Insertion of dimethylsilanone into a Ln–N bond and X-ray crystal structure of the insertion product [MeCpDy(η^2-PzMe$_2$)(μ-η^1:η^2-OSiMe$_2$PzMe$_2$)]
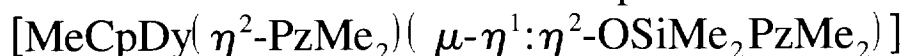
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Abstract

Reaction of MeCp$_3$Ln(MeCp = COLLABCH$_3$C$_5$H$_4$, Ln = Nd, Gd, Dy) with two equivalents of HPzMe$_2$(HPzMe$_2$ = 3,5-dimethylpyrazole) in THF at room temperature yielded complexes [MeCpLn(PzMe$_2$)$_2$] [Ln = Nd(1), Gd(2), Dy(3)], which have been characterized by elemental analysis, IR and MS spectra. The new complexes react with dimethylsilicone grease to give the dimethylsilanone insertion products: [MeCpLn(η^2-PzMe$_2$)(μ-η^1:η^2-OSiMe$_2$PzMe$_2$)]$_2$ [Nd(4), Gd(5), Dy(6)]. The complex **6** has been structurally characterized by X-ray crystallography. **6** crystallizes in the space group $P2_1/n$ with unit cell dimensions $a = 12.066(5)$, $b = 11.601(2)$, $c = 15.307(3)$ Å, $\beta = 105.84(3)°$, $V = 2061(1)$ Å^3, and $Z = 2$ for $D_{calcd} = 1.63$ g cm^{-3}. Least-squares refinement on the basis of 2930 observed reflections were allowed to reach a final R value of 0.031. The molecule is centrosymmetric dimer in which each dysprosium is coordinated by one methylcyclopentadienyl group, two bridging oxygens, two nitrogens of the chelating PzMe$_2$ ligand and one nitrogen atom of the bridging PzMe$_2$ ligand to form a distorted octahedron. The Dy–N(bridging) and Si–N bond lengths are 2.454(5) and 1.803(5) Å, respectively. The average Dy–C(ring), Dy–O and Dy–N(chelating) distances are 2.684(16), 2.294(10), and 2.344(25) Å, respectively. © 1997 Elsevier Science S.A.

Keywords: Dysprosium; Gadolinium; Neodymium; Organolanthanide; Methylcyclopentadienyl; 3,5-Dimethylpyrazolyl

1. Introduction

The bifunctionality and unsaturation of pyrazole give it an interesting coordination chemistry as a ligand [1–3]. The pyrazole-type heterocycle ions have been widely used as chelating ligands in the study of transition-metal complexes. Recently, there has been renewed interest arising from novel reactions such as activation of small molecules (e.g., H$_2$, O$_2$, N$_2$, CO) and C–H bonds by pyrazolyl-containing transition-metal organometallic complexes [4–7]. However, the knowledge of pyrazolates of organolanthanides is rather limited. As a matter of fact, interest in pyrazolyl-containing lanthanide-metal organometallic complexes with Ln–C

bond has evolved only most recently [8–11]. Since the results of the last two decades have witnessed that the organolanthanide complexes have the potential for some unique chemistry distinct from anything possible with main-group or transition-metal organometallic complexes [12–14], the organolanthanide pyrazolates probably have some unprecedented structures and unusual reactivities. In our previous communication [15], we have found that methylcyclopentadienyllanthanide pyrazolate (MeCpYb(PzMe$_2$)$_2$)$_2$ could undergo the insertion of Me$_2$SiO into an Yb–N bond. This unique reaction obviously still remains to be explored. In order to investigate this reaction further, we report herein the synthesis and the Me$_2$SiO insertion of [MeCpLn(PzMe$_2$)] (Ln = Nd, Gd, Dy) as well as the X-ray crystal structure of the insertion product [MeCpDy(η^2-PzMe$_2$)(μ-η^1:η^2-OSiMe$_2$PzMe$_2$)]$_2$.

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2. Experimental section

2.1. Materials and instrumentation

The title complexes are extremely air and moisture sensitive. Therefore, all the manipulations were carried out under purified argon using Schlenk technique with rigorous exclusion air and moisture. THF was refluxed and distilled over sodium benzophenone ketyl immediately before use. n-Hexane was distilled over finely divided LiAlH$_4$ prior to use. 3,5-Dimethylpyrazole [16] and MeCp$_3$Ln(Ln = Nd, Gd, Dy) [17] were prepared as previously described. The high-vacuum dimethylsilicone grease was purchased and was used as received. Elemental analyses for carbon, hydrogen and nitrogen were performed on a PE 2400 analyzer. Metal analyses for lanthanides were accomplished using the literature method [18]. Silicon analysis was performed on a Jarrell–Ash 1100 + 2000 ICP Quantometer. Infrared spectra were obtained on a PE 983G spectrometer with samples prepared as Nujol mulls in CsI pellets. Mass spectra were recorded on a VG ZAB-HS mass spectrometer operating in EI mode.

2.2. Syntheses of 1–3

MeCp$_3$Nd (0.218 g, 0.57 mmol) and HPzMe$_2$ (0.11 g, 1.14 mmol) were mixed in tetrahydrofuran(THF) solution (15 ml). After stirring for 48 h at ambient temperature, the reaction solution was concentrated by reduced pressure to about 2 ml. Then 20 ml of n-hexane was added to it and a pale-blue solid was deposited. 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-blue powder of 1.

According to a similar procedure, 2 and 3 could be readily obtained with good yields.

MeCpNd(PzMe$_2$)$_2$(1): pale blue, yield, 62%, m.p. 126°C (dec.). Anal. Found: C, 46.12; H, 5.16; N, 13.27; Nd, 34.65. C$_{16}$H$_{21}$N$_4$Nd Calcd.: C, 46.46; H, 5.11; N, 13.55; Nd, 34.87%. IR (cm^{-1}): 3196m, 3126m, 3105m, 3050m, 3030m, 2919s, 2855s, 2728m, 1592m, 1463s, 1440m, 1377s, 1367m, 1306m, 1154m, 1029m, 1010m, 885m, 780m, 672m, 436wb, 403wb, 245w, 208m. MS: m/e [fragment, relative intensity (%)] = 79 [MeCp, 16.7], 95 [PzMe$_2$, 24.9], 96 [HPzMe$_2$, 36.2], 223 [MeCpNd, 4.6], 237 [NdPzMe$_2$, 6.1], 334 [Nd(PzMe$_2$)$_2$, 0.9].

MeCpGd(PzMe$_2$)$_2$(2): colorless, yield, 69%, m.p. 135° (dec.). Anal. Found: C, 44.89; H, 4.87; N, 13.19; Gd, 36.71. C$_{16}$H$_{21}$N$_4$Gd Calcd.: C, 45.04; H, 4.96; N, 13.13; Gd, 36.87. IR (cm^{-1}): 3196m, 3126m, 3107m, 3045m, 3030m, 2916s, 2856s, 2728m, 2330m, 1591m, 1461s, 1442m, 1377s, 1365m, 1305m, 1153m, 1030m, 1010m, 886m, 780m, 670m, 438wb, 404wb, 245w,

207m. MS: m/e [fragment, relative intensity (%)] = 79 [MeCp, 87.2], 95 [PzMe$_2$, 32.4], 237 [MeCpGd, 12.6], 253 [GdPzMe$_2$, 3.7], 332 [MeCpGdPzMe$_2$, 2.1], 427 [MeCpGd(PzMe$_2$)$_2$, 0.2], 506 [Gd(PzMe$_2$)$_2$, 0.7], 775 [M$_2$-MeCp, 0.3].

MeCpDy(PzMe$_2$)$_2$(3): pale, yield, 60%, m.p. 148°C (dec.). Anal. Found: C, 44.26; H, 4.82; N, 12.79; Dy, 37.87. C$_{16}$H$_{21}$N$_4$Dy Calcd.: C, 44.50; H, 4.90; N, 12.98; Dy, 37.63. IR (cm^{-1}): 3198m, 3127m, 3108m, 3045m, 3030m, 2920s, 2858s, 2729m, 2330m, 1592m, 1461sb, 1440m, 1377s, 1367m, 1028m, 1010m, 885m, 781m, 671m, 438wb, 404wb, 245m, 205m. MS: m/e [fragment, relative intensity (%)] = 79 [MeCp, 67.2], 95 [PzMe$_2$, 29.6], 243 [MeCpDy, 16.5], 338 [MeCp-DyPzMe$_2$, 6.2], 433 [M, 0.8], 518 [Dy$_2$(PzMe$_2$)$_2$, 1.2], 708 [M$_2$-2MeCp, 0.9], 787 [M$_2$-MeCp, 0.3].

2.3. Insertion of dimethylsilanone into a Ln–N bond for complexes 1–3

To a THF solution (15 ml) of [MeCpLn(PzMe$_2$)$_2$] (0.4 mmol), 0.03 g of high-vacuum dimethylsilicone grease dissolved in THF was slowly added. After stirring for 48 h at room temperature, the reaction solution was concentrated under reduced pressure to ca. 2 ml. Then, 10 ml of n-hexane was slowly diffused into it and a crystal product was obtained.

MeCpNd(PzMe$_2$)(OSiMe$_2$PzMe$_2$)(4): blue-purple, yield, 35%, Anal. Found: C, 43.98; H, 5.56; N, 11.17; Si, 5.20; Nd, 29.11. C$_{18}$H$_{27}$ON$_4$SiNd Calcd.: C, 44.32; H, 5.58; N, 11.49; Si, 5.76; Nd, 29.57. IR (cm^{-1}): 3200m, 3130m, 3050m, 2975s, 2920s, 2860s, 1593w, 1440s, 1306w, 1035m, 1010m, 886m, 835m, 782m, 675w, 438w, 406w.

MeCpGd(PzMe$_2$)(OSiMe$_2$PzMe$_2$)(5): pale-yellow, yield, 47%. Anal. Found: C, 41.81; H, 5.31; N, 10.72; Si, 5.21; Gd, 30.36. C$_{18}$H$_{27}$ON$_4$SiGd Calcd.: C, 41.83; H, 5.26; N, 10.81; Si, 5.43; Gd, 30.43. IR (cm^{-1}): 3199m, 3130m, 3107m, 2976s, 2919s, 2860s, 1592m, 1440s, 1306w, 1032m, 1010m, 885m, 834m, 780m, 672w, 436w, 408w.

MeCpDy(PzMe$_2$)(OSiMe$_2$PzMe$_2$)(6): yellow, yield, 40%. Anal. Found: C, 42.14; H, 5.42; N, 10.97; Si, 5.36; Dy, 32.67. C$_{18}$H$_{27}$ON$_4$SiDy Calcd.: C, 42.72; H, 5.38; N, 11.08; Si, 5.55; Dy, 32.67. IR (cm^{-1}): 3199m, 3130m, 3107m, 2976s, 2919s, 2860s, 1592m, 1440m, 1306m, 1030m, 1010m, 885m, 833m, 781m, 672w, 437w, 405w.

2.4. X-ray crystal structure determination of 6

The crystal of 6 suitable for X-ray analysis was sealed under argon in a Lindemann glass capillary. The intensities were recorded on an Enraf–Nonius CAD4 diffractometer with graphite-monochromated Mo K_α radiation. The $\omega - 2\theta$ scan mode was utilized. Accu-

rate cell parameters were obtained by the least-squares refinement of the setting angles of 25 reflections with $12.21° < \theta < 15.56°$. The intensities were corrected for Lorentz-polarization effects and empirical absorption. A summary of the data collection parameters is given in Table 1.

The structure was solved by the direct method using the TEXSAN program [19]. All nonhydrogen atoms were found from the difference Fourier syntheses. 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. All calculations were performed on a Micro VAX 3100 computer. The atomic coordinates and equivalent thermal parameters of all the nonhydrogen atoms are listed in Table 2.

3. Results and discussion

3.1. Syntheses and spectroscopic characterization of 1–3

Complexes $MeCpLn(PzMe_2)_2$ (Ln = Nd, Gd, Dy) can be prepared by reaction of $(MeCp)_3Ln$ with two

Table 1
Crystal and data collection parameters of 6

Formula	$C_{36}H_{54}O_2N_8Si_2Dy_2$
Molecular weight	1012.04
Crystal size (mm)	0.38×0.32×0.25
Crystal color	yellow-green
Crystal system	monoclinic
Space group	$P2_1/n$
Lattice parameters	
a (Å)	12.066(5)
b (Å)	11.601(2)
c (Å)	15.307(3)
β (°)	105.85(3)
V (Å^3)	2061(1)
Z	2
Dc (g cm^{-3})	1.63
F (000)	1004
Radiation	Mo K$_\alpha$ ($\lambda = 0.71069$ Å)
μ (cm^{-1})	37.27
Scan width (°)	0.80+0.35 tan θ
Scan speed (° min^{-1})	< 5.49
hkl range	0–14, 0–13, −18–18
2 θ_{max} (°)	49.9
No. of reflections measured	4000
No. of unique reflections observed	3866
No. of reflections observed [$I > 3\sigma(I)$]	2930
No. of variables	226
R	0.031
R_ω	0.040
S	1.16
W	$1/\sigma^2$ (F)
$(\Delta/\sigma)_{max}$	0.07
$\Delta\rho_{max}$ (e Å^{-3})	0.61

Table 2
Atomic coordinates and equivalent thermal parameters for complex 6

Atom	x	y	z	B(eq)
Dy	0.35496(2)	0.02209(2)	0.01203(2)	2.68(1)
Si	0.4396(1)	0.1182(1)	−0.1810(1)	2.97(6)
O	0.4662(3)	0.0508(3)	−0.0852(3)	2.8(1)
N(1)	0.2658(5)	0.1981(4)	−0.0312(4)	3.8(2)
N(2)	0.3647(4)	0.2239(4)	0.0365(3)	3.6(2)
N(3)	0.3680(4)	0.0091(4)	0.1745(3)	3.5(2)
N(4)	0.4506(4)	−0.0616(4)	0.2289(3)	3.1(2)
C(1)	0.3675(6)	0.3378(6)	0.0470(5)	4.4(3)
C(2)	0.2715(7)	0.3855(6)	−0.0111(5)	4.8(3)
C(3)	0.2106(6)	0.2977(6)	−0.0600(5)	4.3(3)
C(4)	0.465(1)	0.3941(8)	0.1175(7)	8.1(5)
C(5)	0.0992(7)	0.2952(8)	−0.1343(6)	6.7(4)
C(6)	0.4300(6)	−0.0736(6)	0.3119(4)	3.6(3)
C(7)	0.3337(7)	−0.0096(6)	0.3096(5)	4.7(3)
C(8)	0.2988(6)	0.0408(6)	0.2239(5)	4.6(3)
C(9)	0.5038(7)	−0.1428(6)	0.3872(4)	4.7(3)
C(10)	0.1996(8)	0.121(1)	0.1852(6)	7.5(5)
C(11)	0.2214(9)	−0.1647(7)	0.0236(6)	6.0(4)
C(12)	0.1478(7)	−0.081(1)	−0.0259(8)	6.8(5)
C(13)	0.1725(7)	−0.0636(8)	−0.1097(6)	6.1(4)
C(14)	0.2611(7)	−0.1367(6)	−0.1096(5)	4.8(3)
C(15)	0.2919(7)	−0.1979(6)	−0.0322(6)	5.2(3)
C(16)	0.206(1)	−0.211(1)	0.104(1)	13(1)
C(17)	0.2985(6)	0.0861(6)	−0.2609(4)	4.2(3)
C(18)	0.4585(6)	0.2760(6)	−0.1694(5)	4.2(3)

$Beq = (8\pi^2/3)\Sigma i \; \Sigma j \; \cup \; ij \; \alpha_i^* \; \alpha_j^* a_i a_j.$

equivalent $HPzMe_2$ in THF at room temperature Eq. (1). These complexes are soluble in ethers such as THF but less soluble in hydrocarbon solvents such as hexane at room temperature. They are highly sensitive toward air and water. All of three compounds has no melting points and decomposes at above 125°C.

$$MeCp_3Ln + 2HPzMe_2 \rightarrow MeCpLn(PzMe_2)_2 + 2MeCpH$$
$$Ln = Nd(1), Gd(2), Dy(3) \tag{1}$$
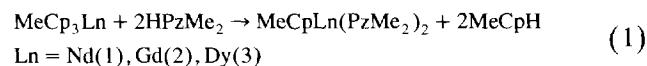
Complexes 1–3 have been characterized by elemental analysis, IR and mass spectra. Satisfactory elemental analyses were obtained. The IR spectra of all the complexes are very similar and display four characteristic absorptions of the η^5-MeCp group at ca. 3045, 1440, 1010, and 780 cm^{-1}; those at 2975, 2855, 1461 and 1365 cm^{-1} to the methyl group. The absorptions for 3,5-dimethylpyrazolyl ligand appear markedly at about 3030, 1592, 1305, 1029, 885 and 672 cm^{-1}. From the IR spectra of all the complexes, two nonligand bands are observed at 438 and 404 cm^{-1}. This suggests that $PzMe_2$ groups have two different modes for binding to metal. The higher wave number may be attributed to the absorption of the Ln–N(chelating) stretching vibration, while the low wave number is that of the Ln–N(bridging) vibration. The mass spectrum of all these complexes displays a series of peaks representing clearly the fragments derived from dimer $[MeCpLn(\eta^2-PzMe_2)(\mu-PzMe_2)]_2$, although their molecular ions were not observed. The presence of peak corresponding to $[Ln_2(PzMe_2)_2]^+$ in the mass spectra evidently indi-
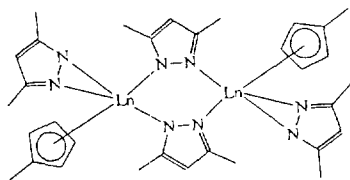
Fig. 1. The proposed structure for complexes 1–3.

cates the pyrazolyl-bridged structure of the complexes. Thus, based on the above analytical and spectral results, the structure of complexes 1–3 may be proposed as shown in Fig. 1.

3.2. Insertion of [Me₂SiO] into Ln–N bond for complexes 1–3

Addition of a THF solution of dimethysilicone grease to MeCpLn(PzMe₂)₂ (Ln = Nd, Gd, Dy) in THF generated the dimethylsilanone insertion products: [MeCpLn(η²-PzMe₂)(μ-η¹:η²-OSiMe₂PzMe₂)]₂ [Nd(4), Gd(5), Dy(6)], which have been fully identified by elementary analysis and IR spectroscopy. Complex 6 has yet been determined by X-ray crystallography. This result is consistent with our previous studies [15]. It is noteworthy that in the insertion, the dimethylsilicone grease must be slowly added. If the dimethylsilicone grease was directly put into the reaction solution at once, a like-cotton precipitate would generate.

Although a number of insertion reactions have been found in organometallic chemistry and the insertion of the Ln–N bond for organolanthanide complexes has also been known [20–22], to our knowledge, the inser-

Table 3
Selected bond distances (Å) of 6

Dy–Dyᵃ	3.654(2)	N(3)–C(8)	1.322(9)
Dy–O	2.285(4)	N(3)–N(4)	1.381(7)
Dy–Oᵃ	2.304(4)	N(4)–C(6)	1.367(7)
Dy–N(1)	2.319(5)	C(1)–C(2)	1.37(1)
Dy–N(2)	2.368(5)	C(1)–C(4)	1.51(1)
Dy–N(3)	2.454(5)	C(2)–C(3)	1.35(1)
Dy–C(14)	2.643(7)	C(3)–C(5)	1.51(1)
Dy–C(13)	2.658(7)	C(6)–C(7)	1.37(1)
Dy–C(12)	2.687(8)	C(6)–C(9)	1.485(9)
Dy–C(15)	2.696(7)	C(7)–C(8)	1.39(1)
Dy–C(11)	2.735(7)	C(8)–C(10)	1.50(1)
Si–O	1.615(4)	C(11)–C(12)	1.39(1)
Si–N(4)ᵃ	1.803(5)	C(11)–C(16)	1.40(2)
Si–C(17)	1.842(7)	C(11)–C(15)	1.41(1)
Si–C(18)	1.847(7)	C(12)–C(13)	1.41(1)
N(1)–C(3)	1.346(8)	C(13)–C(14)	1.36(1)
N(1)–N(2)	1.383(7)	C(14)–C(15)	1.34(1)
N(2)–C(1)	1.331(8)	Dy–Centlᵇ	2.368(1)

ᵃSymmetry operator: 1 − x, − y, − z.
ᵇCent = centroid of MeCp ring.

tion of an Me₂SiO fragment into the M–N bond is unprecedented in organometallic chemistry. This may give a new insight into the reactivity of pyrazolyl organometallic complexes. Further investigations into the mechanism of the insertion reaction and its scope and generality are underway.

3.3. Description and discussion of crystal structure of 6

The molecular structure of 6 is shown in Fig. 2. Selected bond distances and angles are listed in Tables
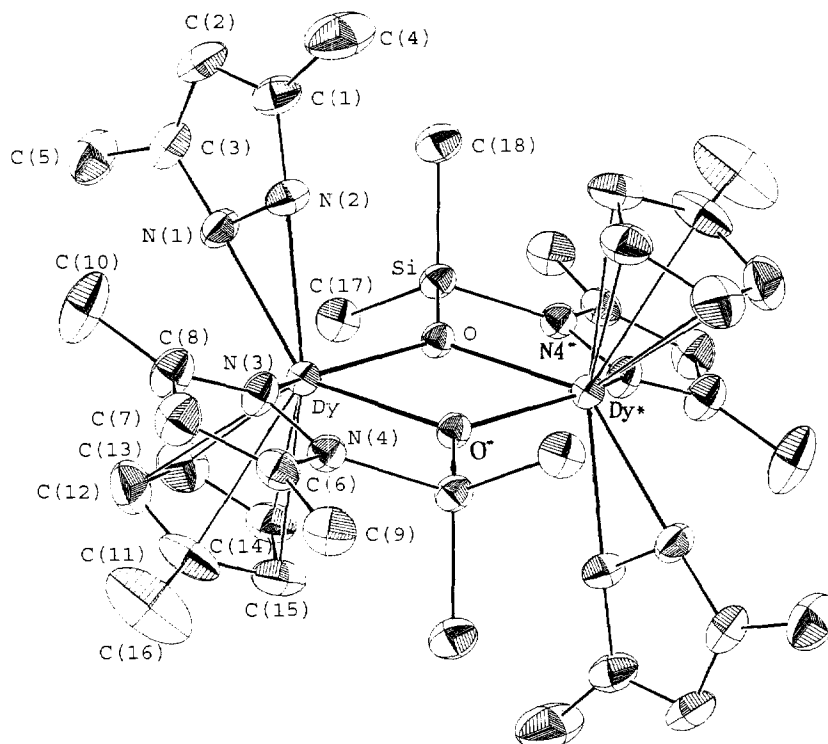

Fig. 2. Molecular structure of [MeCpDy(η²-PzMe₂)(μ-OSiMe₂PzMe₂)]₂.

3 and 4. The complex is a centrosymmetric dimer in which each dysprosium atom is coordinated by one methylcyclopentadienyl group, two bridging oxygens, two nitrogens of the chelating 3,5-dimethylpyrazolyl ligand and one nitrogen atom of the bridging 3,5-dimethylpyrazolyl ligand to form a distorted octahedron. The Dy_2O_2 unit is planar. The MeCp ring lies nearly perpendicular to the plane of the chelating 3,5-dimethylpyrazolyl ring (78.8°), while the bridging 3,5-dimethylpyrazolyl ring is almost parallel to this plane (7.6°). This is probably caused by steric effects between the ligands. Consistent with this, the MeCp ring is in an unusual elliptic conformation with respect to the dysprosium atom. The geometry of 6 is similar to that of the isostructural complex [MeCpYb(η^2-PzMe$_2$)(μ-η^1:η^2-OSiMe$_2$PzMe$_2$)]$_2$, except that bond distances involving the metal atom are generally lengthened [15].

The Dy–C(MeCp) distances range from 2.643(7) to 2.735(7) Å and are in the normal ranges observed for the lanthanide metallocenes. The average Dy–C(MeCp) distance of 2.684(16) Å is compatible with those found in related compounds: [Cp$_2$Dy(μ-OCMe = CHCH$_3$)]$_2$, 2.668(6) Å [23]; Cp$_3$Dy(THF), 2.70 Å [24]. The average Dy–O distance is 2.294(10) Å and at the high end of the range typical for trivalent dimeric oxygen-bridging organolanthanide complexes [23], and is slightly longer than those found in [Cp$_2$Dy(μ-OCMe = CHCH$_3$)]$_2$, average 2.257(4) Å; [C$_8$H$_8$Dy(μ-OCH$_2$CH$_2$CH$_2$CH = CH$_2$)(THF)]$_2$, average 2.260(3) Å [25]. The reason for the lengthening of the Dy–O bond can be attributed to the steric effect caused by the chelating coordination of Dy^{3+} to N atom of the bridging OSiMe$_2$PzMe$_2$ unit.

It is noteworthy that two metal centers in 6 are linked by oxygen bridges instead of nitrogen ones as is usually observed in other dimeric pyrazolyl–metal complexes [1–3]. Presumably because this is favorable space to the center metal to achieve the highest possible coordination number and satisfy the demand of its coordination saturation. If complex 6 were yet a hypothetical pyrazolyl-bridge structure related to those usually found in

pyrazolyl organometallic complexes, the oxygen atoms should become nonbridging coordination. As a result, the steric unsaturation around the center metal ion would be enhanced with diminishing coordination number, thus leading to the change of the coordination mode from pyrazolyl bridges to oxygen bridges. The nitrogen atoms of the chelating 3,5-dimethylpyrazolyl ligand, which exhibit Dy–N distances of 2.319(5) and 2.368(5) Å, are closer to the metal atom than that of the bridging ligand [2.454(5) Å], but the N=N bond distances for the two PzMe$_2$ rings do not differ. The Dy–N(chelating) and Dy–N(bridging) distances are between the values typical for a Ln–N single bond and a N → Ln donor bond [26,27] and are consistent with the corresponding values of other pyrazolyl-containing compounds, respectively, when the difference in the ionic radii is considered, e.g., Yb$_3$(μ-PzMe$_2$)$_6$(η^2-PzMe$_2$)$_3$(μ_3-O)Na$_2$(THF)$_2$ [2.298(5), 2.348(5) and 2.446(5) Å, respectively] [28] and [MeCpYb(η^2-PzMe$_2$)(μ-η^1:η^2-OSiMe$_2$PzMe$_2$)]$_2$ [2.270(6), 2.326(7) and 2.402(7) Å, respectively] [15].

Another remarkable feature of the structure is that the heterobinuclear centers (Yb and Si) are bridged in unusual ways by two different ligands. The coordination environment about the silicon atom has the normal tetrahedral arrangement. The average Si–C distance of 1.845(7) Å is similar to those observed in (C$_5$Me$_5$)Ce[N(SiMe$_3$)$_2$]$_2$, 1.83(8) Å [26]; [(C$_5$Me$_5$)$_2$Sm(THF)]$_2$(μ-OSiMe$_2$OSiMe$_2$O), 1.860(9) Å [29]. The Si–O distance of 1.615(4) Å is nearly equal to the Si–O distance in [(C$_5$Me$_5$)$_2$Sm(THF)]$_2$(μ-OSiMe$_2$OSiMe$_2$O) [average 1.623(4) Å]. The Si–N distance of 1.803(5) Å is slightly longer than those found in (C$_5$Me$_5$)Ce[N(SiMe$_3$)$_2$]$_2$, 1.712(7) and 1.713(7) Å [26]. The O–Dy–O and Dy–O–Dy angles are 74.4(1) and 105.6(1)°, respectively, which are similar to the values usually observed in [Cp$_2$Ln(μ-OR)]$_2$-type complexes [23]. This result revealed that the bridging Ln$_2$O$_2$ unit is rigid and is hardly affected by the changes of the lanthanide ion and R group.

Table 4
Selected bond angles of 6 (°)

O^a–Dy–O	74.4(1)	N(4)–Si–C(18)	108.4(3)
O–Dy–N(1)	89.7(2)	N(4)–Si–C(17)	107.8(3)
O–Dy–N(2)	86.9(2)	C(17)–Si–C(18)	109.3(3)
O–Dy–N(3)	141.5(2)	Si–O–Dy	131.0(2)
O^a–Dy–N(1)	139.7(2)	Dy^a–O–Dy	105.6(1)
O^a–Dy–N(2)	106.7(2)	C(3)–N(1)–Dy	177.1(5)
O^a–Dy–N(3)	72.1(2)	N(2)–N(1)–Dy	74.8(3)
N(1)–Dy–N(2)	34.3(2)	N(1)–N(2)–Dy	70.9(3)
N(1)–Dy–N(3)	103.9(2)	C(8)–N(3)–Dy	133.4(4)
N(2)–Dy–N(3)	85.1(2)	N(4)–N(3)–Dy	118.9(3)
O–Si–N(4)^a	101.9(2)	C(6)–N(4)–Si	132.9(4)
O–Si–C(18)	113.8(3)	N(3)–N(4)–Si	117.5(4)
O–Si–C(17)	115.1(3)	Si–O–Dy^a	123.2(2)

^{a}Symmetry operator: $1 - x$, $- y$, $- z$.

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