Me$_2$-2,6)$_3$]$_2$, 1a. A yellow-orange irregularly-shaped crystal of dimensions 0.20 × 0.25 × 0.30 mm was analyzed at 156 K using a scan speed of 3.5°/min up to a maximum 2θ of 50°. A total of 14 140 reflections were measured of which 6148 had $I > 3\sigma(I)$ and were considered observed.

The structure was solved in the monoclinic space group $P2_1/n$. All hydrogen atoms attached to carbon were included using calculated positions and were constrained to ride upon the appropriate carbon atoms. For methyl groups, at least one of the hydrogen atom positions was located from the difference Fourier map. A disordered THF molecule in the lattice was refined with geometrical restraints. Coordinated THF molecules containing O(5) and O(6) were located at two alternate orientations and were refined with geometrical restraints. The occupancies of the two orientations refined to ratios of 0.60:0.40 and 0.58:0.42, respectively. A total of 639 parameters, including positional and anisotropic thermal parameters for all non-hydrogen

---

(34) Al-Wassil, A. I.; Hitchcock, P. B.; Sarisaban, S.; Smith, J. D.; Wilson, C. L. *J. Chem. Soc., Dalton Trans.* **1985**, 1929−1934.

(35) Modified by C. E. Strouse of the Department of Chemistry, University of California, Los Angeles.

(36) Sheldrick, G. M. *Acta Crystallogr.* **1990**, *A46*, 467−473.

Table 1. Crystallographic Data for $[\mathrm{K(THF)_6}]_2[\mathrm{Sm}(\mu\text{-}\mathrm{NHC_6H_3Me_2}\text{-}2,6)(\mathrm{NHC_6H_3Me_2}\text{-}2,6)_3]_2\cdot 2\mathrm{THF}$, **1a**·2THF, $[\mathrm{K(DME)_2(THF)_3}][\mathrm{Y_2}(\mu\text{-}\mathrm{NHC_6H_3Me_2}\text{-}2,6)_2(\mu\text{-}\mathrm{Cl})(\mathrm{NHC_6H_3Me_2}\text{-}2,6)_4(\mathrm{THF})_2]$, **2**, $\mathrm{Nd(NHC_6H_3{}^iPr_2}\text{-}2,6)_3(\mathrm{THF})_3\cdot\mathrm{THF}$, **3**, and $\mathrm{Yb(NHC_6H_3{}^iPr_2}\text{-}2,6)_3(\mathrm{THF})_2$, **4a**

	1a·2THF	**2**	**3**·THF	**4a**
empirical formula	$C_{120}H_{192}N_8O_{14}K_2Sm_2$	$C_{76}H_{110}N_6O_9ClKY_2$	$C_{52}H_{86}N_3O_4Nd$	$C_{44}H_{70}N_3O_2Yb$
fw	2349.88	1504.10	961.51	846.10
space group	$P2_1/n$	$P2_1/n$	$P2_1$	$P2_1$
a (Å)	12.985(2)	23.335(2)	12.898(1)	9.718(2)
b (Å)	27.122(5)	12.649(1)	16.945(1)	19.119(3)
c (Å)	17.935(3)	27.175(3)	13.290(1)	12.640(2)
β (deg)	100.19(1)	96.36(1)	118.64(2)	112.08(1)
V (Å$^{3)}$	6216(1)	7971(1)	2549.3(3)	2176.3(6)
Z	2	4	2	2
radiation λ (Å)	0.7107	0.7107	0.7107	0.7107
μ (cm$^{-1)}$	10.62	15.96	10.63	21.76
R (R_w),^{a} $I > 3\sigma(I_0)$	0.071 (0.067)	0.095 (0.093)	0.043 (0.048)	0.043 (0.042)
temp, K	156	156	156	156

^{a} $R = \sum||F_o| - |F_c||/\sum|F_c|$; $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$.

Table 2. Crystallographic Data for $\{[\mathrm{Me_2Al}(\mu\text{-}\mathrm{Me_2})]_2\mathrm{Nd}(\mu_3\text{-}\mathrm{NC_6H_5})(\mu\text{-}\mathrm{Me})\mathrm{AlMe}\}_2$, **7**, and $\mathrm{Me_2Al}(\mu\text{-}\mathrm{NHC_6H_5})]_3$, **8**

	7	**8**
empirical formula	$C_{32}H_{70}N_2Al_6Nd_2$	$C_{24}H_{36}N_3Al_3$
fw	933.29	447.51
space group	$P\bar{1}$	$Pcab$
a (Å)	9.618(30	23.510(5)
b (Å)	12.738(4)	25.462(5)
c (Å)	9.608(3)	8.668(2)
α (deg)	99.32(1)	
β (deg)	108.87(1)	
γ (deg)	94.23(1)	
V (Å^3)	1089.1(6)	5188(1)
Z	1	8
radiation λ (Å)	0.7107	0.7107
μ (cm$^{-1)}$	25.07	15.96
R (R_w),^{a} $I > 3\sigma(I_0)$	0.039 (0.045)	0.057 (0.058)
temp, K	156	156

^{a} $R = \sum||F_o| - |F_c||/\sum|F_c|$; $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$.

atoms, were refined using full-matrix least-squares techniques. Refinement converged at $R = 7.1\%$ and $R_w = 6.7\%$. The final difference map showed some residual electron density (maximum 0.98 e Å^{-3}) close to the disordered THF molecule in the lattice.

$[\mathrm{K(DME)_2(THF)_3}][\mathrm{Y_2}(\mu\text{-}\mathrm{NHC_6H_3Me_2}\text{-}2,6)_2(\mu\text{-}\mathrm{Cl})(\mathrm{NHC_6H_3Me_2}\text{-}2,6)_4(\mathrm{THF})_2]$, 2. A colorless irregularly-shaped crystal of dimensions 0.30 × 0.25 × 0.25 mm was analyzed at 156 K using a scan speed of 4.5°/min up to a maximum 2θ of 48°. The intensities of 10 859 reflections were measured of which 9966 were unique and 2788 had $I > 3\sigma(I)$ and were considered observed. The data were quite weak in intensity with only one-third being observed on the basis of 3σ criteria.

The structure was solved in the monoclinic space group of $P2_1/n$. All of the three THF ligands attached to the cation were disordered. These were modeled with geometrical restraints and were given fixed isotropic U values during refinement. All hydrogen atoms attached to carbon except those of the disordered THF ligands were included in calculated positions and were constrained to ride upon the appropriate carbon atoms. For methyl groups at least one of the hydrogen atom positions was located from a difference Fourier map. Due to the low data to parameter ratio, only the non-carbon atoms of the anion and potassium atom of the cation were refined anisotropically. All of the phenyl groups were included as rigid groups with C−C = 1.395 Å and C−H = 1.0 Å. A total of 406 parameters including rigid-group parameters for C_6H_5 were refined using full-matrix least-squares techniques. Refinement converged at $R = 9.5\%$ and $R_w = 9.3\%$.

$\mathrm{Nd(NHC_6H_3{}^iPr_2}\text{-}2,6)_3(\mathrm{THF})_3$, 3. Complex **3** crystallizes from THF with a molecule of THF in the lattice. A light pink irregularly-shaped crystal of dimensions 0.20 × 0.35 × 0.45 mm was analyzed at 156 K using a scan speed of 6°/min up to a maximum 2θ of 50°. The intensities of 4880 reflections were measured of which 3414 had $I > 3\sigma(I)$ and were considered observed.

The structure was solved in the monoclinic space group $P2_1$. All non-methyl hydrogen atoms attached to carbon were included using calculated positions and were constrained to ride upon the appropriate carbon atoms. For methyl groups at least one of the hydrogen atom positions was located from a difference Fourier map. A disordered solvent THF molecule was modeled at two alternate orientations in the ratio 0.76:0.24 and was refined with isotropic temperature factors. A total of 528 parameters including positions and anisotropic thermal parameters for all non-hydrogen atoms were refined using full-matrix least-squares techniques. Refinement converged at $R = 4.3\%$ and $R_w = 4.8\%$. An anomalous dispersion correction was applied to all non-hydrogen atoms. The final difference map was featureless with the largest peak (0.98 e Å^{-3}) in the vicinity of the Nd atom. The correctness of the absolute structure reported was determined by refinement of the Flack parameter.[37]

$\mathrm{Yb(NHC_6H_3{}^iPr_2}\text{-}2,6)_3(\mathrm{THF})_2$, 4a. A red crystal of dimensions 0.15 × 0.25 × 0.25 mm was analyzed at 156 K using a scan speed of 6°/min up to a maximum 2θ of 50°. The intensities of 4198 reflections were measured of which 2933 had $I > 3\sigma(I)$ and were considered observed.

The systematic absences corresponded to either monoclinic space group $P2_1$ or $P2_1/m$. Subsequent refinement of the structure revealed the non-centrosymmetric group, $P2_1$, to be the correct choice. The structure was solved by the conventional heavy-atom method and Fourier techniques. One of the disordered isopropyl groups defined by atoms C(19) to C(21) was refined with geometrical restraints. Another isopropyl group defined with atoms C(31) to C(33) was located at two alternate locations in the ratio 0.69:0.31. All hydrogen atoms attached to carbon except for those of the above disordered group were included in the calculated positions and were constrained to ride upon the appropriate carbon atoms. A total of 454 parameters including positional and anisotropic thermal parameters for all non-hydrogen atoms were refined using full-matrix least-squares techniques. Refinement converged at $R = 4.3\%$ and $R_w = 4.2\%$. The correctness of the absolute structure reported was determined by refinement of the Flack parameter.[37]

$[\mathrm{Y}(\mu\text{-}\mathrm{NHC_6H_3{}^iPr_2}\text{-}2,6)(\mathrm{NHC_6H_3{}^iPr_2}\text{-}2,6)_2]_2$, 5b. A marginally suitable yellow crystal of dimensions 0.06 × 0.07 × 0.33 mm was mounted on a Siemens P4 rotating-anode diffractometer. Determination of Laue symmetry, crystal class, unit cell parameters, and the crystal's orientation matrix was carried out according to standard procedures.[38a] Although the crystal quality was poor, it was decided to proceed with data collection in order to determine the molecular connectivity. Low-temperature (158 K) intensity data were collected using a 2θ-ω technique. All 3502 data were corrected for Lorentz and polarization effects and placed on an approximate absolute scale. The Laue symmetry is $2/m$. On the basis of systematic extinctions, the space group is either $P2_1$ or $P2_1/m$. All attempts to solve the structure in space group $P2_1/m$ proved unsuccessful. It was therefore decided to assign space group $P2_1$ as the more probable space group.

---

(37) Flack, H. D. *Acta Crystallogr.* **1983**, *A39*, 876−881.

(38) (a) *XSCANS Version 2.10*; Siemens Analytical X-Ray Instruments, Inc.: Madison, WI, 1990−1995. (b) *UCLA Crystallographic Computing Package*; University of California: Los Angeles, CA, 1981.

The crystallographic calculations were carried out using a locally modified version of the UCLA Crystallographic Computing Package[38b] and the SHELXTL[39] program. The analytical scattering factors for neutral atoms were used throughout the analysis.[40] The structure was solved by direct methods and refined by full-matrix least-squares techniques (SHELXTL). Due to the poor quality of the data, it was necessary to refine the ligands as fixed groups. The model converged with R1 = 0.0971 for 1718 data with $F_o > 4\sigma(F_o)$, and wR2 = 0.2687 and GOF = 1.23 for 321 parameters refined against all 3408 data.

$[(Me_4Al)_2Nd(\mu_3\text{-}NC_6H_5)(\mu\text{-}Me)AlMe_2]_2$, 7. A blue crystal of dimensions 0.20 × 0.15 × 0.05 mm was analyzed at 156 K using a scan speed of 4.5°/min up to a maximum 2θ of 50°. The intensities of 3827 reflections were measured of which 2976 had $I > 3\sigma(I)$ and were considered observed.

The structure was solved by conventional heavy atom methods and Fourier techniques in the space group $P\bar{1}$. A total of 190 parameters including positional and anisotropic thermal parameters for all non-hydrogen atoms were refined using full-matrix least-squares techniques. Refinement converged at $R = 3.9\%$ and $R_w = 4.5\%$. The largest peaks on the final difference electron density map (1.04 e Å^{-3}) were near Nd.

$[Me_2Al(\mu\text{-}NHC_6H_5)]_3$, 8. A colorless parallelpiped of dimensions 0.35 × 0.15 × 0.15 mm was analyzed at 156 K using a scan speed of 3.0°/min up to a maximum 2θ of 50°. The intensities of 5156 reflections were measured of which 1386 had $I > 3\sigma(I)$ and were considered observed.

The structure was solved using SHELX86 in the orthorhombic space group *Pcab*. All hydrogen atoms were included in calculated positions and were constrained to ride upon the appropriate carbon atoms. A total of 271 parameters including positional and anisotropic thermal parameters for all non-hydrogen atoms were refined using full-matrix least-squares techniques. Refinement converged at $R = 5.7\%$ and $R_w = 5.8\%$. The final difference electron density map was featureless.

Results

(2,6-Dimethylphenyl)amido Complexes. Synthesis. $SmCl_3$ reacts with 4 equiv of $KNHC_6H_3Me_2$-2,6 in THF to give the pale green complex, **1a**, which is insoluble in toluene but easily crystallizes from THF at −40 °C in >60% yield. ^1H NMR spectroscopy shows that the same complex is obtained when only 3 equiv of $KNHC_6H_3Me_2$ is used; i.e., **1a** appears to be the preferred product in this system. The ^1H and ^{13}C NMR spectra of paramagnetic **1a** indicated the presence of a single type of $NHC_6H_3Me_2$ ligand, but since these data were not structurally definitive, an X-ray diffraction study was carried out. **1a** crystallizes in the solid state as the potassium salt of a bimetallic dianion, Figure 1. The formation of **1a** is shown in eq 1.

$$2SmCl_3 + 8KNHC_6H_3Me_2\text{-}2,6 \xrightarrow{THF} \underset{\mathbf{1a}}{[K(THF)_6]_2[Sm(\mu\text{-}NHC_6H_3Me_2\text{-}2,6)(NHC_6H_3Me_2\text{-}2,6)_3]_2} + 6KCl \quad (1)$$

When **1a** was dried for a prolonged period under high vacuum (10^{-5} Torr), a green-yellow powder was obtained which had an elemental analysis consistent with only one THF per samarium. Unfortunately, the low solubility of this material prevented any further characterization. $NdCl_3$ reacts similarly with $KNHC_6H_3Me_2$-2,6 to produce a complex, $[K(THF)_6]_2[Nd(\mu\text{-}NHC_6H_3Me_2\text{-}2,6)(NHC_6H_3Me_2\text{-}2,6)_3]_2$, **1b**, which has analogous unit cell parameters.

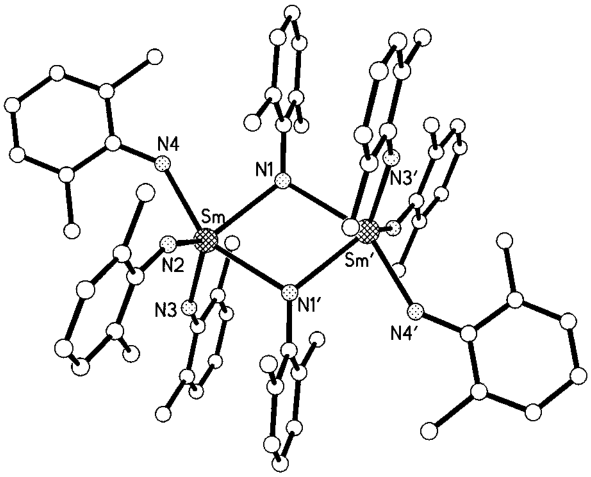

Figure 1. Structure of the $[Sm(\mu\text{-}NHC_6H_3Me_2\text{-}2,6)(NHC_6H_3Me_2\text{-}2,6)_3]_2^{2-}$ ion in **1a**.

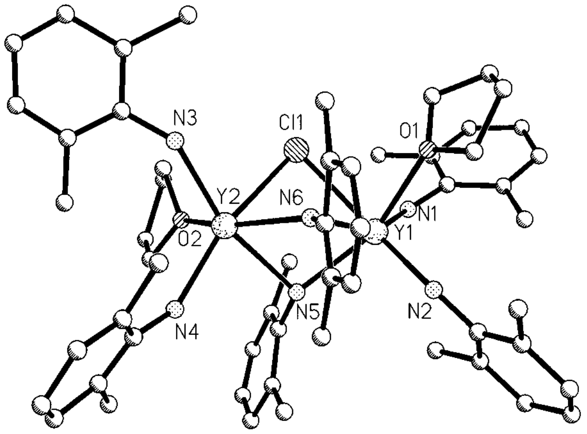

Figure 2. Structure of the $[Y_2(\mu\text{-}NHC_6H_3Me_2\text{-}2,6)_2(\mu\text{-}Cl)(NHC_6H_3Me_2\text{-}2,6)_4(THF)_2]^-$ ion in **2**.

Under similar reaction conditions, YCl_3 does not follow the same reaction pathway. Instead, a complex is isolated which has two types of methyl resonances in the ^1H NMR spectrum in a 1:2 ratio. Crystallization of this toluene-insoluble product formed crystals which readily lose THF. Recrystallization from DME gave crystals of a mixed THF/DME complex which were suitable for definitive structural characterization. X-ray crystallography revealed that the complex was the trimetallic ion pair $[K(DME)_2(THF)_3][Y_2(\mu\text{-}Cl)(\mu\text{-}NHC_6H_3Me_2\text{-}2,6)_2(NHC_6H_3Me_2\text{-}2,6)_4(THF)_2]$, **2** (Figure 2). The formation of **2** can be described as shown in eq 2.

$$2YCl_3 + 6KNHC_6H_3Me_2\text{-}2,6 \xrightarrow{THF} \xrightarrow{DME} 5KCl + \underset{\mathbf{2}}{[K(DME)_2(THF)_3][Y_2(\mu\text{-}Cl)(\mu\text{-}NHC_6H_3Me_2\text{-}2,6)_2(NHC_6H_3Me_2\text{-}2,6)_4(THF)_2]} \quad (2)$$

Structure of $[K(THF)_6]_2[Sm(\mu\text{-}NHC_6H_3Me_2\text{-}2,6)(NHC_6H_3Me_2\text{-}2,6)_3]_2$, 1a. The ions comprising complex **1a** are sufficiently separated in the solid state that they are noninteracting. The $[Sm(\mu\text{-}NHC_6H_3Me_2\text{-}2,6)(NHC_6H_3Me_2\text{-}2,6)_3]_2^{2-}$ anion is a rare case of an anionic lanthanide complex containing only amido ligands. The closest example is the mixed-metal diisopropylamido complex $(^iPr_2N)_2Nd(\mu\text{-}N^iPr_2)_2Li(THF)$, **9**, which was recently structurally characterized.[22d]

The structure of the dianion in **1a** is shown in Figure 1, and important bond lengths and distances are given in Table 3. The two sides of the anion are related by an inversion center. The five $NHC_6H_3Me_2$ ligands form a distorted trigonal bipyramid around samarium. Equatorial N−Sm−N angles involving N(1), N(2), and N(3) range from 115.5(3) to 121.3(3)°, whereas the

---

[39] Sheldrick, G. M. *SHELXTL*; Siemens Analytical X-Ray Instruments, Inc.; Madison, WI, 1990−1995.

[40] *International Tables for X-Ray Crystallography*; Kluwer Academic Publishers: Dordrecht, The Netherlands, 1992; Vol. C.

Table 3. Selected Bond Distances (Å) and Angles (deg) for $[K(THF)_6]_2[Sm(\mu\text{-}NHC_6H_3Me_2\text{-}2,6)(NHC_6H_3Me_2\text{-}2,6)_3]_2$, **1a**, $[K(DME)_2(THF)_3][Y_2(\mu\text{-}NHC_6H_3Me_2\text{-}2,6)_2(\mu\text{-}Cl)(NHC_6H_3Me_2\text{-}2,6)_4(THF)_2]$, **2**, $Nd(NHC_6H_3{}^iPr_2\text{-}2,6)_3(THF)_3$, **3**, and $Yb(NHC_6H_3{}^iPr_2\text{-}2,6)_3(THF)_2$, **4a**

1a		**2**		**3**		**4a**	
Sm−N(1)	2.468(7)	Y(1)−N(1)	2.26(2)	Nd−N(1)	2.304(8)	Yb−N(1)	2.17(1)
Sm−N(2)	2.356(9)	Y(1)−N(2)	2.28(2)	Nd−N(2)	2.320(8)	Yb−N(2)	2.20(2)
Sm−N(3)	2.340(8)	Y(2)−N(3)	2.29(2)	Nd−N(1)	2.304(8)	Yb−N(3)	2.14(1)
Sm−N(4)	2.367(9)	Y(2)−N(4)	2.30(2)	Nd−O(1)	2.593(8)	Yb−O(1)	2.35(1)
Sm−N(1′)	2.614(7)	Y(1)−N(5)	2.40(2)	Nd−O(2)	2.580(8)	Yb−O(2)	2.32(1)
Sm- - -Sm′	4.051(1)	Y(1)−N(6)	2.54(2)	Nd−O(3)	2.591(8)		
		Y(2)−N(5)	2.55(2)				
		Y(2)−N(6)	2.39(2)				
		Y(1)−O(1)	2.39(2)				
		Y(2)−O(2)	2.40(2)				
		Y(1)−Cl	2.806(8)				
		Y(2)−Cl	2.807(8)				
N(1)−Sm−N(2)	115.5(3)	Y(1)−Cl−Y(2)	80.0(2)	N(1)−Nd−N(2)	120.5(4)	N(1)−Yb−N(2)	132.3(4)
N(1)−Sm−N(3)	121.3(3)	Y(1)−N(5)−Y(2)	93.4(7)	N(1)−Nd−N(3)	103.0(4)	N(1)−Yb−N(3)	94.5(5)
N(1)−Sm−N(4)	80.0(3)	Y(1)−N(6)−Y(2)	94.1(8)	N(1)−Nd−O(1)	84.6(3)	N(1)−Yb−O(1)	88.0(4)
N(1)−Sm−N(1′)	74.3(3)	N(1)−Y(1)−N(2)	114.2(7)	N(1)−Nd−O(2)	154.0(3)	N(1)−Yb−O(2)	88.6(4)
N(2)−Sm−N(3)	119.7(3)	N(1)−Y(1)−O(1)	88.0(7)	N(1)−Nd−O(3)	82.8(3)	N(2)−Yb−O(1)	84.9(4)
N(2)−Sm−N(4)	98.9(3)	N(2)−Y(1)−O(1)	88.6(7)	N(2)−Nd−O(1)	82.8(3)	N(2)−Yb−O(2)	85.3(4)
N(3)−Sm−N(4)	108.6(3)	N(3)−Y(2)−N(4)	114.3(7)	N(2)−Nd−O(2)	76.7(4)	N(3)−Yb−O(1)	104.9(4)
Sm−N(1)−Sm′	105.7(3)	N(3)−Y(2)−O(2)	87.2(7)	N(2)−Nd−O(3)	148.7(3)	O(1)−Yb−O(2)	163.3(3)
		N(4)−Y(2)−O(2)	88.0(7)	N(3)−Nd−O(1)	161.8(3)		
		N(5)−Y(1)−N(6)	76.5(7)	N(3)−Nd−O(2)	88.7(3)		
		N(5)−Y(2)−N(6)	76.5(7)	N(3)−Nd−O(3)	85.8(3)		

axial N(4)−Sm−N(1′) angle is 153.1(3)°. It is interesting to note that use of the analogous aryloxide $KOC_6H_3Me_2\text{-}2,6$ in a similar reaction did not produce an analogous dianion. Instead, the neutral compound $[Nd(\mu\text{-}OC_6H_3Me_2\text{-}2,6)(OC_6H_3Me_2\text{-}2,6)_2(THF)_2]_2$ was obtained.[15a]

As expected, the terminal $Sm-N(NHC_6H_3Me_2)$ distances, 2.340(8)−2.367(9) Å, are shorter than the 2.468(7) and 2.614(7) Å bridging distances. The bridging arylamide ligands are located asymmetrically between the two metal centers such that each samarium has one close and one distant interaction. Hence, N(1) is 2.468(7) Å away from Sm and 2.614(7) Å from Sm′. In comparison, in **9** the terminal $Nd-N{}^iPr_2$ distances are 2.283(17)−2.291(16) Å and the bridging distances are 2.393(15) and 2.406(16) Å.[22d] Since Sm is 0.025 Å[41] smaller than Nd and the structure of **9** contains agostic interactions which increase its effective coordination number, the Ln−N distances in **1a** appear to be longer than expected. The Sm−N distances in **1a** are also long compared to the 2.259(9) Å Eu−N distances in $Eu[N(SiMe_3]_3$.[21b] The Sm−N distances in five-coordinate **1a** are more similar to the 2.331(3) Å Sm−NHPh distance in the formally eight-coordinate complex $(C_5Me_5)_2Sm(NHPh)(THF)$.[24]

$[K(DME)_2(THF)_3][Y_2(\mu\text{-}NHC_6H_3Me_2\text{-}2,6)_2(\mu\text{-}Cl)(NHC_6H_3Me_2\text{-}2,6)_4(THF)_2]$, 2. As in **1a**, the ion pair in **2** is well separated in the solid state. Both yttrium atoms in **2** (Figure 2) are surrounded by a distorted octahedron of ligands such that the anion has the structure of a confacial bioctahedron. (Donor atom)−Y−(donor atom) angles (Table 3) range from 76.4(7) to 115.2(7)° for cis ligands and from 151.1(8) to 156.7(7)° for trans ligands.

The 2.26(2)−2.30(2) Å terminal $Y-N(NHC_6H_3Me_2)$ distances are shorter than the bridging distances as expected and are also shorter than the Sm−N distances in **1a** when the differences in radii and coordination number are considered. The bridging arylamide ligands are located asymmetrically between the two yttrium atoms such that each yttrium has one close and one distant interaction. Hence, N(5) is 2.40(2) Å away from Y(1) and 2.55(2) Å from Y(2), whereas N(6) is 2.54(2) Å away from Y(1) and 2.39(2) Å away from Y(2). The bridging chloride ligand, on the other hand, is symmetrically located with 2.806(8) and 2.807(8) Å Y−Cl lengths. The Y−(μ-Cl) distance is in the range of analogous lengths found in $Y_{14}(OCMe_3)_{28}Cl_{10}O_2(THF)_4$,[42] 2.730(12)−2.820(11) Å, and $(C_5Me_5)_2Y(\mu\text{-}Cl)YCl(C_5Me_5)_2$,[43] 2.776(2) Å, but it is longer than the 2.704(1) and 2.684(1) Å distances found in $[(C_5H_4SiMe_3)_2Y(\mu\text{-}Cl)]_2$.[44]

Disorder occurs in the positions of the β-carbon atoms of the THF ligands in the cation and precludes a discussion of the bond distances in this unit.

(2,6-Diisopropylphenyl)amido Complexes. Synthesis. In contrast to the reactions of $KNHC_6H_3Me_2\text{-}2,6$ with lanthanide trichlorides, the bulkier reagent $KNHC_6H_3{}^iPr_2\text{-}2,6$ reacts with $NdCl_3$ in THF to form a product, **3**, which is highly soluble in toluene and hexanes. The paramagnetism of the complex limited the structural information obtainable by NMR spectroscopy, and an X-ray crystal structure determination was carried out to establish the identity of **3** as the neutral complex $Nd(NHC_6H_3{}^iPr_2\text{-}2,6)_3(THF)_3$ (Figure 3, eq 3). Reactions run with

$$NdCl_3 + 3KNHC_6H_3{}^iPr_2\text{-}2,6 \xrightarrow{THF} \underset{\mathbf{3}}{Nd(NHC_6H_3{}^iPr_2\text{-}2,6)_3(THF)_3} \quad (3)$$

excess $KNHC_6H_3{}^iPr_2$ also led to the isolation of neutral **3** instead of an anionic complex analogous to **1a**. Hence, with this metal/ligand combination, a neutral product is apparently preferred. It is interesting to note that, under similar conditions, the chlorides $LnCl_3$ (Ln = La, Nd, Er, Lu) react with 3 or 4 equiv of $KOC_6H_3{}^iPr_2\text{-}2,6$ to form the anionic complexes $K[Ln(OC_6H_3\text{-}{}^iPr_2\text{-}2,6)_4]$, which exhibit infinite chains via potassium−arene interactions in the cases of Ln = Nd and Er and a layer structure in the case of Ln = La.[8a] On the other hand, the analogous

---

(41) Shannon, R. D. *Acta Crystallogr.* **1976**, *A32*, 751−767.

(42) Evans, W. J.; Sollberger, M. S. *Inorg. Chem.* **1988**, *27*, 4417−4423.

(43) Evans, W. J.; Peterson, T. T.; Rausch, M. D.; Hunter, W. E.; Zhang, H.; Atwood, J. L. *Organometallics* **1985**, *4*, 554−559.

(44) Evans, W. J.; Sollberger, M. S.; Shreeve, J. L.; Olofson, J. M.; Hain, J. H., Jr.; Ziller, J. W. *Inorg. Chem.* **1992**, *31*, 2492−2501.

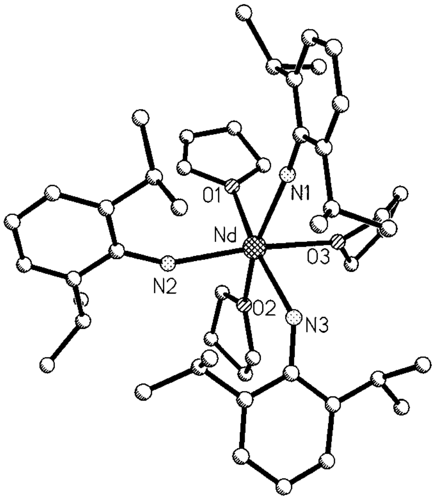

Figure 3. Molecular structure of [Nd($NHC_6H_3{}^iPr_2$-2,6)$_3$(THF)$_3$], **3**.

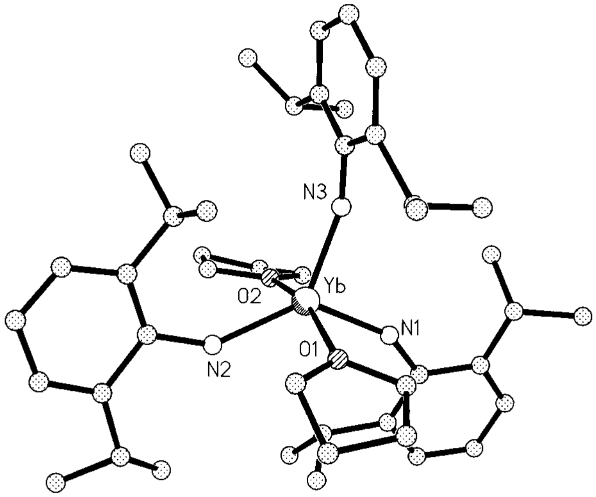

Figure 4. Molecular structure of [Yb($NHC_6H_3{}^iPr_2$-2,6)$_3$(THF)$_2$], **4a**.

aryloxide reactions with Ln = Pr, Sm, Gd, and Yb form the neutral complexes Ln($OC_6H_3{}^iPr_2$-2,6)$_3$(THF)$_2$.[8b]

$YbCl_3$ reacts with $KNHC_6H_3{}^iPr_2$-2,6 to form a product, **4a**, which, like **3**, is soluble in nonpolar solvents. Complex **4a** can be easily crystallized from hexanes at room temperature by slow evaporation, and X-ray crystallography revealed that with this smaller metal a five-coordinate disolvated complex, Yb($NHC_6H_3{}^iPr_2$-2,6)$_3$(THF)$_2$ (Figure 4, eq 4) was formed. YCl_3

$$YbCl_3 + 3KNHC_6H_3{}^iPr_2\text{-}2{,}6 \xrightarrow{THF} \underset{\mathbf{4a}}{Yb(NHC_6H_3{}^iPr_2\text{-}2{,}6)_3(THF)_2} \quad (4)$$

is similar to $YbCl_3$ in that it forms an analogous compound Y($NHC_6H_3{}^iPr_2$-2,6)$_3$(THF)$_2$, **4b**, which is consistent with the similar radii of these metals.

[Yb(μ-$NHC_6H_3{}^iPr_2$-2,6)($NHC_6H_3{}^iPr_2$-2,6)$_2$]$_2$, 5a, and [Y(μ-$NHC_6H_3{}^iPr_2$-2,6)($NHC_6H_3{}^iPr_2$-2,6)$_2$]$_2$, 5b. The reaction of hydrocarbon-soluble Ln[N($SiMe_3$)$_2$]$_3$ complexes[21] with the amine $NH_2C_6H_3{}^iPr_2$-2,6 was also investigated to determine if THF-free complexes could be obtained with arylamido ligands. Using Ln[N($SiMe_3$)$_2$]$_3$ complexes as precursors is a well established technique in alkoxide chemistry.[4] Yb(N($SiMe_3$)$_2$)$_3$ reacts with $NH_2C_6H_3{}^iPr_2$-2,6 in toluene to form the blue complex **5a**. Due to poor solubility in nonpolar solvents and high reactivity toward donor solvents, suitable crystals of **5a** could not be grown. Although the yttrium analog, **5b**, is equally reactive toward donor solvents, it is slightly more soluble and crystals could be grown from hot toluene, which allow complete characterization by X-ray crystallography (Figure 5, eq 5).

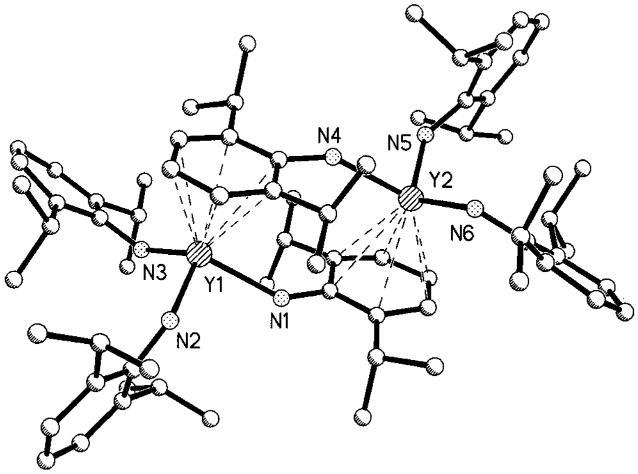

Figure 5. Molecular structure of [Y(μ-$NHC_6H_3{}^iPr_2$-2,6)($NHC_6H_3{}^iPr_2$-2,6)$_2$]$_2$, **5b**.

$$2Y(N(SiMe_3)_2)_3 + 6NH_2C_6H_3{}^iPr_2\text{-}2{,}6 \rightarrow \underset{\mathbf{5b}}{[Y(\mu\text{-}NHC_6H_3{}^iPr_2\text{-}2{,}6)(NHC_6H_3{}^iPr_2\text{-}2{,}6)_2]_2} \quad (5)$$

As expected, **5b** reacts with THF to produce **4b** quantitatively as indicated by NMR spectroscopy (eq 6).

$$\underset{\mathbf{5b}}{[Y(\mu\text{-}NHC_6H_3{}^iPr_2\text{-}2{,}6)(NHC_6H_3{}^iPr_2\text{-}2{,}6)_2]_2} + 4THF \rightarrow \underset{\mathbf{4b}}{Y(NHC_6H_3{}^iPr_2\text{-}2{,}6)_3(THF)_2} \quad (6)$$

Structure of [Nd($NHC_6H_3{}^iPr_2$-2,6)$_3$(THF)$_3$], 3. The three $NHC_6H_3{}^iPr_2$-2,6 ligands and the three THF molecules in **3** roughly define a distorted octahedron with the two sets of ligands oriented in a facial arrangement. The angles (Table 3) involving pairs of THF are less than 90°, whereas angles involving pairs of arylamido ligands are larger than 90°. The overall arrangement is similar to those in Y($OC_6H_3Me_2$-2,6)$_3$(THF)$_3$[45] and Ce($OSiPh_3$)$_3$(THF)$_3$.[46]

The 2.321(14) Å average Nd−N distance in six-coordinate **3** matches the 2.283(17)−2.319(16) Å range of terminal Nd−N distances in ($^iPr_2N$)$_2$Nd(μ-N^iPr_2)$_2$Li(THF), **9**.[23d] The Nd−N distances in **3** provide another example suggesting that the 2.38(2) Å average Sm−N distance in **1a** is long. The Nd−O(THF) distances, which range from 2.580(7) to 2.593(8) Å, are significantly larger than the 2.493(7) and 2.529(9) Å Nd−O(THF) lengths in six-coordinate (2,6-$Me_2C_6H_3O$)$_2$(THF)$_2$Nd(μ-$OC_6H_3Me_2$-2,6)$_2$$AlMe_2$[47] and formally eight-coordinate [(THF)$_2$Li(μ-Cl)$_2$]$_2$[(C_5H_4Me)Nd(THF)],[48] respectively.

Structure of Yb($NHC_6H_3{}^iPr_2$-2,6)$_3$(THF)$_2$, 4a. Complex **4a** is isomorphous with the recently reported aryloxides Ln($OC_6H_3{}^iPr_2$-2,6)$_3$(THF)$_2$ in which Ln = Pr, Gd, Er, or Lu.[8b] The metal center in **4a** is approximately trigonal bipyramidal with the three largest amido ligands in the equatorial positions as

---

(45) Evans, W. J.; Olofson, J. M.; Ziller, J. W. *Inorg. Chem.* **1989**, *28*, 4308−4309.

(46) Gradeff, P. S.; Yunlu, K.; Deming, T. J.; Olofson, J. M.; Doedens, R. J.; Evans, W. J. *Inorg. Chem.* **1990**, *29*, 420−424.

(47) Evans, W. J.; Ansari, M. A.; Ziller, J. W. *Inorg. Chem.* **1995**, *34*, 3079−3082.

(48) Guan, J.; Jin, S.; Lin Y.; Shen, Q. *Organometallics* **1992**, *11*, 2483−2487.

expected. The 2.14(1)−2.20(1) Å Yb−N distances are shorter than the 2.321(14) Å average Nd−N distance in **3** as expected for a smaller metal (Yb is 0.115 Å smaller than Nd)[41] and a lower coordinate complex. However, the 2.32(1) and 2.35(1) Å Yb−O(THF) distances are much shorter than the 2.580(8)−2.593(8) Å distances found in **3**. The Yb−O(THF) distances in **4a** are quite normal compared with those found in five-coordinate $Lu(OC_6H_3{}^iPr_2\text{-}2,6)_3(THF)_2$,[8b] 2.296(2) Å, and $[Y(OC_6H_3Me_2\text{-}2,6)_3(THF)]_3$, 2.348(6) Å.[45] Hence, in a direct comparison of **4a** and $Lu(OC_6H_3{}^iPr_2\text{-}2,6)_3(THF)_2$,[8a] the Ln−O(THF) distances are similar and the 2.041(4)−2.048(4) Å Ln−$O(OC_6H_3{}^iPr_2\text{-}2,6)$ distances are 0.1−0.15 Å shorter than the Ln−$N(NHC_6H_3{}^iPr_2\text{-}2,6)$ lengths.

Structure of $Y(\mu\text{-}NHC_6H_3{}^iPr_2\text{-}2,6)(NHC_6H_3{}^iPr_2\text{-}2,6)_2]_2$, 5b. In complex **5b** (Figure 5), each yttrium is ligated by only three nitrogen donor atoms. However, each yttrium is also oriented toward an aryl ring of an amide ligand on an adjacent yttrium such that the aryl ring centroid and the three nitrogen atoms form a tetrahedron around the metal. **5b** is the first structurally characterized yttrium complex showing such an Y−(η^6-arene) interaction, although examples are known for the (diisopropylaryl)oxide compounds $[U(OC_6H_3{}^iPr_2\text{-}2,6)_3]_2$,[49] $[Nd(OC_6H_3{}^iPr_2\text{-}2,6)_3]_2$,[8b] and $[Sm(OC_6H_3{}^iPr_2\text{-}2,6)_3]_2$.[8b] Complex **5b** is not isomorphous with these compounds, however. Unfortunately, the quality of the structure of **5b** does not allow a detailed discussion of bond distances and angles.

A Mixed-Metal Complex from an Unsubstituted Arylamido Ligand. A reaction involving the unsubstituted NHC_6H_5 ligand was carried out to examine the importance of 2,6-substitution in forming tractable lanthanide arylamido complexes. Reaction of 3 equiv of $KNHC_6H_5$ with 1 equiv of $NdCl_3$ in THF produced a pale blue material which was insoluble in THF. Elemental analysis was consistent with the components of the reaction, namely the formula $[Nd(NHC_6H_5)_3(KCl)_3]$, eq 7.

$$NdCl_3 + 3KNHPh \rightarrow \underset{\mathbf{6}}{[Nd(NHPh)_3(KCl)_3]} \qquad (7)$$

Recently, we showed that trialkylaluminum compounds will solubilize insoluble materials of this type.[23] For example, for the dimethylamido complexes, the reactions in Scheme 1 have been observed.

Scheme 1

$$\begin{aligned} &LnCl_3 + 3LiNMe_2 \rightarrow Ln(NMe_2)_3(LiCl)_3 \xrightarrow{3MMe_3,\ -3LiCl} \\ &\quad Ln(NMe_2)_3(MMe_3)_3 \xrightarrow{MMe_3} \\ &\quad Ln[(\mu\text{-}Me)_2MMe_2][(\mu\text{-}Me)(\mu\text{-}NMe_2)MMe_2]_2 + \\ &\quad 0.5[Me_2NMMe_2]_2 \xrightarrow{\text{excess } MMe_3} Ln[(\mu\text{-}Me)_2MMe_2]_3 + \\ &\qquad [Me_2NMMe_2]_2 \end{aligned}$$

Given the success in forming tractable compounds by this type of reaction, insoluble complex **6** was treated with Al_2Me_6 in hexanes. This produced a blue solution from which blue and colorless crystals were isolated over a period of several days at ambient temperature. To definitively characterize these products, both were studied by X-ray diffraction. The blue material was found to be a heteroleptic heterometallic cluster containing two neodymium and six aluminum centers, $\{[Me_2Al(\mu\text{-}Me_2)]_2Nd(\mu_3\text{-}NC_6H_5)(\mu\text{-}Me)AlMe\}_2$, **7**, and the colorless crystals were identified as the homometallic cyclic aluminum amido compound $(Me_2AlNHPh)_3$, **8.**

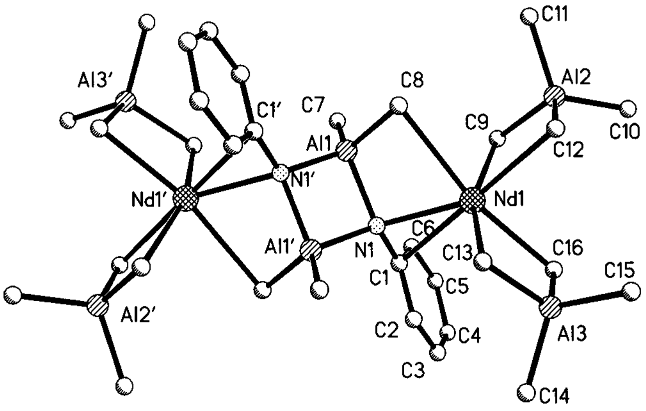

Figure 6. Molecular structure of $\{[Me_2Al(\mu\text{-}Me_2)]_2Nd(\mu_3\text{-}NC_6H_5)(\mu\text{-}Me)AlMe\}_2$, **7**.

The formation of **7** and **8** may be related to Scheme 1 except that further reaction occurs to form methane. A theoretical stoichiometric rationalization of the products is given in equations 8 and 9.

$$\begin{aligned} &2[Nd(NHC_6H_5)_3(KCl)_3] + 3Al_2Me_6 \rightarrow \\ &\qquad 2Nd[(\mu\text{-}NHC_6H_5)(\mu\text{-}Me)AlMe_2]_3 + 6KCl \quad (8) \end{aligned}$$

$$\begin{aligned} &4Nd[(\mu\text{-}NHC_6H_5)(\mu\text{-}Me)AlMe_2]_3 + 9Al_2Me_6 \rightarrow \\ &\quad 2\underset{\mathbf{7}}{\{[Me_2Al(\mu\text{-}Me_2)]_2Nd(\mu_3\text{-}NC_6H_5)(\mu\text{-}Me)AlMe\}_2} + \\ &\qquad 2\underset{\mathbf{8}}{(Me_2AlNHC_6H_5)_3} + 2MeH + 2NH_2C_6H_5 \quad (9) \end{aligned}$$

Structure of $\{[Me_2Al(\mu\text{-}Me_2)]_2Nd(\mu_3\text{-}NC_6H_5)(\mu\text{-}Me)AlMe\}_2$, 7, and $(Me_2AlNHPh)_3$, 8. Complex **7** (Figure 6) is a dimer in which each neodymium center is seven-coordinate. Four coordination positions are occupied by two chelating $[(\mu\text{-}Me)_2AlMe_2]^-$ ligands, and the other three are filled by a tridentate $[(\mu\text{-}Me)(\mu_3\text{-}NC_6H_5)AlMe]^-$ group, which formally can be derived by the loss of a methyl group from $AlMe_3$ and a hydrogen from the $[NHC_6H_5]^-$ ligand. The $[(\mu\text{-}Me)(\mu_3\text{-}NC_6H_5)\text{-}AlMe]^-$ groups generate the dimer through N−Al bonds.

The 2.612(6)−2.707(7) Å range of Nd−Me distances involving the $[(\mu\text{-}Me)_2AlMe_2]^-$ anion in **7** can be compared to the 2.589(14) Å average distance observed in $Nd[(\mu\text{-}Me)_2AlMe_2]_3$, which has a narrower 2.563(14)−2.609(14) Å range. Each $[(\mu\text{-}Me)(\mu\text{-}NC_6H_5)AlMe]^-$ unit coordinates to the neodymium through a 2.859(7) Å Nd−C(8) distance, which is significantly larger than the other Nd−C lengths in the molecule. Coordination of the $[(\mu\text{-}Me)(\mu_3\text{-}NC_6H_5)AlMe]^-$ unit also occurs through nitrogen via a 2.401(5)Å Nd−N bond. This bond is longer than the 2.321(14) Å average terminal Nd−N distance in **3** and the 2.283(17)−2.291(16) Å terminal Nd−N distances in $({}^iPr_2N)_2\text{-}Nd(\mu\text{-}N^iPr_2)_2Li(THF)$, **9**,[23d] as expected for a bridging atom. It matches well with the 2.393(15) and 2.406(16) Å bridging Nd−N bonds in **9**. The ipso carbon, C(1), is 2.723(6) Å from Nd(1), a distance which is shorter than Nd−C(8) and is in the range of the 2.703(7)−2.895(7) Nd−$C(C_5H_4Me)$ distances reported for $[(C_5H_4Me)_3Nd]_4$[50] and the average 2.76(3) Å Nd−$C(C_5Me_5)$ distance found in $(C_5Me_5)_2NdCH(SiMe_3)_2$.[51] The

---

(49) Van Der Sluys, W. G.; Burns, C. J.; Huffman, J. C.; Sattelberger, A. P. *J. Am. Chem. Soc.* **1988**, *110*, 5924−5925.

(50) Burns, J. H.; Baldwin, W. H.; Fink, F. H. *Inorg. Chem.* **1974**, *13*, 1916−1920.

(51) Jeske, G.; Lauke, H.; Mauermann, H.; Swepston, P. N.; Schumann, H.; Marks, T. J. *J. Am. Chem Soc.* **1985**, *107*, 8091−8103.

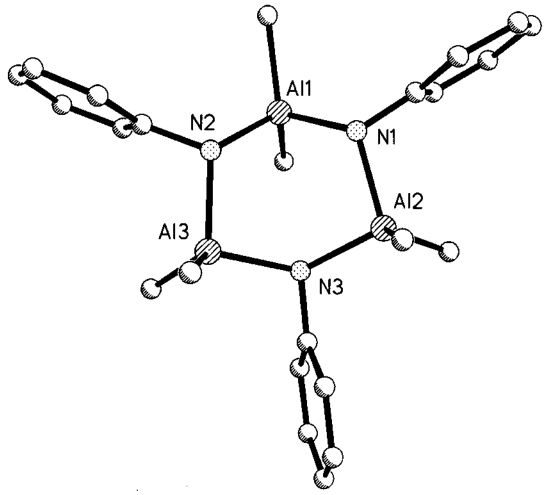

Figure 7. Molecular structure of $[Me_2Al(\mu\text{-}NHC_6H_5)]_3$, **8**.

geometry around N(1) is distorted tetrahedral with the six angles ranging from 87.03(3) to 134.93(4)°.

The internal part of the molecule has a $(Me_2AlNRR')_2$ structural motif which is commonly observed in other systems and apparently is quite stable.[52] In compound **7**, R = Ph and R' = $[Me_2Al(\mu\text{-}Me)_2]_2Nd$. The 1.925(5) and 1.923(6) Å Al−N distances are equiv and can be compared with the 1.96(1) Å Al−N distances in $[(Me_2Al(\mu\text{-}NMe_2)]_2$.[53] The 1.963(7) Å Al−C distances involving a terminal methyl are shorter than the 2.014(7) Å lengths involving a bridging methyl as expected and are in the typical range for terminal Al−Me bonds.[53]

The synthesis of $[Me_2AlNHC_6H_5]_n$ has previously been reported,[34] and the mass spectral data indicated the presence of a trimer in the gas phase. The X-ray diffraction study established that complex **8** is trimeric in the solid state (Figure 7). It consists of a six-membered ring composed of alternating Me_2Al and NHC_6H_5 units. A careful examination of the molecule reveals that it has a skew-boat conformation with Al(1) and N(3) occupying the apical positions. All of the aluminum and nitrogen centers have a distorted tetrahedral geometry with angles around Al and N varying from 95.92(3) to 121.33(7)° and from 108.70(5) to 123.54(4)°, respectively. The Al−N distances range from 1.955(7) to 1.988(7) Å and are similar to those found in other trimers[52] and in **7**. The overall arrangement is similar to that found in $[Me_2AlNH_2]_3$.[52]

Table 4. Selected Bond Distances (Å) and Angles (deg) for $\{[Me_2Al(\mu\text{-}Me_2)]_2Nd(\mu_3\text{-}NC_6H_5)(\mu\text{-}Me)AlMe\}_2$, **7**

Nd(1)−C(1)	2.723(6)	Al(1)−C(7)	1.963(7)
Nd(1)−N(1)	2.401(5)	Al(1)−C(8)	2.014(7)
Nd(1)−C(8)	2.859(7)	Al(2)−C(9)	2.077(8)
Nd(1)−C(9)	2.641(6)	Al(2)−C(10)	1.968(8)
Nd(1)−C(12)	2.707(7)	Al(2)−C(11)	1.947(8)
Nd(1)−C(13)	2.612(6)	Al(2)−C(12)	2.071(7)
Nd(1)−C(16)	2.616(7)	Al(3)−C(13)	2.105(7)
Al(1)−N(1)	1.925(5)	Al(3)−C(14)	1.987(8)
Al(1)−N(1′)	1.923(6)	Al(3)−C(15)	1.966(7)
N(1)−Nd(1)−C(1)	31.23(2)	N(1)−Al(1)−N(1′)	89.72(2)
N(1)−Nd(1)−C(8)	69.93(2)	N(1)−Al(1)−C(7)	118.98(2)
N(1)−Nd(1)−C(9)	103.50(2)	N(1)−Al(1)−C(8)	100.90(2)
N(1)−Nd(1)−C(12)	150.85(2)	N(1′)−Al(1)−C(7)	120.28(2)
N(1)−Nd(1)−C(13)	95.80(2)	N(1′)−Al(1)−C(8)	105.94(2)
N(1)−Nd(1)−C(16)	119.94(2)	C(9)−Al(2)−C(10)	107.64(2)
C(1)−Nd(1)−C(8)	98.51(2)	C(9)−Al(2)−C(11)	107.20(2)
C(1)−Nd(1)−C(9)	94.90(2)	C(9)−Al(2)−C(12)	110.79(2)
C(8)−Nd(1)−C(9)	83.75(2)	C(10)−Al(2)−C(11)	116.30(2)
C(8)−Nd(1)−C(12)	81.73(2)	C(10)−Al(2)−C(12)	107.74(2)
C(8)−Nd(1)−C(13)	103.28(2)	C(11)−Al(2)−C(12)	107.16(2)
C(8)−Nd(1)−C(16)	168.74(2)	C(13)−Al(3)−C(14)	107.27(2)
C(9)−Nd(1)−C(12)	79.32(2)	C(13)−Al(3)−C(15)	107.32(2)
C(12)−Nd(1)−C(13)	83.90(2)	C(13)−Al(3)−C(16)	109.52(2)
C(13)−Nd(1)−C(16)	81.87(2)	C(14)−Al(3)−C(15)	116.24(2)
C(1)−N(1)−Al(1)	118.33(4)	C(15)−Al(3)−C(16)	106.17(2)
C(1)−N(1)−Nd(1)	87.03(3)	Nd(1)−C(9)−Al(2)	85.74(2)
N(1)−C(1)−Nd(1)	61.74(3)	Nd(1)−C(12)−Al(2)	84.14(2)
		Nd(1)−C(13)−Al(3)	84.19(2)
		Nd(1)−C(16)−Al(3)	84.41(2)

Table 5. Selected Bond Distances (Å) and Angles (deg) for $[Me_2Al(\mu\text{-}NHC_6H_5)]_3$, **8**

Al(1)−N(1)	1.949(7)	Al(2)−C(21)	1.942(9)
Al(1)−N(2)	1.955(7)	Al(2)−C(22)	1.954(9)
Al(2)−N(1)	1.988(7)	Al(3)−C(23)	1.967(9)
Al(2)−N(3)	1.965(7)	Al(3)−C(24)	1.959(9)
Al(3)−N(3)	1.971(7)	N(1)−C(1)	1.461(1)
Al(3)−N(2)	1.983(7)	N(2)−C(7)	1.472(1)
Al(1)−C(19)	1.971(9)	N(3)−C(13)	1.447(1)
Al(1)−C(20)	1.979(9)		
N(1)−Al(1)−N(2)	95.92(3)	C(23)−Al(3)−N(3)	112.84(3)
N(1)−Al(1)−C(19)	108.76(3)	C(24)−Al(3)−N(2)	111.78(4)
N(1)−Al(1)−C(20)	111.75(3)	C(24)−Al(3)−N(4)	105.46(3)
N(2)−Al(1)−C(19)	109.61(3)	C(21)−Al(3)−N(3)	105.56(3)
N(2)−Al(2)−C(20)	111.19(3)	N(3)−Al(2)−N(1)	99.26(3)
C(19)−Al(2)−C(20)	117.48(3)	C(1)−N(1)−Al(1)	113.71(5)
C(21)−Al(2)−C(22)	121.13(4)	C(1)−N(1)−Al(2)	108.70(5)
C(21)−Al(2)−N(1)	110.69(4)	Al(1)−N(1)−Al(2)	119.12(5)
C(21)−Al(2)−N(3)	105.56(3)	C(7)−N(2)−Al(1)	113.00(5)
C(22)−Al(2)−N(1)	103.98(3)	C(7)−N(2)−Al(3)	110.10(5)
C(22)−Al(2)−N(3)	114.09(4)	Al(1)−N(2)−Al(3)	118.35(3)
N(3)−Al(2)−N(1)	99.26(3)	C(13)−N(3)−Al(2)	112.73(5)
C(23)−Al(3)−C(24)	121.06(4)	C(13)−N(3)−Al(3)	108.73(5)
C(23)−Al(3)−N(2)	104.43(3)	Al(2)−N(3)−Al(3)	123.54(5)

Discussion

Arylamido groups are clearly viable ligands for yttrium and the lanthanide metals. A variety of structural types can be accessed which are soluble and sufficiently stable to be crystallographically characterized. The various types identified in this preliminary study include anionic (**1a** and **2**), neutral solvated (**3** and **4a**), and neutral unsolvated (**5b**) homometallic species as well as heterometallic (**7**) complexes. The syntheses are applicable to both large- and small-radius metals. The isolation of a particular structural type appears to depend on the exact metal−ligand combination employed and the method of synthesis. Hence, in the few examples studied to date, 2,6-dimethyl substitution favored anionic complexes in **1a** and **2**, whereas attempts to prepare anionic analogs with the 2,6-diisopropyl system were unsuccessful. With this ligand, the neutral species were preferred. Both solvated monometallic and unsolvated bimetallic complexes could be isolated, and conversion of the unsolvated species to the solvated analog was facile.

Detailed comparisons between arylamido ligands and aryloxide ligands are probably premature at this point, but some general comments can be made with the data in hand. Synthetically, variations in terms of preferences for neutral or anionic products depending on the ligand and reaction conditions are found with both the arylamido and aryloxide systems. The actual preferences are not the same however. For example, neutral arylamido complexes **3**, **4a**, and **4b** can be obtained from halide precursors, whereas the analogous neutral aryloxides require amide precursors for some metals.[8] Structural similarity is found (a) between $[Y(\mu\text{-}NHC_6H_3{}^iPr_2\text{-}2,6)(NHC_6H_3{}^iPr_2\text{-}2,6)_2]_2$, **5b**, and the aryloxide analogs $[Ln(\mu\text{-}OC_6H_3{}^iPr_2\text{-}2,6)(OC_6H_3\text{-}{}^iPr_2\text{-}2,6)_2]_2$ (Ln = Nd, Sm),[8b] (b) between $[Yb(NHC_6H_3{}^iPr_2$-

---

(52) Interrante, L. V.; Sigel, G. A; Garbauskas, M.; Hejna, C.; Slack, G. A. *Inorg. Chem.* **1989**, *28*, 252−257.

(53) (a) Hess, H.; Hinderer, A.; Steinhauser, S. *Z. Anorg. Allg. Chem.* **1970**, *377*, 1−10. (b)Beachley, O. T.; Coates, G. E.; Kohnstam; G. J. *J. Chem. Soc.* **1965**, 3248−3252.

$2,6)_3(THF)_2]$, **4a**, and $[Ln(OC_6H_3{}^iPr_2\text{-}2,6)_3(THF)_2]$ (Ln = Pr, Gd, Er, Lu),[8b] and (c) between $[Nd(NHC_6H_3{}^iPr_2\text{-}2,6)_3(THF)_3]$, **3**, and the 2,6-dimethylphenoxide complex $[Y(OC_6H_3Me_2\text{-}2,6)_3\text{-}(THF)_3]$.[45] The overall ligand arrangement in the anionic complex $[Y_2(\mu\text{-}NHC_6H_3Me_2\text{-}2,6)_2(\mu\text{-}Cl)(NHC_6H_3Me_2\text{-}2,6)_4\text{-}(THF)_2]^-$, **2**, can be compared with that in the cationic complex $[Y_2(\mu\text{-}OCMe_3)_2(\mu\text{-}Cl)(OCMe_3)_2(THF)_4]^+$.[54] These comparsions suggest that, by selecting the appropriately-substituted arylamido ligand and reaction conditions, one can obtain most of the simple structural types of mono- and bimetallic alkoxides and aryloxides with NHAr ligands. The effects of the arylamido ligands on reactivity vis-à-vis aryloxide, alkoxide, and cyclopentadienyl coligands remain to be evaluated.

Acknowledgment. For support of this research, we thank the Division of Chemical Sciences, Office of Basic Energy Sciences, Department of Energy.

Supporting Information Available: More fully labeled structural diagrams, descriptions of the X-ray experimental procedures, and tables of crystal data, positional parameters, bond distances and angles, and thermal parameters (64 pages). Ordering information is given on any current masthead page.

IC951499E

---

(54) Evans, W. J.; Olofson, J. M.; Ziller, J. W. *J. Am. Chem. Soc.* **1990**, *112*, 2308−2314.