

Chloro, Alkyl and Aryl Complexes of Rare Earth Metals Supported by Bulky Tetrasubstituted Guanidinate Ligands

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The reactions of anhydrous LnCl_3 ($\text{Ln} = \text{Y, Nd, Sm, Lu}$) with two equiv. of sodium N,N' -dicyclohexyl- N'' -bis(trimethylsilyl)guanidinate $\text{Na}[(\text{Me}_3\text{Si})_2\text{NC}(\text{NCy})_2]$, obtained from $\text{Na}[\text{N}(\text{SiMe}_3)_2]$ and the 1,3-dicyclohexyl-substituted carbodiimide $\text{CyN}=\text{C}=\text{NCy}$ in THF, yield the monochloro bis(guanidinate) tetrahydrofuranate complexes $[(\text{Me}_3\text{Si})_2\text{NC}(\text{NCy})_2]_2\text{-LnCl}(\text{THF})$ [$\text{Ln} = \text{Y}$ (**1**), Nd (**2**), Sm (**3**) and Lu (**4**)]. The analogous reactions of YCl_3 and LuCl_3 with the lithium guanidinate $[\text{Li}(\text{Et}_2\text{O})][(\text{Me}_3\text{Si})_2\text{NC}(\text{NCy})_2]$ afford the bis(guanidinate) "ate" complexes $[(\text{Me}_3\text{Si})_2\text{NC}(\text{NCy})_2]_2\text{Ln}(\mu\text{-Cl})_2\text{Li}(\text{THF})_2$ [$\text{Ln} = \text{Y}$ (**5**) and Lu (**6**)]. Treatment of **5** with dimethoxyethane results in the formation of $[(\text{Me}_3\text{Si})_2\text{NC}(\text{NCy})_2]_2\text{Y}(\mu\text{-Cl})_2\text{-}$

$\text{Li}(\text{DME})$ (**7**). The carbyl complexes $[(\text{Me}_3\text{Si})_2\text{NC}(\text{NCy})_2]_2\text{Y-}t\text{Bu}$ (**8**), $[(\text{Me}_3\text{Si})_2\text{NC}(\text{NCy})_2]_2\text{Y}(\mu\text{-Me})_2\text{Li}(\text{TMEDA})$ (**10**) and $[(\text{Me}_3\text{Si})_2\text{NC}(\text{NCy})_2]_2\text{YPh}(\text{THF})$ (**13**) were obtained by interaction of complex **1** with RLi ($\text{R} = t\text{Bu, Me or Ph}$). The molecular structures of **1, 6, 7, 8** and the side product $[\text{Li}(\text{TMEDA})][(\text{Me}_3\text{Si})_2\text{NC}(\text{NCy})_2]$ have been determined by single-crystal X-ray analyses. Agostic interactions between the yttrium atom and the *tert*-butyl group in complex **8** in the solid state as well as in solution have been substantiated by ^{13}C NMR spectroscopy and X-ray analysis.

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Introduction

The organometallic chemistry of the rare earth metals has made considerable progress in the course of the past two decades and has been generally dominated by the synthesis of cyclopentadienyl sandwich and half-sandwich complexes.^[1] These complexes have been and remain of special interest because of their potential as catalysts in a wide range of transformations of unsaturated substrates.^[2] Recently, research activity has been directed to the substitution of the cyclopentadienyl ligands by other coordinating systems in order to obtain complexes with modified structures and reactivities. To this end, many research groups have focused their work on "harder", mono-anionic polydentate N- and/or O- coordinating ligands providing enough steric bulk to prevent further coordination of Lewis bases, dimerisation or ligand redistribution reactions but still possessing high reactivity.^[3] Ligand frameworks containing electronegative nitrogen atoms as donor atoms have turned out to be the most promising ligands since they show a high affinity for the hard Lewis acidic atoms of the rare earths metals^[4] combined with structural diversity. Guanidinate

anions $[\text{R}_2\text{NC}(\text{NR}'_2)]^-$ are isoelectronic with the cyclopentadienyl anion and have been widely used as supporting ligands for non-transition and d-block transition metals^[5] and also, in recent years, for rare earth metals.^[6] Based on their anionic character, the facile modification of their electronic and steric properties by variation of the substituents at the nitrogen atoms and their flexible coordination behavior, tetrasubstituted guanidinate anions are very attractive ligand systems for the synthesis of kinetically stable, low-coordinate rare earth metal complexes. We have already used the guanidinate anion $[(\text{Me}_3\text{Si})_2\text{NC}(\text{NiPr})_2]^-$ for the successful synthesis of the hydrido complex $\{[(\text{Me}_3\text{Si})_2\text{NC}(\text{NiPr})_2]_2\text{Lu}(\mu\text{-H})\}_2$ which was found to be an active catalyst for the polymerisation of ethylene, propylene and styrene.^[7] Here we report on the synthesis, properties and structures of some chloro, alkyl and aryl derivatives of bis(guanidinate)-coordinated complexes of some rare earth metals.

Results and Discussion

In order to prepare low-coordinate organometallic complexes of rare earth metals which would be predicted to be resistant towards dimerisation, ligand redistribution and further coordination by Lewis bases, we used the bulky guanidinate ligand $[(\text{Me}_3\text{Si})_2\text{NC}(\text{NCy})_2]^-$ bearing cyclohexyl groups at the coordinating nitrogen atoms. The respective sodium and lithium guanidates are available by treatment of $\text{Na}[\text{N}(\text{SiMe}_3)_2]$ or $[\text{Li}(\text{Et}_2\text{O})][\text{N}(\text{SiMe}_3)_2]$ with 1,3-dicy-

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clohexylcarbodiimide, $\text{CyN}=\text{C}=\text{NCy}$, in THF and can be isolated in a pure state.^[6a] Addition of anhydrous LnCl_3 ($\text{Ln} = \text{Y}, \text{Nd}, \text{Sm}, \text{Lu}$) to freshly prepared THF solutions of the sodium guanidinate (1:2 mol ratio) at room temperature allows the isolation of the monomeric crystalline lanthanide bis(guanidinate) chlorides $[(\text{Me}_3\text{Si})_2\text{NC}(\text{NCy})_2]_2\text{-LnCl}(\text{THF})$ [$\text{Ln} = \text{Y}$ (**1**), Nd (**2**), Sm (**3**) and Lu (**4**)] from the respective solution in yields of 60 to 80% (Scheme 1).

The reactions of YCl_3 and LuCl_3 with the lithium salt $[\text{Li}(\text{Et}_2\text{O})][(\text{Me}_3\text{Si})_2\text{NC}(\text{NCy})_2]$ instead of the sodium analogue afford the monomeric “ate” complexes $[(\text{Me}_3\text{Si})_2\text{NC}(\text{NCy})_2]_2\text{Ln}(\mu\text{-Cl})_2\text{Li}(\text{THF})_2$ [$\text{Ln} = \text{Y}$ (**5**), Lu (**6**)] in yields of 74 and 70%, respectively (Scheme 2). In contrast, the metathesis of YCl_3 with $[\text{Li}(\text{Et}_2\text{O})][(\text{Me}_3\text{Si})_2\text{NC}(\text{NiPr})_2]$ containing less steric demanding isopropyl instead of cyclohexyl groups results in the formation of the dimeric complex $\{[(\text{Me}_3\text{Si})_2\text{NC}(\text{NiPr})_2]_2\text{Y}(\mu\text{-Cl})\}_2$.^[6b,6c] Furthermore, treatment of **5** with dimethoxyethane results in replacement of the two THF ligands coordinated to the lithium atom by a DME molecule producing $[(\text{Me}_3\text{Si})_2\text{NC}(\text{NCy})_2]_2\text{Y}(\mu\text{-Cl})_2\text{-Li}(\text{DME})$ (**7**). Though LaCl_3 clearly reacts with sodium or lithium *N,N'*-dicyclohexyl-*N''*-bis(trimethylsilyl)guanidinate under comparable reaction conditions, no THF-soluble lanthanum complex could be isolated.

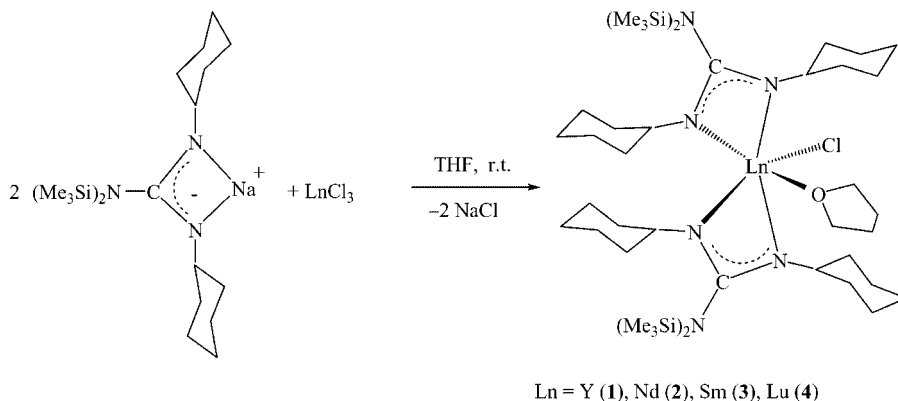
The colourless (**1**, **4**, **5** to **7**), pale blue (**2**) or pale yellow (**3**) crystalline complexes are moisture- and air-sensitive. In an inert atmosphere they can be stored without decomposi-

tion at room temperature. They are soluble in ethers and aromatic hydrocarbons and moderately soluble in hexane and pentane but it should be added that the solubilities of the monochloro bis(guanidinate) complexes **1** to **4** are noticeably higher than those of the related “ate” complexes **5** and **6**.

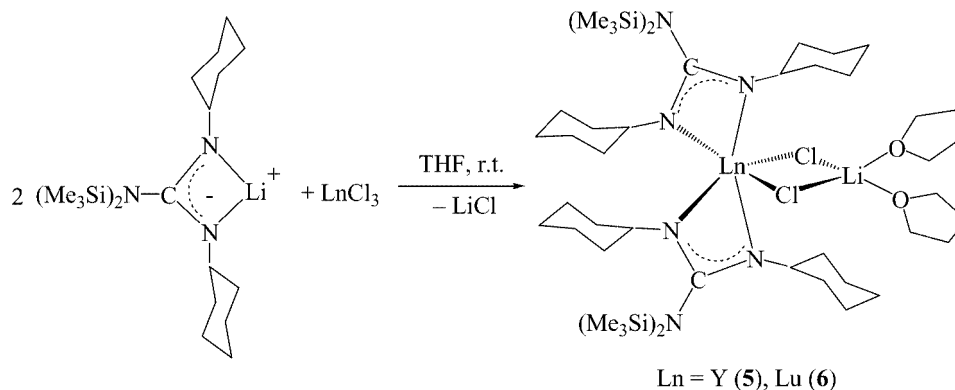
The ^1H and ^{13}C NMR spectra of the diamagnetic complexes **1**, **4**, **5**, **6** and **7** in $[\text{D}_6]\text{benzene}$ at 20°C show the expected sets of resonances due to the guanidinate moiety and the coordinated THF and DME molecules. The ^1H NMR signals of the THF methylene protons in **1**, **4**, **5** and **6** appear as broad singlets reflecting the labile coordination. Crystals suitable for single-crystal X-ray diffraction studies of **1**, **6** and **7** were obtained from hexane solutions by slow evaporation of the solvent at room temperature (**1** and **7**) or by cooling the solution to -20°C (**6**). The molecular structures of **1**, **6** and **7** are depicted in Figure 1, Figure 2 and Figure 3, respectively. The crystal and structural refinement data are listed in Table 1.

Complex **1** crystallises as the monomeric hexane solvate $[(\text{Me}_3\text{Si})_2\text{NC}(\text{NCy})_2]_2\text{YCl}(\text{THF})(\text{C}_6\text{H}_{14})_{1/2}$ in the monoclinic space group $P2_1/c$ with four molecules in the unit cell. The molecular structure shows the yttrium atom hexacoordinated by two chelating guanidinate anions, one chlorine atom and one THF molecule (Figure 1).

The distances $\text{Y-N}(1,2)$ [2.387(5), 2.327(5) Å] and $\text{Y-N}(4,5)$ [2.377(4), 2.344(5) Å] as well as the distances



Scheme 1.



Scheme 2.

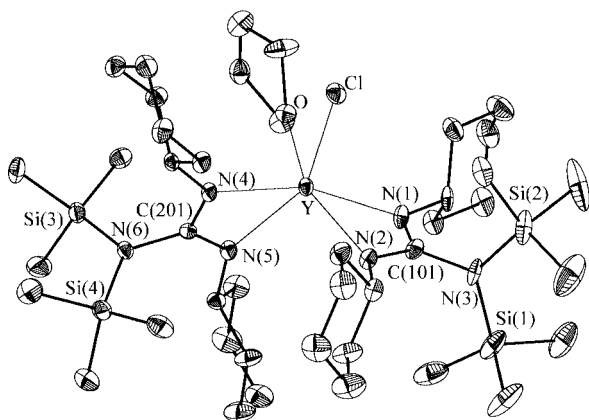


Figure 1. ORTEP diagram (30% probability thermal ellipsoids) of $[(\text{Me}_3\text{Si})_2\text{NC}(\text{NCy})_2]_2\text{YCl}(\text{THF})$ (**1**) showing the non-hydrogen atom numbering scheme. Hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: Y–N(1) 2.387(5), Y–N(2) 2.327(5), Y–N(4) 2.377(4), Y–N(5) 2.344(5), Y–Cl 2.584(2), Y–O 2.406(4), C(101)–N(1) 1.335(8), C(101)–N(2) 1.332(7), C(101)–N(3) 1.442(7), C(201)–N(4) 1.314(8), C(201)–N(5) 1.348(7), C(201)–N(6) 1.451(7); N(1)–Y–N(2) 56.87(17), N(4)–Y–N(5) 56.84(17), N(1)–C(101)–N(2) 114.7(5), N(4)–C(201)–N(5) 115.2(5), O–Y–Cl 84.55(11).

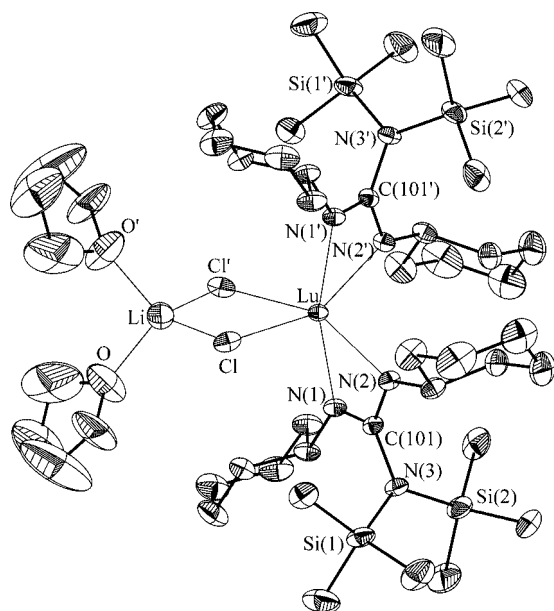


Figure 2. ORTEP diagram (30% probability thermal ellipsoids) of $[(\text{Me}_3\text{Si})_2\text{NC}(\text{NCy})_2]_2\text{Lu}(\mu\text{-Cl})_2\text{Li}(\text{THF})_2$ (**6**) showing the non-hydrogen atom numbering scheme. Hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: Lu–N(1) 2.320(5), Lu–N(2) 2.291(5), Lu–Cl 2.7468(17), Li–Cl 2.304(14), Li–O 1.932(16), C(101)–N(1) 1.316(7), C(101)–N(2) 1.339(7), C(101)–N(3) 1.439(7); N(1)–Lu–N(2) 57.74(7), N(1)–Lu–N(2') 109.49(17), N(1')–Lu–N(2') 57.74(17), N(1)–C(101)–N(2) 114.0(5), C(101)–Lu–C(101A) 130.3(2), Cl–Lu–Cl' 83.90(6), Cl–Li–Cl' 105.7(9). Symmetry operation: $-x, y, \text{ to } -z + 0.5$.

C(101)–N(1,2) [1.335(8), 1.332(7) Å] and C(201)–N(4,5) [1.314(8), 1.348(7) Å] in the guanidinate ligands differ only slightly from each other, thus indicating electron delocalisation within the anionic NCN units. The considerably longer distances C(101)–N(3) [1.442(7) Å] and C(201)–N(6)

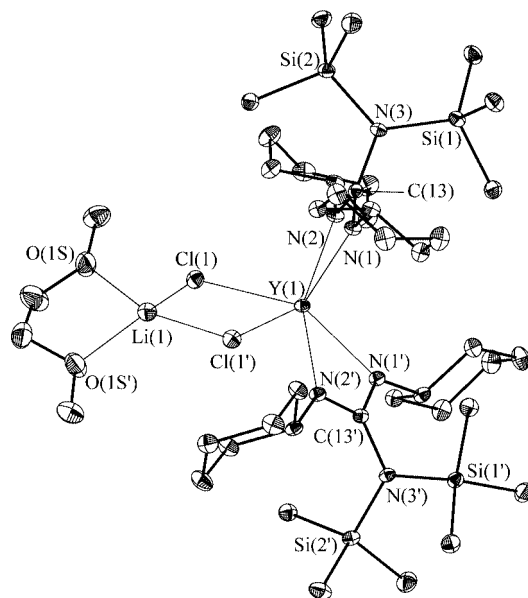


Figure 3. ORTEP diagram (30% probability thermal ellipsoids) of $[(\text{Me}_3\text{Si})_2\text{NC}(\text{NCy})_2]_2\text{Y}(\mu\text{-Cl})_2\text{Li}(\text{DME})$ (**7**) showing the non-hydrogen atom numbering scheme. Hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: Y(1)–N(1) 2.3517(10), Y(1)–N(2) 2.3566(10), Y(1)–Cl(1) 2.6693(3), Li(1)–Cl(1) 1.2311(2), Li(1)–O(1S') 1.980(3), N(1)–C(13) 1.3304(14), N(2)–C(13) 1.3325(15), N(3)–C(13) 1.4377(16); N(1)–Y(1)–N(2) 56.80(3), Cl(1)–Y(1)–Cl(1') 82.106(14), N(1)–C(13)–N(2) 114.47(11), C(13)–Y(1)–C(13') 125.77(5), O(1S')–Li(1)–O(1S) 81.14(14), Cl(1')–Li(1)–Cl(1) 98.70. Symmetry operation: $-x, y, \text{ to } -z + 0.5$.

[1.451(7) Å] indicate that the $\text{N}(\text{SiMe}_3)_2$ moiety does not take part in the conjugation. The opposite orientation of the $\text{N}(\text{SiMe}_3)_2$ and cyclohexyl groups relative to the NCN planes corresponds to the minimisation of their mutual steric repulsion. The dihedral angles between the planes formed by the SiNSi and the NCN fragments as well as between the mean plane of the cyclohexyl groups and the plane of the NCN fragment are close to 90° (89.7 and 82.9, and 73.8 and 96.6°, respectively).

Complex **6** crystallises in the monoclinic space group $C2/c$ with four molecules in the unit cell. The lutetium atom is hexacoordinated by the four nitrogen atoms of the two bidentate guanidinate ligands and by two chlorine atoms. The two chlorine atoms form bridges to the lithium atom which is in turn coordinated to two THF molecules (Figure 2).

As in the molecular structure of **1**, the small differences between the Lu–N(1,2) distances [2.320(5), 2.291(5) Å] and the C(101)–N(1,2) distances [1.316(7), 1.339(7) Å] indicate electron delocalisation within the anionic NCN fragments. The lengths of the lutetium–nitrogen bonds are very close to those in the related lutetium complex $[(\text{Me}_3\text{Si})_2\text{NC}(\text{N}i\text{Pr})_2]_2\text{Lu}(\mu\text{-Cl})_2\text{Li}(\text{THF})_2$ [2.285(1)–2.346(1) Å] containing less sterically demanding isopropyl-substituted guanidinate ligands^[7] and to the lengths of the Lu–N bonds in $[\text{Li}(\text{THF})_4][(\text{C}_5\text{H}_5)_2\text{Lu}(\text{NPh}_2)_2]$ [2.290(7), 2.293(7) Å]^[8] but are much shorter than the coordinate $\text{N} \rightarrow \text{Lu}$ bonds in $(\eta^8\text{-C}_8\text{H}_8)\text{Lu}[o\text{-C}_6\text{H}_4\text{CH}_2\text{N}(\text{CH}_3)_2](\text{THF})$ [2.479(6) Å]^[9] and

Table 1. Crystallographic data and structure refinement details for **1**, **6**, **7**, **8** and **11**.

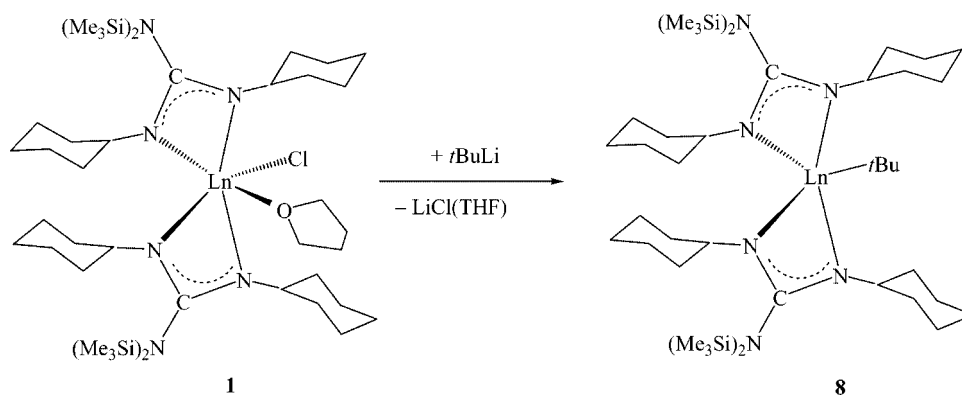
	1	6	7	8	11
Empirical formula	C ₄₅ H ₉₅ ClLiN ₆ OSi ₄ Y	C ₄₆ H ₉₆ Cl ₂ LiLuN ₆ O ₂ Si ₄	C ₄₂ H ₉₀ Cl ₂ LiN ₆ O ₂ Si ₄ Y	C ₄₂ H ₈₉ N ₆ Si ₄ Y	C ₂₅ H ₅₆ LiN ₅ Si ₂
Formula mass	972.99	1130.46	990.31	879.46	489.87
<i>T</i> [K]	173(2)	173(2)	100(2)	100(2)	100(2)
Crystal system	monoclinic	monoclinic	monoclinic	monoclinic	monoclinic
Space group	<i>P</i> 2 ₁ / <i>c</i> (No. 14)	<i>C</i> 2/ <i>c</i> (No. 15)	<i>C</i> 2/ <i>c</i> (No. 15)	<i>P</i> 2 ₁ / <i>c</i> (No. 14)	<i>P</i> 2 ₁ / <i>c</i> (No. 14)
<i>a</i> [Å]	17.9072(3)	26.4406(9)	24.6189(13)	13.9177(11)	17.583(3)
<i>b</i> [Å]	11.5050(1)	13.6217(4)	13.9815(7)	18.2575(15)	10.6598(16)
<i>c</i> [Å]	27.7509(4)	19.1255(4)	17.7688(9)	20.0347(16)	17.615(3)
<i>α</i> [°]	90	90	90	90	90
<i>β</i> [°]	100.082(1)	119.992(1)	116.150(1)	92.452(2)	106.652(2)
<i>γ</i> [°]	90	90	90	90	90
<i>V</i> [Å ³]	5629.02(13)	5966.0(3)	5490.1(5)	5086.2(7)	3163.3(8)
<i>Z</i>	4	4	4	4	4
Density (calcd.) [g cm ^{−3}]	1.148	1.259	1.198	1.149	1.029
<i>μ</i> [mm ^{−1}]	1.204	1.862	1.284	1.274	0.132
<i>T</i> _{max} / <i>T</i> _{min}	0.7590/0.3488	0.8448/0.6565	0.7151/0.5440	0.8832/0.7497	0.9491/0.9430
<i>R</i> (000)	2108	2376	2128	1912	1088
Crystal size [mm]	0.45 × 0.22 × 0.16	0.38 × 0.22 × 0.15	0.54 × 0.49 × 0.28	0.24 × 0.16 × 0.10	0.45 × 0.40 × 0.40
<i>θ</i> range [°]	1.15–27.50	1.74–27.50	1.72–24.50	1.84–29.08	1.94–25.00
Completeness to <i>θ</i> [%]	99.7	99.4	99.7	99.2	99.9
	−22 ≤ <i>h</i> ≤ 23	−34 ≤ <i>h</i> ≤ 34	−27 ≤ <i>h</i> ≤ 28	−18 ≤ <i>h</i> ≤ 18	−20 ≤ <i>h</i> ≤ 20
Index ranges	−14 ≤ <i>k</i> ≤ 12	−14 ≤ <i>k</i> ≤ 17	−16 ≤ <i>k</i> ≤ 9	−24 ≤ <i>k</i> ≤ 24	−12 ≤ <i>k</i> ≤ 12
	−36 ≤ <i>l</i> ≤ 33	−24 ≤ <i>l</i> ≤ 24	−20 ≤ <i>l</i> ≤ 20	−26 ≤ <i>l</i> ≤ 27	−20 ≤ <i>l</i> ≤ 20
Reflections collected	40939	21775	14137	53204	24254
Independent reflections	12878 [<i>R</i> _{int} = 0.2185]	6830 [<i>R</i> _{int} = 0.0712]	4568 [<i>R</i> _{int} = 0.0186]	13505 [<i>R</i> _{int} = 0.0600]	5559 [<i>R</i> _{int} = 0.0302]
Data/restraints/parameters	12878/0/536	6830/2/297	4568/7/445	13505/0/834	5559/0/522
Goodness-of-fit on <i>F</i> ²	0.979	1.112	1.052	0.997	1.062
<i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)]	<i>R</i> ₁ = 0.0949, <i>wR</i> ₂ = 0.1499	<i>R</i> ₁ = 0.0598, <i>wR</i> ₂ = 0.1428	<i>R</i> ₁ = 0.0268, <i>wR</i> ₂ = 0.0671	<i>R</i> ₁ = 0.0444, <i>wR</i> ₂ = 0.0925	<i>R</i> ₁ = 0.0414, <i>wR</i> ₂ = 0.1123
<i>R</i> indices (all data)	<i>R</i> ₁ = 0.2331, <i>wR</i> ₂ = 0.1996	<i>R</i> ₁ = 0.0753, <i>wR</i> ₂ = 0.1518	<i>R</i> ₁ = 0.0311, <i>wR</i> ₂ = 0.0687	<i>R</i> ₁ = 0.0772, <i>wR</i> ₂ = 0.1038	<i>R</i> ₁ = 0.0505, <i>wR</i> ₂ = 0.1177
Largest diff. peak/hole [e Å ^{−3}]	0.483/−0.783	2.634/−0.767	0.420/−0.279	1.422/−0.612	0.889/−0.259

Lu[*o*-C₆H₄CH₂N(CH₃)₂]₃ [2.468(6), 2.478(5) and 2.588(5) Å].^[10] Since the silylamine nitrogen is not involved in the conjugation, the (Si)N–C bond is substantially longer [1.439(7) Å] than the C–N(1,2) bonds. The bridging Lu–Cl distances in **6** [both 2.747(2) Å] are longer than the terminal Lu–Cl distances in [(Me₃Si)₂NC(NiPr)₂]₂Lu(μ-Cl)₂Li(THF)₂ [2.600(1) and 2.622(1) Å]^[7] and (tBu₂C₅H₃)₂Lu(μ-Cl)₂Li(TMEDA) [2.60(1) Å]^[11] which can be attributed to the stronger steric repulsions of the bulkier cyclohexyl groups and the THF molecules coordinated to the lithium atom. The angle C(101)–Lu–C(101A) [130.3(2)°], defined as a bite angle, is slightly smaller than the corresponding angle in [(Me₃Si)₂NC(NiPr)₂]₂Lu(μ-Cl)₂Li(THF)₂ [132.30(6)°]^[7] but larger than the centroid-metal-centroid angle in (tBu₂C₅H₃)₂Lu(μ-Cl)₂Li(TMEDA) [127.9(1)°].^[11]

Complex **7** crystallises in the monoclinic space group *C*2/*c*. The unit cell contains four molecules and the coordination environment of the yttrium atom (Figure 3) is analogous to that of the lutetium atom in **6**. The Y–N(1,2) distances [2.352(1), 2.357(1) Å] differ only very slightly and are in the range of the corresponding distances for the related yttrium guanidinate and amidinate complexes {[(Me₃Si)₂NC(NiPr)₂]₂Y(μ-Cl)₂}₂ [2.326(4)–2.388(4) Å],^[6b] {[(PhC(=NSiMe₃)₂)₂Y(μ-H)]₂}₂ [2.327(3)–2.389(3) Å]^[12a] and [PhC(=NSiMe₃)₂]₂Y(μ-Cl)₂Li(TMEDA) [2.334(2)–2.373(2) Å].^[13] The Y–Cl distances [2.669(1) Å] are slightly longer than those in the metallocene type “ate” complexes Cp*₂Y(μ-Cl)₂-

Li(THF)₂ [2.646(2), 2.655(2) Å]^[14] and [(1,3-Me₃Si)₂-C₅H₃]₂Y(μ-Cl)₂Li(THF)₂ [2.626(1), 2.631(1) Å]^[15] but shorter than the Y–Cl bonds in the dimeric complex {[(Me₃Si)₂NC(NiPr)₂]₂Y(μ-Cl)₂}₂ [2.7128(15), 2.7166(15) Å].^[12b] The bite angle C(13)–Y(1)–C(13') [125.77(5)°] is substantially smaller than that in **6** [130.3(2)°]. As expected, the distance of the yttrium atom to the bridging Cl atoms [2.6693(3) Å] is significantly longer than to the terminal Cl atom in **1** [2.584(2) Å].

Complex **1** turned out to be suitable for alkylation and arylation reactions. The alkylation with *t*BuLi, carried out in hexane at 0 °C, affords the THF-free complex [(Me₃Si)₂-NC(NCy)₂]₂Y-*t*Bu (**8**) (Scheme 3) which was isolated as colourless crystals in a yield of 52%. ¹H NMR spectroscopic monitoring of the course of the reaction revealed that **8** is actually formed quantitatively. However, its isolation in a crystalline state is hampered by its very high solubility in hexane and pentane. The NMR spectra of **8**, recorded in [D₆]benzene at ambient temperature, conditions under which the complex is stable for at least the three days over which measurements were made, show three remarkable features: 1) The ¹H NMR signal of the methyl protons of the *tert*-butyl group appears as a broadened singlet at δ = 1.48 ppm and the corresponding carbon atoms cause the appearance of two ¹³C{¹H} NMR signals at δ = 30.6 and 30.7 ppm which can be interpreted as a doublet with a coupling constant ²*J*_{Y,C} = 2.3 Hz. The tertiary carbon atom



Scheme 3.

of the *tert*-butyl group bonded to the yttrium atom gives rise to a $^{13}\text{C}\{^1\text{H}\}$ NMR doublet at $\delta = 37.5$ ppm with a coupling constant $^1J_{\text{Y,C}} = 56$ Hz. 2) The methine protons of the four cyclohexyl groups appear as two broad multiplet signals at $\delta = 3.45$ and 3.63 ppm with an intensity ratio of 1:3 which collapse to a very broad multiplet at $\delta = 3.54$ ppm in the ^1H NMR spectrum in $[\text{D}_8]\text{toluene}$ below -10°C . The methine carbon atoms display a $^{13}\text{C}\{^1\text{H}\}$ NMR signal at $\delta = 55.2$ ppm and their methylene carbon atoms show a single set of five signals at 24.9 , 25.9 , 26.1 , 26.2 and 26.4 ppm. These observations indicate non-equivalence of the guanidinate ligands apparently resulting from the steric repulsion of the bulky *t*Bu and cyclohexyl groups. 3) The methylsilyl protons give rise to three singlet signals at $\delta = 0.28$, 0.32 and 0.36 ppm in an intensity ratio of 1:3:2 at room temperature and in $[\text{D}_8]\text{toluene}$ below -10°C . They correspond to the three $^{13}\text{C}\{^1\text{H}\}$ NMR signals of the methylsilyl carbon atoms at 2.3 , 2.4 and 2.8 ppm. The different shielding of the $\text{CH}_3(\text{Si})$ groups is not clear. It may be caused by restricted rotation of the $\text{N}(\text{SiMe}_3)_2$ units due to the neighbourhood of the bulky cyclohexyl moieties.

Crystals of **8** suitable for X-ray diffraction studies were obtained by prolonged cooling of concentrated hexane solutions to -30°C . The molecular structure of **8** is shown in Figure 4 and the crystal and structure refinement data are listed in Table 1.

The coordination sphere of the yttrium atom is composed of the four nitrogen atoms of the two bidentate guanidinate ligands and the tertiary carbon atom of the *tert*-butyl group resulting in a formal coordination number of 5 for yttrium, a lower number than for other organo-yttrium compounds.^[1] The most striking feature in the structure of **8** is the strongly distorted geometry of the *t*Bu ligand. The angles $\text{C}(41)\text{--C}(39)\text{--Y}(1)$ [$91.71(16)^\circ$] and $\text{C}(42)\text{--C}(39)\text{--Y}(1)$ [$98.99(16)^\circ$] are substantially smaller and the angle $\text{C}(40)\text{--C}(39)\text{--Y}(1)$ [$135.62(17)^\circ$] is much larger than the value expected for an sp^3 hybridised carbon atom, thus leading to rather close contacts between yttrium and the methyl carbon atoms $\text{C}(41)$ [$2.877(3)\text{ \AA}$] and $\text{C}(42)$ [$3.038(3)\text{ \AA}$] and the hydrogens belonging to them. The distance $\text{Y}(1)\text{--C}(40)$ remains very long [$3.639(3)\text{ \AA}$] and indicates the absence of an interaction between the methyl group and yttrium. Despite the fact that the C–C distances

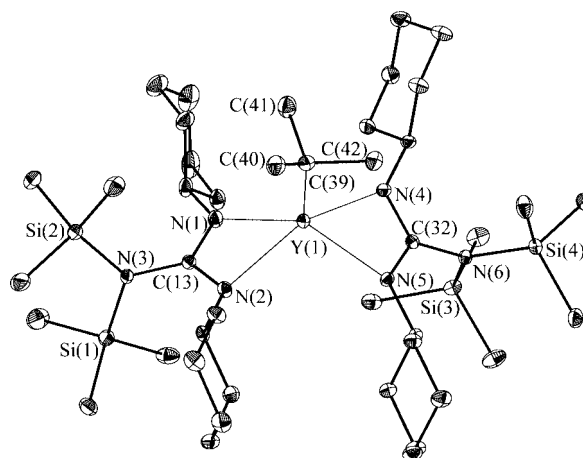


Figure 4. ORTEP diagram (30% probability thermal ellipsoids) of $[(\text{Me}_3\text{Si})_2\text{NC}(\text{NCy})_2]_2\text{Y-}t\text{Bu}$ (**8**) showing the non-hydrogen atom numbering scheme. Hydrogen atoms are omitted for clarity. Selected bond lengths [$\text{\AA}$] and angles [$^\circ$]: $\text{Y}(1)\text{--N}(1)$ $2.3360(19)$, $\text{Y}(1)\text{--N}(2)$ $2.3545(17)$, $\text{Y}(1)\text{--N}(4)$ $2.3990(17)$, $\text{Y}(1)\text{--N}(5)$ $2.3167(17)$, $\text{Y}(1)\text{--C}(39)$ $2.399(2)$, $\text{N}(1)\text{--C}(13)$ $1.338(3)$, $\text{N}(2)\text{--C}(13)$ $1.333(3)$, $\text{N}(3)\text{--C}(13)$ $1.432(3)$, $\text{N}(4)\text{--C}(32)$ $1.334(3)$, $\text{N}(5)\text{--C}(32)$ $1.341(3)$, $\text{N}(6)\text{--C}(32)$ $1.429(3)$, $\text{C}(39)\text{--C}(40)$ $1.515(4)$, $\text{C}(39)\text{--C}(41)$ $1.518(4)$, $\text{C}(39)\text{--C}(42)$ $1.527(3)$; $\text{N}(1)\text{--Y}(1)\text{--N}(2)$ $57.05(6)$, $\text{N}(4)\text{--Y}(1)\text{--N}(5)$ $57.14(6)$, $\text{N}(1)\text{--C}(13)\text{--N}(2)$ $114.03(19)$, $\text{N}(4)\text{--C}(32)\text{--N}(5)$ $115.03(18)$, $\text{C}(39)\text{--Y}(1)\text{--C}(13)$ $112.08(7)$, $\text{C}(39)\text{--Y}(1)\text{--C}(32)$ $116.23(7)$, $\text{C}(40)\text{--C}(39)\text{--Y}(1)$ $135.62(17)$, $\text{C}(41)\text{--C}(39)\text{--Y}(1)$ $91.71(16)$, $\text{C}(42)\text{--C}(39)\text{--Y}(1)$ $98.99(16)$.

within the *tert*-butyl group do not change considerably [$\text{C}(39)\text{--C}(40) = 1.515(4)$, $\text{C}(39)\text{--C}(41) = 1.518(4)$ and $\text{C}(39)\text{--C}(42) = 1.527(2)\text{ \AA}$] we suggest that agostic interactions are present in **8**. To evaluate qualitatively the hindrance of the *t*Bu group to rotation around the $\text{Y}(1)\text{--C}(39)$ bond, the MOLDRW program^[17] was used to estimate the changes in the energies of non-bonding interactions as a function of the torsion angle $\text{N}(5)\text{--Y}(1)\text{--C}(39)\text{--C}(42)$. As shown in Figure 5, the minimum energy corresponds exactly to a torsion angle of 22.5° estimated for **8** from its molecular structure. In this case, even the shortest intramolecular distances between the carbon atoms $\text{C}(40)$ and $\text{C}(42)$ and the carbon atoms of the cyclohexyl and the SiMe_3 groups are rather long ranging from 3.653 to $4.122\text{ \AA}$, thus excluding steric hindrance. According to the diagram the first and, at the same time, the highest maximum of energy corresponds to

a torsion angle of between 163.0 and 172.1°. Such an orientation of the *tert*-butyl group would cause a short contact of 2.700 Å between the C(41) methyl carbon atom and the C(8) methylene carbon atom of the cyclohexyl ring thus provoking steric repulsion. In the case of a torsion angle of 242.8–252.8° corresponding to the second maximum, the shortest intramolecular contact of 2.800 Å would be between the C(42) methyl carbon atom and the C(8) methylene carbon atom of the cyclohexyl moiety. In the last two cases, the distances to the methyl carbon atoms of the SiMe₃ groups are in the range of van der Waals contacts. These data clearly show that the hindrance to rotation of the *t*Bu group is caused by agostic interactions with the yttrium atom. At this point it should be noted that [(Me₃Si)₂NC(NiPr)₂]₂Y-*t*Bu, containing the less steric demanding *i*Pr groups, shows no signs of agostic interactions. In this compound the Y–C bond [2.332(9) Å]^[6b] is noticeably shorter than that in **8** [2.399(2) Å] and in other *N,N*- and *N,O*-coordinated alkyl yttrium complexes.^[16] The bonding situation within the four-membered metallocycles in **8** is different from that in **7**. Whereas in complex **7** both guanidinate ligands are bonded to the metal atom in a symmetric fashion, the Y–N distances in **8** range from 2.3167(17) to 2.3990(17) Å. The very small differences in the bond lengths within the coordinating NCN fragments in **8** [C(13)–N(1) = 1.338(3), C(13)–N(2) = 1.333(3), C(32)–N(4) = 1.334(3) and C(32)–N(5) = 1.341(3) Å] are indicative of delocalised π systems.

Analogous to the synthesis of **8**, we treated equimolar amounts of **1** and MeLi in order to obtain the corresponding methyl yttrium complex. In fact, the NMR-scale reaction carried out in [D₈]toluene at 0 °C occurred with formation of [(Me₃Si)₂NC(NCy)₂]₂YMe (**9**) as indicated by the appearance of a broad signal at –0.36 ppm in the ¹H NMR spectrum which could be assigned to the protons of the yttrium bonded methyl group. However, the compound was no longer formed when the reaction was carried out on a preparative scale in hexane at 0 °C. On the other hand, the reaction of **1** with two equiv. of MeLi in hexane at 0 °C and in the presence of TMEDA afforded the corresponding “ate” complex [(Me₃Si)₂NC(NCy)₂]₂Y(μ-Me)₂Li(TMEDA) (**10**) as a colourless microcrystalline solid in 61 % yield. As

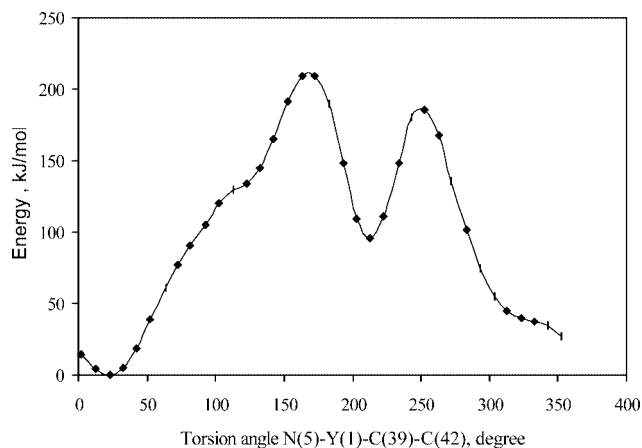
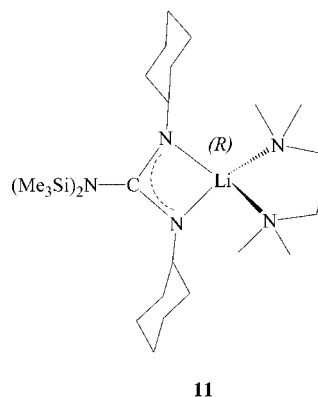
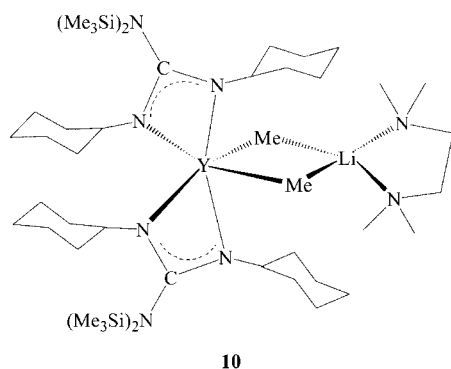


Figure 5. Energy diagram of the non-bonding interactions in complex **8** as function of the torsion angle N(5)–Y(1)–C(39)–C(42).

a side product, lithium guanidinate [Li(TMEDA)][(Me₃Si)₂NC(NCy)₂] (**11**) was isolated in a yield of 7%.

The moisture- and air-sensitive complex **10** is soluble in THF and toluene and moderately soluble in hexane. [D₆]benzene solutions of **10** are stable at room temperature for several days. The NMR spectra of **10** recorded in [D₆]benzene show a broad ¹H singlet signal at –0.51 ppm and a broad ¹³C{¹H} resonance at δ = 11.6 ppm with no resolved yttrium coupling for the yttrium bonded methyl groups. These chemical shift values are very close to those reported for the related methyl complexes [(Me₃Si)₂NC(NiPr)₂Y(μ-Me)₂Li(TMEDA)]^[6b] and [PhC(NSiMe₃)₂Y(μ-Me)₂Li(TMEDA)]^[12a,12b] but are noticeably lower-field compared with those of the metallocene type complexes such as Cp*₂Y(μ-Me)₂Li(OEt₂).^[12c] The guanidinate fragments give rise to a single set of signals indicating the equivalence of both ligands.

The lithium guanidinate [Li(TMEDA)][(Me₃Si)₂NC(NCy)₂] (**11**), formed as a side product, was characterised by ¹H and ¹³C NMR spectroscopy as well as by an X-ray structure analysis. An ORTEP drawing of its molecular structure is shown in Figure 6 and the crystal and structure refinement data are listed in Table 1. Unlike [(Me₃Si)₂NC(NCy)₂]₂Li₂^[18] obtained from the reaction of ether-free



$\text{Li}[\text{N}(\text{SiMe}_3)_2]$ with $\text{CyN}=\text{C}=\text{NCy}$ in toluene, complex **11** was found to be monomeric in the solid state.

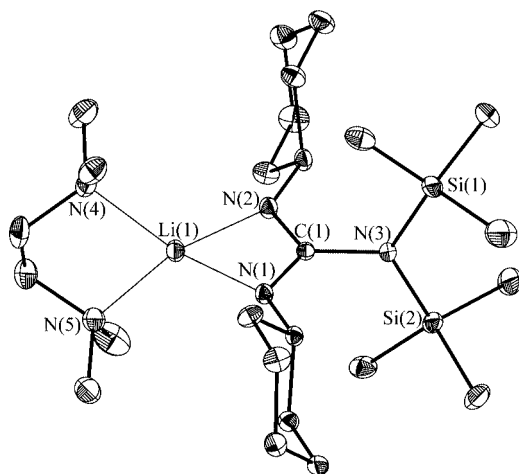


Figure 6. ORTEP diagram (30% probability thermal ellipsoids) of $[\text{Li}(\text{TMEDA})][(\text{Me}_3\text{Si})_2\text{NC}(\text{NCy})_2]$ (**11**) showing the non-hydrogen atom numbering scheme. Hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: Li(1)–N(1) 1.969(3), Li(1)–N(2) 1.971(3), Li(1)–N(4) 2.110(3), Li(1)–N(5) 2.089(3), N(1)–C(1) 1.3258(19), N(2)–C(1) 1.3217(19), N(3)–C(1) 1.4655(19); N(1)–Li(1)–N(2) 69.46(10), N(5)–Li(1)–N(4) 87.01(11).

At first, the reaction of **1** with $\text{LiCH}_2\text{SiMe}_3$ was carried out in an NMR tube in $[\text{D}_8]\text{toluene}$ at 0°C and the ^1H NMR spectrum confirmed the formation of the alkylated product $[(\text{Me}_3\text{Si})_2\text{NC}(\text{NCy})_2]_2\text{YCH}_2\text{SiMe}_3$ (**12**) by the appearance of a characteristic doublet signal at -0.16 ppm with a coupling constant $^2J_{\text{Y,H}} = 3.0$ Hz for the yttrium bonded methylene group. However, the reaction carried out on a preparative scale in hexane yielded an inseparable mixture of **12** and compounds which are most likely thermal decomposition products since the signal of TMS was detected in the ^1H NMR spectrum of the reaction mixture.

The guanidinate supported phenyl yttrium derivative $[(\text{Me}_3\text{Si})_2\text{NC}(\text{NCy})_2]_2\text{YPh}(\text{THF})$ (**13**) was synthesised by treatment of **1** with equimolar amounts of phenyllithium in THF (Scheme 4) and was isolated as a colourless microcrystalline solid in 61% yield. It is soluble in ethers, toluene and hexane. Under NMR conditions ($[\text{D}_6]\text{benzene}$ solution, room temperature, inert atmosphere, sealed tube) it is stable for several days but decomposes immediately in the pres-

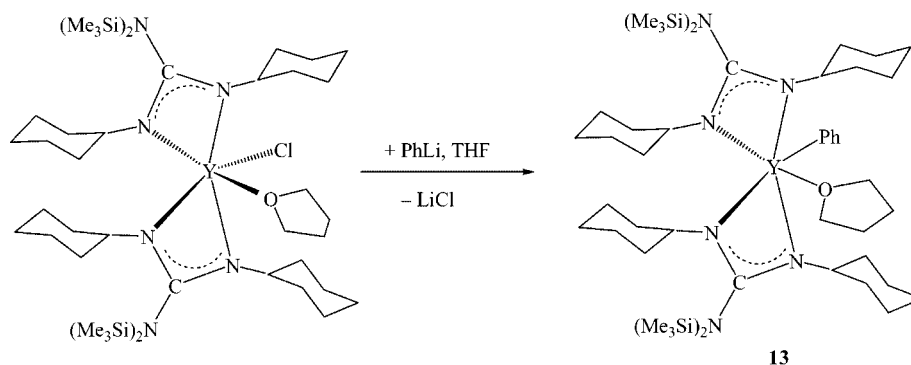
ence of air or moisture. The ^1H NMR spectrum of **13** shows a complex multiplet in the region of 7.20–7.45 ppm for the five phenyl protons and two broad multiplets of equal intensity at $\delta = 3.24$ and 3.55 ppm for the methine protons of the cyclohexyl groups. The methine carbon atoms give rise to two $^{13}\text{C}\{^1\text{H}\}$ singlet signals at $\delta = 54.8$ and 56.9 ppm. The presence of the coordinated THF molecule is apparent from two broad ^1H singlet signals at $\delta = 1.79$ and 3.75 ppm and two $^{13}\text{C}\{^1\text{H}\}$ resonances at $\delta = 25.2$ and 68.7 ppm.

Conclusions

The *N,N'*-dicyclohexyl-*N''*-bis(trimethylsilyl)-substituted guanidinate anion is a suitable ligand for the synthesis of stable monomeric monochloro and “ate” complexes of yttrium, neodymium, samarium and lutetium. Alkyl and phenyl complexes of yttrium with very low coordination numbers stabilised by this guanidinate ligand have been synthesised and characterised. Agostic interactions between yttrium and the methyl groups of the *tert*-butyl ligand in $[(\text{Me}_3\text{Si})_2\text{NC}(\text{NCy})_2]_2\text{Y}-t\text{Bu}$ (**8**) in the solid state as well as in solution have been confirmed by X-ray structural analysis and NMR spectroscopy.

Experimental Section

All experiments were performed in evacuated tubes using standard Schlenk techniques with rigorous exclusion of traces of moisture and air. After drying over KOH, THF was purified by distillation from sodium/benzophenone ketyl. Hexane and toluene were dried by distillation from sodium/triglyme and benzophenone ketyl prior to use. $[\text{D}_6]\text{benzene}$ was dried with sodium and condensed in vacuo into the NMR tubes prior to use. *N,N'*-dicyclohexylcarbodiimide and *t*BuLi were purchased from Acros. Anhydrous LuCl_3 ,^[19] $[\text{Li}(\text{Et}_2\text{O})][\text{N}(\text{SiMe}_3)_2]$ ^[20] and $\text{Na}[\text{N}(\text{SiMe}_3)_2]$ ^[21] were prepared according to literature procedures. All other commercially available chemicals were used after appropriate purification. NMR spectra were recorded on a Bruker DPX 200 spectrometer (^1H , 200 MHz; ^{13}C , 50 MHz). Chemical shifts for ^1H and ^{13}C spectra were referenced internally using the residual solvent resonances and are reported relative to TMS. IR spectra were recorded as Nujol mulls on a Specord M80 instrument. Lanthanide metal analyses were carried out by complexometric titration. The C,H elemental analyses were carried out by the microanalytical laboratory of the IOMC.



Scheme 4.

Synthesis of [(Me₃Si)₂NC(NCy)₂]₂YCl(THF) (1): To a solution of Na[N(SiMe₃)₂] (1.00 g, 5.45 mmol) in THF (30 mL) was added CyN=C=NCy (1.12 g, 5.45 mmol) slowly at 20 °C and after 45 min stirring YCl₃ (0.53 g, 2.72 mmol) was added. The reaction mixture was stirred for further 12 h and the NaCl formed was filtered off and from the clear solution and the solvent was evaporated in vacuo. The remaining solid was extracted twice with toluene (2 × 20 mL). After filtration of the toluene extracts, the toluene was evaporated in vacuo. The remaining off-white solid was dissolved in hexane (30 mL). The resultant solution was slowly concentrated at room temperature to a quarter of its volume and was then cooled to −30 °C. The crystalline precipitate formed overnight was washed with cold hexane and then dried in vacuo at room temperature for 40 min yielding **1** (1.67 g, 66%) as a colourless crystalline solid. C₄₂H₈₈ClN₆OSi₄Y (929.2): calcd. C 54.28, H 9.47, Y 9.56; found C 53.83, H 9.12, Y 9.83. ¹H NMR (200 MHz, [D₆]benzene): δ = 0.43 [s, 36 H, Si(CH₃)₃], 1.12–1.88 (br. m, 44 H, CH₂/Cy, β-CH₂/THF), 3.29 (br. m, 4 H, CH/Cy), 3.94 (br. s, 4 H, α-CH₂/THF) ppm. ¹³C{¹H} NMR (50 MHz, [D₆]benzene): δ = 3.1 [N[Si(CH₃)₃]₂], 25.4 (β-CH₂/THF), 23.1, 26.3, 26.6, 31.9, 37.4 (CH₂/Cy), 55.1 (CH/Cy), 70.1 (α-CH₂/THF), 169.1 (CN₃) ppm. IR (Nujol, KBr): ν̄ = 1620 (s), 1320 (m), 1240 (s), 1270 (m), 1200 (m), 1150 (m), 1100 (m), 1050 (m), 950 (s), 930 (s), 860 (m), 830 (s) cm^{−1}.

Synthesis of [(Me₃Si)₂NC(NCy)₂]₂NdCl(THF) (2): Complex **2** was synthesised following the standard procedure described for **1** from Na[N(SiMe₃)₂] (1.80 g, 9.81 mmol), CyN=C=NCy (2.02 g, 9.81 mmol) and NdCl₃ (1.22 g, 4.90 mmol) in THF (30 mL). Complex **2** was isolated as a pale blue crystalline solid (1.67 g, 79%). C₄₂H₈₈ClN₆NdOSi₄ (984.6): calcd. C 51.23, H 8.93, Nd 14.64; found C 50.80, H 9.28, Nd 14.48. IR (Nujol, KBr): ν̄ = 1620 (s), 1330 (m), 1290 (m), 1240 (s), 1160 (s), 1120 (s), 1050 (m), 990 (s), 950 (s), 930 (s), 850 (s), 830 (s) cm^{−1}.

Synthesis of [(Me₃Si)₂NC(NCy)₂]₂SmCl(THF) (3): Complex **3** was synthesised following the standard procedure described for **1** from Na[N(SiMe₃)₂] (1.00 g, 5.45 mmol), CyN=C=NCy (1.12 g, 5.45 mmol) and SmCl₃ (0.7 g, 2.72 mmol) in THF (30 mL). Complex **3** was isolated as a pale yellow crystalline solid (1.50 g, 56%). C₄₂H₈₈ClN₆OSi₄Sm (990.6): calcd. C 50.92, H 8.88, Sm 17.17; found C 50.61, H 8.49, Sm 17.51. IR (Nujol, KBr): ν̄ = 1620 (s), 1335 (m), 1290 (s), 1240 (s), 1170 (m), 1120 (m), 1060 (m), 990 (s), 930 (s), 930 (s), 850 (s), 830 (s) cm^{−1}.

Synthesis of [(Me₃Si)₂NC(NCy)₂]₂LuCl(THF) (4): Complex **4** was synthesised following the standard procedure described for **1** from Na[N(SiMe₃)₂] (1.35 g, 7.36 mmol), CyN=C=NCy (1.51 g, 7.36 mmol) and LuCl₃ (1.03 g, 3.68 mmol) in THF (30 mL). Complex **4** was isolated as a colourless crystalline solid (1.67 g, 69%). C₄₂H₈₈ClLuN₆OSi₄ (1015.3): calcd. C 49.68, H 8.66, Lu 17.23; found C 49.30, H 8.16, Lu 17.58. ¹H NMR (200 MHz, [D₆]benzene): δ = 0.35 [s, 36 H, Si(CH₃)₃], 1.01–2.09 (br. m, 44 H, CH₂/Cy, β-CH₂/THF), 3.15 (br. m, 4 H, CH/Cy), 3.61 (br. s, 4 H, α-CH₂/THF) ppm. ¹³C{¹H} NMR (50 MHz, [D₆]benzene): δ = 2.8 [N[Si(CH₃)₃]₂], 25.7 (β-CH₂/THF), 22.8, 23.1, 25.1, 29.4, 31.2 (CH₂/Cy), 55.7 (CH/Cy), 68.1 (α-CH₂/THF), 169.6 (CN₃) ppm. IR (Nujol, KBr): ν̄ = 1640 (m), 1305 (m), 1260 (s), 1250 (s), 1200 (m), 1150 (m), 1050 (s), 970 (m), 950 (s), 860 (s), 840 (s) cm^{−1}.

Synthesis of [(Me₃Si)₂NC(NCy)₂]₂Y(μ-Cl)₂Li(THF)₂ (5): Complex **5** was synthesised following the standard procedure described for **1** from [Li(Et₂O)][N(SiMe₃)₂] (1.28 g, 5.30 mmol), CyN=C=NCy (1.09 g, 5.30 mmol) and YCl₃ (0.52 g, 2.65 mmol) in THF (30 mL). Complex **5** was isolated as colourless crystalline solid (2.03 g, 74%). C₄₆H₉₆Cl₂LiN₆O₂Si₄Y (1043.7): calcd. C 52.93, H 9.19, Y 8.51; found C 52.57, H 8.81, Y 8.23. ¹H NMR (200 MHz, [D₆]benzene):

δ = 0.37 [s, 36 H, Si(CH₃)₃], 1.30–2.03 (br. m, 48 H, CH₂/Cy, β-CH₂/THF), 3.41 (br. m, 4 H, CH/Cy), 3.79 (br. s, 8 H, α-CH₂/THF) ppm. ¹³C{¹H} NMR (50 MHz, [D₆]benzene): δ = 2.8 [N[Si(CH₃)₃]₂], 25.2 (β-CH₂/THF), 26.1, 26.4, 37.1 (CH₂/Cy), 54.8 (CH/Cy), 71.0 (α-CH₂/THF), 169.0 (CN₃) ppm. IR (Nujol, KBr): ν̄ = 1620 (m), 1340 (m), 1290 (m), 1240 (s), 1210 (m), 1100 (m), 1060 (m), 970 (m), 950 (s), 860 (m), 830 (s) cm^{−1}.

Synthesis of [(Me₃Si)₂NC(NCy)₂]₂Lu(μ-Cl)₂Li(THF)₂ (6): Complex **6** was synthesised following the standard procedure described for **1** from [Li(Et₂O)][N(SiMe₃)₂] (1.56 g, 6.49 mmol), CyN=C=NCy (1.34 g, 6.49 mmol) and LuCl₃ (0.91 g, 3.24 mmol) in THF (30 mL). Complex **6** was isolated as colourless crystalline solid (2.54 g, 70%). C₄₆H₉₆Cl₂LiLuN₆O₂Si₄ (1129.8): calcd. C 48.90, H 8.49, Lu 15.48; found C 48.48, H 8.10, Lu 15.31. ¹H NMR (200 MHz, [D₆]benzene): δ = 0.38 [s, 36 H, Si(CH₃)₃], 1.21–2.11 (br. m, 48 H, CH₂/Cy, β-CH₂/THF), 3.56 (br. m, 4 H, CH/Cy), 3.75 (br. s, 8 H, α-CH₂/THF) ppm. ¹³C{¹H} NMR (50 MHz, [D₆]benzene): δ = 2.9 [N[Si(CH₃)₃]₂], 25.4 (β-CH₂/THF), 14.1, 22.8, 26.0, 26.3, 36.9, (CH₂/Cy), 54.9 (CH/Cy), 68.8 (α-CH₂/THF), 171.2 (CN₃) ppm. IR (Nujol, KBr): ν̄ = 1630 (m), 1350 (m), 1300 (m), 1250 (s), 1210 (m), 1100 (m), 1050 (s), 950 (s), 920 (s), 870 (m), 830 (s) cm^{−1}.

Synthesis of [(Me₃Si)₂NC(NCy)₂]₂Y(μ-Cl)₂Li(DME) (7): Complex **5** (1.10 g, 1.05 mmol) was dissolved in DME (10 mL). Volatiles were evaporated in vacuo and the solid residue was recrystallised from hexane. Complex **7** was isolated as a colourless crystalline solid (0.77 g, 74%). C₄₂H₉₀Cl₂LiN₆O₂Si₄Y (989.7): calcd. C 50.97, H 9.09, Y 8.98; found C 50.60, H 8.71, Y 8.51. ¹H NMR (200 MHz, [D₆]benzene): δ = 0.23 [s, 36 H, Si(CH₃)₃], 1.42–2.02 (br. m, 40 H, CH₂/Cy), 2.79 (s, 4 H, CH₂/DME), 3.15 (s, 6 H, CH₃/DME), 3.46 (br. m, 4 H, CH/Cy) ppm. ¹³C{¹H} NMR (50 MHz, [D₆]benzene): δ = 2.8 [N[Si(CH₃)₃]₂], 26.1, 26.2, 26.4, 33.4, 37.2 (CH₂/Cy), 54.8 (CH/Cy), 58.8 (OCH₃/DME), 70.2 (CH₂/DME), 168.6 (CN₃) ppm. IR (Nujol, KBr): ν̄ = 1640 (s), 1320 (m), 1260 (s), 1240 (s), 1100 (w), 1060 (m), 950 (s), 880 (m), 830 (s) cm^{−1}.

Synthesis of [(Me₃Si)₂NC(NCy)₂]₂Y-*t*Bu (8): To a solution of **1** (0.82 g, 0.88 mmol) in hexane (20 mL) was added a solution of *t*BuLi in hexane (0.58 mL, 1.5 M solution, 0.88 mmol) slowly at 0 °C and the reaction mixture was stirred for 1 h. The mixture was then warmed to room temperature and was stirred again for 1 h. The pale-yellow solution was filtered and concentrated in vacuo to approximately a quarter of its initial volume. The concentrated solution was cooled to −30 °C and kept at that temperature overnight. The mother liquor was then decanted from the precipitate formed. The latter was washed with cold hexane and was dried in vacuo at room temperature for 30 min yielding **8** as colourless crystals (0.40 g, 52%). C₄₂H₈₉N₆Si₄Y (879.4): calcd. C 57.36, H 10.12, Y 10.10; found C 56.99, H 9.81, Y 9.79. ¹H NMR (200 MHz, [D₆]benzene): δ = 0.28, 0.32, 0.36 [3 s, 36 H, Si(CH₃)₃], 1.48 [s, 9 H, C(CH₃)₃], 1.27–2.04 (br. m, 40 H, CH₂/Cy), 3.45, 3.63 (2 br. m, 4 H, CH/Cy) ppm. ¹³C{¹H} NMR (50 MHz, [D₆]benzene): δ = 2.3, 2.4, 2.8 [N[Si(CH₃)₃]₂], 24.9, 25.9, 26.1, 26.2, 26.4 (CH₂/Cy), 30.65 [d, ²J = 2.3 Hz, C(CH₃)₃], 37.5 [d, ¹J_{YC} = 56 Hz, C(CH₃)₃], 55.2 (CH/Cy), 168.7 (CN₃) ppm. IR (Nujol, KBr): ν̄ = 1620 (s), 1330 (m), 1220 (s), 1260 (m), 1205 (m), 1150 (m), 950 (s), 930 (s), 830 (s) cm^{−1}.

NMR Tube Synthesis of [(Me₃Si)₂NC(NCy)₂]₂YMe (9): A solution of MeLi in diethyl ether (0.028 mL, 1.6 M, 0.0448 mmol) was added to a solution of **1** (41.62 mg, 0.0448 mmol) in [D₈]toluene (2 mL) in an NMR tube at 0 °C which was then sealed. The reaction mixture was warmed to room temperature, shaken for 30 min and then left for 45 min to allow the LiCl to settle. ¹H NMR (200 MHz,

[D₆]benzene): δ = −0.36 (br. s, 3 H, YCH₃), 0.46, 0.47 [s, 36 H, NSi(CH₃)₃], 1.32–2.03 (br. m, 40 H, CH₂/Cy), 3.47, 3.95 (br. m, together 4 H, CH/Cy) ppm.

Synthesis of [(Me₃Si)₂NC(NCy)₂Y(μ-Me)₂Li(TMEDA) (10): To a solution of **1** (0.97 g, 1.04 mmol) in hexane (20 mL) were added TMEDA (0.24 g, 2.08 mmol) and a solution of MeLi in diethyl ether (1.3 mL, 1.6 M solution, 2.08 mmol) slowly at 0 °C. The reaction mixture was stirred for 45 min and was then warmed to room temperature and again stirred for 1.5 h. The pale-yellow solution was filtered and concentrated in vacuo to approximately half of its initial volume. When the precipitation of crystals started, the solution was cooled to −10 °C and kept at that temperature for 2 h. The mother liquor was decanted and the small amount of colourless crystals was washed with cold hexane, dried in vacuo at room temperature for 15 min and identified as the side product **11** (0.07 g, 7%). The decanted mother liquor was concentrated to the half of its initial volume, cooled to −30 °C and left at that temperature for one week. The crystalline solid formed was separated by decantation, washed with cold hexane and dried in vacuo leaving colourless crystals of **10** (0.40 g, 61%). C₄₆H₁₀₂LiN₈Si₄Y (974.7): calcd. C 56.68, H 10.46, Y 9.12; found C 56.31, H 10.02, Y 9.33. ¹H NMR (200 MHz, [D₆]benzene): δ = −0.51 (br. s, 6 H, μ-CH₃), 0.53 [s, 36 H, Si(CH₃)₃], 1.32–2.00 [br. m, 44 H, CH₂/Cy, (NCH₂)₂], 2.12 [s, 12 H, N(CH₃)₂], 3.58 (br. m, 4 H, CH/Cy). ¹³C{¹H} NMR (50 MHz, [D₆]benzene): δ = 3.1 [N[Si(CH₃)₃]₂], 11.6 (br., μ-CH₃), 14.3, 23.0, 26.6, 26.7, 31.2 (CH₂/Cy), 46.2 ([N(CH₃)₂]₂), 55.2 (CH/Cy), 57.6 (NCH₂), 167.6 (CN₃) ppm. **11**: C₂₅H₅₆LiN₅Si₂ (489.8): calcd. C 61.29, H 11.43; found C 61.56, H 11.81. ¹H NMR (200 MHz, [D₆]benzene): δ = 0.31 [s, 18 H, Si(CH₃)₃], 1.15–2.00 [br. m, 24 H, CH₂/Cy, (NCH₂)₂], 2.15 [s, 12 H, N(CH₃)₂], 3.42 (m, 4 H, CH/Cy). ¹³C{¹H} NMR (50 MHz, [D₆]benzene): δ = 3.0 [N[Si(CH₃)₃]₂], 26.6, 26.7, 31.2 (CH₂/Cy), 46.6 [N(CH₃)₂], 54.8 (CH/Cy), 57.4 (NCH₂), 165.3 (CN₃) ppm.

NMR Tube Synthesis of [(Me₃Si)₂NC(NCy)₂YCH₂SiMe₃ (12): In an inert atmosphere, compound **1** (36.00 mg, 0.0387 mmol), LiCH₂SiMe₃ (3.64 mg, 0.0387 mmol) and [D₈]toluene (2 mL) were mixed in an NMR tube at 0 °C which was then sealed. The reaction mixture was warmed to room temperature, shaken for 30 min then left for 30 min for the LiCl to settle. The spectroscopic investigation of the solution product indicated the formation of **12**: ¹H NMR (200 MHz, [D₈]toluene): δ = −0.16 (d, ²J_{Y,H} = 3.0 Hz, 2 H, YCH₂), 0.37 [s, 36 H, NSi(CH₃)₃], 0.52 [s, 9 H, CH₂Si(CH₃)₃], 1.24–2.00 (br. m, 40 H, CH₂/Cy), 3.46 (br. m, 4 H, CH/Cy) ppm.

Synthesis of [(Me₃Si)₂NC(NCy)₂YPh(THF) (13): A solution of phenyllithium (0.10 g, 1.20 mmol) in THF (10 mL) was slowly added at 0 °C to a solution of **1** (1.12 g, 1.20 mmol) in THF (20 mL) and the reaction mixture was stirred for 2 h. After warming to room temperature the solvent was evaporated in vacuo. The remaining off-white solid was extracted with hexane (40 mL). The extract was filtered and concentrated to a quarter of its initial volume, cooled to −30 °C and left at that temperature for one week. The crystalline solid formed was separated from the mother liquor by decantation, washed with cold hexane and dried in vacuo at room temperature for 20 min leaving colourless crystals of **13** (0.66 g, 61%). C₄₈H₉₃N₆O₄Si₄Y (970.8): calcd. C 59.38, H 9.57, Y 9.15; found C 59.00, H 9.19, Y 9.41. ¹H NMR (200 MHz, [D₆]benzene): δ = 0.53 [s, 36 H, Si(CH₃)₃], 1.33–2.10 (br. m, 44 H, CH₂/Cy, β-CH₂/THF), 3.24, 3.55 (br. m, 4 H, CH/Cy), 3.75 (br. s, 4 H, α-CH₂/THF), 7.20–7.45 (m, 5 H, Ar) ppm. ¹³C{¹H} NMR (50 MHz, [D₆]benzene): δ = 3.4 [N[Si(CH₃)₃]₂], 25.2 (β-CH₂/THF), 22.8, 25.8, 26.4, 26.9, 37.2 (CH₂/Cy), 54.8, 56.9 (CH/Cy), 68.7 (α-CH₂/THF), 127.1, 127.6, 128.0, 137.2 (Ar), 169.4 (CN₃), 177.8 (d, ¹J_{Y,C} = 51 Hz, ipso-C, Ar) ppm.

X-ray Crystallographic Study: The crystal data and details of data collection are given in Table 1. X-ray data were collected on a Siemens SMART CCD diffractometer (graphite-monochromated Mo-K_α radiation, λ = 0.71073 Å, ω -scan technique) with an area-detector at −100 °C. The intensity data were integrated with the SAINT program.^[22] SADABS^[23] was used to perform area-detector scaling and absorption corrections. The structures were solved by direct methods and were refined on F^2 using all reflections with SHELXTL.^[24] All non-hydrogen atoms were refined anisotropically. The hydrogen atoms of the THF ligands in **1** and **6** were placed in calculated positions and refined in the “riding-model”. All other hydrogen atoms in **1** and **6** as well as in **7**, **8** and **11** were found from the Fourier syntheses and refined isotropically. CCDC-281699 (for **1**), -281698 (for **6**), -281697 (for **7**), -281695 (for **8**) and -281696 (for **11**) 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.

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