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Rare Earth and Alkaline Earth Metal Complexes with Me_2Si-Bridged Cyclopentadienyl-Imidazolin-2-Imine Ligands and Their Use as Constrained-Geometry Hydroamination Catalysts

Tarun K. Panda,[a] Cristian G. Hrib,[a] Peter G. Jones,[a] Jelena Jenter,[b] Peter W. Roesky,[b] and Matthias Tamm*[a]

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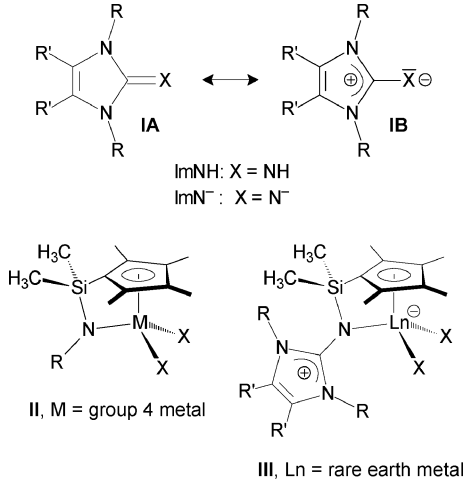
The imidazolin-2-imino-functionalized tetramethylcyclopentadiene, **3**-H, has been prepared by the reaction of two equivalents of 1,3-diisopropyl-4,5-dimethylimidazolin-2-imine (**1**) with 5-(chlorodimethylsilyl)-1,2,3,4-tetramethyl-1,3-cyclopentadiene (**2**). The reactions of **3**-H with the trimethylsilylmethyl (neosilyl) $[Ln(CH_2SiMe_3)_3(THF)_2]$ (Ln = Sc, Y, Lu) complexes afford tetramethylsilane and the constrained-geometry $[(\eta^5{:}\eta^1\text{-}\mathbf{3})Ln(CH_2SiMe_3)_2]$ (Ln = Sc, **4a**; Ln = Y, **4b**; Ln = Lu, **4c**) complexes, whereas the analogous bis(trimethylsilyl)amido (HMDS) calcium complex, $[(\eta^5{:}\eta^1\text{-}\mathbf{3})\text{-}Ca(HMDS)(THF)]$ (**5**), can be obtained from **3**-H and $[Ca(HMDS)_2(THF)_2]$ with loss of hexamethyldisilazane, $(Me_3Si)_2NH$. The molecular structures of **4a**–**4c** and **5** have been established by X-ray diffraction analyses, which confirm in all cases the formation of complexes with a chelating Me_2Si-bridged cyclopentadienyl-imidazolin-2-imine ligand. The presence of short Ln–N and Ca–N bonds is indicative of the strong electron-donating capacity of the imidazolin-2-imino nitrogen atom, which is based on the ability of the imidazolium ring to effectively stabilize a positive charge. The rare earth metal complexes **4a**–**4c** can be used as efficient catalysts for the hydroamination/cyclization reaction of terminal aminoalkenes and aminoalkynes.

Introduction

Imidazolin-2-imines (ImNH) and imidazolin-2-imides (ImN^-) can be described by two limiting resonance structures, **IA** and **IB**, which indicates that the ability of the imidazolium ring to stabilize a positive charge leads to highly basic ligands with a strong electron-donating capacity towards transition metals (Scheme 1).[1–3] We have recently established a general method for the preparation of these ligands from stable carbenes of the imidazolin-2-ylidene type and trimethylsilyl azide. This procedure resembles the Staudinger reaction[4] between phosphanes and azides and furnishes 2-trimethylsilyliminoimidazolines (X = $SiMe_3$),[3] which are suitable precursors for the synthesis of transition metal complexes incorporating ancillary imidazolin-2-iminato ligands (X = N^-).[5] Owing to their ability to act as 2σ,4π-electron donors, these ligands can be regarded as monodentate analogues of cyclopentadienyl derivatives (C_5R_5) and also as monoanionic imido ligands in a similar fashion to that described for related phosphoraneiminato ligands.[6] These characteristics have been exploited for the development of imidazolin-2-iminato tungsten alkylidyne complexes as catalysts for efficient room-temperature alkyne metathesis,[7] and also for the preparation of lanthanide complexes with very short Ln–N bonds, which can serve as accurate models for elusive mononuclear lanthanide imido complexes.[8]



Scheme 1. Mesomeric structures of imidazolin-2-imines and imides, and schematic representation of silylene-linked cyclopentadienyl-amido and cyclopentadienyl-imino complexes.

[a] Institut für Anorganische und Analytische Chemie, Technische Universität Carolo-Wilhelmina zu Braunschweig, Hagenring 30, 38106 Braunschweig, Germany
Fax: +49-531-391-5309
E-mail: m.tamm@tu-bs.de
[b] Institut für Anorganische Chemie, Universität Karlsruhe, Engesserstr. 15, 76128 Karlsruhe, Germany
Fax: +49-721-608-4854
E-mail: roesky@chemie.uni-karlsruhe.de

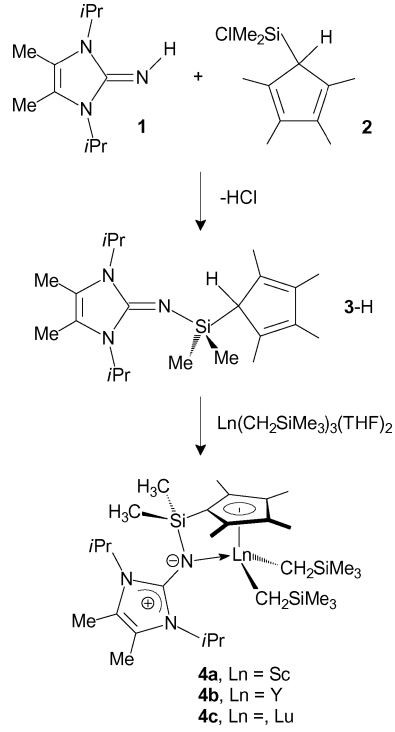
Imidazolin-2-imines (X = NH, Scheme 1) are not only valuable ligands or ligand precursors in their own right, but can also serve as useful building blocks for the design and preparation of novel multidentate poly(imidazolin-2-imine) ligands. Yet again, these ligands attain their unique properties from their ability to effectively delocalize a positive charge over the imidazole moiety to produce compounds with considerably enhanced basicity and N-nucleophilicity.[9–12] For instance, the unusual stability of coordinatively unsaturated 16-electron ruthenium and molybdenum half-sandwich complexes supported by ethylene-bridged bis(imidazolin-2-imine) ligands can be ascribed to the strongly π-basic nature of the novel bidentate ligands,[10] which also holds true for the high reactivity of copper(I) bis(imidazolin-2-imine) complexes and allows for effective CO_2 and O_2 fixation, C–Cl bond activation and Cu^I disproportionation.[11] Recently, the pronounced electron donor properties of these ligands have also been demonstrated by the synthesis and structural characterization of lanthanide complexes containing a bis(imidazolin-2-imino)pyridine pincer ligand, which confirms that the imine moieties act as ylidic amido-type ligands upon metal complexation.[12]

In a similar fashion, tethering of an imidazolin-2-imine unit to a cyclopentadienyl ring through a Me_2Si bridge leads to cyclopentadienyl-imidazolin-2-imine ligands, which can be expected to form functional "constrained-geometry" *ansa*-cyclopentadienyl-amido complexes, despite the overall neutral charge of the imine moiety. This concept has been realized by the preparation of chromium(III) complexes[13] that are structurally closely related to well-established and commercialized type **II** *ansa*-cyclopentadienyl-amido complexes containing tetravalent group 4 metals (Scheme 1).[14–16] The introduction of other trivalent metal atoms such as rare earth elements (group 3 metals and lanthanides) should also lead to isostructural complexes, as the resulting cyclopentadienyl-imidazolin-2-imine complexes, [(η^5:η^1-C_5R_4-$SiMe_2$-NIm)LnX_2] (**III**), require two monoanionic X ligands to attain an overall neutral charge.[17] In contrast, "conventional" silylene-linked cyclopentadienyl-amido complexes of the [(η^5:η^1-C_5R_4-$SiMe_2$-NR)LnX] (Ln = rare earth metal) type contain only one additional anionic ligand,[18] and ever since their introduction in the early 1990s,[19] these systems have attracted considerable interest because of their remarkable activity in various stoichiometric and catalytic processes.[18,20–25] *Monoalkyl* complexes have been of particular importance, and this contribution establishes the corresponding type **III** rare earth metal *dialkyl* complexes and compares their properties with those of their silylene-linked cyclopentadienyl-amido counterparts.

Results and Discussion

Ligand Synthesis

The imidazolin-2-imino-tetramethylcyclopentadiene ligand, **3**-H, was isolated as a yellow oil from the reaction of 5-(chlorodimethylsilyl)-1,2,3,4-tetramethyl-1,3-cyclopentadiene (**2**) with two equivalents of 1,3-diisopropyl-4,5-dimethylimidazolin-2-imine, Im$^{i\mathrm{Pr}}$NH (**1**). One equivalent of the imine serves as a hydrochloric acid scavenger and precipitates from the reaction mixture as the corresponding 2-aminoimidazolium chloride, **1**·HCl (Scheme 2).[13] The formation of cyclopentadiene **3**-H from imine **1** can easily be followed by ^{1}H NMR spectroscopy since four additional resonances are observed for the (tetramethylcyclopentadienyl)dimethylsilyl moiety, while the imine NH resonance disappears. The resonances of the imidazolin-2-imine moieties are only slightly shifted in comparison to those of imine **1** and are almost identical to those reported for the corresponding 2-(trimethylsilylimino)imidazoline molecule.[3,5b] No fluxional behaviour is observed for the cyclopentadiene moiety, and the ^{1}H NMR spectrum exhibits a singlet at δ = 3.20 ppm for the CH hydrogen atom along with two signals at about 2.22 and 1.97 ppm for the 2,4- and 3,5-methyl groups, respectively, which reveals that compound **3**-H adopts C_s symmetry with the silylene bridge in the allylic position. In the ^{13}C NMR spectra, product formation is indicated by a characteristic high-field shift of about 10 ppm for the imidazoline C2 (NCN) resonance (from 153.4 ppm in **1** to 144.2 ppm in **3**-H). The cyclopentadiene CH carbon resonance is observed at δ = 59.8 ppm, whereas the resonances for the tertiary carbon atoms in the 2,5- and 3,4-positions appear at δ = 134.5 and 133.9 ppm, respectively.



Scheme 2. Synthesis of cyclopentadienyl-imidazolin-2-imine complexes.

Synthesis and Characterization of Rare Earth Metal Complexes

Following the salt-free route developed for the preparation of trimethylsilylmethyl ("neosilyl") complexes of the

$[(\eta^5{:}\eta^1\text{-}C_5Me_4\text{-}SiMe_2\text{-}NR)Ln(CH_2SiMe_3)(THF)_n]$ (n = 1, 2) type,[20,21] the acid–base reaction between the rare earth metal $[Ln(CH_2SiMe_3)_3(THF)_2]$ (Ln = Sc, Y, Lu) trialkyl complexes and cyclopentadiene **3**-H in hexane at ambient temperature afforded the solvent-free $[(\eta^5{:}\eta^1\text{-}C_5Me_4\text{-}SiMe_2\text{-}NIm^{iPr})Ln(CH_2SiMe_3)_2]$ (Ln = Sc, **4a**; Ln = Y, **4b**; Ln = Lu, **4c**) complexes, which can be isolated in good yields as colourless crystalline solids from THF/pentane solutions at –30 °C (Scheme 2). As expected for time-averaged C_s-symmetric structures in solution, the ^{1}H NMR spectra of **4a**–**4c** in C_6D_6 exhibit four characteristic singlet resonances in a 6:6:6:6 ratio for four different types of methyl groups present in the cyclopentadienyl-imine ligand along with a low-field septet resonance at about 4.8 ppm for the isopropyl CH hydrogen atoms. The corresponding isopropyl CH_3 groups give rise to broad signals in the 1.23 to 1.08 ppm range, which indicates dynamic behaviour at room temperature on the NMR timescale. For the neosilyl (CH_2SiMe_3) groups, one singlet ($SiMe_3$) and two doublets with $^2J_{^1H,^1H}$ = 11 Hz are observed at high fields for each complex, which reveals the presence of diastereotopic CH_2 hydrogen atoms. These observations are in agreement with the assumption that the dynamic behaviour of complexes **4** in solution is mainly a result of rotation around the N–C_{imine} bond axes and does not involve cleavage of the Ln–N bonds. It should also be noted that the ^{1}H NMR spectrum of yttrium derivative **4b** in [D$_8$]THF shows a well-resolved doublet of doublets with a $^2J_{^{89}Y,^1H}$ coupling constant of 2.7 Hz, which falls in the range previously observed for neosilyl yttrium complexes.[20b,21e]

Single crystals of complexes **4a**–**4c** could be obtained from THF/hexane solutions, and their molecular structures could be established by X-ray diffraction analyses. **4a** (Ln = Sc) and **4c** (Ln = Lu) are isostructural and crystallize as hexane hemisolvates in the space group $P2_1/c$, whereas yttrium compound **4b** crystallizes without solvent incorporation in the space group $P2_1/n$ with two independent molecules in the asymmetric unit. The overall structural parameters of the three complexes are very similar, and pertinent data are summarized in Table 1. As a representative example, two different views of the molecular structure of the lutetium complex **4c** are shown in Figure 1. Coordination of the Cp-imine ligand, **3**, in a chelating $\eta^5{:}\eta^1$-fashion is confirmed for all complexes, and **4a**–**4c** exhibit a three-legged piano-stool geometry with a distorted pseudotetrahedral environment around the metal atoms. The solid-state

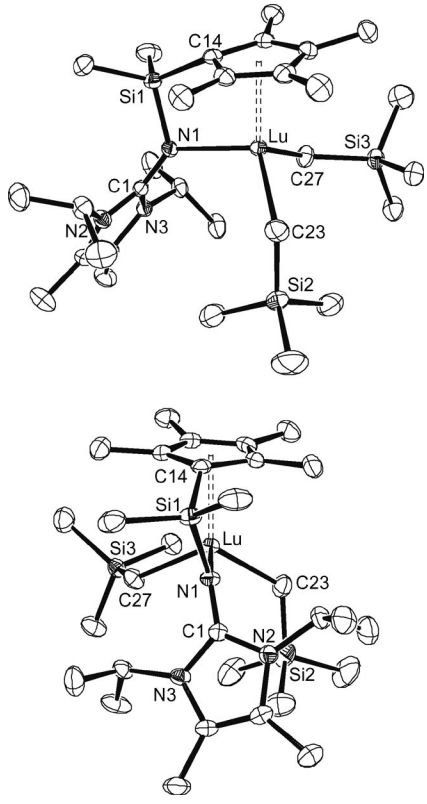


Figure 1. ORTEP drawings of **4c** with thermal displacement parameters drawn at 50% probability.

Table 1. Selected bond lengths [Å] and angles [°] in complexes **4** and **5**.

	4a [M = Sc]	**4b** [M = Y][a]	**4c** [M = Lu]	**5** [M = Ca]
M–N1	2.2135(16)	2.354(2)/2.352(2)	2.298(2)	2.448(2)
M–C23	2.228(2)	2.403(3)/2.400(3)	2.365(3)	
M–C27	2.253(2)	2.417(3)/2.416(3)	2.341(3)	
M–C(Cp)	2.410(2)–2.651(2)	2.568(2)/2.562(2)–2.711(3)/2.738(2)	2.515(3)–2.735(3)	2.601(3)–2.887(3)
M–Cp_{ct}[b]	2.221	2.356/2.360	2.327	2.471
M–Si1	3.0480(7)	3.1931(8)/3.1715(8)	3.1378(8)	3.2263(10)
N1–Si1	1.7425(15)	1.755(2)/1.748(2)	1.746(2)	1.731(2)
N1–C1	1.345(2)	1.337(3)/1.342(3)	1.342(3)	1.330(3)
M–N1–Si1	100.11(7)	100.98(9)/100.31(10)	100.90(9)	99.62(9)
M–N1–C1	130.97(12)	132.36(16)/130.13(17)	130.48(17)	132.39(16)
C1–N1–Si1	128.83(13)	126.59(18)/129.51(18)	128.47(18)	127.02(18)
N1–Si1–C14	96.83(8)	99.23(11)/98.54(11)	97.96(11)	102.07(12)
Cp_{ct}–M–N1[b]	101.1	96.1/95.4	97.3	94.6
Cp–C14–Si1[c]	23.6	23.5/23.6	22.8	18.2
C23–M–C27	104.56(8)	105.41(10)/109.60(11)	106.42(11)	
N1–M–C23	105.09(6)	114.68(9)/110.86(9)	108.13(10)	
N1–M–C27	107.04(7)	108.07(9)/105.49(9)	105.40(9)	

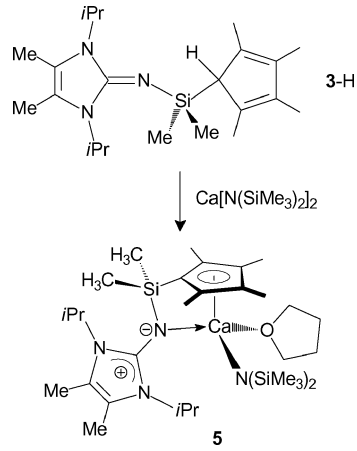
[a] Two independent molecules in the asymmetric unit. [b] Cp_{ct} = centroid of the cyclopentadienyl ring. [c] Dihedral angle between the Cp plane and the C14–Si bond.

structures of all of the complexes deviate quite significantly from C_s symmetry, and the Si1–N1–C1 planes subtend angles of 14.6° (**4a**), 11.1/19.3° (**4b**) and 15.3° (**4c**), respectively, with the best plane containing the centroid of the Cp ring, the N1 atom and the metal atom. This distortion is presumably a result of the *syn* and *anti* orientation of the neosilyl $SiMe_3$ groups towards the Cp ring, which leads to a twisting of the imidazole ring in order to accommodate the isopropyl groups. Despite this imidazole slippage, the near perpendicular orientation of the heterocycles towards the C1–N1–Si1 plane [interplanar angles of 85.1° (**4a**), 80.1/76.3° (**4b**) and 83.6° (**4c**)] rules out any significant π-interaction between the exocyclic nitrogen atom and the imidazole system. In comparison to the molecular structures of uncoordinated *N*-silylated imidazolin-2-imines,[3] this orientation leads to a pronounced elongation of the C1–N1 bonds and to more obtuse N2–C1–N3 angles (Table 1). This reveals an increase of the imidazolium-amide character, as indicated by mesomeric form **IB** and the ylidic presentation of complexes **4** in Scheme 1. As a consequence of this charge separation, relatively short Ln–N1 bonds are observed, which in all cases confirm the strong donating capability of the planar, three-coordinate N1 nitrogen atom. The angle sums at N1 in **4a**–**4c** lie within 0.1° of 360.0° (Table 1).

The Y–N1 and Lu–N1 distances of 2.354(2)/2.352(2) Å (**4b**) and 2.298(2) Å (**4c**) fall in the range observed for the related $[(\eta^5{:}\eta^1\text{-}C_5Me_4\text{-}SiMe_2\text{-}N\text{-}C_6H_5)Ln(CH_2SiMe_3)(THF)_2]$ neosilyl complexes containing two THF ligands [Y–N 2.327(5) Å, Lu–N 2.283(5) Å];[21e] they are longer, however, than the metal–nitrogen bond lengths observed for mono(tetrahydrofuran) complexes such as $[(\eta^5{:}\eta^1\text{-}C_5Me_4\text{-}SiMe_2\text{-}N\textit{t}Bu)Y(CH_2SiMe_3)(THF)]$ [2.208(6) Å][20b] and $[(\eta^5{:}\eta^1\text{-}C_5Me_4\text{-}SiMe_2\text{-}NXy)Lu(CH_2SiMe_3)(THF)]$ [2.188(2) Å, Xy = 2,6-dimethylphenyl].[21a] The Sc–N1 distance of 2.2135(16) Å is also longer than previously observed for other scandium complexes of the Cp-amido type, which range from 2.072 to 2.104 Å.[19b,25a] This elongation might be a consequence of a slightly reduced electron-donating ability of the neutral imine moiety in comparison with the anionic amido group; however, a particularly strong steric interaction of the *N*-isopropyl groups and *two* neosilyl groups must also be taken into account. Finally, it should be noted that the angles at the N1 and Si1 atoms, which are associated with the constrained geometry of the ligand system, are very similar to those in structurally characterized silylene-linked cyclopentadienyl-amido rare earth metal complexes (see for instance ref.[21f] for X-ray crystal structures of half-sandwich complexes over the full size range of group 3 and lanthanide metals).

Synthesis and Characterization of a Constrained-Geometry Calcium Complex

In a similar fashion to that described for the structural analogy between complexes of type **II** and **III** (Scheme 1), complexation of a divalent metal by the Cp-imine ligand, **3**, would potentially lead to complexes that are isostructural with silylene-linked cyclopentadienyl-amido complexes of the $[(\eta^5{:}\eta^1\text{-}C_5R_4\text{-}SiMe_2\text{-}NR)LnX]$ type. In view of the diagonal relationship between calcium and yttrium and of their comparable ionic radii,[26] we aimed towards the synthesis of a Ca^{II} complex of the $[(\eta^5{:}\eta^1\text{-}C_5R_4\text{-}SiMe_2\text{-}NIm)CaX]$ type containing one additional monoanionic ligand, X. Calcium bis(hexamethyldisilazide), $[Ca(HMDS)_2(THF)_2]$ [HMDS = $N(SiMe_3)_2$], seemed to be a promising starting material for developing a salt-free route,[27] and its reaction with **3**-H in hexane afforded the THF complex, $[(\eta^5{:}\eta^1\text{-}C_5Me_4\text{-}SiMe_2\text{-}NIm^{iPr})Ca(HMDS)(THF)]$ (**5**), in good yield as a colourless solid after recrystallization from a THF/pentane solution at –30 °C (Scheme 3). The ^1H NMR spectrum of **5** in C_6D_6 is very similar to the spectra recorded for complexes **4** (vide supra) and reveals the time-averaged C_s symmetry of the molecule in solution despite the presence of one additional THF ligand, as indicated by the observation of two multiplets at 3.61–3.54 and 1.44–1.37 ppm. The bis(trimethylsilyl)amide ligand gives rise to one high-field resonance at δ = 0.18 ppm.



Scheme 3. Synthesis of a cyclopentadienyl-imidazolin-2-imine calcium complex.

Although there has been ongoing interest in alkaline earth organometallics[28] and particularly in the cyclopentadienyl chemistry of these elements,[28b] **5** represents—to the best of our knowledge—the first structurally characterized constrained-geometry (CG) alkaline earth metal complex containing a silylene-bridged Cp–N ligand, despite the fact that Grignard reagents have been employed frequently as intermediates for the synthesis of other CG complexes (CGC).[29] Therefore, its molecular structure was determined by X-ray diffraction analysis, and an ORTEP presentation is shown in Figure 2. In agreement with the NMR spectroscopic data, the solid-state molecular structure of **5** contains one coordinated THF ligand, which leads to a three-legged piano-stool geometry with a strongly distorted pseudotetrahedral environment around the metal atom. This distortion can be mainly attributed to the steric requirements of the $N(SiMe_3)_2$ ligand, as indicated by the large N1–Ca–N4 angle of 118.10(7)°. The Cp-imine ligand,

however, is coordinated in a relatively symmetric fashion, and the angles of 11.0° and 89.4° between the Si1–N1–C1 plane and the planes containing either the centroid of the Cp ring, the N1 atom and the metal atom or the imidazole ring indicate approximately coplanar or almost perfectly perpendicular orientations, respectively. The N1 atom resides in an irregular trigonal-planar environment, and the sum of the angles at N1 is 359.0°.

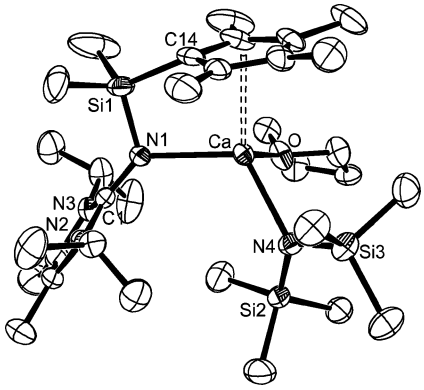


Figure 2. ORTEP drawing of **5** with thermal displacement parameters drawn at 50% probability. The THF ligand is disordered over two positions, and only one position is shown. Selected bond lengths [Å] and angles [°]: Ca–N4 2.357(2), N4–Si2 1.683(3), N4–Si3 1.692(2), N1–Ca–N4 118.10(7), Ca–N4–Si2 118.69(12), Ca–N4–Si3 116.96(12), Si2–N4–Si3 123.77(13); see also Table 1 for additional data.

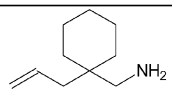
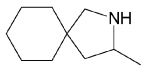
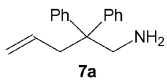
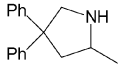
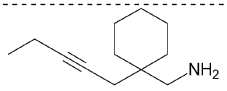
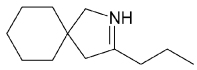
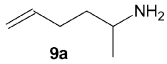
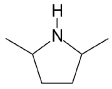
As expected from the larger atomic radius of Ca^{2+},[26] the metal–N1 and metal–C(Cp) distances are elongated in comparison with the corresponding values determined for the Ln^{III} complexes, **4** (Table 1). The Ca–C(Cp) bond lengths are in satisfactory agreement with the corresponding distances reported for other cyclopentadienyl-calcium complexes;[30] their variation from 2.601(3) to 2.887(3) Å, however, indicates a slightly more pronounced deviation from an ideal η^5-coordination mode than observed for complexes **4**. The calcium–nitrogen distances are Ca–N1 2.448(2) Å and Ca–N4 2.357(2) Å, which is in agreement with a slightly more tightly bound HMDS ligand; the Ca–N4 bond length is slightly longer than the analogous distances found in $[Ca(HMDS)_2]_2$ [2.282(6) and 2.267(7) Å], $[Ca(HMDS)_2(DME)]$ [2.271(3) Å][31] and $[Ca(HMDS)_2(THF)_2]$ [2.294(3) and 2.309(3) Å].[32] The Ca–N4–Si2 and Ca–N4–Si3 angles of 118.69(12)° and 116.96(12)°, respectively, show that the HMDS ligand is symmetrically bound and that there is no indication of a structural distortion as a result of an "agostic" interaction, as observed for the related half-sandwich complex, $[(C_5iPr_4H)Ca(HMDS)(THF)]$.[33] Analogous Ln···$H_3C$–Si contacts have also been observed in the unsolvated $[(\eta^5{:}\eta^1\text{-}C_5R_4\text{-}SiMe_2\text{-}N\mathit{t}Bu)Ln(HMDS)]$ (Ln = Y, Sm) complexes,[22a,25b] which represent the most closely structurally related rare earth metal analogues to the calcium complex, **5**, presented in this publication.

Catalytic Hydroamination Studies

The catalytic addition of an organic amine N–H bond to alkenes or alkynes (hydroamination) to give nitrogen-containing molecules is of great interest.[34] Currently, most amines are made in multistep syntheses that produce significant amounts of waste. Therefore, hydroamination offers an attractive alternative route to nitrogen-containing molecules that are important for the preparation of fine chemicals and pharmaceuticals. It has been shown that hydroamination can be catalyzed by d- and f-block transition metals[22,35,36] and s-block metals,[37] and the scope of catalytic hydroamination has been recently reviewed.[34] In lanthanide chemistry, it was shown by T. J. Marks et al. that amido and alkyl metallocene complexes represent efficient catalysts for the hydroamination/cyclization of primary aminoalkenes, allenes and alkynes.[22,34k] Moreover, "constrained-geometry" organolanthanides of $[(\eta^5{:}\eta^1\text{-}C_5Me_4\text{-}SiMe_2\text{-}N\mathit{t}Bu)LnE(SiMe_3)_2]$ (Ln = Sm, Nd, Yb, Lu; E = CH, N) composition were used as precatalysts for aminoalkene hydroamination/cyclization and are significantly more active than the corresponding metallocenes $[(\eta^5\text{-}C_5Me_5)_2LnE(SiMe_3)_2]$.[22a]

We have used compounds **4a**–**4c** in the intramolecular hydroamination/cyclization reaction of terminal aminoalkenes and of one aminoalkyne (Table 2). Our intention was to evaluate the catalytic activity of compounds **4a**–**4c** in comparison to other rare earth metal complexes. In our substrate screening, we focused on challenging nonactivated aminoalkenes. The rigorously anaerobic reaction of the catalyst with dry, degassed substrates proceeds regiospecifically. All substrates are converted into the cyclic product under mild conditions using compounds **4a**–**4c** as catalysts with low catalyst loadings of 2 to 6 mol-%. Kinetic studies were undertaken by in situ ^1H NMR spectroscopy. The reaction of a 20-fold molar excess of the substrates was monitored with constant catalyst concentration until substrate consumption was complete. The decrease of the substrate peak was integrated vs. the product signals. As observed for metallocene catalysts of the lanthanides,[34k] the rates increase with increasing ionic radius, which shows yttrium compound **4b** to be the most active. In rate, we observe significant deviations from ideal zero-order kinetics. By using compound **4b**, all substrates were converted at room temperature (entries 2, 5, 8 and 11), whereas for the scandium compound a reaction temperature of 60 °C was required (entries 1, 4, 7 and 10). Substrates **6a**, **7a**, and **8a**, bearing bulky geminal substituents in the β-position to the amino group (Thorpe–Ingold effect), could be cyclized within a few minutes (entries 1–3 and 4–6).[38] By using less bulky substituents in the β-positions, significantly lower rates are observed for all catalysts (entries 10–12). A comparison of compound **4b** using substrate **9a** with the CG $[(\eta^5{:}\eta^1\text{-}C_5Me_4\text{-}SiMe_2\text{-}N\mathit{t}Bu)LnE(SiMe_3)_2]$ compounds[22a] shows a slower turnover frequency for **4b** by a factor of about three. In contrast, a comparison of **4b** with CG actinide complexes using substrate **7a** shows a similar turnover frequency to $[(\eta^5{:}\eta^1\text{-}C_5Me_4\text{-}SiMe_2\text{-}N\mathit{t}Bu)U(NMe_2)_2]$ but a lower turnover frequency than $[(\eta^5{:}\eta^1\text{-}C_5Me_4\text{-}SiMe_2N\mathit{t}Bu)Th(NMe_2)_2]$.[39]

Table 2. Hydroamination reaction of terminal aminoalkenes and alkynes catalyzed by **4a**–**4c**.[a]

Entry	Substrate	Product	Catalyst	Cat. [mol-%]	T [°C]	T [min]	Conv.[b] [%]
1	 **6a**	 **6b**	**4a**	5	60	90	99
2			**4b**	5	r.t.	3	quant.
3			**4c**	5	r.t.	17	99
4	 **7a**	 **7b**	**4a**	6	60	60	99
5			**4b**	4	r.t.	3	quant.
6			**4c**	5	r.t.	19	99
7	 **8a**	 **8b**	**4a**	4	60	10	quant.
8			**4b**	5	r.t.	5	quant.
9			**4c**	4	r.t.	19	quant.
10	 **9a**	 **9b**	**4a**	2	60	6000	99 (*cis*:*trans* 1:12)
			4a	2	120	3840	99 (*cis*:*trans* 1:12)
11			**4b**	3	r.t.	240	99 (*cis*:*trans* 1:9)
			4b	3	60	60	99 (*cis*:*trans* 1:9)
12			**4c**	2	r.t.	1200	99 (*cis*:*trans* 1:15)
			4c	2	60	300	99 (*cis*:*trans* 1:15)

[a] Conditions: Cat. 10 mg, C_6D_6. [b] Calculated by ^{1}H NMR spectroscopy.

Conclusions

With this contribution, we have introduced novel constrained-geometry rare earth and alkaline earth metal complexes by employing the monoanionic Me_2Si-bridged cyclopentadienyl-imidazolin-2-imine ligand, **3**, which forms stable chelate complexes of the [(η^5:η^1-C_5Me_4-$SiMe_2$-NIm$^{i\mathrm{Pr}}$)M] type with short metal–nitrogen bonds. The strong electron-donating capacity of the tethered nitrogen donor atom stems from the ability of the imidazole ring to effectively stabilize a positive charge, and this ligand can thus be regarded as a monoanionic analogue of dianionic silylene-linked cyclopentadienyl-amido ligands. Accordingly, the use of ligands such as **3** allows the preparation of complexes with an isolobal and isostructural relationship to well-established Cp-amido complexes of the [(η^5:η^1-C_5Me_4-$SiMe_2$-NR)M] type if the charge of the metal atom is reduced by one (e.g., by going from M^{4+} to M^{3+}),[17] and the rare earth metal complexes, **4**, presented herein are related to Cp-amido complexes of group 4 metals. Complexes **4** are active catalysts for the hydroamination/cyclization of aminoalkenes and aminoalkynes. Future work will be aimed towards the activation of these complexes by alkyl scavengers, which should afford cationic monoalkyl complexes as active olefin polymerization catalysts, in a similar fashion to that described for the related group 4 systems.[15] Finally, the use of the Cp-imine ligand **3** allowed the isolation of the first constrained-geometry calcium complex **5**, and the full potential of **5** and other alkaline earth metal complexes for applications in homogeneous catalysis will be further explored.

Experimental Section

General: All manipulations of air-sensitive materials were performed with rigorous exclusion of oxygen and moisture in flame-dried Schlenk-type glassware either on a dual manifold Schlenk line, interfaced to a high vacuum (10^{-4} Torr) line, or in an argon-filled MBraun glove box. All solvents were dried using an M. Braun solvent purification system. Deuterated solvents were obtained from Sigma Aldrich (all ≥ 99 atom-% D) and were degassed, dried, and stored in the argon-filled M. Braun glove box. NMR spectra were recorded with Bruker DPX 200 and 400 MHz spectrometers. Chemical shifts are referenced to internal solvent resonances and are reported relative to tetramethylsilane. Elemental analyses (C, H, N) were carried out with an Elementar vario EL. The 2-iminoimidazoline **1** and [Ln(CH_2SiMe_3)$_3$(THF)$_2$] (Ln = Sc, Y, Lu) were prepared according to published procedures.[3,40] [Ca(HMDS)$_2$(THF)$_2$] was prepared from CaI_2 and NaN($SiMe_3$)$_2$ according to a modified literature procedure;[27] a detailed protocol is given below. 5-(Chlorodimethylsilyl)-1,2,3,4-tetramethyl-1,3-cyclopentadiene (**2**) was purchased from Boulder Scientific Company and distilled prior to use.

Preparation of 3-H: A general procedure for the preparation of **3**-H was reported in a previous publication.[13] A detailed protocol is described as follows: a solution of the 2-iminoimidazoline **1** (2 equiv.) in hexane was treated with one equivalent of **2** at ambient temperature and was stirred for 90 min. The solution was separated from the cloudy precipitate of **1**·HCl by filtration through a glass frit, and the filtrate solvent was removed in vacuo. Tetramethylcyclopentadiene **3**-H was obtained as a pale yellow oil containing excess **2**, which can be purified by heating under vacuum for several hours at 70 °C. Yield 98%. $C_{22}H_{39}N_3Si$ (373.65): calcd. C 70.72, H 10.52, N 11.25; found C 69.80, H 10.59, N 11.60. ^{1}H NMR (400 MHz, C_6D_6, 25 °C): δ = 4.63 (sept, 2 H, C*H*CH$_3$), 3.20 (s, 1 H, *ipso*-CH), 2.22 (s, 6 H, *o*-CCH$_3$), 1.97 (s, 6 H, *m*-CCH$_3$), 1.71

(s, 6 H, NCCH$_3$), 1.17 (d, 12 H, CHC*H*$_3$), 0.34 (s, 6 H, SiCH$_3$) ppm. ^{13}C{^{1}H} NMR (100.62 MHz, C_6D_6, 25 °C): δ = 144.2 (NCN), 134.5 (*m*-C), 133.9 (*o*-C), 114.0 (N*C*CH$_3$), 59.8 (*ipso*-C), 44.9 (*C*HCH$_3$), 21.5 (CH*C*H$_3$), 15.0 (*o*-C*C*H$_3$), 11.6 (*m*-C*C*H$_3$), 10.0 (NC*C*H$_3$), 1.7 (SiCH$_3$) ppm.

Preparation of Scandium Complex 4a: In a 50 mL flask, [Sc(CH$_2$SiMe$_3$)$_3$(THF)$_2$] (150 mg, 0.33 mmol) was stirred for 5 min in hexane (10 mL), after which a mixture of **3**-H (125 mg, 0.33 mmol) in hexane (5 mL) was added. The mixture was stirred at room temperature for 12 h, and then volatiles were removed under vacuum. The residue was washed in pentane and crystallized from THF/pentane (2:1) at –30 °C to obtain colourless single crystals. Yield 160 mg (76%). **4a**·(hexane)$_{0.5}$: $C_{30}H_{60}N_3ScSi_3$ (592.0): calcd. C 60.86, H 10.21, N 7.09; found C 60.16, H 9.34, N 6.89. ^{1}H NMR (200 MHz, C_6D_6, 25 °C): δ = 4.93 [sept, 2 H, CH(CH$_3$)$_2$], 2.47 (s, 6 H, C$_5$Me$_4$), 2.39 (s, 6 H, C$_5$Me$_4$), 1.50 (s, 6 H, CH$_3$), 1.23 (br., 12 H, CH$_3$), 0.45 (s, 6 H, SiMe$_2$), 0.34 (s, 18 H, SiMe$_3$), –0.34 (d, $^2J_{H,H}$ = 11 Hz, 2 H, CH$_2$), –0.36 (d, $^2J_{H,H}$ = 11 Hz, 2 H, CH$_2$) ppm. ^{13}C{^{1}H} NMR (100.6 MHz, [D$_8$]THF, 25 °C): δ = 151.2 (NCN), 126.5 (*m*-C), 123.7 (*o*-C), 118.3 (N*C*CH$_3$), 100.1 (*ipso*-C), 46.8 (*C*HCH$_3$), 30.3 (Sc-*C*H$_2$SiMe$_3$), 21.2 (CH*C*H$_3$), 15.0 (*o*-C*C*H$_3$), 12.3 (*m*-C*C*H$_3$), 10.6 (NC*C*H$_3$), 5.7 [CH$_2$Si(*C*H$_3$)$_3$], 4.7 [Si(*C*H$_3$)$_2$] ppm.

Preparation of Yttrium Complex 4b: In a 50 mL flask, [Y(CH$_2$SiMe$_3$)$_3$(THF)$_2$] (200 mg, 0.40 mmol) was stirred for 5 min in hexane (10 mL), after which a mixture of **3**-H (150 mg, 0.40 mmol) in hexane (5 mL) was added. The mixture was stirred at room temperature for 16 h, and then volatiles were removed under vacuum. The residue was washed in pentane and crystallized from THF/pentane (2:1) at –30 °C to obtain colourless single crystals. Yield 210 mg (83%). **4b**·(hexane)$_{0.5}$: $C_{30}H_{60}N_3Si_3Y$ (635.9): calcd. C 56.65, H 9.50, N 6.60; found C 55.97, H 8.95, N 6.46. ^{1}H NMR (400 MHz, C_6D_6, 25 °C): δ = 4.85 [sept, 2 H, CH(CH$_3$)$_2$], 2.49 (s, 6 H, C$_5$Me$_4$), 2.36 (s, 6 H, C$_5$Me$_4$), 1.48 (s, 6 H, CH$_3$), 1.08 (d, 12 H, CH$_3$), 0.45 (s, 6 H, SiMe$_2$), 0.36 (s, 18 H, SiMe$_3$), –0.58 (dd, $^2J_{H,H}$ = 11, $^2J_{^{89}Y,H}$ = 2.7 Hz, 2 H, CH$_2$), –0.96 (dd, $^2J_{H,H}$ = 11, $^2J_{^{89}Y,H}$ = 2.7 Hz, 2 H, CH$_2$) ppm. ^{13}C{^{1}H} NMR (100.6 MHz, [D$_8$]-THF, 25 °C): δ = 151.4 (NCN), 126.2 (*m*-C), 123.8 (*o*-C), 118.9 (N*C*CH$_3$), 100.4 (*ipso*-C), 46.4 (*C*HCH$_3$), 30.7 (d, $J_{Y,C}$ = 40.4 Hz, Y-*C*H$_2$SiMe$_3$), 22.2 (CH*C*H$_3$), 15.0 (*o*-C*C*H$_3$), 12.1 (*m*-C*C*H$_3$), 9.6 (NC*C*H$_3$), 5.9 [CH$_2$Si(*C*H$_3$)$_3$], 4.8 [Si(*C*H$_3$)$_2$] ppm.

Preparation of Lutetium Complex 4c: In a 50 mL flask, [Lu(CH$_2$SiMe$_3$)$_3$(THF)$_2$] (150 mg, 0.26 mmol) was stirred for 5 min in hexane (10 mL), after which a mixture of **3**-H (97 mg, 0.26 mmol) in hexane (5 mL) was added. The reaction mixture was stirred at room temperature for 14 h, and then the volatiles were removed under vacuum. The residue was washed in pentane and crystallized from THF/pentane (2:1) at –30 °C to obtain colourless single crystals. Yield 160 mg (80.4%). **4c**·(hexane)$_{0.5}$: $C_{30}H_{60}LuN_3Si_3$ (722.0): calcd. C 49.90, H 8.37, N 5.82; found: C 49.33, H 7.91, N 5.61. ^{1}H NMR (200 MHz, C_6D_6, 25 °C): δ = 4.89 [sept, 2 H, CH(CH$_3$)$_2$], 2.52 (s, 6 H, C$_5$Me$_4$), 2.37 (s, 6 H, C$_5$Me$_4$), 1.47 (s, 6 H, CH$_3$), 1.08 (br., 12 H, CH$_3$), 0.37 (s, 6 H, SiMe$_2$), 0.35 (s, 18 H, SiMe$_3$), –0.78 (d, $^2J_{H,H}$ = 11 Hz, 2 H, CH$_2$), –1.15 (d, $^2J_{H,H}$ = 11 Hz, 2 H, CH$_2$) ppm. ^{1}H NMR (400 MHz, [D$_8$]THF, 25 °C): δ = 4.97 [sept, 2 H, CH(CH$_3$)$_2$], 2.25 (s, 6 H, C$_5$Me$_4$), 2.11 (s, 6 H, C$_5$Me$_4$), 1.47 (d, ^2J = 9.4 Hz, 12 H, CH$_3$), 0.45 (s, 6 H, CH$_3$), 0.01 (s, 6 H, SiMe$_2$), –0.15 (s, 18 H, SiMe$_3$), –1.36 (s, 2 H, CH$_2$) ppm. ^{13}C{^{1}H} NMR (50.3 MHz, C_6D_6, 25 °C): δ = 152.2 (NCN), 125.8 (*m*-C), 122.9 (*o*-C), 120.4 (N*C*CH$_3$), 100.2 (*ipso*-C), 47.3 (*C*HCH$_3$), 37.3 (Lu-*C*H$_2$SiMe$_3$), 22.6 (CH*C*H$_3$), 14.9 (*o*-C*C*H$_3$), 12.0 (*m*-C*C*H$_3$), 10.0 (NC*C*H$_3$), 5.9 [CH$_2$Si(*C*H$_3$)$_3$], 4.7 [Si(*C*H$_3$)$_2$] ppm.

Preparation of [Ca(HMDS)$_2$(THF)$_2$]: In a 50 mL flask, CaI$_2$ (294 mg, 1.0 mmol) was treated with NaN(SiMe$_3$)$_2$ (367 mg, 2.0 mmol) in THF (20 mL) at ambient temperature. The reaction mixture was stirred for 12 h. The solvent was evaporated under vacuum, and the residue was dissolved in pentane. The solution was filtered, and a fluffy white powder was obtained from the filtrate after removal of pentane under vacuum. The ^{1}H NMR spectrum of this compound is in good agreement with the literature values. Yield 480 mg (95%). $C_{20}H_{52}CaN_2O_2Si_4$ (505.1): calcd. C 47.56, H 10.37, N 5.54; found C 47.20, H 9.98, N 5.21. ^{1}H NMR (200 MHz, C_6D_6, 25 °C): δ = 3.44 (br., 8 H, THF), 1.16 (br., 8 H, THF), 0.35 (s, 36 H, SiMe$_3$) ppm. ^{13}C{^{1}H} NMR (50.3 MHz, C_6D_6, 25 °C): δ = 67.2 (THF), 25.5 (THF), 6.0 (SiMe$_3$) ppm.

Preparation of Calcium Complex 5: In a 50 mL flask, [Ca(HMDS)$_2$-(THF)$_2$] (131 mg, 0.26 mmol) was stirred for 5 min in hexane (10 mL), after which a mixture of **3**-H (97 mg, 0.26 mmol) in hexane (5 mL) was added to the reaction flask. The reaction mixture was stirred at room temperature for 20 h, and then the volatiles were removed under vacuum. The residue was washed in pentane several times and crystallized from THF/pentane (2:1) at –30 °C to obtain colourless crystals of X-ray quality. Yield 120 mg (71%). $C_{32}H_{64}CaN_4OSi_3$ (645.2): calcd. C 59.56, H 9.99, N 8.68; found C 58.96, H 9.70, N 8.52. ^{1}H NMR (200 MHz, C_6D_6, 25 °C): δ = 4.82 [sept, 2 H, CH(CH$_3$)$_2$], 3.61–3.54 (m, 4 H, THF), 2.52 (s, 6 H, C$_5$Me$_4$), 2.37 (s, 6 H, C$_5$Me$_4$), 1.49 (s, 6 H, CH$_3$), 1.44–1.37 (m, 4 H, THF), 1.07 (d, 12 H, CH$_3$), 0.58 (s, 6 H, SiMe$_2$), 0.18 (s, 18 H, SiMe$_3$) ppm. ^{13}C{^{1}H} NMR (50.3 MHz, C_6D_6, 25 °C): δ = 152.2 (NCN), 125.8 (*m*-C), 122.9 (*o*-C), 120.4 (N*C*CH$_3$), 67.5 (*ipso*-C), 45.3 (*C*HCH$_3$), 25.3 (THF), 21.5 (CH*C*H$_3$), 14.2 (*o*-C*C*H$_3$), 9.2 (NC*C*H$_3$), 5.7 (SiMe$_3$), 4.8 (SiMe$_2$) ppm.

Hydroamination Reactions: The catalyst was weighed under argon gas into an NMR tube. C_6D_6 (≈ 0.5 mL) was condensed into the NMR tube, and the mixture was frozen to –196 °C. The reactant was injected onto the solid mixture, and the whole sample was melted and mixed just before insertion into the core of the NMR machine (t_0). The ratio between the reactant and the product was calculated by comparison of the integrations of the corresponding signals. SiMe$_4$ was used as an internal standard for the kinetic measurements. The substrates, *C*-(1-allylcyclohexyl)methylamine (**6a**),[37b] 2,2-diphenylpent-4-enylamine (**7a**),[37b] [1-(pent-2-ynyl)cyclohexyl]methanamine (**8a**)[36q] and 2-amino-5-hexene (**9a**),[41] were synthesized according to literature procedures. ^{1}H NMR spectra of 3-methyl-2-azaspiro[4.5]decane (**6b**),[37b] 2-methyl-4,4-diphenylpyrrolidine (**7b**),[37b] 3-propyl-2-azaspiro[4.5]dec-2-ene (**8b**)[36q] and 2,5-dimethylpyrrolidine(**9b**)[41b] conform with the literature.

Single Crystal X-ray Structure Determinations: CCDC-683442 (for **4c**), -683443 (for **4a**), -683444 (for **4b**) and -683445 (for **5**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. The hydrogen atoms were included in the model at geometrically calculated positions and refined using either a riding model or with rigid methyl groups. Special features: in **4a** and **4c**, the hexane molecules, which lie across inversion centres, were refined isotropically. The CH$_3$ groups of **4a** at Si3 are disordered over two positions. The CH$_2$ groups of the THF molecule in **5** are disordered over two positions. The Flack parameter of **5** refined to –0.02(3). Diffractometer: Bruker SMART. Program system: SHELXL-97 (G. M. Sheldrick, University of Göttingen). See Table 3 for crystallographic data.

Table 3. Crystal data and structure refinement for **4a**, **4b**, **4c** and **5**.

	4a [M = Sc]	**4b** [M = Y]	**4c** [M = Lu]	**5** [M = Ca]
Empirical formula	$C_{33}H_{67}N_3ScSi_3$	$C_{30}H_{60}N_3YSi_3$	$C_{33}H_{67}N_3LuSi_3$	$C_{32}H_{64}N_4OCaSi_3$
M_r [g mol^{-1}]	635.13	635.99	765.14	645.22
T [K]	133(2)	133(2)	133(2)	133(2)
λ [Å]	0.71073	0.71073	0.71073	0.71073
Crystal system	monoclinic	monoclinic	monoclinic	monoclinic
Space group	$P2_1/c$	$P2_1/n$	$P2_1/c$	Cc
a [Å]	10.4951(14)	10.6675(5)	10.5398(10)	13.4917(6)
b [Å]	19.585(2)	21.5952(10)	19.6595(18)	17.2912(8)
c [Å]	19.170(2)	32.1593(14)	19.1864(18)	16.7587(8)
β [°]	100.329(8)	95.090(1)	100.346(3)	96.642(4)
V [Å^3]	3876.5(8)	7379.2(6)	3910.9(6)	3883.4(3)
Z	4	8	4	4
$\rho_{calcd.}$ [Mg m^{-3}]	1.088	1.145	1.299	1.104
μ [mm^{-1}]	0.306	1.699	2.640	0.282
F(000)	1396	2736	1596	1416
Crystal size [mm^3]	0.50 × 0.41 × 0.40	0.45 × 0.31 × 0.18	0.29 × 0.23 × 0.16	0.47 × 0.31 × 0.31
$2\theta_{max}$ [°]	61	56.6	61	56.6
Reflections collected	74789	136526	82938	27034
Independent reflections	11779	18295	11922	9444
R(int)	0.0451	0.0739	0.0472	0.0399
Max./min. transmission	0.887/0.719	0.750/0.595	0.677/0.554	0.918/0.879
Goodness of fit	1.07	1.04	1.09	1.02
$R_1[I > 2\sigma(I)]$	0.0485	0.0418	0.0281	0.0412
wR_2	0.1487	0.1053	0.0668	0.0967
$\Delta\rho$ [e Å^{-3}]	0.596/–0.769	1.360/–0.796	2.025/–1.420	0.338/–0.373

Acknowledgments

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