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Metalation of aromatic heterocycles by yttrium alkyl complexes that contain a linked amido-cyclopentadienyl ligand: synthesis, structure and Lewis base adduct formation

Stefan Arndt [a], Alexander Trifonov [a], Thomas P. Spaniol [a], Jun Okuda [a,*], Masanori Kitamura [b,1], Tamotsu Takahashi [b]

[a] *Institut für Anorganische Chemie und Analytische Chemie, Johannes Gutenberg-Universität, Duesberg-Weg 10-14, D-55099 Mainz, Germany*
[b] *Catalysis Research Center and Graduate School of Pharmaceutical Sciences, Hokkaido University, Kita 11 Jo, Nishi 10 Chome, Kita-ku, Sapporo 060-0811, Japan*

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Abstract

The reaction of the half-sandwich alkyl complex $[Y(\eta^5:\eta^1\text{-}C_5Me_4SiMe_2NCMe_3)(CH_2SiMe_3)(THF)]$ with furan and thiophene gives metalation products $[Y(\eta^5:\eta^1\text{-}C_5Me_4SiMe_2NCMe_3)(\mu\text{-}2\text{-}C_4H_3X)]_2$ (X = O, S) which are sparingly soluble in hydrocarbons due to the dimeric structure. Single crystal X-ray structure analysis of the 2-thienyl complex confirms a six-membered core with bridging sulfur atoms and trans-disposed amido-tetramethylcyclopentadienyl ligands. In contrast to THF and pyridine, 1,2-dimethoxyethane (DME) forms isolable, crystalline adducts $[Y(\eta^5:\eta^1\text{-}C_5Me_4SiMe_2NCMe_3)(2\text{-}C_4H_3X)(DME)]$. Single crystal X-ray structure analysis of the 2-furyl derivative shows a four-legged piano stool configuration. The reaction of $[Y(\eta^5:\eta^1\text{-}C_5Me_4SiMe_2NCMe_3)(CH_2SiMe_3)(THF)]$ with excess DME gives the isolable, five-coordinate complex $[Y(\eta^5:\eta^1\text{-}C_5Me_4SiMe_2NCMe_3)(CH_2SiMe_3)(DME)]$ that does not react with furan or thiophene, indicating an associative mechanism. $[Y(\eta^5:\eta^1\text{-}C_5Me_4SiMe_2NCMe_3)(CH_2SiMe_3)(THF)]$ reacts with pyrrole to give the sparingly soluble pyrrolide that can be studied by crystallography as a DME adduct $[Y(\eta^5:\eta^1\text{-}C_5Me_4SiMe_2NCMe_3)(\eta^1\text{-}\kappa N\text{-}C_4H_4N)(DME)]$. The reaction of $[Y(\eta^5:\eta^1\text{-}C_5Me_4CH_2SiMe_2NCMe_3)(CH_2SiMe_3)(THF)]$ that contains the longer CH_2SiMe_2-bridge reacts with furan to a mixture of a hydrocarbon-soluble dimer and the labile THF adduct, whilst the reaction with thiophene results in the selective formation of the monomeric $[Y(\eta^5:\eta^1\text{-}C_5Me_4CH_2SiMe_2NCMe_3)(2\text{-}C_4H_3S)(THF)]$ which was characterized by crystallography. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Yttrium; Amido-cyclopentadienyl ligand; Half-sandwich complexes; C–H bond activation; Heterocycles

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1. Introduction

Metallocenes of the rare earth metals have been known for quite some time to activate C–H bonds in both saturated and unsaturated organic substrates [1]. Extensive systematic studies by Bercaw et al. have established the σ-bond metathesis as a general reaction type whenever metal complexes with f^xd^0-electron configuration undergo C–H activation processes [2]. One of the most common reactions is the ortho-metalation of aromatic molecules by decamethyl lanthanocenes $[Ln(C_5Me_5)_2X]$ (X = H, alkyl) [3]. More recently, this type of reaction of thiophene was combined with ethylene insertion chemistry of the resulting 2-thienyl complex to synthesize polyethylenes with 2-thienyl-end groups [4]. We have reported that the labile yttrium alkyl complex $[Y(\eta^5:\eta^1\text{-}C_5Me_4SiMe_2NCMe_3)(CH_2SiMe_3)(THF)]$ (**1**) [5] cleanly undergoes σ-bond metathesis with aromatic heterocycles such as furan and thiophene, whilst, not unexpectedly, undergoes protonolysis with pyrrole [6]. The products of these reactions are sparingly soluble due to their dimeric structure and were found to dissolve only in strong Lewis-bases such as THF or pyridine. We report here the structure of some of these derivatives

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* Corresponding author. Tel.: +49-6131-3923737; fax: +49-6131-3925605.
E-mail address: okuda@mail.uni-mainz.de (J. Okuda).

[1] Exchange research fellow at the University of Mainz, 2001.

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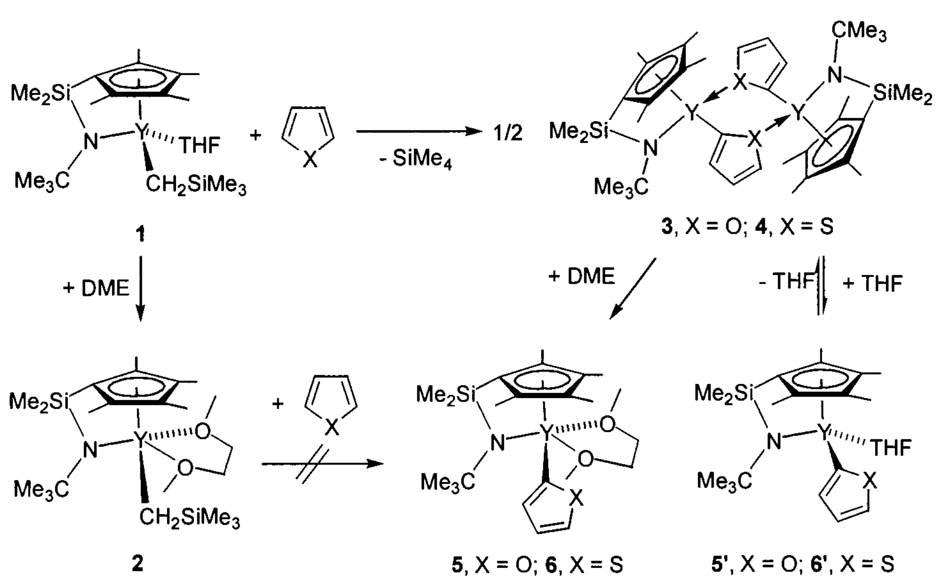


Scheme 1.

and the extension of the reaction to a system containing the longer CH_2SiMe_2 instead of the $SiMe_2$ link. Such a change in the ancillary ligand was recently found to result in significantly higher solubility and reactivity [7].

2. Results and discussion

When the alkyl complex [$Y(\eta^5:\eta^1-C_5Me_4SiMe_2NCMe_3)(CH_2SiMe_3)(THF)$] (**1**) [5] is treated in pentane with excess of furan or thiophene at 25 °C, tetramethylsilane is formed and sparingly soluble dimeric complexes [$Y(\eta^5:\eta^1-C_5Me_4SiMe_2NCMe_3)(\mu-2-C_4H_3X)]_2$ (X = O, **3**; S, **4**) precipitates in good yields (Scheme 1). In analogy to the crystallographically characterized 2-thienyl permethylyttrocene complex [$Y(\eta^5-C_5Me_5)_2(\mu-2-C_4H_3S)]_2$, [4] the crystal structure determination confirmed a centrosymmetric dimeric structure for **4** (Fig. 1). The $C_5Me_4SiMe_2NCMe_3$ ligands are arranged in a transoidal fashion. The two 'metallocene-like' $Y(\eta^5:\eta^1-C_5Me_4SiMe_2NCMe_3)$ fragments are connected by two bridging 2-thienyl ligands forming a puckered six-membered ring core. In addition to the short yttrium–carbon bond length between Y and C19 (2.50(1) Å), the ring atoms seem to form an η^5-interaction with the second yttrium atom. Interatomic distances between the metal atom and the ring atoms are in the range of 2.82(1) and 2.947(5) Å, whereby the latter distance involves the sulfur atom. As was previously observed for the crystal structure of the 2-furyl derivative **3**, [5] there is disorder in the bridging 2-thienyl groups (that may be explained by the η^5-interaction). The distances between yttrium and the (disordered) positions for the sulfur atom are 2.912(5) and 2.947(5) Å.

Whereas, the dimeric complexes **3** and **4** easily form back from THF solutions due to the lability of the THF adducts **5′** and **6′**, the 2-furyl complex **3** can be crystallized from DME to give single crystals of the DME adduct **5** which were found to be amenable to X-ray structure analysis. The results show a four-legged piano-stool molecule with yttrium–oxygen bond lengths in the range of 2.387(2) and 2.482(2) Å (for the two crystallographically independent molecules) (Fig. 2). The longer yttrium–oxygen bond distances are *trans* to the amido-nitrogen atom of the ancillary ligand. The angles at the yttrium center add to 341. The NMR spectra of **5** in pyridine-d_5 display a molecule with a mirror plane due to the complete dissociation of the DME molecule which appears as two singlets at 3.28

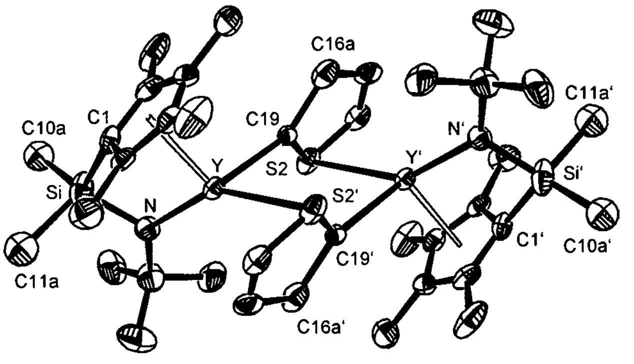


Fig. 1. ORTEP diagram of the molecular structure of **4**. Thermal ellipsoids are drawn at 30% probability level. Hydrogen atoms are omitted for the sake of clarity; selected bond distances (Å) and angles (°): Y–C16(=S′), 2.912(5); Y–C17, 2.84(1); Y–C18, 2.82(1); Y–C19^1, 2.87(1); Y–S(=C16′), 2.947(5); Y–C19, 2.50(1); Y–N, 2.233(9); Y–Cp_{cent}, 2.34(1); Y···Y′, 4.381(2); C1–Si–N, 97.7(5); Si–N–Y, 102.8(5); Cp_{cent}–Y–C19, 110.7(4); Cp_{cent}–Y–N, 98.6(4); C19–Y–N, 105.6(4).

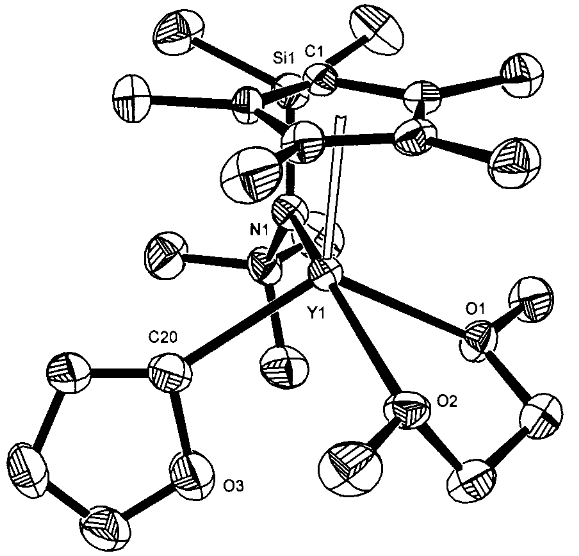
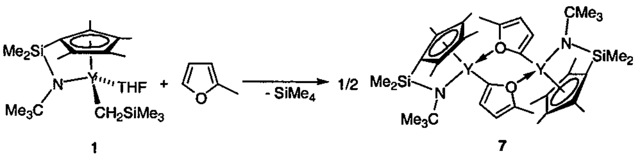


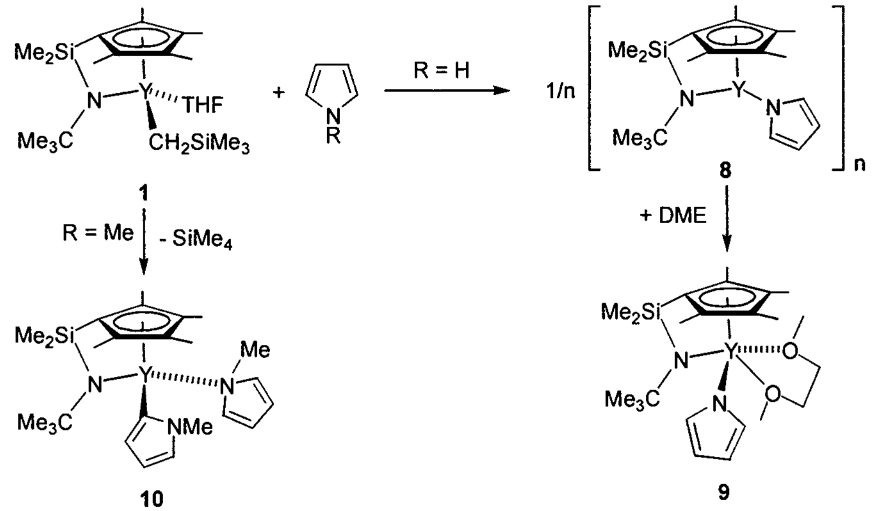
Fig. 2. ORTEP diagram of the molecular structure of **5**. Thermal ellipsoids are drawn at 50% probability level. Hydrogen atoms are omitted for the sake of clarity; selected bond distances (Å) and angles (°): Y1–C20, 2.463(3); Y1–N1, 2.241(2); Y1–O1, 2.387(2); Y1–O2, 2.473(2); Y–Cp_{cent}, 2.351(1); C1–Si1–N1, 97.5(1); Si1–N1–Y1, 105.0(1); Cp_{cent}–Y1–C20, 116.1(1); Cp_{cent}–Y1–N1, 97.2(1); Cp_{cent}–Y1–O1, 114.9(1); Cp_{cent}–Y1–O2, 105.3(1); N1–Y1–C20, 101.1(1); C20–Y1–O2, 81.91(9); O2–Y1–O1, 66.06(7); O1–Y1–N1, 91.71(8).

ppm for the 6 methoxy and at 3.50 ppm for the 4 methylene protons. The 2-furyl group gives rise to a doublet for the 3-proton at 6.57 ppm ($^3J_{HH} = 3.0$ Hz), a double doublet for the 4-proton at 6.52 ppm ($^3J_{HH} =$ 3.0, 1.4 Hz), and a doublet for the 5-proton at 7.89 ppm ($^3J_{HH} = 1.4$ Hz). In the ^{13}C-NMR spectrum the 2-carbon appears as a doublet at 209.2 ppm with $^1J_{YC} = 52.3$ Hz. The corresponding resonance in the THF adduct **5′** is found at 204.4 ppm with $^1J_{YC} = 59.0$ Hz [6].

When the alkyl complex $[Y(\eta^5:\eta^1\text{-}C_5Me_4SiMe_2NCMe_3)(CH_2SiMe_3)(THF)]$ (**1**) is recrystallized from 1,2-dimethoxyethane (DME), the labile THF molecule was completely displaced to give the DME adduct $[Y(\eta^5:\eta^1\text{-}C_5Me_4SiMe_2NCMe_3)(CH_2SiMe_3)(DME)]$ (**2**). This complex does not undergo any metalation reaction with furan or thiophene even at elevated temperatures, indicating that an associative mechanism may be operative when **1** is involved. Due to the insolubility of **2** in THF, the NMR spectra were recorded in pyridine-d_5 at 25 °C. Both ^{1}H- and ^{13}C-NMR spectra show the presence of a mirror plane with the coordinated DME completely dissociated (singlets at 3.27 for the 6 methoxy and at 3.48 ppm for the 4 methylene protons). The CH_2 group attached to the yttrium gives rise to a doublet at −0.64 ppm with $^2J_{YH} = 2.9$ Hz in the ^{1}H-NMR and a doublet at 23.0 ppm with $^1J_{YC} = 39.6$ Hz in the ^{13}C-NMR spectrum. The corresponding signal for the THF complex **1** in C_6D_6 is found at 26.2 ppm with $^1J_{YC} = 45$ Hz, the higher value is in agreement with a lower coordination number [6]. 2-Methylfuran can be similarly metalated by **1** to give $[Y(\eta^5:\eta^1\text{-}C_5Me_4SiMe_2NCMe_3)(\mu\text{-}2\text{-}(OC_4H_2Me\text{-}5))]_2$ (**7**) according to Eq. (1), but the solubility in benzene is not high enough to study its structure in hydrocarbon solution. The NMR spectroscopic feature in THF-d_8 is analogous to that of the 2-furyl complex **3** and its THF adduct **5′**.



(1)



Scheme 2.

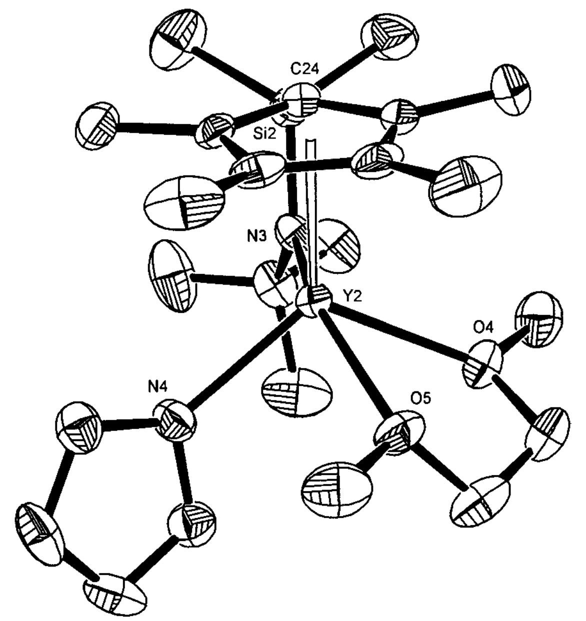
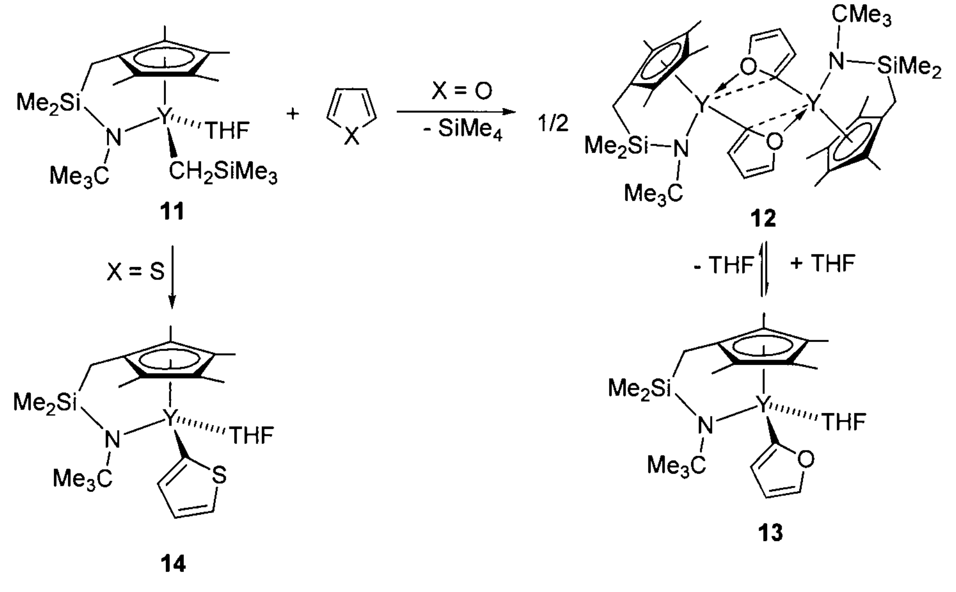


Fig. 3. ORTEP diagram of the molecular structure of **9**. Thermal ellipsoids are drawn at 50% probability level. Hydrogen atoms are omitted for the sake of clarity; selected bond distances (Å) and angles (°): Y1–N1, 2.246(2); Y1–N2, 2.337(2); Y1–O1, 2.386(2); Y1–O2, 2.439(2); Y1–Cp_{cent}, 2.356(2); C1–Si1–N1, 97.7(1); Si1–N1–Y1, 104.53(9); Cp_{cent}–Y1–N1, 97.37(7); Cp_{cent}–Y1–N2, 120.50(7); Cp_{cent}–Y1–O1, 111.54(7); Cp_{cent}–Y1–O2, 105.36(7); N1–Y1–N2, 99.34(7); N1–Y1–O2, 153.69(6); O1–Y1–O2, 65.94(6); O2–Y1–N2, 80.53(6).

DME was found to be also a suitable Lewis base to dissolve the insoluble pyrrolide **8** formed by the protonolysis of the alkyl **1** with pyrrole (Scheme 2). Recrystallization of **8** from DME gives crystals of the DME adduct **9**, which are suitable for X-ray structure analysis (Fig. 3). The molecular structure of **9** in the crystal is as expected, showing a four-legged piano stool configuration. The Y–N bond distances for the pyrrolide ligand (in both crystallographically independent molecules) are 2.337(2) and 2.319(2) Å, whereas, the Y–N distances for the ancillary ligands are 2.246(2) and 2.247(2) Å. These values are within the expected range for Y–N bond lengths such as those of 2.184(7) and 2.255(8) and in $[Y(\eta^5{:}\eta^1\text{-}C_5Me_4SiMe_2NCMe_3)\{N(SiMe_3)_2\}]$ [8a]. Generally, the distance of the metal to the amido nitrogen atom of the chelating ligand appears to be by about 3% longer than that to the silylamido nitrogen, as found in the samarium complex $[Sm(\eta^5{:}\eta^1\text{-}C_5Me_4SiMe_2NCMe_3)\{N(SiMe_3)_2\}]$ [8b]. The NMR spectra are identical with those obtained from pyridine-d_5 solutions of **8** except that free DME can be detected. *N*-Methylpyrrole reacts with **1** under orthometalation to give a 2-*N*-methylpyrrolide complex as a *N*-methylpyrrole adduct **10**.

When the alkyl complex containing the CH_2SiMe_2 link $[Y(\eta^5{:}\eta^1\text{-}C_5Me_4CH_2SiMe_2NCMe_3)(CH_2SiMe_3)(THF)]$ (**11**) [7] was reacted with furan, a mixture of both the dimer **12** and the THF adduct was formed (Scheme 3). The new THF-free complex **12** was soluble in hydrocarbons and NMR spectra in C_6D_6 showed the presence of a symmetrical molecule. Most interestingly, a triplet at 201.7 ppm with $^1J_{YC} = 24.7$ Hz was detected in the ^{13}C-NMR spectrum, indicating a dimeric structure in which not only the oxygen, but the 2-carbon of the furyl group is interacting with both yttrium atoms. As expected, however, when the ^{13}C-NMR spectrum of **12** was recorded in THF-d_8, a doublet at 208.0 ppm with $^1J_{YC} = 55.0$ Hz was observed for the 2-furyl carbon atom.



Scheme 3.

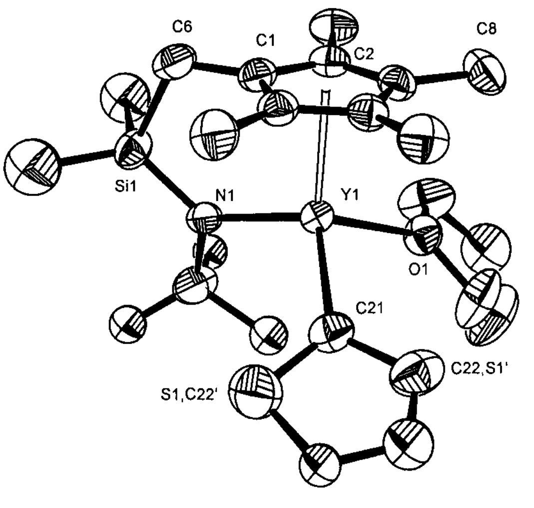
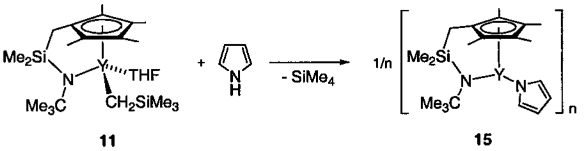


Fig. 4. ORTEP diagram of the molecular structure of **14**. Thermal ellipsoids are drawn at 50% probability level. Hydrogen atoms are omitted for the sake of clarity; selected bond distances (Å) and angle (°): Y1–C21, 2.436(3); Y1–N1, 2.218(3); Y1–O1, 2.335(2); Y1–$\mathrm{Cp_{cent}}$, 2.324(3); C1–C6–Si1, 115.7(2); C6–Si1–N1, 106.7(2); Si1–N1–Y1, 123.5(1); C21–Y1–$\mathrm{Cp_{cent}}$, 111.01; N1–Y1–$\mathrm{Cp_{cent}}$, 106.0(1); O1–Y–$\mathrm{Cp_{cent}}$, 109.7(1); N1–Y1–O1, 114.39(9); O1–Y1–C21, 102.7(1); C21–Y1–N1, 113.0(1).

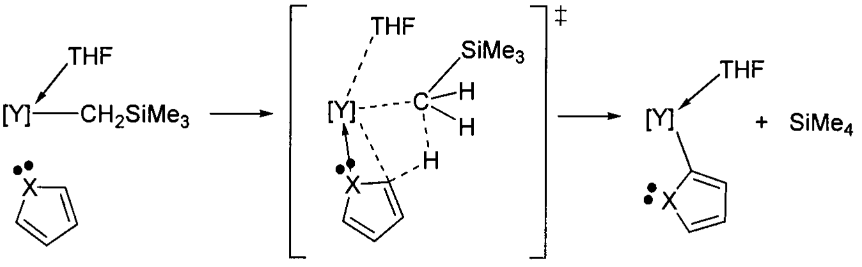
The reaction of the alkyl **11** with thiophene smoothly gives the THF adduct [Y(η^5:η^1-$C_5Me_4CH_2SiMe_2$-$NCMe_3$)(2-C_4H_3S)(THF)] (**14**) selectively as hydrocarbon-soluble, colorless crystals. At room temperature, the chiral molecule has a mirror plane due to the usual lability of the THF. In the ^{1}H-NMR spectrum the 2-thienyl group shows resonances at 7.39 (d, $^3J_{HH} = 2.8$ Hz, C_4H_3S-3), 7.46 (dd, $^3J_{HH} = 2.8$ Hz, 4.4 Hz, C_4H_3S-4), and 7.76 ppm (d, $^3J_{HH} = 4.4$ Hz, C_4H_3S-5). In the ^{13}C-NMR spectrum the 2-carbon gives rise to a doublet at 178.2 ppm with $^1J_{YC} = 42$ Hz, as compared with a resonance at 176.7 ppm with $^1J_{YC} = 55$ Hz for **6**′ in THF-d_8. The decamethylyttrocene complex [Y(η^5-$C_5Me_5)_2$(2-C_4H_3S)(THF)] shows a resonance for the corresponding carbon atom at 180.24 ppm with $^1J_{YC} =$ 62 Hz in THF-d_8. [3e] The single crystal X-ray structure analysis of **14** confirmed the postulated structure of a three-legged piano-stool molecule (Fig. 4). The yttrium-2-thienyl carbon distance is 2.436(3) Å (as well as 2.415(3) Å in the second crystallographically independent molecule) and comparable to that in the dimeric complex **4**. The sum of the angles at the yttrium center is 330° (as well as 327°). Other metrical parameters such as Y–N and Y–O bond lengths are similar to those of the parent alkyl **11** [7]. The 2-thienyl group is disordered with identical positions for S1 and C22 (as well as for S2 and C42) [9]. Finally pyrrole reacts with **11** to give the pyrrolide complex **15** that is only soluble in pyridine or THF (Eq. (2)).



(2)

3. Conclusion

The two alkyl complexes [Y{η^5:η^1-$C_5Me_4(CH_2)_x$-$SiMe_2NCMe_3$}(CH_2SiMe_3)(THF)] (**1**, $x = 0$; **11**, $x = 1$) smoothly undergo σ-bond metathesis with furan and thiophene to give tetramethylsilane and ortho-metalated products. Depending on the ancillary ligand, dimeric, THF, or DME adducts can be isolated and structurally characterized. In agreement with the negative activation entropy and large kinetic isotope effect for the reaction of **1** with thiophene, [6] all reactions appear to follow associative pathways (Scheme 4), since the DME adducts of the alkyls [Y{η^5:η^1-$C_5Me_4(CH_2)_x$-$SiMe_2NCMe_3$}(CH_2SiMe_3)(DME)] do not react with furan and thiophene. Thus yttrium complexes with a linked amido-cyclopentadienyl ligand have three ligand sites that are accessible (one X- and two L-type ligands; in principle up to five orbitals are available). This is in contrast to the situation in scandium complexes [Sc{η^5:η^1-$C_5Me_4SiMe_2NCMe_3$}X(L)], where the dimeric hydride [Sc(η^5:η^1-$C_5Me_4SiMe_2NCMe_3$)(PMe_3)-(μ-H)]$_2$ is the only five-coordinate species [10]. Metallocene hydrido and alkyl derivatives commonly accommodate one X and one L ligands, but are relatively more reactive toward C,H-bond activation reactions [11]. Despite the sterically open ligand sphere, the



Scheme 4.

strongly π-donating amido group apparently renders the Group 3 metal less electrophilic. The dramatic solubility difference upon extending the linking group from $SiMe_2$ to CH_2SiMe_2 is ascribed to the decreased electrophilicity of the yttrium center [7]. This is may be due to the increased steric demand of the longer bridge with additional conformational flexibility.

4. Experimental

4.1. General considerations

All operations were performed under an inert atmosphere of Ar using standard Schlenk-line or glovebox techniques. After drying over KOH, THF was distilled from sodium benzophenone ketyl. Hexane and $C_6H_5CH_3$ were purified by distillation from Na–triglyme benzophenone ketyl. Anhydrous yttrium trichloride (ALFA or Strem) was used as received. The alkyl complexes $[Y\{\eta^5{:}\eta^1\text{-}C_5Me_4(CH_2)_xSiMe_2NCMe_3\}(CH_2SiMe_3)(THF)]$ (**1**, $x = 0$; **11**, $x = 1$) were prepared according to published procedures [5b,7]. All other chemicals were commercially available and used after appropriate purification. NMR spectra were recorded on a Bruker DRX 400 spectrometer (^1H, 400 MHz; ^{13}C, 101 MHz; ^{89}Y, 19.6 MHz) at 25 °C, unless otherwise stated. Chemical shifts for ^1H and ^{13}C spectra were referenced internally using the residual solvent resonances and reported relative to tetramethylsilane. ^{89}Y spectra were referenced externally to a 1 M solution of YCl_3 in D_2O. Elemental analyses were performed by the Microanalytical Laboratory of this Department. In many cases the results were not satisfactory and the best values from repeated runs were given. Moreover, the results were inconsistent from run to run and therefore, not reproducible. We ascribe this difficulty observed also by other workers [12] to the extreme sensitivity of the material.

4.2. $[Y(\eta^5{:}\eta^1\text{-}C_5Me_4SiMe_2NCMe_3)(CH_2SiMe_3)(DME)]$ (2)

A suspension of $[Y(\eta^5{:}\eta^1\text{-}C_5Me_4SiMe_2NCMe_3)(CH_2SiMe_3)(THF)]$ (**1**) (200 mg, 402 μmol) in 3 ml of dimethoxyethane (DME) was stirred at 25 °C for 16 h. After standing for 5 h at −40 °C, the supernatant was decanted to afford colorless microcrystals (172 mg, 82%). ^1H-NMR (pyridine-d_5): δ −0.64 (d, $^2J_{YH} = 2.9$ Hz, 2H, YCH_2), 0.08 (s, 9H, CH_2SiCH_3), 0.75 (s, 6H, $SiMe_2$), 1.35 (s, 9H, $NCCH_3$), 1.80, 2.16 (s, 2 × 6H, C_5CH_3), 3.27 (s, 2 × 3H, OCH_3), 3.48 (s, 2 × 2H, OCH_2). ^{13}C-NMR (pyridine-d_5): δ 4.6 (CH_2SiCH_3), 8.6 ($SiMe_2$), 11.0, 14.2 (C_5CH_3), 23.0 (d, $^1J_{YC} = 39.6$ Hz), 35.1 (CCH_3), 53.5 (DME), 58.1 (CCH_3), 71.5 (DME), 106.6 (C_5Me_4 attached to $SiMe_2$), 121.4, 124.6 (C_5Me_4). Anal. Calc. for $C_{23}H_{48}NO_2Si_2Y$: C, 53.57; H, 9.38; N, 2.72. Found: C, 52.73; H, 9.78; N, 3.06%.

4.3. $[Y(\eta^5{:}\eta^1\text{-}C_5Me_4SiMe_2NCMe_3)(C_4H_3O\text{-}2)(DME)]$ (5)

To a solution of **1** (200 mg, 402 μmol) in C_5H_{12} (5 ml) was added neat furan (470 mg, 6.9 mmol). After stirring the reaction mixture for 2 h at 25 °C, colorless microcrystals formed. The supernatant was decanted and the precipitate was dissolved in DME (5 ml). After 20 h at −40 °C, colorless crystals (48 mg, 24%) were obtained. Single crystals for X-ray structure analysis were grown from DME solutions at 25 °C. ^1H-NMR (pyridine-d_5): δ 0.81 (s, 6H, $SiMe_2$), 1.39 (s, 9H, $NCCH_3$), 1.99, 2.09 (s, 2 × 6H, C_5CH_3), 3.28 (s, 2 × 3H, OCH_3), 3.51 (2 × 2H, OCH_2), 6.52 (dd, $^3J_{HH} = 3.0$ Hz, 1.4 Hz, 1H, 4-C_4H_3O), 6.57 (d, $^3J_{HH} = 3.0$ Hz, 1H, 3-C_4H_3O), 7.89 (d, $^3J_{HH} = 1.4$ Hz, 1H, 5-C_4H_3O). ^{13}C-NMR (pyridine-d_5): δ 9.1 ($SiMe_2$), 11.5, 14.7 (C_5CH_3), 35.4 (CCH_3), 54.5 (DME), 58.6 (CCH_3), 72.0 (DME), 107.3 (C_5Me_4 attached to $SiMe_2$), 108.5, 118.4 (C_4H_3O), 122.7, 126.2 (C_5Me_4), 143.7 (C_4H_3O), 209.2 (d, $^1J_{YC} = 52.3$ Hz, 2-C_4H_3O). Anal. Calc. for $C_{23}H_{40}NO_2Si_2Y$: C, 55.74; H, 8.14; N, 2.83. Found: C, 54.71; H, 8.73; N, 3.52%.

4.4. $[Y(\eta^5{:}\eta^1\text{-}C_5Me_4SiMe_2NCMe_3)\{2\text{-}(OC_4H_2Me\text{-}5)\}]_2$ (7)

To a solution of **1** (200 mg, 402 μmol) in C_5H_{12} (5 ml) was added 2-methylfuran (550 mg, 6.7 mmol). The solution was stirred for 4.5 h at 25 °C, and cooled down to −40 °C. After standing for 2 days at this temperature, yellow microcrystals were obtained (101 mg, 60%). ^1H-NMR (THF-d_8): δ 0.39 (s, 6H, $SiCH_3$), 1.26 (s, 9H, $NCCH_3$), 2.01, 2.02 (s, 2 × 6H, C_5CH_3), 2.20 (s, 3H, $C_4H_2CH_3$), 5.59 (br, 1H, $C_4H_2CH_3$), 6.06 (d, $^3J_{HH} = 2.6$ Hz, 1H, $C_4H_2CH_3$). ^{13}C-NMR (THF-d_8): δ 8.8 ($SiCH_3$), 11.6 (C_5CH_3), 13.9 ($C_4H_2CH_3$), 14.9 (C_5CH_3), 35.3 (CCH_3), 54.6 (CCH_3), 104.3 ($C_4H_2CH_3$), 107.0 (C_5CH_3 attached to $SiMe_2$), 120.4 ($C_4H_2CH_3$), 121.6, 126.7 (C_5CH_3), 151.4 ($C_4H_2CH_3$), 206.6 (d, $^1J_{YC} = 60.0$ Hz, $C_4H_2CH_3$). Anal. Calc. for $C_{24}H_{40}NO_2SiY$: C, 58.64; H, 8.20; N, 2.85. Found: C, 56.31; H, 8.00; N, 3.68%.

4.5. $[Y(\eta^5{:}\eta^1\text{-}C_5Me_4SiMe_2NCMe_3)(\eta^1\text{-}\kappa N\text{-}C_4H_4N)(DME)]$ (9)

To a solution of **1** (200 mg, 402 μmol) in C_5H_{12} (9 ml) was added neat pyrrole (28 μl, 0.4 mmol). After stirring for 3 h at 25 °C, colorless microcrystals formed. The supernatant was decanted and the precipitate was dissolved in DME (18 ml). The solution was left standing for 6 days at −40 °C, giving colorless crystals (48 mg, 24%). Single crystals for X-ray structure analysis were grown from DME solutions at 25 °C. ^{1}H-NMR (pyridine-d_5): δ 0.79 (s, 6H, SiMe$_2$), 1.40 (s, 9H, NCCH$_3$), 1.72, 2.05 (s, 2 × 6H, C$_5$CH$_3$), 3.27 (s, 2 × 3H, OCH$_3$), 3.49 (s, 2 × 2H, OCH$_2$), 6.67 (s, 2H, C$_4$H$_4$N), 7.07 (s, 2H, C$_4$H$_4$N). ^{13}C-NMR (pyridine-d_5): δ 9.0 (SiMe$_2$), 11.3, 15.0 (C$_5$*C*H$_3$), 34.8 (C*C*H$_3$), 54.7 (DME), 58.5 (*C*CH$_3$), 71.9 (DME), 107.3 (C$_5$Me$_4$ attached to SiMe$_2$), 108.6 (C$_4$H$_4$N), 124.7 (C$_5$Me$_4$), 127.2 (C$_4$H$_4$N); one C$_5$Me$_4$ signal is obscured by solvent signals. Anal. Calc. for C$_{23}$H$_{41}$N$_2$O$_2$SiY: C, 55.86; H, 8.36; N, 5.66. Found: C, 55.62; H, 8.48; N, 6.04%.

4.6. *[Y(η^5:η^1-C$_5$Me$_4$SiMe$_2$NCMe$_3$){C$_4$H$_3$NCH$_3$)}-2-{C$_4$H$_4$NCH$_3$)}$_{0.75}$] (**10**)*

To a solution of [Y(η^5:η^1-C$_5$Me$_4$SiMe$_2$N^{t}Bu)(CH$_2$SiMe$_3$)(THF)] (100 mg, 201 μmol) in C$_6$H$_{14}$ (2 ml) was added *N*-methylpyrrole (457 mg, 5.6 mmol). The solution was stirred at 25 °C for 8 h, and then cooled down to −40 °C for 7 days to give colorless microcrystals (76 mg, 79%). ^{1}H-NMR (pyridine-d_5): δ 0.74 (s, 6H, SiCH$_3$), 1.43 (s, 9H, NCCH$_3$), 1.61, 1.64, 1.93, 2.02 (s, 4 × 3H, C$_5$CH$_3$), 3.40 (s, 2.25H, C$_4$H$_4$NC*H*$_3$), 3.75 (s, 3H, C$_4$H$_3$NC*H*$_3$), 5.74 (m, 1H, C$_4$*H*$_3$NCH$_3$), 5.81 (t, $^3J_{\mathrm{HH}} = 3.0$ Hz, 1H, C$_4$*H*$_3$NCH$_3$), 6.28 (m, 2 × 0.75H, C$_4$*H*$_4$NCH$_3$), 6.43 (m, 1H, C$_4$*H*$_3$NCH$_3$), 7.21 (br, 2 × 0.75H, C$_4$*H*$_4$NCH$_3$).

4.7. *[Y(η^5:η^1-C$_5$Me$_4$CH$_2$SiMe$_2$NCMe$_3$)(μ-2-C$_4$H$_3$O)]$_2$ (**12**)*

To a solution of [Y(η^5:η^1-C$_5$Me$_4$CH$_2$SiMe$_2$NCMe$_3$)(CH$_2$SiMe$_3$)(THF)] (**11**) (496 mg, 1.0 mmol) in 2 ml of C$_6$H$_6$ was added at ambient temperature a 20-fold excess of neat furan (1.362 g, 20.0 mmol) and the reaction mixture stirred for 6 h. The volatiles were removed in vacuo and 20 ml of C$_5$H$_{12}$ was added, the mixture was cooled at −30 °C to form a precipitate. Removal of the supernatant and drying under vacuum afforded [Y(η^5:η^1-C$_5$Me$_4$CH$_2$SiMe$_2$NCMe$_3$)(η-2-C$_4$H$_3$O)]$_2$ (195 mg, 46%) as colorless powder. ^{1}H-NMR (C$_6$D$_6$): δ 0.57 (s, 6H, SiCH$_3$), 1.32 (s, 9H, CMe$_3$), 1.61, 1.95 (s, 2 × 6H, C$_5$CH$_3$), 2.18 (s, 2H, CH$_2$), 6.16 (dd, $^3J_{\mathrm{HH}} = 3.2$, 1.0 Hz, 1H, C$_4$H$_3$O-4), 6.80 (d, $^3J_{\mathrm{HH}} = 3.2$ Hz, 1H, C$_4$H$_3$O-3), 7.49 (d, $^3J_{\mathrm{HH}} = 1.0$ Hz, 1H, C$_4$H$_3$O-5). ^{13}C{^{1}H}-NMR (C$_6$D$_6$): δ 8.6 (SiCH$_3$), 11.4 (C$_5$*C*H$_3$), 11.6 (C$_5$*C*H$_3$), 18.1 (CH$_2$), 35.7 (C(*C*H$_3$)$_3$), 54.0 (*C*(CH$_3$)$_3$), 112.1 (C$_4$H$_3$O), 116.5, 117.9 (C$_5$Me$_4$), 124.5 (C$_5$Me$_4$ attached to CH$_2$), 146.2 (C$_4$H$_3$O), 201.7 (t, $^1J_{\mathrm{YC}} = 24.7$ Hz, C$_4$H$_3$O-2), one carbon signal is obscured by solvent signals. ^{1}H-NMR (THF-d_8): δ 0.21 (s, 6H, SiCH$_3$), 1.27 (s, 9H, CMe$_3$), 1.90 (s, 2H, CH$_2$), 1.91, 1.98 (s, 2 × 6H, C$_5$CH$_3$), 6.07 (bs, 1H, C$_4$H$_3$O-3), 6.22 (d, $J_{\mathrm{HH}} = 2.8$ Hz, 1H, C$_4$H$_3$O-4), 7.49 (bs, 1H, C$_4$H$_3$O-5). ^{13}C{^{1}H}-NMR (THF-d_8): δ 8.8 (SiCH$_3$), 11.5, 12.3 (C$_5$*C*H$_3$), 18.4 (CH$_2$), 34.5 (C(*C*H$_3$)$_3$), 54.2 (*C*(CH$_3$)$_3$), 108.1 (C$_4$H$_3$O-4), 115.8, 115.9 (C$_5$Me$_4$), 119.3 (d, $J_{\mathrm{YC}} = 2.9$ Hz, C$_4$H$_3$O-3), 124.1 (C$_5$Me$_4$ attached to CH$_2$), 143.0 (C$_4$H$_3$O-5), 208.0 (d, $J_{\mathrm{YC}} = 55.0$ Hz, C$_4$H$_3$O-2). ^{89}Y-NMR (C$_6$D$_6$): δ 263.7. Anal. Calc. for C$_{20}$H$_{32}$NOSiY: C, 57.27; H, 7.69; N, 3.34. Found: C, 54.11; H, 8.27; N, 3.16%.

4.8. *[Y(η^5:η^1-C$_5$Me$_4$CH$_2$SiMe$_2$NCMe$_3$)-(2-C$_4$H$_3$S)(THF)] (**14**)*

To a solution of **11** (395 mg, 770 μmol) in C$_6$H$_{14}$ (15 ml) was added a solution of thiophene (650 mg, 7.71 mmol) in C$_6$H$_{14}$ (5 ml). The reaction mixture was stirred for 4 h at 25 °C, concentrated in vacuum and cooled to 0 °C to give colorless crystals (270 mg, 69%). Single crystals for X-ray strucutre analysis were obtained by slow cooling of a C$_6$H$_{14}$ solution to 0 °C. ^{1}H-NMR (C$_6$D$_6$): δ 0.53 (s, 6H, SiCH$_3$), 1.03 (m, 4H, β-CH$_2$, THF), 1.37 (s, 9H, NCCH$_3$), 1.96, 2.12 (s, 2 × 6H, C$_5$CH$_3$), 2.26 (s, 2H, CH$_2$), 3.42 (m, 4H, α-CH$_2$, THF), 7.39 (d, $^3J_{\mathrm{HH}} = 2.8$ Hz, 1H, C$_4$H$_3$S-3), 7.46 (dd, $^3J_{\mathrm{HH}} = 2.8$ Hz, 4.4 Hz, 1H, C$_4$H$_3$S-4), 7.76 (d, $^3J_{\mathrm{HH}} = 4.4$ Hz, 1H, C$_4$H$_3$S-5). ^{13}C{^{1}H}-NMR (C$_6$D$_6$): δ 8.3 (SiMe$_2$), 11.5, 11.6 (C$_5$*C*H$_3$), 18.1 (CH$_2$), 24.8 (β-CH$_2$, THF), 35.1 (C*C*H$_3$), 53.7 (*C*CH$_3$), 70.6 (α-CH$_2$, THF), 116.2, 117.3 (C$_5$Me$_4$), 124.8, 127.5, 129.2 (C$_4$H$_3$S), 134.3 (C$_5$Me$_4$ attached to CH$_2$), 178.2 (d, $^1J_{\mathrm{YC}} = 42$ Hz, C$_4$H$_3$S-2). ^{89}Y-NMR (C$_6$D$_6$): δ 355.1. Anal. Calc. for C$_{24}$H$_{40}$NOSSiY: C, 56.82; H, 7.88; N, 2.75; S, 6.32. Found: C, 56.90; H, 7.89; N, 2.72; S, 6.31%.

4.9. *[Y(η^5:η^1-C$_5$Me$_4$CH$_2$SiMe$_2$NCMe$_3$)(η^1-κN-C$_4$H$_4$N)] (**15**)*

To a solution of **10** (248 mg, 0.5 mmol) in 1 ml of C$_6$H$_6$ was added at ambient temperature neat pyrrole (34 mg, 0.5 mmol) and the reaction mixture stirred for 5 h. The volatiles were removed in vacuo and 10 ml of C$_6$H$_{14}$ was added to the residue. Removal of the supernatant and drying under vacuum afforded [Y(η^5:η^1-C$_5$Me$_4$CH$_2$SiMe$_2$NCMe$_3$)(η^1-NC$_4$H$_4$)] (93 mg, 44%) as colorless powder. ^{1}H-NMR (pyridine-d_5): δ 0.63 (s, 6H, SiCH$_3$), 1.38 (s, 9H, CMe$_3$), 1.57, 2.04 (s, 2 × 6H, C$_5$CH$_3$), 2.27 (s, 2H, CH$_2$), 6.73 (br s, 2H, NC$_4$H$_4$), 7.23 (br s, 2H, NC$_4$H$_4$). ^{13}C{^{1}H}-NMR (pyridine-d_5): δ 8.8 (SiCH$_3$), 11.8, 12.7 (C$_5$*C*H$_3$), 18.2 (CH$_2$), 33.9 (C(*C*H$_3$)$_3$), 54.3 (*C*(CH$_3$)$_3$), 108.3 (NC$_4$H$_4$), 115.4, 116.5 (C$_5$Me$_4$), 124.6 (NC$_4$H$_4$), 126.2 (C$_5$Me$_4$ attached to CH$_2$). ^{1}H-NMR (THF): δ 0.27 (s, 6H, SiCH$_3$), 1.31 (s, 9H, CMe$_3$), 1.98 (s, 2H, CH$_2$), 2.00, 2.08 (s, 2 × 6H, C$_5$CH$_3$), 5.92 (s, 2H, NC$_4$H$_4$), 6.59 (s, 2H, NC$_4$H$_4$). ^{13}C{^{1}H}-NMR (THF-d_8): δ 9.1 (SiCH$_3$), 11.6, 12.5 (C$_5$*C*H$_3$), 18.6 (CH$_2$), 35.0 (C(*C*H$_3$)$_3$), 54.3 (*C*(CH$_3$)$_3$), 107.5 (NC$_4$H$_4$), 116.0, 116.6 (C$_5$Me$_4$), 125.2 (NC$_4$H$_4$), 125.4 (C_5Me_4 attached to CH_2). ^{89}Y-NMR (C_6D_6): δ 193.4. Anal. Calc. for $C_{20}H_{33}N_2SiY$: C, 57.40; H, 7.95; N, 6.69. Found: C, 56.27; H, 7.94; N, 7.04%.

*4.10. X-ray crystal structure analysis and determination of the structures of **4**, **5**, **9**, and **14***

Single crystals of $[Y(\eta^5{:}\eta^1\text{-}C_5Me_4SiMe_2NCMe_3)(\mu\text{-}C_4H_3S\text{-}2)]_2$ (**4**) [6] were obtained by standing a 0.2 mmol l^{-1} C_5H_{12} solution of **1** and thiophene at −30 °C for 5 days. For the structures of **5**, **9**, and **14**, data sets were obtained with a Bruker AXS diffractometer at −90 °C in the ω-scan mode. The data corrections were carried out using the program system SAINT [13]. The structures **5** and **14** were solved by Patterson and Fourier methods using the program SHELXS-86 [14a], the structure of **9** was solved by isotypical replacement using the atomic coordinates of **5**. The refinements were carried out using the program SHELXL-97 based on F^2 [14b]. Anisotropic thermal parameters were refined for the non-hydrogen atoms (except for disordered groups). For compounds **5** and **9**, all hydrogen atoms could be located in Fourier difference maps and were refined in their positions with isotropic thermal parameters. Due to disorder in the structure of **14**, the atoms S1 and C22 (as well as S2 and C42 for the second crystallographically independent molecule) occupy identical positions in the crystal structure. Hydrogen atoms were included into calculated positions. X-ray crystal structural analysis and determination of the structure of **4**: The data set was obtained with an Enraf–Nonius diffactometer at 23 °C in the ω-scan mode. The data correction was carried out using the program system WINGX [15]. The structure was solved with direct methods and refined

Table 1
Experimental data for the crystal structure determination of the complexes **4**, **5**, **9**, and **14**

Compound	**4**	**5**	**9**	**14**
Crystal data				
Empirical formula	$C_{38}H_{60}N_2S_2Si_2Y_2$	$C_{23}H_{40}NO_3SiY$	$C_{23}H_{41}N_2O_2SiY$	$C_{24}H_{40}NOSSiY$
Formula weight	843.02	495.57	494.59	507.63
Crystal color	Colorless	Colorless	Colorless	Colorless
Crystal size (mm)	0.12 × 0.18 × 0.40	0.02 × 0.10 × 0.24	0.115 × 0.260 × 0.447	0.18 × 0.24 × 0.38
Crystal system	Monoclinic	Orthorhombic	Orthorhombic	Monoclinic
Space group	$P2_1/n$	$Pbca$	$Pbca$	$P2_1/c$
a (Å)	12.4201(9)	16.5945(9)	16.446(1)	17.338(1)
b (Å)	12.2075(8)	15.7342(8)	15.681(1)	18.662(1)
c (Å)	14.352(1)	39.432(2)	39.590(2)	17.110(1)
α (°)	90	90	90	90
β (°)	106.393(7)	90	90	102.666(1)
γ (°)	90	90	90	90
V (Å^3)	2087.6(3)	10295.7(9)	10210(1)	5401.4(5)
Z	4/2	16	16	8
D_{calc} (g cm^{-3})	1.341	1.279	1.287	1.245
μ (mm^{-1})	2.951	2.334	2.351	2.295
F(000)	880	4192	4192	2144
Data collection				
$2\theta_{max}$ (°)	48.0	56.6	56.6	46.6
Index ranges	$-14 \le h \le 10$, $0 \le k \le 13$, $-15 \le l \le 16$	$-22 \le h \le 22$, $-20 \le k \le 20$, $-52 \le l \le 52$	$-21 \le h \le 21$, $-20 \le k \le 20$, $-52 \le l \le 51$	$-23 \le h \le 23$, $-24 \le k \le 22$, $-21 \le l \le 22$
Solution and refinement				
No of reflections measured	4668	90 881	90 347	36 882
No of independent reflections	3262 [R_{int} = 0.0983]	12 758 [R_{int} = 0.1322]	12 663 [R_{int} = 0.0817]	12 980 [R_{int} = 0.0538]
No of observed reflections	1341	6034	7500	8047
No of parameters	217	844	852	525
Goodness-of-fit	1.170	1.023	0.857	0.945
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0696$, $wR_2 = 0.1371$	$R_1 = 0.0382$, $wR_2 = 0.0677$	$R_1 = 0.0339$, $wR_2 = 0.0598$	$R_1 = 0.0459$, $wR_2 = 0.1168$
Final R indices (all data)	$R_1 = 0.2667$, $wR_2 = 0.1941$	$R_1 = 0.1256$, $wR_2 = 0.0825$	$R_1 = 0.0808$, $wR_2 = 0.0665$	$R_1 = 0.0857$, $wR_2 = 0.1272$
Largest e-max, e-min (e Å^{-3})	0.752 and −0.744	0.425 and −0.695	0.397 and −0.383	0.962 and −1.601
Extinction coefficient		0.00051(3)	0.00006(3)	0.0011(2)

using the program SHELXL-97. The hydrogen atoms were included into calculated positions (whereby torsional refinement was carried out for the hydrogen atoms of the methyl groups). For this compound, orientational disorder was found within the thienyl ring (with identical positions for the atoms S and C16). Results are given in Table 1.

5. Supplementary material

Crystallographic data for the structural analyses have been deposited with the Cambridge Crystallographic Data Centre, CCDC, no. 170820 for compound **4**, 170821 for compound **5**, 170822 for compound **9**, and 170823 for compound **14**. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ UK (Fax: +44-1223-336033 or e-mail deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk.

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References

[1] (a) P.L. Watson, J. Am. Chem. Soc. 104 (1982) 337;
(b) P.L. Watson, J. Am. Chem. Soc. 105 (1983) 6491;
(c) P.L. Watson, G.W. Parshall, Acc. Chem. Res. 18 (1985) 51.

[2] M.E. Thompson, S.M. Baxter, A.R. Bulls, B.J. Burger, M.C. Nolan, B.D. Santarsiero, W.P. Schaefer, J.E. Bercaw, J. Am. Chem. Soc. 109 (1987) 203.

[3] (a) P.L. Watson, J. Chem. Soc. Chem. Commun. (1983) 276;
(b) W.J. Evans, T.A. Ulibarri, J.W. Ziller, Organometallics 10 (1991) 134;
(c) K.H. den Haan, Y. Wielstra, J.H. Teuben, Organometallics 6 (1987) 2053;
(d) M. Booij, A. Meetsma, J.H. Teuben, Organometallics 10 (1991) 3246;
(e) B.J. Deelman, M. Booij, A. Meetsma, J.H. Teuben, H. Kooijman, A.L. Spek, Organometallics 14 (1995) 2306;
(f) N.S. Radu, S.L. Buchwald, B. Scott, C.J. Burns, Organometallics 15 (1996) 3913.

[4] (a) S.N. Ringelberg, A. Meetsma, B. Hessen, J.H. Teuben, J. Am. Chem. Soc. 121 (1999) 6082;
(b) B. Hessen, S.N. Ringelberg, G.-J. Meppelder, J.H. Teuben, Polym. Preprints 41 (1) (2000) 397;
(c) S.N. Ringelberg, Doctoral Thesis, University of Groningen, 2001.

[5] (a) K.C. Hultzsch, T.P. Spaniol, J. Okuda, Angew. Chem. Int. Ed. 38 (1999) 227;
(b) K.C. Hultzsch, P. Voth, K. Beckerle, T.P. Spaniol, J. Okuda, Organometallics 19 (2000) 228;
(c) S. Arndt, P. Voth, T.P. Spaniol, J. Okuda, Organometallics 19 (2000) 4690.

[6] S. Arndt, T.P. Spaniol, J. Okuda, Eur. J. Inorg. Chem. (2001) 73.

[7] A.A. Trifonov, T.P. Spaniol, J. Okuda, Organometallics, 20 (2001) 4869.

[8] (a) Y. Mu, W.E. Piers, M.-A. MacDonald, M.J. Zaworotko, Can. J. Chem. 73 (1995) 2333;
(b) S. Tian, V.M. Arrendondo, C.L. Stern, T.J. Marks, Organometallics 18 (1999) 2568.

[9] (a) For a related disorder of the 2-thienyl ligand in Cp*RhCl(PMe$_3$)(C$_4$H$_3$S-2), see L. Dong, S.B. Duckett, K.F. Ohman, W.D. Jones, J. Am. Chem. Soc. 114 (1992) 151;
(b) Structure of thiophene W.R. Harschbarger, S.H. Bauer, Acta. Crystallogr. B26 (1970) 1010.

[10] (a) P.J. Shapiro, E. Bunel, W.P. Schaefer, J.E. Bercaw, Organometallics 9 (1990) 867;
(b) P.J. Shapiro, W.D. Cotter, W.P. Schaefer, J.A. Labinger, J.E. Bercaw, J. Am. Chem. Soc. 116 (1994) 4623.

[11] P. Chirik, J.E. Bercaw, in: A. Togni, R.H. Halterman (Eds.), Metallocenes, Wiley-VCH, Weinheim, 1999, p. 1999.

[12] J.P. Mitchell, S. Hajela, S.K. Brookhart, K.I. Hardcastle, L.M. Henling, J.E. Bercaw, J. Am. Chem. Soc. 118 (1996) 1045.

[13] Siemens. ASTRO, SAINT and SADABS. Data Collection and Processing Software for the SMART System. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA, 1996.

[14] (a) G.M. Sheldrick, SHELXS-86, A Program for Crystal Structure Solution, University of Göttingen, Germany, 1986;
(b) G.M. Sheldrick, SHELXS-97, A Program for Crystal Structure Refinement, University of Göttingen, Germany, 1997.

[15] L.J. Farraguia, WINGX—Version 1.64.02, An Integrated System of Windows Programs for the Solution, Refinement and Analysis of Single Crystal X-Ray Diffraction Data, J. Appl. Cryst. 32 (1999) 837.