Synthesis and Dimethylsilicone Insertion into the Ln−N Bond of Cyclopentadienyl Lanthanide Pyrazolate Complexes

Xi-geng Zhou, Zu-en Huang,* Rui-fang Cai, Li-bei Zhang, and Li-xin Zhang

Department of Chemistry, Fudan University, Shanghai 200433, People's Republic of China

Xiao-ying Huang

The State Key Laboratory of Structural Chemistry, Fuzhou 350002, People's Republic of China

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Reactions of Cp_3Ln (Cp = C_5H_5; Ln = Ho, Dy, Yb, Sm) with 2 equiv of $HPzMe_2$ ($HPzMe_2$ = 3,5-dimethylpyrazole) in THF at room temperature yield complexes $CpLn(PzMe_2)_2$ [Ln = Ho (**1**), Dy (**2**)], $Cp_2Yb(PzMe_2)(HPzMe_2)$ (**3**), and $Sm(PzMe_2)_3$ (**5**), respectively, indicating that the number of cyclopentadienyl groups liberated from a Cp_3Ln moiety is largely influenced by the size of the lanthanide ion. Reaction of Cp_3Er and 1 equiv of $HPzMe_2$ under the same conditions gave $Cp_2Er(PzMe_2)(THF)$ (**4**). The structures of **3** and **4** were determined by X-ray diffraction. In both complexes the central metal ions are coordinated to four ligands in a typical "bent metallocene" geometry. Complexes **1** and **2** react with dimethylsilicone grease to give the corresponding Me_2SiO insertion products $[CpLn(PzMe_2)(OSiMe_2PzMe_2)]_2$ [Ln = Ho (**6**), Dy (**7**)]. The results of the investigation show that the insertion of dimethylsilicone into the Ln−N bond is only possible for the monocyclopentadienyl-type organolanthanide pyrazolates. X-ray diffraction reveals complex **6** to be a centrosymmetric dimer in which each holmium atom is coordinated to one cyclopentadienyl group, two bridging oxygen atoms, and three nitrogen atoms, two from the chelating $PzMe_2$ ligand and one from the bridging 3,5-dimethylpyrazolyl siloxide ligand to form a distorted octahedron.

Introduction

There is currently considerable interest in studying the reactivities of the Ln−N bonds of organolanthanide complexes.[1−8] Pyrazole-type heterocycle ions represent an important class of ligands in organometallic chemistry.[9−12] Although the coordination of these ligands to lanthanides has been extensively investigated, knowledge of the reactivity for organolanthanide pyrazolates is rather limited to date.[13−17] We have previously reported the insertion of dimethylsilicone into the Ln−N bond of $[(C_5H_4Me)Ln(PzMe_2)_2]_2$.[4,5,8] It is well-known that changes in the substitution pattern of the cyclopentadienyl ligands can substantially affect the reactivity and catalytic activity of organolanthanide complexes.[18−20] To better understand the influence of the cyclopentadienyl ring and to further develop the insertion reaction, in this work we present an extension of this reaction to other lanthanocene pyrazolates, such as $(C_5H_5)Ln(PzMe_2)_2$ (Ln = Dy, Ho).

Experimental Section

Materials and Methods. All manipulations were carried out under argon with rigorous exclusion of air and moisture using Schlenk, vacuum-line, and glovebox techniques. All solvents were refluxed and distilled over sodium benzophenone ketyl immediately before use. Cp_3Ln (Ln = Sm, Dy, Ho, Er, Yb)[21] and 3,5-dimethylpyrazole ($HPzMe_2$)[22] were prepared by the literature procedure. The dimethylsilicone grease (China)

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was purchased and was used as received. Elemental analyses for carbon, hydrogen, and nitrogen were performed on a Rapid CHN−O analyzer. Metal analyses for lanthanides were accomplished using the literature method.[23] Infrared spectra were obtained on a NICOLE FT-IR 5DX spectrometer with samples prepared as Nujol mulls. Mass spectra were recorded on a HP5989A instrument operating in EI mode. Crystal samples of the respective complexes were rapidly introduced by the direct inlet techniques with a source temperature of 200 °C. The values of *m/z* are referred to the isotopes ^{12}C, ^{1}H, ^{14}N, ^{152}Sm, ^{164}Dy, ^{165}Ho, ^{166}Er, and ^{174}Yb. ^{1}H NMR data were obtained on a Bruker MSL-300 NMR spectrometer and were referenced to residual aryl protons in C_6D_6 (δ 7.15).

$CpHo(PzMe_2)_2$ (1). Cp_3Ho (0.193 g, 0.536 mmol) and $HPzMe_2$ (0.103 g, 1.07 mmol) were mixed in 20 mL of THF. After stirring for 48 h at room temperature, the reaction solution was concentrated by reduced pressure to about 2 mL. Addition of 15 mL of *n*-hexane resulted in the precipitation of a pale-yellow solid. The resulting mixture was centrifuged, and the solution was decanted. The precipitate was washed with *n*-hexane and dried under vacuum to afford a pale-yellow powder of **1**. Yield: 0.180 g (80%). Anal. Calcd for $C_{15}H_{19}N_4$-Ho: C, 42.87; H, 4.56; N, 13.33; Ho, 39.25. Found: C, 42.63; H, 4.61; N, 13.40; Ho, 39.02. IR (KBr pellet, cm^{-1}): 3127 m, 3108 w, 3072 w, 1592 m, 1461 s, 1376 s, 1306 m, 1154 m, 1030 m, 1012 m, 778 s, 670 m, 481 m, 465 w, 436 w. MS: *m/e* [fragment, relative intensity %] = 420 [M, 2], 355 [M − Cp, 13], 324 [M − $HPzMe_2$, 8], 260 [M − Cp − $PzMe_2$, 9], 230 [M − $2PzMe_2$, 78], 95 [$PzMe_2$, 37], 65 [Cp, 100].

$CpDy(PzMe_2)_2$ (2). Using the same procedure, reaction of 0.225 g (0.629 mmol) of Cp_3Dy and 0.121 g (1.26 mmol) of $HPzMe_2$ in THF gave **2** as a colorless solid. Yield: 0.226 g (86%). Anal. Calcd for $C_{15}H_{19}N_4Dy$: C, 43.12; H, 4.58; N, 13.40; Dy, 38.89. Found: C, 42.88; H, 4.57; N, 13.51; Dy, 38.67. IR (KBr pellet, cm^{-1}): 3127 m, 3108 w, 3073 w, 1592 m, 1544 w, 1462 s, 1378 s, 1306 m, 1154 m, 1030 m, 1012 m, 778 s, 670 m, 481 w, 466 w, 436 w. MS: *m/e* [fragment, relative intensity %] = 419 [M, 1], 354 [M − Cp, 3], 323 [M − $HPzMe_2$, 2], 259 [M − Cp − $PzMe_2$, 5], 229 [M − $2PzMe_2$, 65], 95 [$PzMe_2$, 42], 65 [Cp, 100].

$Cp_2Yb(PzMe_2)(HPzMe_2)$ (**3**). To a mixture of Cp_3Yb (0.278 g, 0.755 mmol) and $HPzMe_2$ (0.145 g, 1.51 mmol) was added 20 mL of THF. After stirring for 60 h at ambient temperature, the reaction solution was concentrated to about 3 mL. Orange crystals were obtained by slow diffusion of *n*-hexane at 5 °C. Yield: 0.194 g (52%). Anal. Calcd for $C_{20}H_{25}N_4Yb$: C, 48.58; H, 5.10; N, 11.32; Yb, 35.00. Found: C, 47.86; H, 5.15; N, 11.12; Yb, 35.27. IR (cm^{-1}): 3353 m, 3197 w, 3132 m, 3099 m, 3033 w, 1594 m, 1572 w, 1544 m, 1519 m, 1462 s, 1378 s, 1338 w, 1328 w, 1306 m, 1256 m, 1181 w, 1144 m, 1044 m, 1028 m, 1012 m, 934 s, 825 m, 800 m, 775 s, 738 w, 662 m, 491 m, 469 m. MS: *m/e* [fragment, relative intensity %] = 399 [M − $HPzMe_2$, 26.26], 334 [M − $HPzMe_2$ − Cp, 69.87], 303 [M − $2HPzMe_2$, 5.49], 269 [$YbPzMe_2$, 65.86], 239 [CpYb, 16.16], 174 [Yb, 7.18], 96 [$HPzMe_2$, 100], 66 [CpH, 49.05].

$Cp_2Er(PzMe_2)(THF)$ (**4**). To a mixture of 0.381 g (1.05 mmol) of Cp_3Er and 0.101 g (1.05 mmol) of $HPzMe_2$ was added 20 mL of THF at room temperature. After stirring for 24 h, the solution was concentrated to ca. 3 mL in vacuo. Next, *n*-hexane was added until the formation of a cloudy precipitate was observed. Pink crystals were formed by cooling to −15 °C. Yield: 0.35 g (72%). Anal. Calcd for $C_{19}H_{25}N_2OEr$: C, 49.11; H, 5.42; N, 6.03; Er, 36.00. Found: C, 48.86; H, 5.35; N, 6.12; Er, 36.17. IR (cm^{-1}): 3102 m, 1544 w, 1516 m, 1462 s, 1378 s, 1306 m, 1181 m, 1144 m, 1078 m, 1012 s, 972 m, 891 m, 775 s, 662 m, 483 m, 465 m. MS: *m/z* [fragment, relative intensity %] = 391 [M − THF, 28.08], 325 [M − THF − Cp, 100], 295 [M − THF − $HPzMe_2$, 22], 261 [M − THF − 2Cp, 4], 231 [CpEr, 11], 182 [ErO, 1], 166 [Er, 11], 95 [$PzMe_2$, 20], 65 [Cp, 37], 720 [M′ + 2 − CpH, 2], 654 [M′ + 2 − 2Cp, 1], 624 [M′ + 2 − Cp − $PzMe_2$, 1] (M′ = $[M - THF]_2$).

$Sm(PzMe_2)_3$ (**5**). To a THF solution (15 mL) of Cp_3Sm (0.208 g, 0.602 mmol) was added 0.116 g (1.20 mmol) of $HPzMe_2$, dissolved in 6 mL of THF. The resulting solution was stirred at room temperature. The color of reaction solution changed slowly from orange to yellow. After ca. 2 h, a yellow precipitate started to form slowly. After stirring at room temperature for 48 h, the reaction mixture was centrifuged. The precipitate was collected, washed twice with 8 mL of THF and 10 mL of hexane, respectively, and dried in a vacuum to give a pale-yellow solid product, which was found to be pure $Sm(PzMe_2)_3$ (**5**). Yield: 0.136 g (78%). Anal. Calcd for $C_{15}H_{21}N_6Sm$: Sm, 34.51. Found: Sm, 34.42. IR (cm^{-1}): 3066 w, 1459 s, 1446 s, 1378 m, 1356 m, 1281m, 1122 w, 1181 m, 1147 m, 1075 m, 1016 m, 922 m, 869 m, 778 s, 731 s, 688 s, 509 w, 490 m, 459 w. ^{1}H NMR (C_6D_6): δ 2.08 (s, 18H, $C_3N_2H(CH_3)_2$), 12.63 (br s, 3H, $C_3N_2H(CH_3)_2$). MS (EI): 437 [M, 1], 341 [M − $HPzMe_2$, 8], 246 [M − $2PzMe_2$ − 1, 19], 95 [$PzMe_2$, 100].

The clear supernatant solution from the centrifugation was concentrated to about 5 mL in vacuo and was then stored in −18 °C to afford orange crystals, which were confirmed to be $Cp_3Sm(THF)$ by X-ray crystallographic analysis.[24]

$[CpHo(PzMe_2)(OSiMe_2PzMe_2)]_2$ (**6**). To a THF solution of **1** (0.164 g, 0.39 mmol) was added 0.060 g of dimethylsilicone grease dissolved in THF. The reaction solution was stirred for 48 h and was then concentrated to ca. 3 mL under reduced pressure. A yellow crystalline product was obtained by slow diffusion of *n*-hexane. Yield: 0.09 g (48%). Anal. Calcd for $C_{34}H_{50}N_8O_2Si_2Ho_2$: C, 41.30; H, 5.10; N, 11.33; Ho, 33.36. Found: C, 41.12; H, 5.14; N, 11.07; Ho, 33.41. IR (cm^{-1}): 3123 m, 3102 m, 3090 w, 1544 w, 1516 m, 1462 s, 1378 s, 1338 w, 1325 w, 1253 m, 1181 w, 1144 m, 1044 m, 1012 m, 944 s, 935 m, 825 m, 800 m, 769 s, 762 s, 666 m, 481 m, 466 m, 422 m. MS: *m/z* [fragment, relative intensity %] = 956 [M + 2 − $2CH_3$, 4], 925 [M + 2 − Cp, 19], 895 [M + 2 − $PzMe_2$, 1], 829 [M + 2 − CpH − $PzMe_2$, 1], 503 [$Ho(OSiMe_2PzMe_2)_2$, 15], 494 [M/2, 4], 429 [$Ho(PzMe_2)(OSiMe_2PzMe_2)$, 100], 398 [M/2 − $HPzMe_2$, 18], 334 [$Ho(OSiMe_2PzMe_2)$, 4], 324 [M/2 − $HOSiMe_2$-$PzMe_2$, 11], 304 [M/2 − $2PzMe_2$, 1], 260 [$Ho(PzMe_2)$, 2], 230 [CpHo, 2], 165 [Ho, 1], 95 [$PzMe_2$, 2], 65 [Cp, 3].

$[CpDy(PzMe_2)(OSiMe_2PzMe_2)]_2$ (**7**). Using the same procedure, 0.10 g of dimethylsilicone grease and 0.212 g (0.507 mmol) of **2** in 15 mL of THF gave **7** as colorless crystals. Yield: 0.12 g (50%). Anal. Calcd for $C_{34}H_{50}N_8O_2Si_2Dy_2$: C, 41.50; H, 5.12; N, 11.38; Dy, 33.03. Found: C, 41.12; H, 5.14; N, 11.50; Dy, 33.21. IR (cm^{-1}): 3120 m, 3085 m, 1541 w, 1516 m, 1462 s, 1378 s, 1334 w, 1325 w, 1253 s, 1140 m, 1094 m, 1044 m, 1012 m, 940 sb, 825 s, 797 s, 769 s, 762 s, 666 m, 481 m, 466 m, 422 m. MS: *m/z* [fragment, relative intensity %] = 920 [M − CpH, 13], 825 [M − CpH − $PzMe_2$, 1], 502 [$Dy(OSiMe_2PzMe_2)_2$, 9], 493 [M/2, 3], 463 [M/2 − 2Me, 2], 428 [$Dy(PzMe_2)(OSiMe_2PzMe_2)$, 100], 397 [M/2 − $HPzMe_2$, 28], 324 [M/2 − $OSiMe_2PzMe_2$, 23], 302 [M/2 − $2PzMe_2$ − 1, 5], 259 [$Dy(PzMe_2)$, 4], 229 [CpDy, 6], 164 [Dy, 3], 96 [$HPzMe_2$, 40], 66 [CpH, 37].

X-ray Crystallographic Study of $Cp_2Yb(PzMe_2)$-$(HPzMe_2)$ (3). A orange crystal with approximate dimensions 0.55 × 0.35 × 0.25 mm was sealed under argon in a thin-walled glass capillary and mounted on an Enraf-Nonius CAD-4 diffractometer. Final cell parameters are based on a least-squares analysis of 25 reflections in well-separated regions of reciprocal space, all having 11.52° < θ < 22.07°. Relevant crystal and data collection parameters are given in Table 1.

All 4752 unique data were corrected for the effects of absorption and for Lorentz and polarization factors. The structure was solved by direct methods with the program

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[23] Qian, C. T.; Ye, C. Q.; Lu, H. Z.; Zhou, J. L.; Ge, Y. W. *J. Organomet. Chem.* **1983**, *247*, 161.

[24] The X-ray crystal structure of $(C_5H_5)_3Sm(THF)$ has recently been reported in the literature.[27a]

Table 1. Crystal and Data Collection Parameters of Complexes 3, 4, and 6

	3	**4**	**6**
formula	$YbC_{20}H_{25}N_4$	$ErON_2C_{19}H_{25}$	$Ho_2C_{34}H_{50}O_2N_8Si_2$
molecular weight	494.48	464.68	988.85
crystal color, shape	orange	pink	yellow
crystal system	monoclinic	monoclinic	monoclinic
space group	$P2_1/n$	$P2_1/c$	$P2_1/n$
lattice params			
a (Å)	10.418(2)	8.187(2)	11.754(2)
b (Å)	11.498(3)	14.543(5)	11.519(2)
c (Å)	16.300(4)	16.146(5)	15.095(4)
β (deg)	94.70(2)	100.93(2)	104.10(1)
V (Å^3)	1979.7(9)	1887(1)	1982(1)
Z	4	4	2
D_c (g cm^{-3})	1.659	1.635	1.657
F(000)	972	916	976
radiation ($\lambda = 0.71069$ Å)	Mo Kα	Mo Kα	Mo Kα
temperature (K)	296	296	296
scan type	$\omega-2\theta$	$\omega-2\theta$	$\omega-2\theta$
μ (mm^{-1})	4.719	4.510	4.109
hkl range	0 to 13, 0 to 14, −20 to 20	−10 to 10, 0 to 17, 0 to 19	0 to 15, −14 to 0, −19 to 19
$2\theta_{max}$	54	52	54
no. of reflns measured	4752	3980	4740
no. of unique reflns	4570	3868	4578
no. of reflns observed	3352 [$I > 3\sigma(I)$]	1785 [$I > 2\sigma(I)$]	3673 [$I > 3\sigma(I)$]
no. of variables	226	208	218
w	$1/\sigma^2(F)$	$1/\sigma^2(F)$	$1/\sigma^2(F)$
R	0.043	0.076	0.042
R_w	0.053	0.076	0.051
S	1.55	1.30	1.49
$(\Delta/\sigma)_{max}$	0.0009	0.002	0.0007
$\Delta\rho_{max}$ (e Å^{-3})	2.35	1.22	2.06

MITHRIL.[25] Hydrogen atoms were placed in calculated idealized positions. All calculations were performed by using the TEXSAN crystallographic software package of the Molecular Structure Corp. program.[26]

X-ray Crystallographic Study of $Cp_2Er(PzMe_2)(THF)$ (4). A pink crystal of approximate dimensions 0.40 × 0.32 × 0.30 mm was handled as described above for **3**. Final cell parameters are based on a least-squares analysis of 25 reflections in well-separated regions of reciprocal space, all having 9.31° < θ < 15.15°. The intensity was corrected for Lorentz−polarization effects and empirical absorption. The crystal data collection and refinement parameters are collected in Table 1.

The structure was solved by directed methods and refined on F^2 by full-matrix least-squares methods. All non-hydrogen atoms were refined anisotropically. The H atoms were included in calculated positions with isotropic thermal parameters related to those of the supporting carbon atoms, but were not included in refinement.

X-ray Crystal Structure Determination of $[CpHo(PzMe_2)(OSiMe_2PzMe_2)]_2$ (6). A yellow crystal measuring approximately 0.90 × 0.60 × 0.25 mm was handled as described above for **3**. Accurate cell parameters were obtained by the least-squares refinement of the setting angles of 25 reflections with 11.86° < θ < 19.60°. A summary of crystallographic data and data collection parameters is given in Table 1. During data collection, the intensities of three standard reflections measured every 250 reflections showed 7.5% decay. The intensities were corrected for Lorentz and polarization factors and empirical absorption.

A combination of direct methods and difference Fourier techniques provided the locations of all non-hydrogen atoms, which were refined with anisotropic temperature parameters by the use of full-matrix least-squares methods. The H atoms were included in calculated positions with isotropic thermal parameters related to those of the supporting carbon atoms, but were not included in the refinement.

Results and Discussion

Synthesis and Spectroscopic Characterization of Complexes 1−5. Complexes of the type $CpLn(PzMe_2)_2$ [Ln = Ho (**1**), Dy (**2**)] were prepared by reaction of Cp_3Ln with $HPzMe_2$ in THF at room temperature (eq 1).

$$Cp_3Ln + 2HPzMe_2 \rightarrow CpLn(PzMe_2)_2 + 2CpH \quad (1)$$

Surprisingly, although acid displacement of cyclopentadienyl groups from a Cp_3Ln moiety is a well-known synthetic method,[18] attempts to prepare the corresponding ytterbium complex by reacting stoichiometric amounts of Cp_3Yb and $HPzMe_2$ under the same reaction conditions were unsuccessful. Abstraction of only one cyclopentadienyl ligand occurred with the formation of $Cp_2Yb(PzMe_2)(HPzMe_2)$ (**3**). The disubstituted complex $CpYb(PzMe_2)_2$ may be prepared in high yield by reaction of $CpYbCl_2(THF)_3$ with 2 equiv of $NaPzMe_2$. In addition, the corresponding Cp_3Sm derivative also behaves differently. Addition of a THF solution of 2 equiv of $HPzMe_2$ to a THF solution of Cp_3Sm results in the formation of a yellow deposit. This species has been characterized, by analytical and spectroscopic means, as the Cp-free complex $Sm(PzMe_2)_3$ (**5**). Crystallization of the supernatant solution from this reaction gave $Cp_3Sm(THF)$. The formation of $Cp_3Sm(THF)$ is presumably due to ligand redistribution of the initially formed $CpSm(PzMe_2)_2$ (eq 2).[27]

$$3CpSm(PzMe_2)_2 \rightarrow Cp_3Sm + 2Sm(PzMe_2)_3 \quad (2)$$

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[25] Gilmore, C. J. *MITHRIL, Computer Program for the Automatic Solution of Crystal Structure from X-ray Data*; Department of Chemistry, University of Glasgow: Scotland, 1983.

[26] *TEXSAN, TEXRAY Structure analysis Package*, revised; Molecular Structure Corporation: 3200 Research Forest Dr., The Woodlands, TX 77381, 1987.

All of these results are different from those observed for the analogous methylcyclopentadienyl complexes, in which the reactions of $(C_5H_4Me)_3Yb$ and $(C_5H_4Me)_3Sm$ with 2 equiv of $HPzMe_2$ proceeded smoothly and gave the derived products $(C_5H_4Me)Yb(PzMe_2)_2$ and $(C_5H_4Me)Sm(PzMe_2)_2$, respectively.[4,28]

This striking difference in reactivity between the lanthanides would appear to be electronic and/or steric in origin since all of these substrates have similar structures. Presumably, the formation of $Cp_2Yb(PzMe_2)(HPzMe_2)$ is due to the enhanced covalence of the Ln−Cp bond in the series Cp_3Ln (Ln = Sm, Dy, Ho, Yb), as a result of the lanthanide contraction, and because the acidity of CpH is stronger than that of C_5H_5Me. Thus $HPzMe_2$ is not strong enough of an acid to liberate the second Cp group from the more covalent Cp_3Yb moiety to give $CpYb(PzMe_2)_2$. On the other hand, preferred formation of a tris- over a bis(pyrazolate) complex can be ascribed to the smaller size of the Cp group compared to that of the MeC_5H_4 ligand; this leads to greater steric unsaturation in $CpSm(PzMe_2)_2$ and facile ligand redistribution to Cp_3Sm and $Sm(PzMe_2)_3$.

To obtain additional data on the other organolanthanide pyrazolate systems and to determine if related chemistry could occur with the dicyclopentadienyl complexes, the synthesis of the monopyrazolate complex, $Cp_2Er(PzMe_2)(THF)$ (**4**), by reaction of Cp_3Ln with 1 equiv of $HPzMe_2$ was carried out also.

Complexes **1**−**5** have been characterized by elemental analysis and infrared, ^1H NMR, and mass spectroscopies, which confirmed the proposed formula. The structures of complexes **3** and **4** have also been determined by X-ray crystallography. Complexes **1**−**5** exhibit ν(Ln−N) stretching bands in the 481−491 and 459−469 cm^{-1} regions, typical of lanthanide pyrazolate complexes. Compound **3** shows two additional bands in the IR spectrum at 3353 and 1594 cm^{-1}, corresponding to terminal ν(N−H) and δ(N−H) vibrations. In the case of **4** the IR spectrum exhibits, in addition to the characteristic absorption assigned to Cp and $PzMe_2$ groups, two well-defined bands at 891 and 1045 cm^{-1} for coordinated THF.

The mass spectra of all these compounds display a series of peaks clearly representing fragments derived from the parent molecules. Interestingly, the mass spectra of $Cp_2Er(PzMe_2)(THF)$ (**4**) show that when the vaporization temperature of the sample reaches 200 °C, fragment peaks corresponding to $[Cp_2Er(PzMe_2)]_2$ are also observed, indicating that **4** has desolvated to form a dimer during the course of the heating process.

Reactivity of Complexes 1−5 to Dimethylsilicone Grease. Synthesis of $[CpLn(PzMe_2)(OSiMe_2PzMe_2)]_2$ (Ln = Ho (6), Dy (7)). Like the methylcyclopentadienyl lanthanide pyrazolate species, the monocyclopentadienyllanthanide pyrazolates **1** and **2** also exhibit high reactivity; they react with dimethylsilicone grease to give the mono Me_2SiO insertion products, $[CpHo(PzMe_2)(OSiMe_2PzMe_2)]_2$ (**6**) and $[CpDy(PzMe_2)(OSiMe_2PzMe_2)]_2$ (**7**), respectively. Insertion of a second Me_2SiO moiety does not occur even in the presence of a large excess of the dimethylsilicone grease. To better understand the cyclopentadienyl effect, the reaction of **3**−**5** with dimethylsilicone grease was also studied, indicating that the Ln−N bonds in **3**−**5** have not been sufficiently activated to react with dimethylsilicone grease. Presumably, the Ln−N(chelating) bond is stronger than the Ln−N(bridging) bond. In addition, the steric factor of these complexes is also unfavorable to another reagent to attack at the Ln−N(chelating). These results confirm that insertion of dimethylsilicone into a Ln−N bond is only available for the monocyclopentadienyl organolanthanide pyrazolates.

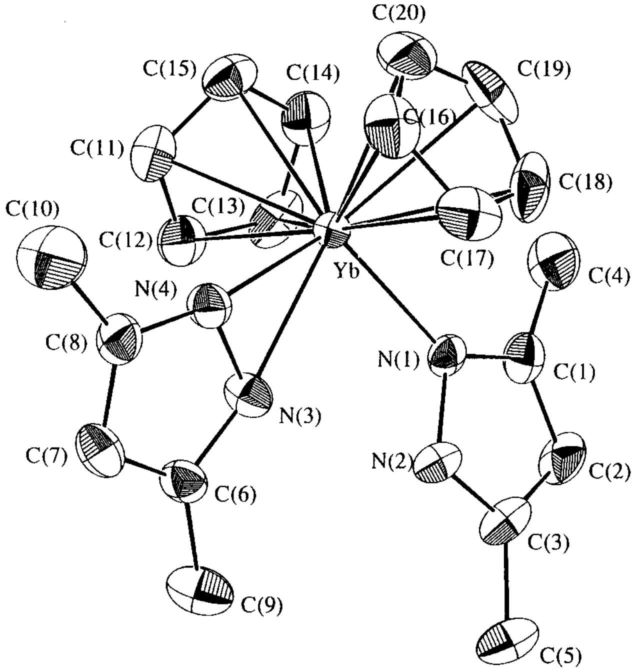

Figure 1. ORTEP diagram of $CpYb(PzMe_2)(HPzMe_2)$ (**3**) with the probability ellipsoids drawn at the 30% level.

Complexes **6** and **7** are moderately sensitive toward moisture and air. They are soluble in THF, but less soluble in *n*-hexane. Their infrared spectra are very similar in appearance and relative intensity, indicating that they have the same structures. In the IR spectra of **6** and **7**, bands are observed at 481, 466, and 422 cm^{-1}, which may be attributed to the absorptions of Ln−N bonds. The two higher wavenumber absorptions are the Ln−N(chelating) stretching vibration, while the low one is the Ln−N(bridging) vibration. The molecular ions and main fragments of two complexes are clearly observed in the mass spectra, indicating that a binuclear core is present.

Structure of Complex 3. Figure 1 shows the molecular structure of **3**. Selected bond distances and angles are listed in Table 2. The molecule crystallizes as well-separated monomeric units. The ytterbium atom is coordinated to two cyclopentadienyl rings and three nitrogen atoms, two from the 3,5-dimethylpyrazolate anion and another from the neutral 3,5-dimethylpyrazole molecule. The coordination geometry is typical "bent metallocene". The Yb−C(Cp) distances range from 2.60(1) to 2.64(1) Å and average 2.62(1) Å. The average value is similar to those found in other Cp_2Yb-containing compounds, such as $[Cp_2Yb(OCMe{=}C{=}CHMe)]_2$, 2.63(1) Å;[29] $Cp_2Yb(OC_{10}H_7)(THF)$, 2.60(2) Å;[30] and $Cp_2Yb(CH_3)(THF)$, 2.60(2) Å.[31] However, consistent with higher

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Table 2. Selected Bonded Distances (Å) and Angles (deg) for Complex 3

Bond Distances			
Yb−N(4)	2.248(6)	Yb−N(3)	2.360(6)
Yb−N(1)	2.414(7)	Yb−C(18)	2.619(9)
Yb−C(19)	2.602(8)	Yb−C(20)	2.62(1)
Yb−C(14)	2.603(9)	Yb−C(15)	2.63(1)
Yb−C(12)	2.606(9)	Yb−C(11)	2.64(1)
Yb−C(13)	2.613(9)	Yb−C(16)	2.64(1)
Yb−C(17)	2.62(1)		
Bond Angles			
N(4)−Yb−N(3)	34.4(2)	N(4)−Yb−N(1)	115.2(2)
N(3)−Yb−N(1)	81.5(2)	N(3)−N(4)−Yb	77.3(4)
Yb−N(1)−N(2)	115.1(4)	Yb−N(1)−C(1)	141.7(5)
Cent−Yb−Cent[a]	127.9		

[a] Cent represents the centroid of cyclopentadienyl ring.

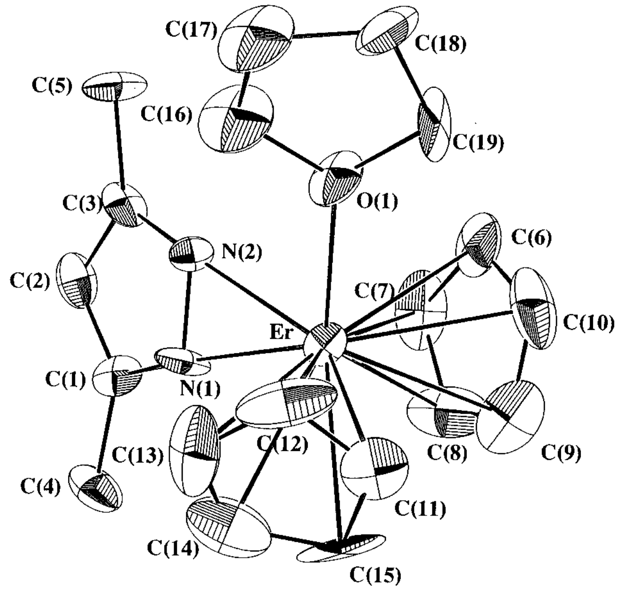

Figure 2. ORTEP diagram of $Cp_2Er(PzMe_2)(THF)$ (**4**) with the probability ellipsoids drawn at the 30% level.

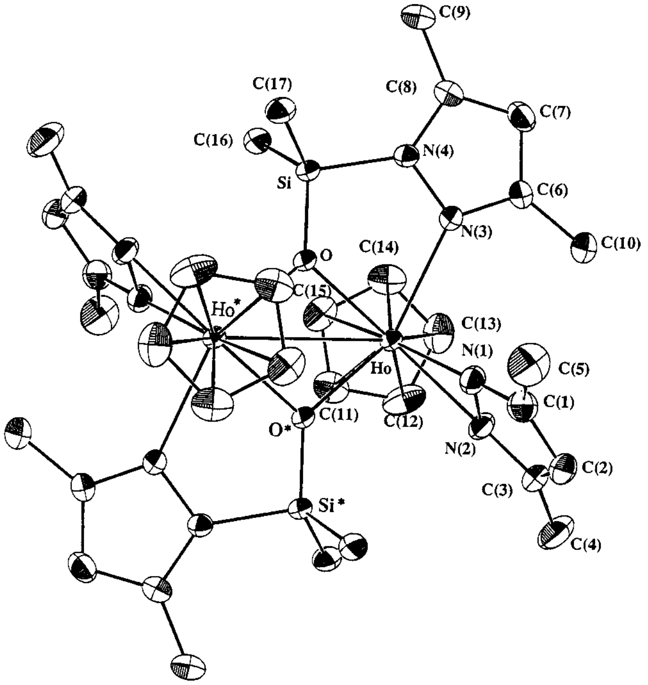

Figure 3. ORTEP diagram of $[CpHo(PzMe_2)(OSiMe_2PzMe_2)$ (**6**) with the probability ellipsoids drawn at the 30% level.

coordination number, the Cent−Yb−Cent angle of 127.9° in **3** is at the low end of the 128.9−131° range observed in the above complexes cited. The dihedral angle between the planes of two 3,5-dimethylpyrazole rings is 156.2°.

The Yb−N(3) and Yb−N(4) distances, 2.360(6) and 2.248(6) Å, are intermediate between the values observed for a Yb−N single-bond distance and an Yb←:N donor bond distance[32] and are comparable to the corresponding values found in $[(C_5H_4Me)Yb(PzMe_2)(OSiMe_2PzMe_2)]_2$ [2.326(7) and 2.270(6) Å][4] and $Yb_3(\mu\text{-}PzMe_2)_6(\eta^2\text{-}PzMe_2)_3(\mu_3\text{-}O)Na_2(THF)_2$ [2.348(5) and 2.298(5) Å].[33] Due to the different bonding mode and nature of the ligand, the Yb−N(1) distance of 2.414(6) Å is clearly longer than the Yb−N(3) and Yb−N(4) distances, but the N=N bond distances for the two ligands differ only slightly. The Yb−N(1) distance is in the range of a Yb^{3+}←:NR_3 donor bond and is the same as that observed in $Cp_3Yb(NCCH_2CH_3)$, 2.414(5) Å.[34]

Structure of Complex 4. The structure of **4** is shown in Figure 3. Selected bond distances and angles are given in Table 3. The overall structure of **4** is similar to that of **3** with a THF molecule taking the place of 3,5-dimethylpyrazole. The erbium atom is coordinated to two η^5-cyclopentadienyl groups, one bidentate 3,5-dimethylpyrazolate ligand and one tetrahydrofuran molecule. The coordination number of the central metal Er is 9. Complex **4** has a Cent−Er−Cent angle of 127.4° and an average Er−C(Cp) distance of 2.63(3) Å, which are in the normal range. As expected, the smaller oxygen atom is closer to the metal than the $HPzMe_2$ nitrogen atom in **3**. The Er−O(THF) distance of 2.32(1) Å is shorter than the values found in complexes $CpErCl_2(THF)_3$, 2.445−2.529 Å,[35] and $Cp_3Er(THF)$, 2.37(4) Å.[36] As in **3**, the Er−N distances of 2.25(2) and 2.28(2) Å are in the range expected for the Ln−N bond interaction with a partial single and donor bond character. When the differences in the metallic radii are subtracted (ca. 0.01 Å for Ho^{3+} and 0.03 Å for Yb^{3+}),[37] the average Er−N length in **4** is reasonable in comparison with the corresponding values in the complexes **3** and **6**. The $PzMe_2$ and THF ring planes are nearly parallel to the C(6)−C(10) ring and C(11)−C(15) ring planes, respectively. The Cent−Er−Cent angle of 127.4° is similar to that in **3**. An unusual feature in **4** is that, although the size of the THF molecule is smaller than that of $HPzMe_2$, leading to less steric crowding in **4** compared to **3**, the best plane of the THF ring makes a 54.1°

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Table 3. Selected Bonded Distances (Å) and Angles (deg) for Complex 4

Bond Distances			
Er−N(1)	2.25(2)	Er−N(2)	2.28(2)
Er−O(1)	2.32(1)	Er−C(11)	2.62(3)
Er−C(6)	2.61(3)	Er−C(12)	2.61(3)
Er−C(7)	2.62(2)	Er−C(13)	2.65(3)
Er−C(8)	2.63(2)	Er−C(14)	2.62(3)
Er−C(9)	2.62(3)	Er−C(15)	2.67(3)
Er−C(10)	2.62(3)		
Bond Angles			
N(1)−Er−N(2)	35.0(5)	N(1)−Er−O(1)	116.9(6)
N(2)−Er−O(1)	83.5(6)	N(2)−N(1)−Er	73(1)
Er−N(2)−N(1)	72(1)	Er−O(1)−C(16)	121(2)
Cent−Er−Cent	127.4	Er−O(1)−C(19)	131(1)

Table 4. Selected Distances (Å) and Angle (deg) for Complex 6[a]

Bond Distances			
Ho−O	2.290(4)	Ho−C(11)	2.655(7)
Ho−O*	2.270(4)	Ho−C(12)	2.645(7)
Ho−N(2)	2.299(5)	Ho−C(13)	2.663(7)
Ho−N(1)	2.345(5)	Ho−C(14)	2.713(7)
Ho−N(3)	2.438(5)	Ho−C(15)	2.693(7)
Si−N(4)	1.806(5)	Si−O	1.614(4)
Si−C(16)	1.842(7)	Si−C(17)	1.853(7)
Ho−Ho*	3.629(1)		
Bond Angles			
O−Ho−O*	74.5(1)	O−Ho−N(2)	88.4(1)
O−Ho−N(1)	86.4(1)	O−Ho−N(3)	141.2(2)
N(2)−Ho−N(1)	34.6(2)	N(2)−Ho−N(3)	104.3(2)
N(1)−Ho−N(3)	84.5(2)	O−Si−N(4)	101.7(2)
Si−O−Ho	131.6(2)	Si−O−Ho*	122.4(2)
Ho−O−Ho*	105.5(1)	N(1)−N(2)−Ho	74.5(3)
N(2)−N(1)−Ho	70.9(3)	N(4)−N(3)−Ho	118.3(3)

[a] Symmetry operator: (*) $-x$, $-y$, $1-z$.

dihedral angle with the plane of the $PzMe_2$ ring, and this value is 30.3° larger than the dihedral angle between the planes of $PzMe_2$ and $HPzMe_2$ rings (23.8°).

Structure of Complex 6. As shown in Figure 3, complex **6** is a centrosymmetric dimer in which each holmium atom is coordinated to one cyclopentadienyl group, two bridging oxygen atoms, and three nitrogen atoms of 3,5-dimethylpyrazolate groups to form a distorted octahedron. The bridging Ho_2O_2 unit is planar. The Cp group is in eclipsed conformation with respect to the holmium atom. The average Ho−C(Cp) distance of 2.674(7) Å is at the high end of the range typical for trivalent lanthanocenes and is slightly longer than that found in the related complex $[Cp_2Ho(\mu\text{-}Cl)]_2$, 2.60(3) Å.[38] The average Ho−O distance is 2.280(4) Å, which is comparable to that in $[(MeOCH_2CH_2C_5H_4)_2Ho(\mu\text{-}OH)]_2$, 2.250(3) Å.[39]

The nitrogen atoms of the chelating 3,5-dimethylpyrazolate ligand, which exhibit Ho−N distances of 2.299(5) and 2.345(5) Å, are closer to the metal atom than that of the bridging 3,5-dimethylpyrazolate ligand [2.438(5) Å], but the N═N distances for the two $PzMe_2$ rings do not differ. When the differences in the ionic radii are considered,[37] all the Ho−N distances are in good agreement with the corresponding values of other pyrazolate-containing complexes, respectively, e.g., $[(C_5H_4Me)Yb(PzMe_2)(OSiMe_2PzMe_2)]_2$ [2.298(5), 2.348(5), and 2.446(5) Å][4] and $[(C_5H_4Me)Dy(PzMe_2)(OSiMe_2PzMe_2)]_2$ [2.319(5), 2.368(5), and 2.454(5) Å].[5] The coordination environment about the silicon atom has the normal tetrahedral arrangement. Both the Si−C and Si−O distances are in the normal ranges. However, the Si−N distance of 1.806(5) Å is longer than those found in $(C_5Me_5)Ce(N(SiMe_3)_2)_2$, 1.712(7) and 1.713(7) Å.[40]

Conclusions

The results of this study offer an interesting contrast to the known methylcyclopentadienyl-type organolanthanide pyrazolate complexes. With a methylcyclopentadienyl group as a coligand, $(C_5H_4Me)Ln(PzMe_2)_2$ complexes are available for all the lanthanides from Nd to Yb, and these complexes undergo smooth insertion of Me_2SiO into Ln−N bond to give $[(C_5H_4Me)Ln(PzMe_2)(OSiMe_2PzMe_2)]_2$. In contrast, for the present cyclopentadienyl ligand system, under the same reaction conditions, insertion is only available for the elements between middle and heavy lanthanides. The heavy rare earth elements underwent abstraction of only one Cp ligand, whereas the putative $CpLn(PzMe_2)_2$ for the light and middle lanthanides underwent facile ligand redistribution to Cp_3Ln and $Ln(PzMe_2)_3$.

All these results confirm that the insertion of dimethylsilicone into the Ln−N bond is only possible for the monocyclopentadienyl organolanthanide pyrazolates.

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Supporting Information Available: Text giving the details of data collection, data, and structure solution and refinement, tables of bond lengths, bond angles, torsion angles, and positional and thermal parameters for **3**, **4**, and **6**. This material is available free of charge via the Internet at http://pubs.acs.org.

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