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New Interventions by silicone grease in synthesis

Daniel Werner,^[a] Nazli E. Rad,^[b] Zhifang Guo,^[b] Glen B. Deacon,^[a] and Peter C. Junk^{*,[b]}

Dedicated to our good friend, Professor Thomas Schleid on the occasion of his 65th birthday.

In redox-transmetallation protolysis (RTP) reactions in tetrahydrofuran (thf) between excess scandium or cerium metal, $\text{Hg}(\text{C}_6\text{F}_5)_2$ and 3,5-dimethylpyrazole (Me_2pzH) in silicone greased Schlenk flasks, formation of the 3,5-dimethyl-1-pyrazolyl(dimethyl)siloxide ($\text{Me}_2\text{pzSiMe}_2\text{O}$) ligand was observed.

Thus the former reaction gave $[\text{Sc}_2(\text{Me}_2\text{pz})_4(\text{Me}_2\text{pzSiMe}_2\text{O})_2]$ **1** in good yield, whilst the latter gave a mixture of $[\text{Ce}_4\text{O}(\text{Me}_2\text{pz})_9(\text{Me}_2\text{pzSiMe}_2\text{O})_2]$ **2a**, $[\text{Ce}_4\text{O}(\text{Me}_2\text{pz})_{11}]$ **2b**, both mixed oxidation state species, and the Ce^{V} complex $[\text{Ce}(\text{Me}_2\text{pz})_4(\text{Me}_2\text{pzH})]$ **2c**.

Introduction

Silicone grease is frequently the lubricant of choice for vacuum taps and joints in Schlenk lines used for the manipulation of highly reactive organometallics, alkoxides, organoamides and related species. Nevertheless, it is not always an innocent bystander, and sufficient examples of its reactivity to produce unexpected and exotic products have occurred as to warrant two reviews.^[1–2] Since then a number of further examples of such reactivity have emerged.^[3–4] Notably there has been a recent report of the formation of mixed alkoxido/siloxido compounds of Ce^{IV} , Sr/Zr , and Sn/In , which are of interest as possible sources of metal/silicon oxide composites.^[5] It has earlier been shown that Me_2SiO from grease can insert into a $\text{Yb}-\text{N}$ bond of $[\text{Yb}(\text{MeCp})(\text{Me}_2\text{pz})_2]$ (MeCp = methylcyclopentadienyl; Me_2pz = 3,5-dimethylpyrazolate) to give $[\text{Yb}(\text{Me}_2\text{pz})(\text{MeCp})(\text{Me}_2\text{pzSiMe}_2\text{O})_2]$ ($\text{Me}_2\text{pzSiMe}_2\text{O}$ = 3,5-dimethyl-1-pyrazolyl(dimethyl)siloxide)^[6] and similar reactions were observed for $[\text{LnCp}(\text{Me}_2\text{pz})_2]$ ($\text{Ln} = \text{Dy}, \text{Ho}$).^[7] However reactions of grease with pyrazolate complexes do not necessarily lead to insertion, as sodium 3,5-di-*tert*-butylpyrazolate yields $[\text{Na}_4(\text{tBu}_2\text{pz})_2(\text{thf})_2(\text{OSiMe}_2)_2\text{O}]$ with the $\text{OSiMe}_2\text{OSiMe}_2\text{O}$ disiloxide ligand,^[8] and the same ligand was also obtained in silicone-grease-derived $\{\text{Ba}_6(\text{dmpz})_8(\text{thf})_6(\text{OSiMe}_2)_2\text{O}\}_2$.^[9] On the other hand, Me_2SiO can insert into other $\text{M}-\text{N}$ bonds, e.g. the $\text{Li}-\text{N}$ bond of lithiated 6-methyl-2-aminopyridine.^[10] In this contribution, we report that the $\text{Me}_2\text{pzSiMe}_2\text{O}$ ligand is also formed in redox transmetallation/protolysis (RTP) reactions of two free rare earth metals in silicone greased Schlenk flasks.

Results and discussion

Synthesis and Characterisation

The rare earth 3,5-dimethylpyrazolate complex, $[\text{Sc}_2(\text{Me}_2\text{pz})_4(\text{Me}_2\text{pzSiMe}_2\text{O})_2]$ **1** [Scheme 1 1] with a pyrazolylsiloxide ligand was isolated following redox-transmetallation protolysis (RTP) reactions in thf between excess rare earth metal, $\text{Hg}(\text{C}_6\text{F}_5)_2$ and 3,5-dimethylpyrazole. $[\text{Sc}_2(\text{Me}_2\text{pz})_4(\text{Me}_2\text{pzSiMe}_2\text{O})_2]$ **1** was obtained in 55% yield after the reaction mixture was stirred for one week, unsuccessful crystallization attempts were made including heating and partial evaporation, and the resulting solution was stored for several weeks (see experimental) with exposure to silicone stopcock grease at all stages. Thus, depolymerisation of $[\text{SiMe}_2\text{O}]_n$ grease and insertion into $\text{Sc}-\text{N}$ bonds occurred [Scheme 1 eq(1)]. The presence of a resonance at $\delta = 0.29$ ppm in the ^1H NMR spectrum of **1** can be attributed to methyl H atoms of SiMe_2O and is consistent with the X-ray crystal structure (below). The reaction was repeated using different solvents (acetonitrile and DME) in place of THF and in each case the same compound was isolated and identified by unit cell measurements. Meaningful microanalyses could not be obtained due to extreme air sensitivity and international transport to the analyst, but a Sc analysis on a freshly prepared sample was close to the expected value for the single crystal composition (see below).

The formation of $[\text{Ce}_4\text{O}(\text{Me}_2\text{pz})_9(\text{Me}_2\text{pzSiMe}_2\text{O})_2]$ **2a**, $[\text{Ce}_4\text{O}(\text{Me}_2\text{pz})_{11}]$ **2b**, and $[\text{Ce}(\text{Me}_2\text{pz})_4(\text{Me}_2\text{pzH})]$ **2c** [Scheme 1 2a–2c] resulted from an attempt to increase the yield of $[\text{Ce}_2(\text{Me}_2\text{pz})_6(\text{thf})_2]$ [Scheme 1 eq(2)] from the RTP reaction between Ce metal, $\text{Hg}(\text{C}_6\text{F}_5)_2$ and 3,5-dimethylpyrazole in thf.^[11] After the filtered reaction mixture was evaporated to dryness, only 60–70% of the resulting powder could be manually recovered. Accordingly the remaining solid was extracted with toluene and heated at 60 °C in a silicone greased flask, whereupon the colour of the solution became deep red and crystallization from toluene/hexane yielded three sets of crystals, which were identified by X-ray crystallography. **2a** contained an Me_2SiO group that has inserted into a $\text{Ce}-\text{N}$ bond of a $\text{Ce}-\text{Me}_2\text{pz}$ fragment. Pure bulk material could not be

[a] D. Werner, G. B. Deacon

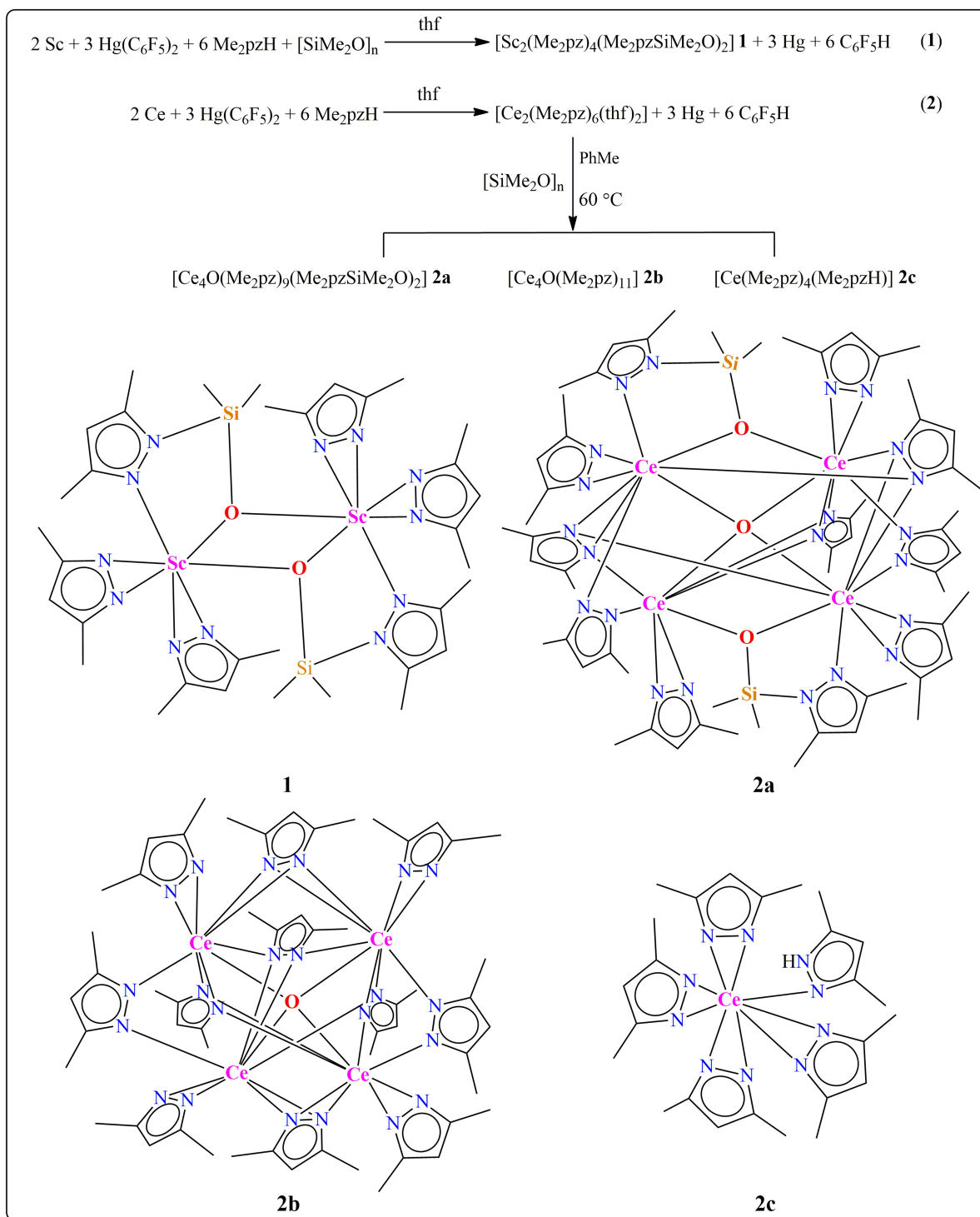
School of Chemistry, Monash University, Clayton 3800, Australia.

[b] N. E. Rad, Z. Guo, P. C. Junk

College of Science & Engineering, James Cook University, Townsville 4811, Qld, Australia.

E-mail: peter.junk@jcu.edu.au

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Scheme 1. Synthetic routes towards compounds **1**, **2a**, **2b** and **2c**.

separated for microanalyses. Formation of **2b** (and **2c**) presumably arises when no further “Me₂SiO” can be extracted from the grease. Both **2a** and **2b** are mixed oxidation state species (formally 3 Ce^{III}:1 Ce^{IV}) on the basis of stoichiometry (below), and are related by replacement of 2 Me₂pz by two Me₂pz-(SiMe₂O) ligands. Whilst adventitious oxygen, entering owing to

extraction of grease by toluene, is the most likely source of the oxido ligands of **2a** and **2b**, reduction of Me₂SiO by the excess of Ce metal is also a possible contributor.

[Ce(Me₂pz)₄(Me₂pzH)] **2c**, a Ce^{IV} species, crystallised as deep red blocks, similar to [Ce(Me₂pz)₄L] (L = thf, Me₂pzH or O) and toluene solvates of the L = 0 species,^[12] and contrasts **2a** (pale

pink) or **2b** (white). It is a different crystal form from that previously isolated.^[12c] Polymorphism has been observed with other $[\text{Ce}(\text{Me}_2\text{pz})_4\text{L}]$ species.^[12] An NMR scale reaction between $[\text{Ce}_2(\text{Me}_2\text{pz})_6(\text{thf})_2]$ and silicone grease in C_6D_6 showed that, on heating, the Me resonance of the grease disappeared and the solution turned the bright red colour of **2c**.

Molecular structures

Complex **1** $[\text{Sc}_2(\text{Me}_2\text{pz})_4(\text{Me}_2\text{pzSiMe}_2\text{O})_2]$ crystallised as colourless crystals from THF and the structure was solved and refined in the triclinic space group $P-1$ with two whole molecules occupying the asymmetric unit. The complex is a near centrosymmetric dimer in which two bridging tridentate ($\mu-1\kappa(\text{N},\text{O}):2\kappa(\text{O})$) pyrazolylsiloxide ligands cap the metals at opposite sides of the dimer. The anionic oxygen of the siloxide ligand bridges between the two scandium atoms. Each seven coordinate scandium atom is ligated by two terminal η^2 -pyrazolates, one pyrazolyl nitrogen and two siloxide oxygen atoms (Figure 1). The Sc–O (ave. 2.115 Å) and Sc–N (ave. 2.191 Å) bond lengths are shorter than the values reported for the Yb–O (2.250(5) Å) and Yb–N (avg. 2.332 Å) in the formally eight-coordinate Yb in $[\text{Yb}(\eta^2\text{-Me}_2\text{pz})(\eta^5\text{-MeCp})(\mu-1\kappa(\text{N},\text{O}):2\kappa(\text{O})\text{OSiMe}_2\text{Me}_2\text{pz})_2]$ due to the larger ionic radius of Yb^{3+} (0.868 Å) compared with Sc^{3+} (0.745 Å),^[6] and the coordination

number difference. Compound **1** shows a similar bond length relationship with those of the centrosymmetric dimer $[\text{HoCp}(\text{Me}_2\text{pz})(\text{OSiMe}_2\text{Me}_2\text{pz})_2]$.^[7] The Si–N bond lengths of compound **1** (Figure 1) are close to the Si–N distance in $[\text{HoCp}(\text{Me}_2\text{pz})(\text{OSiMe}_2\text{Me}_2\text{pz})_2]$ (1.806(5) Å).^[7]

Complex $[\text{Ce}_4\text{O}(\text{Me}_2\text{pz})_9(\text{Me}_2\text{pzSiMe}_2\text{O})_2]$ **2a** (Figure 2) crystallised as light pink crystals and was solved in the orthorhombic space group $Pbcn$ with half the cage within the asymmetric unit. $[\text{Ce}_4\text{O}(\text{Me}_2\text{pz})_{11}]$ **2b** was obtained from the same reaction mixture, and crystallises in the monoclinic space group $C2/c$, with half the molecule occupying the asymmetric unit (Figure 2). There were no obvious signs of a Me_2pzH ligand in either structure, nor was a H^+ located on the oxide ligand, and therefore summation of the anionic charges in both complexes indicate a $\text{Ce}^{\text{III}}_3\text{Ce}^{\text{IV}}$ constitution. However the symmetry of each complex with only two crystallographically different Ce atoms, which have similar Ce–O(N) bond lengths (Table 1), means no oxidation state differentiation can be made and each cerium atom can be considered to have the oxidation state +3.25. In two reported $\text{Ce}^{\text{III}}/\text{Ce}^{\text{IV}}$ alkoxide complexes, one has crystallographic differentiation of atoms with the two oxidation states^[13a] and one does not.^[13b] Both complexes **2a** and **2b** are oxygen centred clusters. The central oxide ligand, bridges to four cerium atoms with tetrahedral stereochemistry. In **2a**, Ce1 is nine coordinate and Ce2 is eight coordinate. Ce1 is coordinated by the central oxygen (O1), a terminal η^2 - Me_2pz

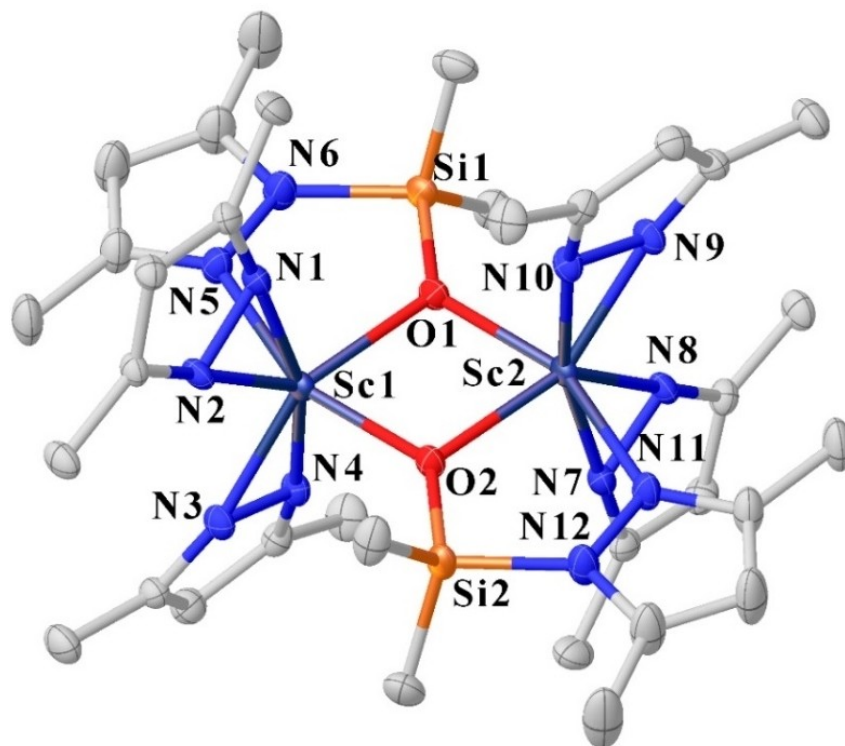


Figure 1. Molecular diagram of $[\text{Sc}_2(\text{Me}_2\text{pz})_4(\text{Me}_2\text{pzSiMe}_2\text{O})_2]$ **1** represented by 50% thermal ellipsoids. The hydrogen molecules have been omitted for clarity. Selected bond lengths (Å) and angles (°) for **1**: Sc1–O1 2.137(3), Sc1–O2 2.091(3), Sc1–N1 2.189(4), Sc1–N2 2.148(3), Sc1–N3 2.147(4), Sc1–N4 2.173(3), Sc1–N5 2.278(4), Sc2–O1 2.091(2), Sc2–O2 2.139(3), Sc2–N7 2.175(4), Sc2–N8 2.163(3), Sc2–N9 2.152(3), Sc2–N10 2.167(3), Sc2–N11 2.278(4), Si1–O1 1.610(3), Si1–N6 1.795(4), Si2–O2 1.611(3), Si2–N12 1.794(4).

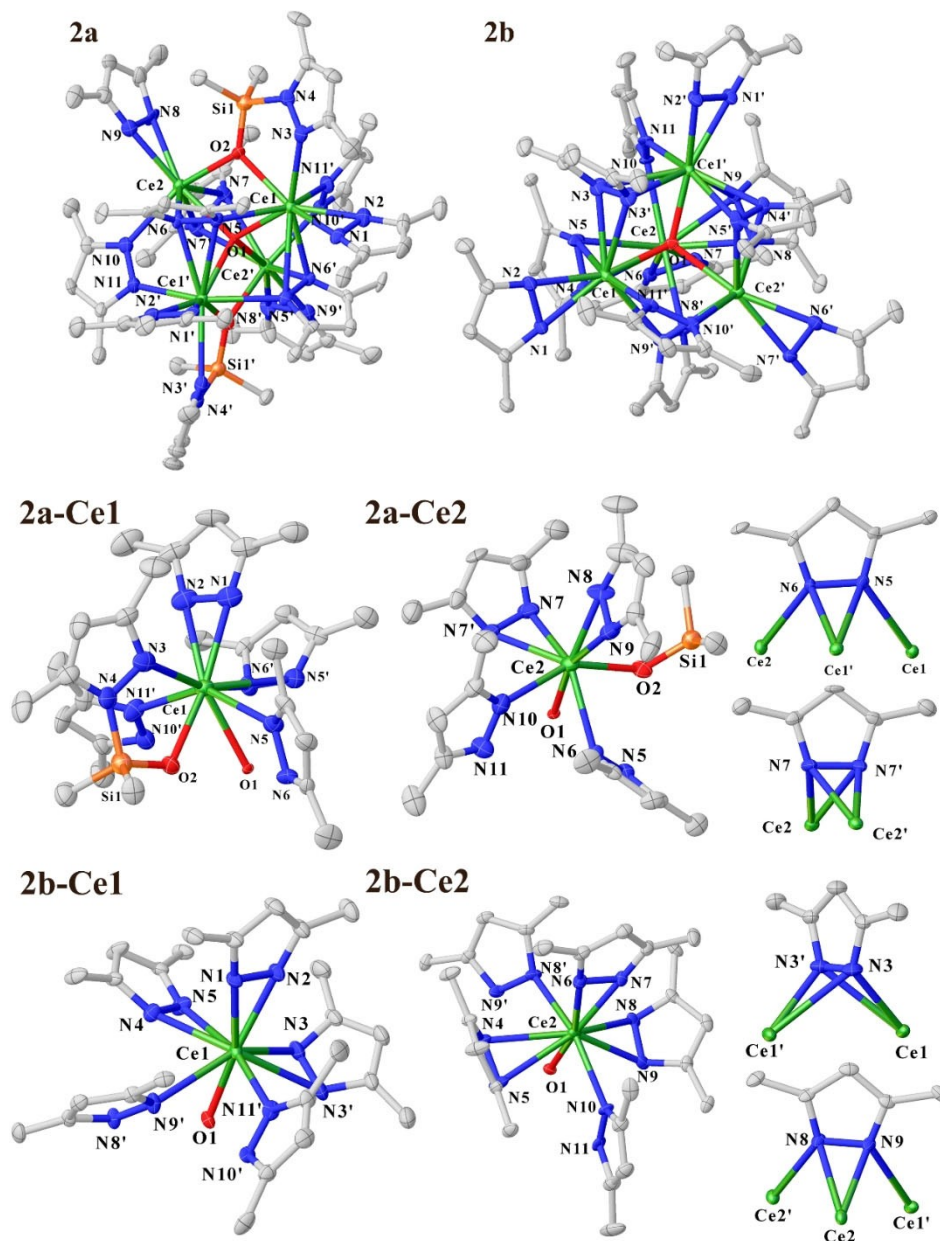


Figure 2. Molecular diagram of $[\text{Ce}_4\text{O}(\text{Me}_2\text{pz})_9(\text{Me}_2\text{pzSiMe}_2\text{O})_2]$ (**2a**) and $[\text{Ce}_4\text{O}(\text{Me}_2\text{pz})_{11}]$ (**2b**) represented by 50% thermal ellipsoids. The hydrogen atoms have been omitted for clarity. Top row: complete structures, second and third rows environment of Ce1 and Ce2 and two of the pyrazolate binding modes of **2a** and **2b** respectively.

(N1,N2), chelation by N5'/N6' of a $\mu_3\text{-}1\kappa(\text{N}):2\eta^2:3\kappa(\text{N}')$ ligand, a single nitrogen (N5) of the symmetry related ligand, a single nitrogen (N11') of a bridging bidentate ($\mu\text{-}1\kappa(\text{N}):2\kappa(\text{N}')$), and N3,O2 of a chelating pyrazolylsiloxide ligand. Ce2 is bonded by the central O1, a chelating (N8,N9) pyrazolate, N6 from a $1\kappa(\text{N}):2\eta^2:3\kappa(\text{N}')$ donor, N7,N7' of a $\mu\text{-}\eta^2:\eta^2\text{-Me}_2\text{pz}$, N10 from a bridging bidentate pyrazolate, and O2 of the pyrrolylsiloxide, which thus bridges Ce1 and Ce2. In **2b**, Ce1 is coordinated by the central oxygen (O1), a terminal Me_2pz (N1 N2), N3,N3' and N4,N5 of $\mu\text{-}\eta^2:\eta^2$ ligands, and N9' from a $\mu_3\text{-}1\kappa(\text{N}):2\eta^2:3\kappa(\text{N}')$ ligand and N11' from a bridging bidentate ligands. Ce2 is bound by O1, a chelating pyrazolate (N6,N7), N4,N5 of a $\mu\text{-}\eta^2:\eta^2\text{-Me}_2\text{pz}$, N8,N9 of a $\mu_3\text{-}1\kappa(\text{N}):2\eta^2:3\kappa(\text{N}')$ ligand, N8' of the symmetry related ligand, and N10 of a bridging bidentate Me_2pz . In **2b**, a $\mu\text{-}\eta^2:\eta^2$ ligand replaces the pyrazolylsiloxide ligand of **2a**.

$[\text{Ce}(\text{Me}_2\text{pz})_4(\text{Me}_2\text{pzH})]$ **2c** crystallises as deep red blocks in the triclinic space group $P\bar{1}$. The structural solution required resolution of significant disorder (see Experimental). The nine coordinate Ce atom is ligated by four terminal η^2 -pyrazolates and one η^1 -pyrazolyl nitrogen atom (Figure 3). While the bond lengths are broadly similar to those of a reported polymorph,^[11] the considerable disorder of the latter precludes a close comparison.

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Table 1. Selected bond lengths (Å) and angles (°) for complexes **2a** and **2b**.

2a		2b		2b		2b	
bond lengths	2a (Å)	bond lengths	2a (Å)	bond lengths	2b (Å)	bond lengths	2b (Å)
Ce1–O1	2.548(5)	Ce2–O1	2.400(5)	Ce1–O1	2.303(2)	Ce2–O1	2.427(2)
Ce1–O2	2.489(7)	Ce2–O2	2.405(7)	Ce1–N1	2.432(3)	Ce2–N4	2.726(4)
Ce1–N1	2.476(10)	Ce2–N6	2.619(9)	Ce1–N2	2.402(4)	Ce2–N5	2.745(5)
Ce1–N2	2.463(9)	Ce2–N7	2.615(10)	Ce1–N3	2.579(4)	Ce2–N6	2.443(4)
Ce1–N3	2.677(9)	Ce2–N8	2.458(9)	Ce1–N4	2.495(4)	Ce2–N7	2.444(3)
Ce1–N5	2.649(8)	Ce2–N9	2.459(9)	Ce1–N5	2.658(4)	Ce2–N8	2.715(4)
Ce1–N5'	2.898(8)	Ce2–N10	2.529(9)	Ce1–N3'	2.754(4)	Ce2–N9	2.650(4)
Ce1–N6'	2.665(8)	Ce2–N7'	2.686(10)	Ce1–N9'	2.734(3)	Ce2–N10	2.564(2)
Ce1–N11'	2.564(9)			Ce1–N11'	2.719(19)	Ce2–N8'	2.647(3)
Si1–N4	1.780(10)	Si1–O2	1.618(7)				
bond angles	2a (°)	bond angles	2a (°)	bond angles	2b (°)	bond angles	2b (°)
Ce1–O1–Ce2	109.20	Ce1–O1–Ce2'	108.80(3)	Ce1–O1–Ce2	108.24(3)	Ce1–O1–Ce2'	109.46(3)
Ce1–O1–Ce1'	105.7(3)	Ce2–O2–Ce1'	111.0(3)	Ce1–O1–Ce1'	115.4(2)	Ce2–O1–Ce2'	105.61(3)

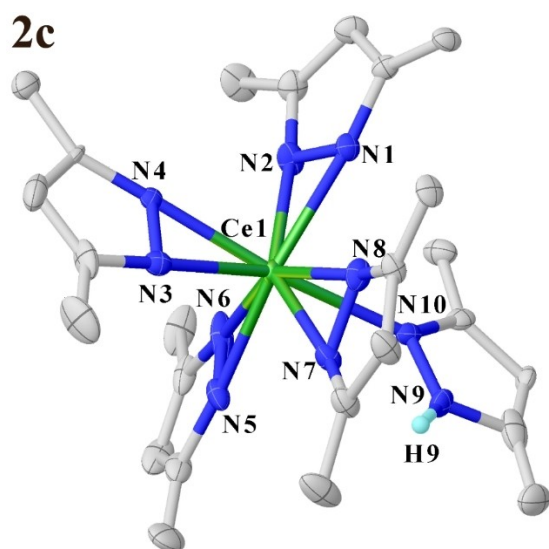


Figure 3. Molecular diagram of $[\text{Ce}(\text{Me}_2\text{pz})_4(\text{Me}_2\text{pzSiMe}_2\text{O})_2]$ **2c** represented by 50% thermal ellipsoids. The hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (°) for complexes **2c**: Ce–N1 2.361(3), Ce–N2 2.338(4), Ce–N3 2.348(5), Ce–N4 2.321(5), Ce–N5 2.307(4), Ce–N6 2.323(4), Ce–N7 2.426(4), Ce–N8 2.385(4), Ce–N10 2.597 (4).

Conclusions

This study provides new examples of the capacity of silicone grease to intervene in syntheses. In one case a scandium complex with the 3,5-dimethyl-1-pyrazolyl(dimethyl)siloxide ligand was isolated in good yield. The other gave a mixture of products which not only included one with the pyrazolylsiloxide ligand, but also products formed when the silicone grease source was exhausted.

Experimental

General

The compounds described here were prepared and handled using vacuum-nitrogen line techniques and a dry box under an atmosphere of purified nitrogen. All solvents were pre-dried with sodium metal and then further dried by distillation over sodium or sodium/benzophenone. Rare earth metals were from Santoku/Molycorp/Eutectix. Large chunks were filed in the drybox before use. 3,5-Dimethylpyrazole (Me_2pzH) was purchased from Aldrich/Sigma-Aldrich. IR spectra were recorded as Nujol mulls between NaCl plates using a Nicolet-Nexus FT-IR spectrometer within the range 4000–600 cm^{-1} . ^1H NMR spectra were recorded on a Bruker 400 MHz spectrometer. Crystals were measured on a Bruker P4 diffractometer or the MX1 beamline at the Australian Synchrotron. CCDC 2181607 for **1**, 2181608 for **2a**, 2181609 for **2b**, and 2181610 for **2c**, contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre.

$[\text{Sc}_2(\text{Me}_2\text{pz})_4(\text{Me}_2\text{pzSiMe}_2\text{O})_2]$ **1**

Scandium filings (0.32 g, 2.3 mmol), $\text{Hg}(\text{C}_6\text{F}_5)_2$ (1.1 g, 2.0 mmol), and Me_2pzH (0.39 g, 4.0 mmol), were added to a Schlenk flask and dissolved with stirring in THF (15 mL), at room temperature for one week. The resulting suspension was filtered through a pad of Celite and concentrated to 5 mL (by exposure to vacuum), stored at $\sim 4^\circ\text{C}$ for one week. As no crystal formation occurred, the mixture was heated and allowed to slowly cool to room temperature. Upon storage at -25°C for several weeks, small colourless crystals of $[\text{Sc}_2(\text{Me}_2\text{pz})_4(\text{Me}_2\text{pzSiMe}_2\text{O})_2]$ were obtained. Yield = 0.97 g (55%); IR (Nujol, cm^{-1}): $\nu = 2726$ (w), 1591 (w), 1519 (m), 1504 (m), 1305 (m), 1154 (m), 1071 (w), 1028 (m), 1009 (w), 956 (w), 845 (vw), 777 (m), 722 (w), 660 cm^{-1} (vw). ^1H NMR (C_6D_6 , 303.2 K): $\delta = 0.44$ (s, 12H, Me-SiMe₂), 1.78 (br s, 36 H, Me), 5.4 ppm (s, 6 H, H4-Me₂pz). Elemental analysis calcd. (%) for $\text{C}_{34}\text{H}_{54}\text{N}_{12}\text{O}_2\text{Sc}_2\text{Si}_2$ ($M = 808.99 \text{ g}\cdot\text{mol}^{-1}$): Sc 11.11; Found from complexometric titration: Sc 10.38.

$[\text{Ce}_4\text{O}(\text{Me}_2\text{pz})_9(\text{Me}_2\text{pzSiMe}_2\text{O})_2]$ **2a**, $[\text{Ce}_4\text{O}(\text{Me}_2\text{pz})_{11}]$ **2b** and $[\text{Ce}(\text{Me}_2\text{pz})_4(\text{Me}_2\text{pzH})]$ **2c**

Ce metal (0.60 g, 4.3 mmol), $\text{Hg}(\text{C}_6\text{F}_5)_2$ (1.22 g, 2.28 mmol) and Me_2pzH (0.43 g, 4.5 mmol) were stirred in THF within a Schlenk flask. After stirring for several days, the solution was filtered from

the metal residues and evaporated to dryness *in vacuo*. Much of the resulting white powder, $[\text{Ce}_2(\text{Me}_2\text{pz})_6(\text{thf})_2]^{(11)}$ (60–70%) was scraped from the Schlenk flask, and the residual powder in the flask was dissolved in PhMe (10 mL) and heated to 60 °C. The solution changed colour from light yellow to deep red within hours of heating. Concentration of the reaction mixture and addition of hexane yielded three crystalline sets: light pink crystals of $[\text{Ce}_4\text{O}(\text{Me}_2\text{pz})_9(\text{Me}_2\text{pzSiMe}_2\text{O})_2]$ **2a**, small colourless crystals of $[\text{Ce}_4\text{O}(\text{Me}_2\text{pz})_{11}]$ **2b**, and deep red crystals $[\text{Ce}(\text{Me}_2\text{pz})_4(\text{Me}_2\text{pzH})]$ **2c**. The compositions were determined by X-ray crystallography.

X-ray crystallography

Complex **2a** was measured on a 'Bruker P4' diffractometer with integration and absorption corrections completed using Apex II program suite.^[14] Complexes **1**, **2b**, and **2c** were determined at the Australian Synchrotron on the MX1 beamline, where the data and integration were completed by Blue-ice^[15] and XDS^[16] software programs. Structural solutions were obtained by SHELXT^[17] using full-matrix least-squares methods against F^2 using SHELXL2018,^[17] in conjunction with the Olex2^[18] graphical user interface. All hydrogen atoms were placed in calculated positions using the riding model.

$[\text{Sc}_2(\text{Me}_2\text{pz})_4(\text{Me}_2\text{pzSiMe}_2\text{O})_2]$ **1**: $\text{C}_{34}\text{H}_{54}\text{N}_{12}\text{O}_2\text{Sc}_2\text{Si}_2$, ($M = 808.99$), triclinic, space group $P-1$ (no. 2), $a = 11.627(2)$ Å, $b = 19.250(4)$ Å, $c = 21.050(4)$ Å, $\alpha = 108.99(3)^\circ$, $\beta = 103.68(3)^\circ$, $\gamma = 94.28(3)^\circ$, $V = 4269.4(17)$ Å³, $Z = 4$, $\mu(\text{MoK}\alpha) = 0.418$ mm⁻¹, 68313 reflections measured, 14963 unique ($R_{\text{int}} = 0.0422$), which were used in all calculations. The final wR_2 was 0.1964 (all data) and R_1 was 0.0768 ($I > 2\sigma(I)$).

$[\text{Ce}_4\text{O}(\text{Me}_2\text{pz})_9(\text{Me}_2\text{pzSiMe}_2\text{O})_2]$ **2a**: $\text{C}_{59}\text{H}_{89}\text{Ce}_4\text{N}_{22}\text{O}_3\text{Si}_2$ ($M = 1771.18$ g/mol): orthorhombic, space group $Pbcn$ (no. 60), $a = 14.5797(11)$ Å, $b = 25.140(2)$ Å, $c = 19.5444(15)$ Å, $V = 7163.7(10)$ Å³, $Z = 4$, $\mu(\text{MoK}\alpha) = 2.584$ mm⁻¹, $D_{\text{calc}} = 1.642$ g/cm³, 42898 reflections measured ($3.22^\circ \leq 2\theta \leq 50^\circ$), 6308 unique ($R_{\text{int}} = 0.1567$) which were used in all calculations. The final R_1 was 0.0504 ($> 2\sigma(I)$) and wR_2 was 0.1600 (all data).

$[\text{Ce}_4\text{O}(\text{Me}_2\text{pz})_{11}]$ **2b**: $\text{C}_{55}\text{H}_{77}\text{Ce}_4\text{N}_{22}\text{O}$ ($M = 1622.86$): monoclinic, space group $C2/c$ (no. 15), $a = 23.059(5)$ Å, $b = 13.156(3)$ Å, $c = 22.579(5)$ Å, $\beta = 111.10(3)^\circ$, $V = 6390(3)$ Å³, $Z = 4$, $\mu = 2.851$ mm⁻¹, $D_{\text{calc}} = 1.687$ g/mm³, 73878 reflections measured ($3.63 \leq 2\theta \leq 63.112$), 9315 unique ($R_{\text{int}} = 0.0730$) which were used in all calculations. The final R_1 was 0.0392 ($I > 2\sigma(I)$) and wR_2 was 0.0963 (all data).

$[\text{Ce}(\text{Me}_2\text{pz})_4(\text{Me}_2\text{pzH})]$ **2c**: $\text{C}_{25}\text{H}_{36}\text{CeN}_{10}$ ($M = 616.76$): triclinic, space group $P-1$ (no. 2), $a = 8.4870(17)$ Å, $b = 9.1640(18)$ Å, $c = 10.570(2)$ Å, $\alpha = 108.16(3)^\circ$, $\beta = 110.10(3)^\circ$, $\gamma = 91.31(3)^\circ$, $V = 725.7(3)$ Å³, $Z = 1$, $\mu = 1.599$ mm⁻¹, $D_{\text{calc}} = 1.411$ g/mm³, 23756 reflections measured ($7.644 \leq 2\theta \leq 63.028$), 4318 unique ($R_{\text{int}} = 0.0739$) which were used in all calculations. The final R_1 was 0.0495 ($I > 2\sigma(I)$) and wR_2 was 0.1264 (all data). The structural solution contained significant disorder, **2c** is modelled as a whole molecule disorder (including the metal atom) over the inversion centre so all atoms are half occupancy. Due to the extensive disorder, each ligand has been restrained to be flat with a fixed 5-membered ring with additional restraints on the C–Me distances.

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

Keywords: Redox transmetallation protolysis (RTP) reactions · Silicone grease · 3,5-dimethylpyrazole · Scandium and mixed oxidation and tetravalent Ce complexes · Crystal structures

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