Novel Insertion of Dimethylsilanone into an Yb–N Bond and Molecular Structure of the Insertion Product [{Yb(η^2-$C_3N_2HMe_2$-3,5)(μ-η^1:η^2-$OSiMe_2C_3N_2HMe_2$-3,5)(η-C_5H_4Me)}$_2$]

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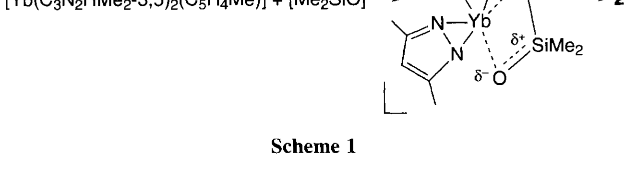
When [Yb($C_3N_2HMe_2$-3,5)$_2$(C_5H_4Me)] ($C_3N_2H_2Me_2$-3,5 = 3,5-dimethylpyrazole) is recrystallized by slow diffusion of hexane into a thf solution which contains a small amount of dimethylsilicone grease, it is converted into to the unexpected complex [{Yb(η^2-$C_3N_2HMe_2$-3,5)(μ-η^1:η^2-$OSiMe_2C_3N_2HMe_2$-3,5)(η-C_5H_4Me)}$_2$] indicating a novel Me_2SiO insertion reaction.

Pyrazole-type heterocycles represent an important class of ligands in organometallic chemistry and the coordination of these ligands to metals and metalloids has been extensively investigated.[1–3] They can act as neutral monodentate, anionic monodentate, *exo*-bidentate, *exo*-bidentate with side-on donating coordination, or *endo*-bidentate ligands on coordination to metal centres. Since their introduction in the 1960s, the syntheses of a number of transition-metal complexes incorporating pyrazolyl ligands have been studied. 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] Despite both these attractive features and the extensive development of pyrazole coordination chemistry in general, knowledge of their cyclopentadienyllanthanide complexes is rather limited to date.[8] On the other hand, there is also increasing interest in activating unsaturated molecules with organolanthanide complexes. Insertion of CO into Ln–N bonds is one of the most interesting reactions in the area.[9,10] Continuing our recent investigations of N-containing systems,[11,12] and to learn more about the pyrazolate ion as a ligand, we report here on the synthesis of a new pyrazolyl-containing organolanthanide complex [Yb($C_3N_2HMe_2$-3,5)$_2$(C_5H_4Me)] and its reactivity with dimethylsilanone-containing materials, in which an unprecedented Me_2SiO insertion into an Ln–N bond was observed.

[Yb(C_5H_4Me)$_3$] (0.41 g, 1.0 mmol) and $C_3N_2H_2Me_2$-3,5 (0.129 g, 2.0 mmol) were mixed in tetrahydrofuran (thf) solution (20 ml)† and allowed to stir at ambient temperature for 72 h, the solvent was then removed under reduced pressure, and the residue was washed with *n*-hexane and dried *in vacuo*, giving 0.25 g of [Yb($C_3N_2HMe_2$-3,5)$_2$(C_5H_4Me)] **1** in 56% yield. When **1** was recrystallized by slow diffusion of hexane into a thf solution of the compound in an H-tube which was sealed at the ground-glass joints with high-vacuum dimethylsilicone grease for several months, it was converted into bright yellow crystals of [{Yb(η^2-$C_3N_2HMe_2$-3,5)(μ-η^1: η^2-$OSiMe_2C_3N_2HMe_2$-3,5)(η-C_5H_4Me)}$_2$] **2** in 26% yield (Scheme 1). Complexes **1** and **2** have been characterized by elemental analysis and spectroscopic properties.‡ Complex **2** was also identified by X-ray crystallography.§

As shown in this study, although pyrazole type ligands have been known for a long time and have been used extensively in organometallic and coordination chemistry, their chemical character is not yet fully understood. To our knowledge, the insertion of an Me_2SiO fragment into an Ln–N bond is unprecedented in organometallic chemistry and may give a new insight into the reactivity of pyrazolyl organometallic complexes.



Scheme 1

Fig. 1 shows an ORTEP drawing of **2**. The complex is a centrosymmetric dimer in which each ytterbium atom is coordinated by one methylcyclopentadienyl group, two bridging oxygens, two nitrogens of the chelating pyrazolyl ligand and one nitrogen atom of the bridging pyrazolyl ligand to form a distorted octahedron. The C_5H_4Me ring lies nearly perpendicular to the plane of the chelating 3,5-dimethylpyrazolyl ring (79.23°), while the bridging 3,5-dimethylpyrazolyl ring is almost parallel to this plane (8.14°). This is probably caused by steric effects between the ligands. Consistent with this, the C_5H_4Me ring is in an unusual eclipsed conformation with respect to the ytterbium atom. The average Yb–O and Yb–C(C_5H_4Me) distances [2.249(5) and 2.644(9) Å, respectively] are at the high end of the range typical for trivalent dimeric organoytterbium complexes,[13–15] and are in good agreement with those found in the more steric crowded complexes [Yb(C_5H_4Me)$_3$] [average Yb–C(C_5H_4Me) 2.64 Å][16] and [Yb_4(C_5H_4Me)$_3$(μ-Cl)$_6$(μ_3-Cl)(μ_4-O)(thf)$_3$] (average Yb–O 2.24 Å).[17]

It is noteworthy that two metal centres in **2** are linked by oxygen bridges instead of nitrogen bridges as is usually observed in other dimeric pyrazolyl–metal complexes.[2] The

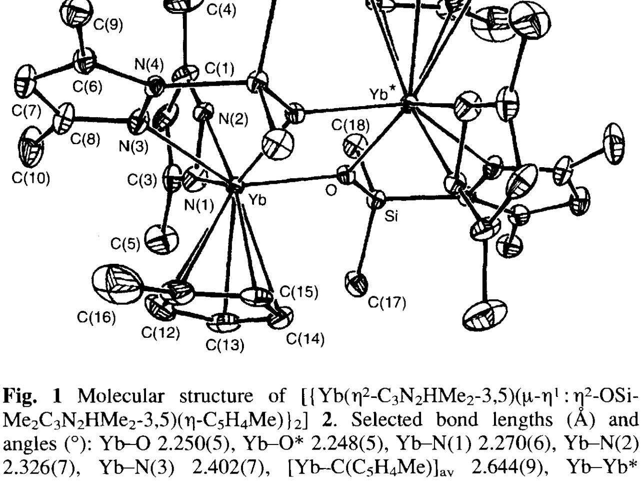


Fig. 1 Molecular structure of [{Yb(η^2-$C_3N_2HMe_2$-3,5)(μ-η^1:η^2-$OSiMe_2C_3N_2HMe_2$-3,5)(η-C_5H_4Me)}$_2$] **2**. Selected bond lengths (Å) and angles (°): Yb–O 2.250(5), Yb–O* 2.248(5), Yb–N(1) 2.270(6), Yb–N(2) 2.326(7), Yb–N(3) 2.402(7), [Yb–C(C_5H_4Me)]$_{av}$ 2.644(9), Yb–Yb* 3.574(1), Si–O 1.615(5), Si–N(4*) 1.792(6), Si–C(18) 1.824(9), Si–C(17) 1.831(9), N(1)–N(2) 1.38(1), N(3)–N(4) 1.395(9); Yb–O–Yb* 105.3(2), O–Yb–O* 74.7(2), N(1)–Yb–N(2) 34.9(2), N(1)–Yb–N(3) 102.3(2), N(2)–Yb–N(3) 84.1(2), C(17)–Si–C(18) 109.3(4), O–Si–C(17) 115.1(3), O–Si–C(18) 114.6(4), O–Si–N(4) 102.1(3), C(17)–Si–N(4) 106.5(4), C(18)–Si–N(4) 108.5(4), N(3)–N(4)–Si 116.2(5), N(4)–N(3)–Yb 119.1(5), O–Yb–N(1) 89.5(2), O–Yb–N(2) 86.1(2), O–Yb–N(3) 142.5(2).

Yb_2O_2 unit is planar. The nitrogen atoms of the chelating 3,5-dimethylpyrazolyl ligand, which exhibit Yb–N distances of 2.270(6) and 2.326(7) Å, are closer to the metal atom than that of the bridging ligand [2.402(7) Å], but the N=N bond distances for the two rings do not differ. The Yb–N (bridging) distance is identical with those found in $[\{Ln[O(CH_2CH_2C_5H_4)_2]\}_2(\mu\text{-}C_3N_2HMe_2\text{-}3,5)(\mu\text{-}OH)]$ (Ln = Y or Lu) (Y–N 2.44 Å, Lu–N 2.39 Å),[8] when the differences in the ionic radii is considered. The Yb–N(chelating) distances are comparable with the corresponding values observed in $[Yb_3(\mu\text{-}C_3N_2HMe_2\text{-}3,5)_6(\eta^2\text{-}C_3N_2HMe_2\text{-}3,5)_3(\mu_3\text{-}O)Na_2(C_3N_2H_2Me_2\text{-}3,5)_2]$ of 2.348(5) and 2.298(5) Å.[18]

Another remarkable feature of the structure is that the heterobinuclear centres (Yb and Si) are bridged in unusual ways by two different ligands.[8] The coordination environment about the silicon atom is approximately tetrahedral. The Si–N distance of 1.792(6) Å is slightly longer than those found in $[Sm(C_5Me_5)\{N(SiMe_3)_2\}]$, 1.712(7)–1.713(7) Å.[19] Evidently, this variation results from the steric bulk of the ligands; the metal–ligand interaction would be enhanced with a reduction in the size of the ligands. The average Si–C and Si–O distances [1.826(9) and 1.616(5) Å, respectively] are similar to those observed in $[\{(C_5Me_5)_2(thf)\}_2(\mu\text{-}OSiMe_2OSiMe_2O)]$, Si–C 1.860(9) and Si–O 1.623(4) Å.[20]

This research is supported by a grant for a key research project from the State Science and Technology Commission and NSF of China.

Received, 20th June 1994; Com. 5/03993B

Footnotes

† All manipulations were performed under argon using Schlenk techniques with rigorous exclusion air and moisture.

‡ Satisfactory elemental analyses were obtained for **1** and **2**. *Spectroscopic data* for **1**: IR (KBr, cm^{-1}): 3196m, 3127m, 3107m, 3080m, 2919s, 2728m, 1592m, 1461s, 1306m, 1154m, 1029m, 1010m, 885m, 781m, 672w, 438w, 404w, 206m. MS(EI): m/z (fragment, relative intensity %) = 96 ($C_3N_2H_2Me_2$, 32.8%), 95 ($C_3N_2HMe_2$, 24.6), 79 (C_5H_4Me, 6.7).

§ *Crystal data for* **2**: M_r = 1033.13, monoclinic, space group $P2_1/n$, a = 12.035(2), b = 11.460(2), c = 15.393(1) Å, β = 106.32(2)°, U = 2037.5(9) $Å^3$, Z = 2, D_c = 1.68 g cm^{-3}, $F(000)$ = 1020, μ = 46.47 cm^{-1}. The intensity data were collected on an Enraf-Nonius CAD-4 diffractometer at 296 K, using graphite-monochromated Mo-Kα radiation (λ = 0.71073 Å), ω–2θ scan mode. 3932 reflections were measured in the range $2 \leqslant 2\theta \leqslant 50°$, 3817 unique reflections, 3054 of which with $I > 3\sigma(I)$ were used for refinement. Intensities were corrected for Lorentz-polarization effects and empirical absorption. The structure was solved by the heavy-atom method using the TEXSAN program and Fourier techniques, refined on F, 226 parameters. R = 0.045, R_w = 0.058 for $w = 1/\sigma^2(F)$. Final difference maps showed no peaks > 1.75 or < −1.36 e $Å^{-3}$. All Δ/ρ values < 0.02. The H atoms were placed at calculated positions. All the calculations were performed on a MICRO VAX 3100 computer. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Information for Authors, Issue No. 1.

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