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Flexibility in the Coordination Chemistry of the 2,3-Dimethylindolide Ligand with Potassium, Yttrium, and Samarium

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The coordination chemistry of the 2,3-dimethylindolide anion (DMI), $(Me_2C_8H_4N)^-$, with potassium, yttrium, and samarium ions is described. In the potassium salt $[K(DMI)(THF)]_n$, **1**, prepared from $Me_2C_8H_4NH$ and KH in THF, the dimethylindole anion binds and bridges potassium ions in three different binding modes, namely η^1, η^3, and η^5, to form a two-dimensional extended structure. In the dimethoxyethane (DME) adduct $[K(DMI)(DME)_2]_2$, **2**, prepared by crystallizing a sample of **1** from DME, DMI exists as a μ-η^1:η^1 ligand. Compound **1** reacts with $SmI_2(THF)_4$ in THF to form the distorted octahedral complex *trans*-$(DMI)_2Sm(THF)_4$, **3**, in which the dimethyindolide anions are bound in the η^1 mode to samarium. Reaction of 2,3-dimethylindole with $Y(CH_2SiMe_3)_3(THF)_2$ afforded the amide complex $(DMI)_3Y(THF)_2$, **4**, in which the dimethylindolide anions are also bound in the η^1 mode to yttrium. Compound **1** also reacts with $(C_5Me_5)_2LnCl_2K(THF)_2$ (Ln = Sm, Y) to form unsolvated amide complexes $(C_5Me_5)_2Ln(DMI)$ (Ln = Sm, **5**; Y, **6**), in which DMI attaches primarily through nitrogen, although the edge of the arene ring is oriented toward the metals at long distances.

Introduction

One of the active areas of f element chemistry is the examination of alternatives to the commonly used cyclopentadienyl groups, C_5R_5, as stabilizing, solubilizing, ancillary ligands.[1−27] One approach to new ancillary ligands is to examine similar ring systems in which heteroatoms are incorporated.[2] Nitrogen- and phosphorus-containing systems have been investigated, and variations range from pyrrole anions, $(C_4R_4N)^-$,[3−5] pyrazole anions, $(C_3R_2N_2)^-$,[6−11] and phosphole anions, $(C_4R_4P)^-$,[12−18] to polypyrazolylborates, $[RB(N_2C_3R_3)_3]^-$,[19] and porphyrinogens, $[R_n(C_4H_2N)_4]^{4-}$.[20−27] Pyrrole anions are intriguing ligands because they can bind in the η^5 mode that is most common for cyclopentadienyl ligands, but they also have a propensity to bind in the η^1 mode, utilizing the electron rich heteroatom. Variation from η^1 to η^3 or η^5 can provide the basis for flexible reactivity because both steric and electronic saturations can be varied considerably.

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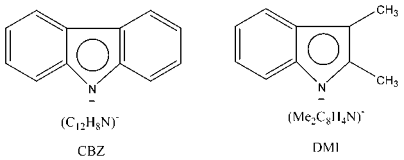

Figure 1. Anionic cyclopentadienyl-like ligands derived from carbazole and 2,3-dimethylindole.

Previous studies of the f element chemistry of the anion $(C_{12}H_8N)^-$ (CBZ) derived from carbazole, Figure 1, suggested that the presence of arene rings on each side of the pyrrole partitioned the binding to the η^1 form.[28-30] Similar η^1 bonding was observed with Yb(II) and the anion derived from 2-phenylindole.[28,31] Given the often dramatic effects of changing substitution on cyclopentadienyl ligands,[32] we were interested in examining related analogues. The 2,3-dimethylindolide ligand (DMI), $(Me_2C_8H_4N)^-$, Figure 1, is sterically similar to carbazole, but the dimethyl substitution provides enhanced solubility and easily identified resonances in ^1H NMR spectra. In addition, this particular indole is readily available and inexpensive.

Only a few structurally characterized complexes containing the 2,3-dimethylindolide anion have been reported.[33,34] In $(Ph_3P)_2Ir(CO)(DMI)$, DMI binds in the η^1 mode to iridium.[33] Deprotonation of neutral 2,3-dimethylindole in $(C_5Me_5)Ir(\eta^6\text{-}Me_2C_8H_4NH)$ has been reported to cause isomerization to $(C_5Me_5)Ir(\eta^5\text{-DMI})$, but no structural data were presented.[35] In $[(\eta^6\text{-}C_6H_4\text{-}(CHMe_2)\text{-}4\text{-Me-}1)Ru(\eta^6\text{-DMI})][BPh_4]$, DMI is coordinated in an η^6 mode to cationic Ru via the arene ring.[34] Since the electrophilic lanthanides can also interact with arene rings of anionic ligands,[36-38] this provides an additional bonding option. We report here on the complexation chemistry of DMI with potassium, yttrium, and samarium.

Experimental Section

The chemistry described below was performed under nitrogen with the rigorous exclusion of air and water by using Schlenk, vacuum line, and glovebox techniques. THF and diethyl ether were dried over activated alumina and sieves. Toluene and hexanes were dried over Q-5 and molecular sieves. Benzene-d_6 was distilled over NaK alloy and benzophenone. NMR spectra were obtained using Bruker DRX-400 and General Electric QE-500 spectrometers. Infrared analyses were recorded on a ReactIR 1000 as thin films. 2,3-Dimethylindole was purchased from Aldrich and used as received. KH was washed with hexanes prior to use. $SmI_2(THF)_2$,[39] $Y(CH_2SiMe_3)_3(THF)_2$,[40] $(C_5Me_5)_2SmCl_2K(THF)_2$, and $(C_5Me_5)_2YCl_2K(THF)_2$[41] were prepared according to literature methods.

$[K(DMI)(THF)]_n$, 1. In a glovebox, KH (65 mg, 1.62 mmol) was added slowly to 2,3-dimethylindole (200 mg, 1.35 mmol) dissolved in 25 mL of THF. The reaction was stirred for 3 h, and no further evolution of gas was observed. The resulting yellow/orange solution was centrifuged to remove excess KH. The solution was evaporated under vacuum, leaving **1** (290 mg, 84%) as a light orange powder. X-ray quality crystals were grown from a saturated THF solution at −32° C.^1H NMR (THF-d_8, 25 °C): δ 1.78 (m, 4H, THF), 2.24 (s, 3H, $Me_2C_8H_4N$), 2.44 (s, 3H, $Me_2C_8H_4N$), 3.62 (m, 4H, THF), 6.53 (t, 1H, $Me_2C_8H_4N$), 6.62 (s, 1H, $Me_2C_8H_4N$), 7.14 (d, 1H, $Me_2C_8H_4N$), 7.24 (d, 1H, $Me_2C_8H_4N$). ^{13}C NMR (THF-d_8, 25 °C): δ 10.3 (s, $Me_2C_8H_4N$), 15.9 (s, $Me_2C_8H_4N$), 26.6 (THF), 68.4 (s, THF), 102 (s), 114 (s), 115 (s), 116 (s), 133 (s), 144 (s), 146 (s). IR (thin film): 2907 w, 2863 w, 2335 s, 2127 w, 2084 s, 1571 w, 1440 w, 1347 w, 1285 m, 1227 w, 1162 m, 1100 s, 1045 s, 842 m, 749 w. Anal. Calcd for $C_{14}H_{18}NOK$: C, 65.83; H, 7.12; N, 5.48; O, 6.26; K, 15.31. Found: C, 65.26; H, 7.48; N, 5.44; K, 15.84.

$[K(DMI)(DME)_2]_2$, 2. Compound **2** was prepared by crystallizing a sample of **1** from dimethoxyethane. ^1H NMR (THF-d_8, 25 °C): δ 2.24 (s, 3H, $Me_2C_8H_4N$), 2.43 (s, 3H, $Me_2C_8H_4N$), 3.23 (s, 6H, DME), 3.44 (t, 4H, DME), 6.58 (t, 1H, $Me_2C_8H_4N$), 6.67 (t, 1H, $Me_2C_8H_4N$), 7.16 (d, 1H, $Me_2C_8H_4N$), 7.24 (s, 1H, $Me_2C_8H_4N$). ^{13}C NMR (THF-d_8, 25 °C): δ 10.4 (s, $Me_2C_8H_4N$), 15.5 (s, $Me_2C_8H_4N$), 58.9 (s, DME), 72.8 (s, DME), 102 (s), 102 (s), 110 (s), 113 (s), 114 (s), 116 (s), 116 (s). IR (thin film): 2910 s, 2860 s, 1598 s, 1463 m, 1440 m, 1347 w, 1285 s, 1243 m, 1200 w, 1112 s, 1085 s, 1007 s, 884 w, 865 w, 838 w, 745 w, 683 w.

$(DMI)_2Sm(THF)_4$, 3. A solution containing **1** (61 mg, 0.237 mmol) in 5 mL of THF was added to a blue solution of $SmI_2(THF)_2$ (65 mg, 0.119 mmol) in 5 mL of THF. The color darkened upon addition of **1**, and a white solid precipitate formed. The reaction was stirred for 3 h, and the resulting slurry was centrifuged to remove KI. The resulting deep blue solution was evaporated under vacuum, leaving **2** as a dark blue solid (74 mg, 86%). X-ray quality crystals of **2** were grown from a saturated THF solution at −32 °C. ^1H NMR (THF-d_8, 25 °C): δ −1.09 (br, $\Delta\upsilon_{1/2}$ = 131 Hz, 6H, $Me_2C_8H_4N$), 6.16 (br, $\Delta\upsilon_{1/2}$ = 103 Hz, 3H, $Me_2C_8H_4N$), 9.11 (br, $\Delta\upsilon_{1/2}$ = 150 Hz, 6H, $Me_2C_8H_4N$), 17.89 (br, $\Delta\upsilon_{1/2}$ = 167 Hz, 3H, $Me_2C_8H_4N$). IR (thin film): 3057 m, 2918 s, 2860 m, 1621 w, 1590 w, 1463 s, 1436 m, 1390 w, 1332 m, 1301 s, 1243 s, 1146 w, 1007 m, 803 w, 741 m, 703 w, 672 w. Anal. Calcd for $C_{36}H_{52}N_2O_4Sm$: C, 59.46; H, 7.22; N, 3.85; O, 8.80; Sm, 20.68. Found: C, 59.24; H, 7.36; N, 3.79; Sm, 20.54.

$(DMI)_3Y(THF)_2$, 4. Addition of 2,3-dimethylindole (96 mg, 0.648 mmol) in 2 mL of toluene to a colorless solution containing $Y(CH_2SiMe_3)_3(THF)_2$ (107 mg, 0.216 mmol) in 10 mL of toluene caused an immediate color change to yellow. The solution was stirred for 2 h, and the solvent was removed, leaving **4** as a yellow powder (138 mg, 97%). X-ray quality crystals were grown from a 1:1 toluene/hexane solution at − 32 °C. ^1H NMR (C_6D_6): δ 0.73 (s, 8H, THF), 2.43 (s, 9H, $Me_2C_8H_4N$), 2.47 (s, 9H, $Me_2C_8H_4N$), 3.32 (s, 8H, THF), 7.18 (t, 3H, $Me_2C_8H_4N$), 7.30 (t, 3H, $Me_2C_8H_4N$), 7.67 (d, 3H, $Me_2C_8H_4N$), 7.77 (d, 3H, $Me_2C_8H_4N$). Anal. Calcd

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Table 1. Experimental Data for the X-ray Diffraction Studies of $[(C_{10}H_{10}N)K(THF)]_n$, **1**, $[(C_{10}H_{10}N)K(DME)_2]_2$, **2**, $(C_{10}H_{10}N)_2Sm(THF)_4$, **3**, $(C_{10}H_{10}N)_3Y(THF)_2$, **4**, $(C_5Me_5)_2Sm(C_{10}H_{10}N)$, **5**, and $(C_5Me_5)_2Y(C_{10}H_{10}N)$, **6**[a]

	1	**2**	**3**	**4**	**5**	**6**
formula	$[C_{28}H_{36}K_2N_2O_2]_n$	$C_{36}H_{60}K_2N_2O_8$	$C_{36}H_{52}N_2O_4Sm$	$C_{38}H_{46}N_3O_2Y{\cdot}C_7H_8$	$C_{30}H_{40}NSm$	$C_{30}H_{40}NY$
fw	510.79	727.06	727.15	757.82	564.98	503.54
temp (K)	158(2)	158(2)	158(2)	158(2)	163(2)	163(2)
crystal system	triclinic	monoclinic	triclinic	monoclinic	orthorhombic	orthorhombic
space group	$P\bar{1}$	$P2_1/n$	$P\bar{1}$	$P2_1/n$	*Pbca*	*Pbca*
a (Å)	10.5982(7)	14.7779(7)	12.2572(9)	8.1331(15)	14.4256(10)	14.4029(6)
b (Å)	11.3815(7)	9.6085(5)	12.5513(9)	25.559(5)	17.3581(12)	17.3947(7)
c (Å)	12.3834(8)	14.9257(7)	14.1586(11)	19.167(4)	20.9642(14)	20.8392(9)
α	74.2900(1)		66.8400(10)			
β (deg)	75.4220(10)	90.8780(10)	76.7920(10)	99.406(4)	90	90
γ	89.2400(1)		60.8340(10)			
V (Å^3)	1389.22(15)	2119.10(18)	1746.9(2)	3930.7(12)	5249.5(6)	5220.9(4)
Z	2	2	2	4	8	8
ρ_{calcd} (mg/m^3)	1.221	1.139	1.382	1.281	1.430	1.281
μ (mm^{-1})	0.367	0.269	1.719	1.524	2.254	2.251
refinement[b] R1 [$I > 2\sigma(I)$]	0.0557	0.0595	0.0467	0.1320	0.0373	0.0373
wR2 (all data)	0.1596	0.1876	0.1191	0.3809	0.0942	0.1075
goodness-of-fit on F^2	1.024	1.021	1.052	1.440	1.034	1.035

[a] Radiation: Mo Kα ($\lambda = 0.710730$ Å). Monochromator: highly oriented graphite. [b] $R = \sum|F_o| - |F_c||/\sum F_o|$; $wR2 = [\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]]^{1/2}$.

for $C_{38}H_{46}N_3O_2Y$: C, 68.55; H, 6.98; N, 6.31; Y, 13.36. Found: C, 68.29; H, 6.99; N, 6.66; Y, 13.32.

$(C_5Me_5)_2Sm(DMI)$, 5. Toluene (5 mL) was added to a mixture of **1** (59 mg, 0.231 mmol) and $(C_5Me_5)_2SmCl_2K(THF)_2$ (155 mg, 229 mmol). After 1 h of stirring, most of the solids dissolved to give a bright orange-red solution. The reaction was stirred for 12 h, and the insoluble materials were removed. The orange solution was evaporated, leaving an oily bright orange solid. This material was extracted with hexanes to form an orange solution and a white precipitate. The insoluble material was separated by centrifugation, and the solvent was evaporated, leaving **4** (103 mg, 79%) as a bright orange solid. ^{1}H NMR (C_6D_6): δ −2.03 (s, 3H, $Me_2C_8H_4N$), 0.16 (s, 30H, C_5Me_5), 3.25 (s, 3H, $Me_2C_8H_4N$), 6.04 (t, 1H, $Me_2C_8H_4N$), 8.66 (d, 1H, $Me_2C_8H_4N$). IR (thin film): 2961 s, 2914 s, 2860 s, 1571 m, 1463 w, 1440 s, 1378 w, 1332 w, 1301 w, 1243 w, 1150 m, 1085 s, 1007 w, 950 m, 799 w, 741 w, 676 m. Anal. Calcd for $C_{30}H_{40}NSm$: C, 63.77; H, 7.15; N, 2.48; Sm, 26.61. Found: C, 63.24; H, 7.21; N, 2.41; Sm, 26.39.

$(C_5Me_5)_2Y(DMI)$, 6. Following the procedure for **5**, we added toluene (8 mL) to a mixture of **1** (173 mg, 0.677 mmol) and $(C_5Me_5)_2YCl_2K(THF)_2$ (414 mg, 0.666 mmol). After 1 h of stirring, most of the solids dissolved to give an orange solution. The reaction was stirred for 10 h, and the insoluble materials were removed. The orange solution was evaporated, leaving an oily orange solid. This material was extracted with hexanes to form an orange solution and a white insoluble precipitate. The insoluble material was separated by centrifugation, and the solvent was evaporated, leaving **5** (170 mg, 79%) as an orange solid. ^{1}H NMR (C_6D_6): δ 1.71 (s, 30H, C_5Me_5), 2.26 (s, 3H, $Me_2C_8H_4N$), 2.48 (s, 3H, $Me_2C_8H_4N$), 6.08 (m, 1H, $Me_2C_8H_4N$), 7.24 (m, 2H, $Me_2C_8H_4N$), 7.81 (s, 1H, $Me_2C_8H_4N$). ^{13}C NMR (C_6D_6, 25 °C): δ 10.7 (s, C_5Me_5), 10.9 (s, $Me_2C_8H_4N$), 11.7 (s, $Me_2C_8H_4N$), 105 (s), 117 (s), 117 (s), 118 (s), 119 (s), 120.5 (s, C_5Me_5), 121 (s). IR (thin film): 2961 s, 2914 s, 2860 s, 1571 m, 1463 w, 1140 s, 1374 w, 1332 w, 1301 m, 1243 w, 1154 m, 1089 s, 1011 w, 953 w, 803 w, 741 w, 660 m. Anal. Calcd for $C_{30}H_{40}NY$: C, 71.56; H, 8.02; N, 2.78; Y, 17.66. Found: C, 71.51; H, 7.98; N, 2.75; Y, 17.13.

X-ray Data Collection, Structure Solution, and Refinement for 1−6. $[K(DMI)(THF)]_n$, 1. The procedure described in detail for **1** was followed for **2**−**6**. A colorless crystal of approximate dimensions 0.13 × 0.28 × 0.36 mm^3 was mounted on a glass fiber and transferred to a Bruker CCD platform diffractometer. The SMART[42] program package was used to determine the unit-cell parameters (see Table 1) and for data collection (20 s/frame scan time for a sphere of diffraction data). The raw frame data were processed using SAINT[43] and SADABS[44] to yield the reflection data file. Subsequent calculations were carried out using the SHELXTL[45] program. There were no systematic absences nor any diffraction symmetry other than the Friedel condition. The centrosymmetric triclinic space group $P\bar{1}$ was assigned and later determined to be correct. The structure was solved by direct methods and refined on F^2 by full-matrix least-squares techniques. The analytical scattering factors[46] for neutral atoms were used throughout the analysis. Hydrogen atoms were included using a riding model.

$[K(DMI)(DME)_2]_2$, 2. A colorless crystal of approximate dimensions 0.27 × 0.30 × 0.44 mm^3 was handled as described for **1** except a 25 s/frame scan time was used. The diffraction symmetry was 2/*m*, and the systematic absences were consistent with the centrosymmetric monoclinic space group $P2_1/n$ which was later determined to be correct. The molecule was located about an inversion center.

***trans*-$(DMI)_2Sm(THF)_4$, 3.** A dark blue crystal of approximate dimensions 0.10 × 0.18 × 0.23 mm^3 was handled as described for **1** except a 30 s/frame scan time was used. There were no systematic absences nor any diffraction symmetry other than the Friedel condition. The centrosymmetric triclinic space group $P\bar{1}$ was assigned and later determined to be correct. Carbon atoms C(34) and C(35) were disordered. The disordered atoms were included using two components with partial site-occupancy factors (0.55/0.45).

$(DMI)_3Y(THF)_2$, 4. A colorless crystal of approximate dimensions 0.11 × 0.17 × 0.19 mm^3 was handled as decribed for **1** except a 30 s/frame scan time was used. The diffraction symmetry was 2/*m*, and the systematic absences were consistent with the centrosymmetric monoclinic space group $P2_1/n$ which was later

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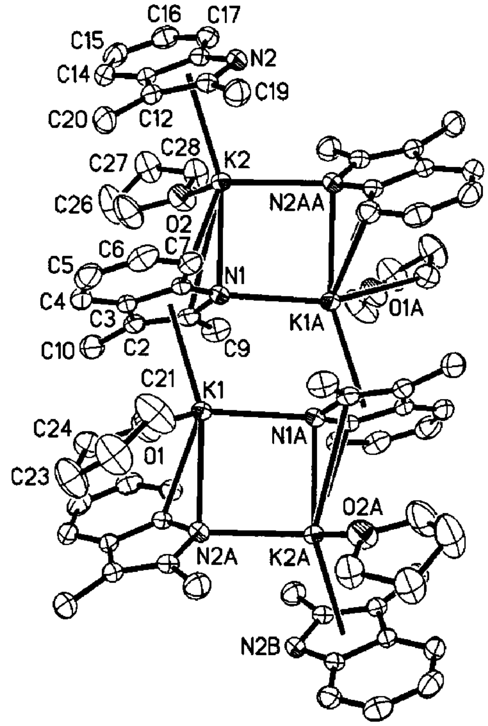

Figure 2. Thermal ellipsoid plot of [K(DMI)(THF)]$_n$, **1**, drawn at the 50% probability level.

determined to be correct. There was one molecule of toluene solvent present per formula unit. Because the quality of the data was poor, only atom connectivity was definitively determined.

$(C_5Me_5)_2$Sm(DMI), 5. An orange crystal of approximate dimensions 0.22 × 0.35 × 0.36 mm^3 was used. The diffraction symmetry was *mmm*, and the systematic absences were consistent with the orthorhombic space group *Pbca* which was later determined to be correct.

$(C_5Me_5)_2$Y(DMI), 6. A pale yellow crystal of approximate dimensions 0.39 × 0.41 × 0.45 mm^3 was mounted and handled as decribed for **1** except a 25 s/frame scan time was used. The diffraction symmetry was *mmm*, and the systematic absences were consistent with the orthorhombic space group *Pbca* which was later determined to be correct. The indole ligand is disordered. It occupied two sites in an approximately 60/40 distribution. Partial site-occupancy factors were assigned (0.60/0.40) to the disordered atoms which were refined anisotropically.

Results

Potassium Salts. 2,3-Dimethylindole, $Me_2C_8H_4NH$, can be readily deprotonated by KH in THF to make a $K^+(Me_2C_8H_4N)^-$ salt, K(DMI), that is a convenient starting material for the synthesis of yttrium and f element complexes. The ^{1}H NMR spectrum of K(DMI) in THF shows a single set of DMI resonances with the methyl groups readily identified at δ 2.24 and 2.44 ppm. In the course of examining the reaction chemistry of K(DMI), crystals of two solvates of this complex were obtained that show the flexibility of the DMI ligand with large metals.

[K(DMI)(THF)]$_n$, 1. When K(DMI) crystallized from THF as a THF solvate, the 2,3-dimethylindolide ion was found to coordinate η^1, η^3, and η^5 to three separate potassium ions in an extended 2-dimensional polymer, Figure 2. Each of the crystallographically independent potassium ions interacts with one η^1-DMI, one η^3-DMI, and one η^5-DMI ligand. In addition, each potassium ion is coordinated by a molecule of THF, giving each a formal coordination number of seven.

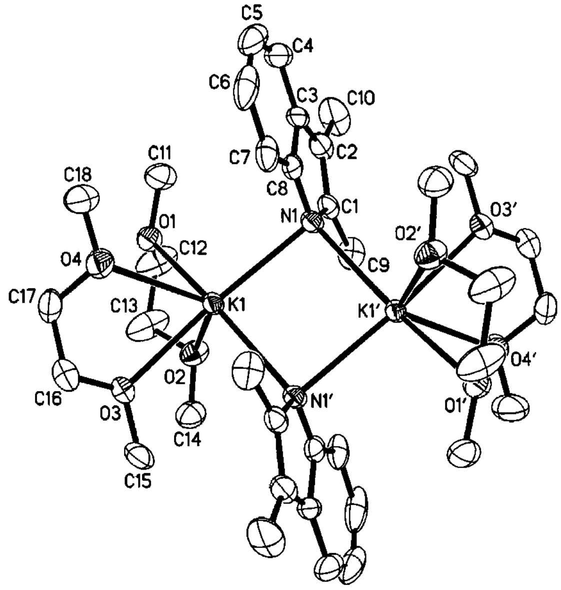

Figure 3. Thermal ellipsoid plot of $[K(DMI)(DME)_2]_2$, **2**, drawn at the 30% probability level.

The K−N distances in **1** vary depending upon the coordination mode. For the η^1-DMI, K1−N1A is 2.768(2) Å, for the η^3-DMI, K2−N2A is 2.906(2) Å, and for the η^5-DMI, K1−N1 is extended to 2.998(2) Å. The K−(ring centroid) distance for the η^5 bound ring is 2.827 Å. The K−O(THF) distance is 2.638(2) Å. These distances can be compared to those in the hexameric pyrazolate $[(Ph_2C_3HN_2)K(THF)]_6$, where the K−N distances range from 2.763(4)−2.869(4) Å and the K−O(THF) distance is 2.716(5) Å.[47] The structure of **1** demonstrates that η^3 and η^5 binding can be achieved with this ligand in addition to the η^1 and η^6 modes previously identified.

$[K(DMI)(DME)_2]_2$, 2. X-ray quality crystals of a dimethoxyethane (DME) adduct of K(DMI), **2**, were also obtained when **1** was crystallized from DME. In **2**, the DMI ligand assumes a μ-η^1:η^1 bridging mode between two potassium ions, Figure 3. Hence, complex **2** demonstrates yet another possible binding mode of the flexible DMI anion. Each potassium ion in **2** is coordinated by two DME molecules in the dimeric complex such that each has a coordination number of six. The K−N distances in **2**, 2.807(2) Å for K1−N1 and 2.826(2) Å for K1−N1′, are slightly longer than the η^1-K−N distance in **1,** as expected for a bridging DMI unit. The K−O distances, 2.774(2) for K1−O1, 2.802(2) for K1−O2, 2.708(2) for K1−O3, and 2.890(3) for K1−O4, are comparable to the 2.74(2)−2.94(4) Å range for the DME-coordinated potassium ion in $[Y_2(NHC_6H_3\text{-}Me\text{-}2,6)_6Cl(THF)_2][K(THF)_3(DME)_2]$.[48]

Lanthanide Complexes. *trans*-$(DMI)_2Sm(THF)_4$, 3. The reaction of K(DMI) with $SmI_2(THF)_2$ was examined in

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Table 2. Selected Bond Distances and Angles for $(DMI)_2Sm(THF)_4$, **3**, $(C_5Me_5)_2Sm(DMI)$, **5**, and $(C_5Me_5)_2Y(DMI)$, **6**

compound	coordination number	M−N distance (Å)	M−Cnt distance (Å)	M−C(arene) (Å)	Cnt−M−Cnt angle (deg)	M−C(C_5Me_5) range (Å)
3	6	2.610(4) 2.601(4)				
5	8	2.399(4)	2.419 2.404	2.946(6) 3.107(5)	137.9	2.669(4)−2.724(4)
6	8	2.385(4) 2.194(7)	2.343 2.331	2.962(6) 3.073(6)	139.2	2.597(2)−2.620(2)

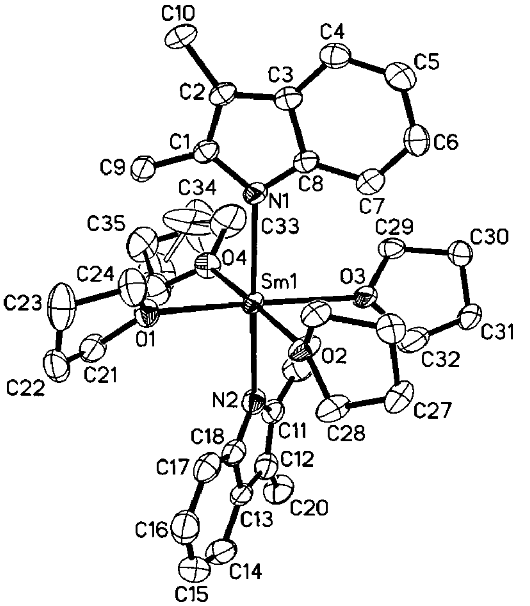
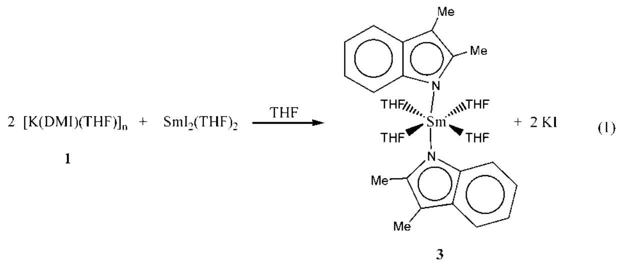


Figure 4. Thermal ellipsoid plot of $(DMI)_2Sm(THF)_4$, **3**, drawn at the 50% probability level.

efforts to make an analogue of the carbazole complexes, *cis*-$(CBZ)_2Sm(THF)_4$ and *trans*-$(CBZ)_2Sm(N\text{-}MeIm)_4$,[30] for the direct comparison of the DMI and CBZ anions with the same lanthanide. The dark blue $(DMI)_2Sm(THF)_4$, **3**, can be made in 86% yield in 4 h according to eq 1.



The ^1H NMR spectrum contains four broad peaks. Two peaks at δ −1.09 and 9.11 ppm were assigned to the methyl groups of the DMI ligand. Two peaks at δ 6.16 and 17.89 ppm in a 3:1 ratio were assigned to the phenyl protons. These shifts are similar to those in *cis*-$(CBZ)_2Sm(THF)_4$, where four broad phenyl resonances were observed in the range 4.79−11.34 ppm in a 1:1:1:1 ratio.

An X-ray diffraction study of crystals grown from THF indicates that the structure is similar to *trans*-$(CBZ)_2Sm(N\text{-}MeIm)_4$ in that the DMI ligands adopt a *trans* η^1 configuration about the Sm(II) center in a distorted octahedral complex, Figure 4. The Sm−N distances in **3**, 2.610(4) and 2.601(4) Å (Table 2), are intermediate between those in the complexes *cis*-$(CBZ)_2Sm(THF)_4$, 2.547(3) and 2.583(3) Å, and *trans*-$(CBZ)_2Sm(N\text{-}MeIm)_4$, 2.694(14) and 2.724(22) Å. The average 2.556(3) Sm−O(THF) distance in **3** is slightly shorter than that in *cis*-$(CBZ)_2Sm(THF)_4$, 2.582(3), and is long compared to the average 2.27(1) Å Sm−O($OPPh_3$) distance found in octahedral $SmI_2(OPPh_3)_4$.[49]

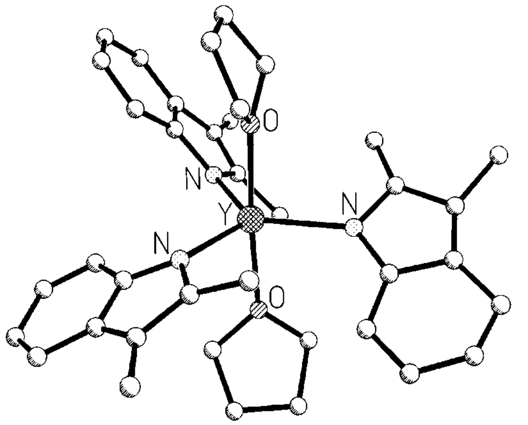
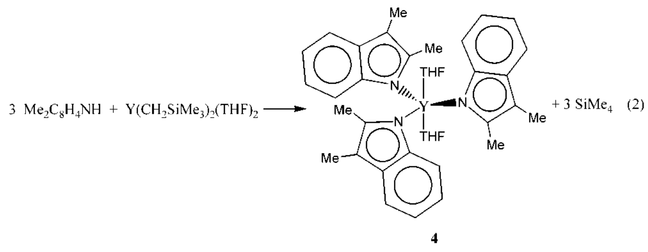


Figure 5. Ball and stick plot of $(DMI)_3Y(THF)_2$, **4**.

$(Me_2C_8H_4N)_3Y(THF)_2$, 4. In an attempt to synthesize a homoleptic $(DMI)_3Ln$ complex analogous to the common series of $(C_5H_5)_3Ln$ complexes,[32] $Y(CH_2SiMe_3)_3(THF)_2$ was treated with neutral 2,3-dimethylindole. This reaction generates tetramethylsilane and a pale yellow powder identified as $(C_{10}H_{10}N)_3Y(THF)_2$, **4**, by ^1H NMR spectroscopy and X-ray crystallography, eq 2.



The ^1H NMR resonances of the methyl groups of **4** were found at δ 2.43 and 2.47 ppm in C_6D_6 which represented only a small shift from those of **1** in THF.

In the structure of **4**, Figure 5, yttrium is bound by three η^1-DMI ligands along with two THF molecules to form a five-coordinate species. The structure of **4** is similar to other group 3 tris(amide)−bis(THF) complexes, $Y[NHC_6H_3(CHMe_2)_2\text{-}2,6]_3(THF)_2$,[48] $Y[N(SiHMe_2)_2]_3(THF)_2$,[50] and La-

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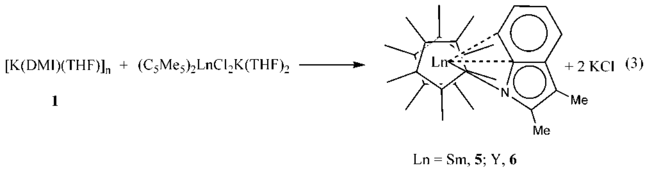
$[N(SiHMe_2)_2]_3(THF)_2$.[51] Because of the poor quality of the X-ray data, the comparison of metrical parameters to complexes in the literature cannot be made. Coordination numbers as low as three have been observed in yttrium and lanthanide chemistry, but they almost always involve extremely bulky ligands such as $[N(SiMe_3)_2]^-$ [50,52−56] and $[OC_6H_3(CMe_3)_2\text{-}2,6]^-$.[57−61] Because compound **4** has a low coordination number, it is interesting that the binding of the DMI ligand does not deviate from the η^1 mode to utilize the ring system to provide additional coordination to the metal center.

$(C_5Me_5)_2$Ln(DMI) (Ln = Sm, 5; Y, 6). Given the propensity of DMI to bind in the η^1mode to samarium and yttrium, its reaction chemistry with $(C_5Me_5)_2LnCl_2K(THF)_2$ was examined to determine if this would be a convenient route to a THF-free $(C_5Me_5)_2Ln(NR_2)$ amide complex, a type of complex that is generally available only with the bulky $[N(SiMe_3)_2]^-$ (ref 62) and $[NPh_2]^-$ (ref 63) ligands or bidentate ligands such as pyrazolate $[Ph_2C_3N_2]^-$ and azaindolate $[C_7H_5N_2]^-$.[64] The reaction of $[K(DMI)(THF)]_n$ with $(C_5Me_5)_2SmCl_2K(THF)_2$ in toluene produced a bright orange solution. $(C_5Me_5)_2Sm(DMI)$, **5**, can be removed from the crude reaction mixture in 80% yield by hexane extraction, eq 3. The methyl resonances of the DMI ligand in this paramagnetic Sm(III) complex were found at δ −2.03 and 3.25 ppm compared to the δ 0.16 ppm shift of the C_5Me_5 methyl groups.



X-ray diffraction studies on bright orange crystals of **5** grown from hexanes revealed a Lewis base free product in which the DMI unit has three atoms oriented toward the Sm(III) center, Figure 6. The 2.399(4) Sm−N1 bond length is about 0.2 Å shorter than the Sm−N(DMI) lengths in **3**. The comparison of the ionic radii of six coordinate Sm(II) and seven coordinate Sm(III) suggests that the length in **5** should be 0.15 Å shorter.[65] In addition to the coordination of the nitrogen, the arene ring is oriented edge on toward the metal with the Sm−C(21) and Sm−C(22) distances 2.946(6) and 3.107(5) Å, respectively. In comparison, the Sm−C(C_5Me_5) lengths range from 2.669(4) to 2.724(4) Å, distances which are typical for eight coordinate trivalent complexes containing a decamethylsamarocene unit.[66] Long distance metal hydrocarbon interactions are not unusual for lanthanide metallocenes.[67−71] The Sm−C distances in **5** can be compared to the Sm−C(arene, $(BPh_4)^-$) distances 2.825(3) and 2.917(3) Å in $(C_5Me_5)_2Sm[(\mu\text{-}Ph)_2BPh]_2$.[64] In contrast, the analogous Sm−C distances in **3** are all greater than 3.6 Å; that is, these DMI carbon atoms are not oriented toward the metal.

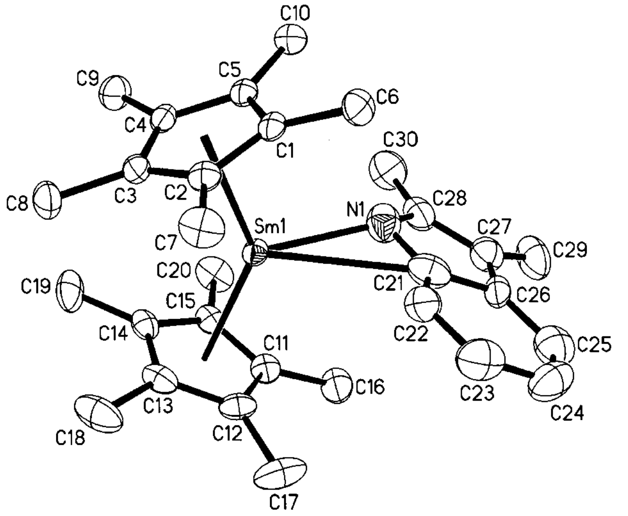


Figure 6. Thermal ellipsoid plot of $(C_5Me_5)_2Sm(DMI)$, **5**, drawn at the 50% probability level.

In a reaction analogous to the synthesis of **5,** the yttrium complex $(C_5Me_5)_2Y(DMI)$, **6**, was made in 82% yield from $[K(DMI)(THF)]_n$ and $(C_5Me_5)_2YCl_2K(THF)_2$. The ^{1}H NMR of **6** showed greater shifts of the methyl resonances of the DMI ligand from those in **1** and **4** to 2.26 and 2.48 ppm in C_6D_6. The C_5Me_5 resonance was observed at 1.71 ppm.

X-ray diffraction showed that the structure of **6** was similar to that of **5**, Figure 7. However, the DMI ligand was found to bind in two different orientations in the crystal with two significantly different Y−N distances: 2.385(4) and 2.194(7) Å. The corresponding Y−C(21) and Y−C(22) distances associated with the longer Y−N bond are 2.962(6) and 3.245-

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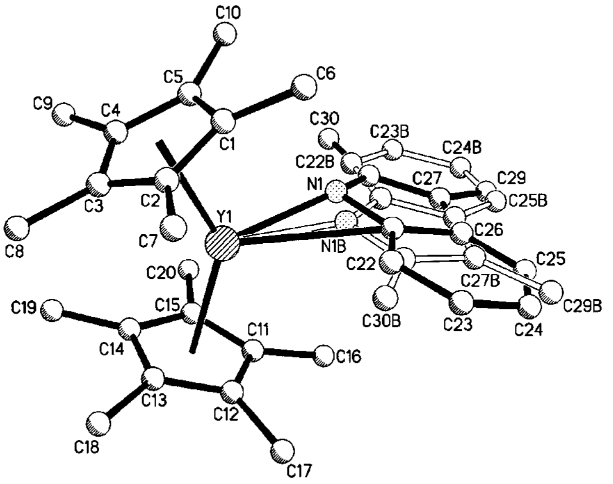

Figure 7. Ball and stick plot of $(C_5Me_5)_2Y(DMI)$, **6**, showing the disorder in the DMI coordination.

(7) Å. The analogous distances associated with the shorter Y−N bond are 3.073(6) and 3.732(11) Å, respectively. The distances in neither of the two disordered structures match well those of **5**. On the basis of the 0.06 Å difference in radii of Y^{3+} and Sm^{3+}, a 2.34 Å Y−N bond distance would have been expected in **6**, along with 2.89 and 3.05 Å Y−C bonds. The molecule with the 2.385(4) Å bond has one Y−C distance longer and the other shorter than expected. The molecule with the 2.194(7) Å distance has much longer Y−C distances such that the arene ring cannot be considered to interact in the same way as in the other orientation and in complex **5**. The origin of this disorder or even how accurately this model describes the disorder is unknown. However, this does suggest that DMI can vary in its η^1 bonding.

Discussion

One of the stimuli for investigating the anion derived from 2,3-dimethylindole, $[Me_2C_8H_4N]^-$ (DMI), as a ligand was that it has the potential to engage in several types of bonding modes. This was realized in the structures of the potassium complexes, **1** and **2**, because η^1, η^3, and η^5 binding modes are all found in these structures. Another feature demonstrated by these compounds is that the DMI ligand readily forms bridges. Hence, polymeric **1** contains μ-η^1:η^3 and μ-η^1:η^3:η^5 bridging DMI ligands and dimeric **2** contains a μ-η^1:η^1 arrangement. These are newly identified bonding options for DMI adding to the previously reported nonbridging η^1 and η^6 modes observed in $(Ph_3P)_2Ir(CO)(DMI)$[33] and $[(\eta^6\text{-}C_6H_4\text{-}(CHMe_2)\text{-}4\text{-}Me\text{-}1)Ru(\eta^6\text{-}DMI)][BPh_4]$.[34]

The structures of **1** and **2** also suggest that interconversion between modes can be facile. Because the $KMe_2C_8H_4N$ salts in **1** and **2** differ only in the coordinating solvent, THF versus DME, it is clear that relatively small changes can significantly change the bonding of this ligand. Furthermore, the fact that η^1, η^3, and η^5 bonding is found in a single crystal of **1** suggests that there is not necessarily one type which is strongly preferred.

In contrast to the variable coordination found in the monovalent potassium complexes, in the divalent and trivalent lanthanide complexes reported here, the DMI ligand binds primarily in a terminal η^1 mode in the presence of THF. In these lanthanide systems, formation of THF polysolvates containing η^1-DMI ligands is preferred to that of structures with less THF and a higher DMI hapticity. This may be related to the charge-to-radius ratio of these ions. The eight coordinate radii of K^+, Sm^{2+}, Sm^{3+}, and $Y^{3+}$are 1.51, 1.27, 1.079, and 1.02 Å, respectively.[65] The smaller metals with higher charge may favor a direct η^1 interaction with nitrogen, although too few examples are known to make a broad generalization.

The η^1 binding preference of DMI in **3** matches that found for the related samarium complex of the anion derived from carbazole, $[C_{12}H_8N]^-$ (CBZ). In $(DMI)_2Sm(THF)_4$, **3**, and the analogous *trans*-$(CBZ)_2Sm(N\text{-}MeIm)_4$ and *cis*-$(CBZ)_2Sm(THF)_4$, the coordination sphere of the metal attached to two η^1 ligands is filled with solvent instead of using the η^3 or η^5 bonding capacity of the ligands. This contrasts strongly with the preference of potassium in the mono-THF solvate **1** to engage in bridging DMI bonding rather than multiple THF solvation. A similar situation occurs in the $(DMI)_3Y(THF)_2$ system. In this case, a coordination number lower than usual is observed for yttrium and neither additional DMI bonding nor additional THF is found.

In the case of the metallocene complexes, $(C_5Me_5)_2Ln(DMI)$ (Ln = Sm, **5**; Y, **6**), it is more reasonable to expect an η^1 binding mode because this would be most easily accommodated by the open wedge of the metallocene. However, the DMI ligand appears to be oriented so that the arene carbon atoms adjacent to nitrogen are also directed at samarium and yttrium with long-range Ln−C(arene) interactions. Because such long-range interactions are common in unsolvated metallocenes, $(C_5Me_5)_2LnZ$, in which Z = $CH(SiMe_3)_2$, $N(SiMe_3)_2$, CCR, or BPh_4,[67−71] this is not unusual for this type of complex. However, this does show that the DMI ligand can orient to increase its interaction with the metal in the presence of the proper ancillary ligand set.

Conclusion

The anion derived from 2,3-dimethylindole coordinates to potassium in several different binding modes and readily forms yttrium and lanthanide complexes. It is a synthetically convenient ligand, which can function as the sole anionic ligand in a complex as well as being compatible with bis(cyclopentadienyl) systems. It provides a convenient alternative to $[N(SiMe_3)_2]^-$ for forming solvate-free $(C_5Me_5)_2Ln(amide)$ complexes. To date, its bonding mode with lanthanides is observed to be primarily η^1; that is, it acts primarily as a bulky terminal amide ligand.

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