ortho-Metalation of aromatic ethers by yttrium alkyl complexes that contain a linked amido-cyclopentadienyl ligand

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, Duesbergweg 10-14, D-55099 Mainz, Germany*
[b] *Catalysis Research Center and Graduate School of Pharmaceutical Sciences, Hokkaido University, Kita-ku, Sapporo 060-0811, Japan*

Dedicated to E.O. Fischer on the occasion of his 85th birthday

Abstract

The reaction of the half-sandwich alkyl complex [Y(η^5:η^1-C$_5$Me$_4$CH$_2$SiMe$_2$N^{t}Bu)(CH$_2$SiMe$_3$)(THF)] (**1**) with anisole smoothly gives the *ortho*-metalation product [Y(η^5:η^1-C$_5$Me$_4$CH$_2$SiMe$_2$N^{t}Bu)(2-C$_6$H$_4$OMe)(THF)] (**2**). 3- and 4-Methylanisole as well as phenetole analogously undergo *ortho*-metalation, whereas thioanisole, *N*,*N*′-dimethylaniline, fluorobenzene, and trifluorobenzene do not react with yttrium complex **1**. 2-Methylanisole reacts with **1** under activation of the ring methyl group to give the 2-methoxybenzyl complex [Y(η^5:η^1-C$_5$Me$_4$CH$_2$SiMe$_2$N^{t}Bu)(CH$_2$C$_6$H$_4$OMe-2)(THF)] (**6**). A single-crystal X-ray structure analysis of the 2-anisyl complex **2** revealed a four-legged piano-stool configuration with the methoxy group coordinated *cis* to the amido-function of the ancillary ligand.
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1. Introduction

The *ortho*-metalation of aromatic molecules is a typical reaction promoted by decamethyl lanthanocenes [Ln(η^5-C$_5$Me$_5$)$_2$X] (X = H, alkyl) [1], which have long been known to activate C–H bonds in both saturated and unsaturated organic substrates via σ-bond metathesis [2–4]. We have reported that the labile yttrium alkyl complex [Y(η^5:η^1-C$_5$Me$_4$SiMe$_2$N^{t}Bu)(CH$_2$SiMe$_3$)(THF)] [5] cleanly undergoes σ-bond metathesis with the aromatic heterocycles furan and thiophene to give structurally characterized 2-furyl and 2-thienyl complexes [6]. This reaction type could also be extended to [Y(η^5:η^1-C$_5$Me$_4$CH$_2$SiMe$_2$N^{t}Bu)(CH$_2$SiMe$_3$)(THF)] (**1**), containing a ligand system with the longer CH$_2$SiMe$_2$ instead of the SiMe$_2$ link [7]. Such a change in the ancillary ligand was recently found to result in

significantly higher solubility and reactivity, intriguingly contrasting with the concept of the so-called "constrained-geometry" catalyst [8]. We report here that alkyl complex **1** selectively undergoes an *ortho*-metalation reaction with anisole.

2. Results and discussion

When the alkyl complex [Y(η^5:η^1-C$_5$Me$_4$CH$_2$SiMe$_2$N^{t}Bu)(CH$_2$SiMe$_3$)(THF)] (**1**) [7] is treated with excess anisole in benzene at ambient temperature, tetramethylsilane is formed and the 2-anisyl complex [Y(η^5:η^1-C$_5$Me$_4$CH$_2$SiMe$_2$N^{t}Bu)(2-C$_6$H$_4$OMe)(THF)] (**2**) is isolated as hydrocarbon-soluble, colorless crystals in good yield (Scheme 1).

The crystal structure determination of **2** revealed a four-legged piano-stool structure, as shown by the ORTEP diagram in Fig. 1. The linked amido-cyclopentadienyl ligand shows the expected coordination features: an η^5-bonded five-membered ring (yttrium–carbon distances in the expected range 2.601(4)–

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* Corresponding author. Tel.: +49-6131-3925333; fax: +49-6131-3925605.
E-mail address: okuda@mail.uni-mainz.de (J. Okuda).
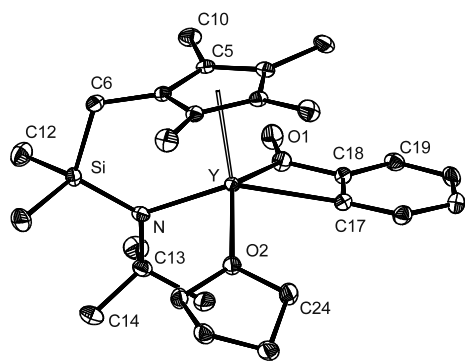[1] Exchange Research Fellow at the University of Mainz, 2001.
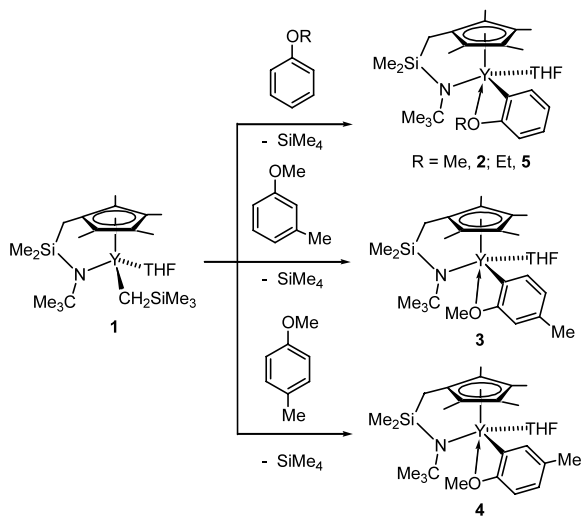
Scheme 1.

Fig. 1. ORTEP diagram of the molecular structure of **2**. Thermal ellipsoids are drawn at the 30% probability level. Hydrogen atoms are omitted for the sake of clarity; selected bond distances (Å) and angles (°):Y–C 17 2.482(3); Y–N, 2.248(3); Y–O1, 2.476(3); Y–O2, 2.384(3); Y–Cp$_{cent}$, 2.327(4); N–Y–O1, 95.8(1); N–Y–O2, 92.8(1); O1–Y–C17, 56.0(1); O2–Y–C17, 91.2(1); Cp$_{cent}$–Y–N, 107.3(1); Cp$_{cent}$–Y–C17, 110.8(1). Cp$_{cent}$: centroid of C1, C2, C3, C4 and C5.

2.640(4) Å), and a planar amido nitrogen atom with Y–N distance of 2.248(3) Å, with the sum of the angles at the nitrogen atom being 360°. These features are comparable to those found in the parent alkyl **1**, in the 1-phenethyl [Y(η^5:η^1-C$_5$Me$_4$CH$_2$SiMe$_2$N^t-Bu){CH(Me)Ph}(THF)] [8], and in the 2-thienyl [Y(η^5:η^1-C$_5$Me$_4$CH$_2$SiMe$_2$N^{t}Bu)(2-C$_5$H$_3$S)(THF)] [7]. However, in contrast to these three-legged piano-stool complexes, the oxygen atom of the 2-anisyl group in complex **2** is bonded to the yttrium center in the lateral sector of the coordination sphere with an Y–O distance of 2.476(3) Å. The bond distance between the oxygen atom of the THF ligand and the yttrium atom is 2.384(3) Å, somewhat larger than the values found in the above-mentioned complexes (2.327(1) Å in **1**; 2.350(8) Å in the 1-phenethyl complex [8], 2.335(2) Å in the 2-thienyl complex [7]). The *ipso*-carbon atom C17 of the 2-anisyl group is bonded with a distance of

2.482(3) Å, which is comparable to the corresponding distance in the 2-thienyl complex of 2.436(3) Å [7]. In agreement with a four-legged piano-stool configuration, the sum of angles at the 16-electron yttrium center is 336°.

The ^{1}H NMR spectrum of **2** in THF-d_8 at 55 °C shows a set of five sharp singlets for the ancillary ligand system [C$_5$Me$_4$CH$_2$SiMe$_2$N^{t}Bu], indicating the presence of a mirror plane. Fast dissociation and coordination of both the THF ligand and the methoxy group at the yttrium center would be in agreement with this spectral feature. Notably, the higher field methyl signal for one pair of C$_5$Me$_4$ groups is broadened, and below +30 °C, considerable broadening of the signals for the other symmetry-related groups become apparent. Unfortunately, the low-temperature limit could not be reached at −60 °C. We believe that the two (possibly interconnected) exchange processes occur in solution. In the ^{13}C NMR spectrum the diagnostic *ipso*-carbon is observed as a doublet at 170 ppm with $^1J_{YC} = 39.7$ Hz. Interestingly, the carbon atom carrying the OMe group also displays a coupling to yttrium of $^2J_{YC} = 2.6$ Hz.

Analogous *ortho*-metalation reactions of alkyl complex **1** occur with 3- and 4-methylanisole as well as with phenetole, resulting in the formation of the corresponding aryl complexes **3–5**. Similar to the parent complex **2**, these derivatives are all fluxional, as can be seen from the temperature-dependence of the ^{1}H NMR spectra of **3–5**. At 60 °C in C$_6$D$_6$, each of the complexes gives rise to a simple pattern consistent with a C_s-symmetric structure. For product **3**, formed from 3-methylanisole, the signal pattern consisting of a singlet at 6.40 ppm and an AB signal set at 6.97 and 7.49 ppm unambiguously indicates metalation at the sterically less encumbered 6-position.

When 2-methylanisole was reacted with **1** under the same conditions as above, *ortho*-metalation did not occur; the product obtained resulted from C–H activation at the 2-methyl group (Scheme 2). In the ^{1}H NMR spectrum of **6** in C$_6$D$_6$ at room temperature, four resonances for the aromatic protons were recorded, in addition to the typical signals for the C_s-symmetric ancillary ligand and THF. The benzyl group Y*CH$_2$* is observed as a singlet at 1.38 ppm in the ^{1}H and as a doublet at 41.9 ppm with $^1J_{YC} = 37.3$ Hz in the 13C spectrum. A related complex [Y(η^5:η^1-C$_5$Me$_4$Si-
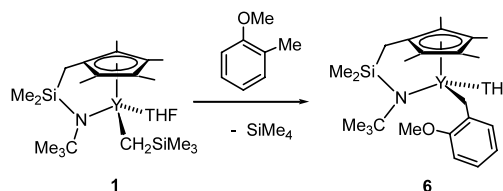
Scheme 2.

Me$_2$N^{t}Bu){2-(NC$_5$H$_4$Me-4)CH$_2$}(NC$_5$H$_4$Me$_2$-2,4)] derived from the C−H activation of the 2-methyl group in 2,4-lutidine has been crystallographically characterized [9].

3. Conclusion

The alkyl complex [Y(η^5:η^1-C$_5$Me$_4$CH$_2$SiMe$_2$N^t-Bu)(CH$_2$SiMe$_3$)(THF)] (**1**) smoothly undergoes σ-bond metathesis with anisole to give tetramethylsilane and the *ortho*-metalated product [Y(η^5:η^1-C$_5$Me$_4$CH$_2$Si-Me$_2$N^{t}Bu)(2-C$_6$H$_4$OMe)(THF)] (**2**). Despite the sterically open ligand sphere, the strongly π-donating amido group apparently renders the yttrium center less electrophilic and a softer Lewis acid [10], so that other substituted arenas with softer functional groups are not activated. This reactivity pattern contrasts to that of decamethylyttrocene hydride [Y(η^5-C$_5$Me$_5$)$_2$H], which is capable of *ortho*-metalating benzene derivatives substituted with, e.g., halogen, NMe$_2$, PMe$_2$ and SMe [1e]. From our observations, it is most probable that the metalation is induced by the coordination of the methoxy group at the 14-electron center (Scheme 3) [7]. In agreement with this associative mechanism, 2-methylanisole is not *ortho*-metalated; instead, its distal methyl group is activated, and benzyl complex **6** results. Finally, the synthetically useful *ortho*-metalation of anisole and its substituted derivatives by alkyllithium, a reaction whose mechanism has been intensively studied, is also proposed to be preceded by the coordination of the methoxy group at the lithium center [11].

4. Experimental

4.1. General considerations

All operations were performed under an inert atmosphere of argon and by using standard Schlenk-line or glovebox techniques. After drying over KOH, THF was distilled from sodium benzophenone ketyl. Hexane and toluene were purified by distillation from sodium/triglyme benzophenone ketyl. The alkyl complex [Y(η^5:η^1-C$_5$Me$_4$CH$_2$SiMe$_2$N^{t}Bu)(CH$_2$SiMe$_3$)(THF)] (**1**) was prepared according to the published procedure [7]. All other chemicals were commercially available and
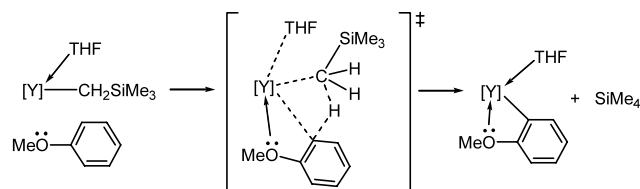
used after appropriate purification. NMR spectra were recorded on a Bruker DRX 400 spectrometer (^{1}H, 400 MHz; ^{13}C, 101 MHz) at 25 °C, unless otherwise stated. Chemical shifts for ^{1}H and ^{13}C spectra were referenced internally using the residual solvent resonances and are reported relative to tetramethylsilane. 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(η^5:η^1-C$_5$Me$_4$CH$_2$SiMe$_2$N^{t}Bu)(2-C$_6$H$_4$OMe) (THF)] (2)

A 20-fold excess of anisole (2.16 g, 20.0 mmol) was added at room temperature to a solution of [Y(η^5:η^1-C$_5$Me$_4$CH$_2$SiMe$_2$N^{t}Bu)(CH$_2$SiMe$_3$)(THF)] (**1**) (0.51 g, 1.0 mmol) in benzene (3 ml), and the mixture was stirred for 12 h at room temperature. All volatiles were removed in vacuo, the residue was taken up in hexane, and the solution was cooled to −30 °C to afford **2** as a colorless powder; yield: 0.36 g (67%). ^{1}H NMR (THF-d_8): δ 0.21 (s, 6H, SiCH$_3$), 1.16 (s, 9H, CMe$_3$), 1.68 (br s, 6H, C$_5$CH$_3$), 1.74 (br, 4H, β-CH$_2$, THF), 1.94 (s, 2H, CH$_2$), 2.05 (s, 6H, C$_5$CH$_3$), 3.57 (br, 4H, α-CH$_2$, THF), 3.87 (s, 3H, OCH$_3$), 6.57 (d, J_{HH} = 8.0 Hz, 1H, C$_6$H$_4$), 6.70 (dd, $^3J_{HH}$ = 6.4, 7.2 Hz, 1H, C$_6$H$_4$), 6.87 (ddd, J_{HH} = 1.5 Hz, 7.2 Hz, 8.0 Hz, 1H, C$_6$H$_4$), 7.31 (d, $^3J_{HH}$ = 6.4 Hz, 1H, C$_6$H$_4$). ^{13}C{^{1}H} NMR (THF-d_8): δ 8.7 (SiMe$_2$), 11.1, 11.9 (C$_5$(CH$_3$)$_4$), 18.4 (CH$_2$SiN), 26.4 (β-CH$_2$, THF), 34.7 (C(CH$_3$)$_3$), 54.9 (C(CH$_3$)$_3$), 56.1 (OCH$_3$), 68.3 (α-CH$_2$, THF), 105.9 (C$_6$H$_4$), 114.6 (br, C$_5$(CH$_3$)$_4$), 114.9 (br, C$_5$(CH$_3$)$_4$), 122.7 (C$_6$H$_4$), 123.7 (C$_5$(CH$_3$)$_4$ attached to CH$_2$), 126.4 (C$_6$H$_4$), 139.0 (C$_6$H$_4$), 168.4 (d, $^2J_{YC}$ = 2.5 Hz, 2-C$_6$H$_4$), 170.0 (d, $^1J_{YC}$ = 39.7 Hz, 1-C$_6$H$_4$). ^{1}H NMR (THF-d_8, 55 °C): δ 0.21 (s, 6H, SiCH$_3$), 1.16 (s, 9H, CMe$_3$), 1.59 (s, 6H, C$_5$CH$_3$), 1.71 (br s, 4H, β-CH$_2$, THF), 1.94 (s, 2H, CH$_2$), 1.99 (s, 6H, C$_5$CH$_3$), 3.55 (br s, 4H, α-CH$_2$, THF), 3.86 (s, 3H, OCH$_3$), 6.56 (d, $^3J_{HH}$ = 8.0 Hz, 1H, C$_6$H$_4$), 6.69 (dd, $^3J_{HH}$ = 6.4 and 7.2 Hz, 1H, C$_6$H$_4$), 6.87 (ddd, J_{HH} = 1.7 Hz, 7.2 Hz, 8.0 Hz, 1H, C$_6$H$_4$), 7.31 (d, $^3J_{HH}$ = 6.4 Hz, 1H, C$_6$H$_4$). ^{13}C{^{1}H} NMR (THF-d_8, 55 °C): δ 8.7 (SiCH$_3$), 10.9, 11.8 (C$_5$(CH$_3$)$_4$), 18.5 (CH$_2$SiN), 26.3 (β-CH$_2$, THF), 34.7 (C(CH$_3$)$_3$), 54.9 (C(CH$_3$)$_3$), 56.0 (OCH$_3$), 68.3 (α-CH$_2$, THF), 105.9 (C$_6$H$_4$), 114.8 (C$_5$(CH$_3$)$_4$), 116.6 (C$_5$(CH$_3$)$_4$), 122.7 (C$_6$H$_4$), 123.8 (C$_5$(CH$_3$)$_4$ attached to CH$_2$), 126.3(C$_6$H$_4$), 139.0 (C$_6$H$_4$), 168.4 (d, $^2J_{YC}$ = 2.6 Hz, 2-C$_6$H$_4$), 170.3 (d, $^1J_{YC}$ = 39.7 Hz, 1-C$_6$H$_4$). Anal. Calc. for C$_{27}$H$_{44}$NO$_2$SiY: C, 61.00; H, 8.34; N, 2.63. Found: C, 59.85; H, 8.15; N, 2.79%.

Scheme 3.

4.3. $[Y(\eta^5:\eta^1-C_5Me_4CH_2SiMe_2N^tBu)\{2-C_6H_4(Me-4)OMe\}(THF)]$ (3)

A 20-fold excess of 3-methylanisole (2.44 g, 20.0 mmol) was added at room temperature to a solution of $[Y(\eta^5:\eta^1-C_5Me_4CH_2SiMe_2N^tBu)(CH_2SiMe_3)(THF)]$ (**1**) (0.51 g, 1.0 mmol) in benzene (4 ml), and the mixture was stirred for 24 h at room temperature. All volatiles were removed in vacuo and the residue taken up in pentane. The solution was cooled at $-30\,^{\circ}C$ to afford **3** as a colorless powder; yield: 0.31 g (57%). ^1H NMR (C_6D_6): δ 0.55 (br s, 6H, SiCH$_3$), 1.26 (br, β-CH$_2$, THF), 1.26 (s, 9H, CMe$_3$), 1.69–2.21 (m, 12H, C$_5$CH$_3$), 2.32 (br s, 2H, CH$_2$), 2.38 (s, 3H, C$_6$H$_3$CH$_3$), 3.55 (s, 3H, OCH$_3$), 3.83 (br, 4H, α-CH$_2$, THF), 6.40 (s, 1H, C$_6$H$_3$), 6.97 (d, $^3J_{HH} = 6.6$ Hz, 1H, C$_6$H$_3$), 7.49 (d, $^3J_{HH} = 6.6$ Hz, 1H, C$_6$H$_3$). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 8.6, 9.2 (br s, SiCH$_3$), 11.2 (C$_5$(CH$_3$)$_4$), 11.9 (br s, C$_5$(CH$_3$)$_4$), 18.2 (CH$_2$SiN), 21.9 (C$_6$H$_3$CH$_3$), 24.9 (β-CH$_2$, THF), 34.5 (C(CH$_3$)$_3$), 54.6 (C(CH$_3$)$_3$), 55.3 (OCH$_3$), 71.5 (α-CH$_2$, THF), 106.5 (C$_6$H$_3$), 113.3, 115.3, 117.7 (s, C$_5$(CH$_3$)$_4$), 123.5, 123.7, 135.5 (C$_6$H$_3$), 138.7 (C$_6$H$_3$), 165.0 (d, $^1J_{YC} = 38.0$ Hz, C$_6$H$_3$), 168.3 (d, $^2J_{YC} = 2.4$ Hz, C$_6$H$_3$). ^1H NMR (C_6D_6, 60 °C): δ 0.48 (s, 6H, SiCH$_3$), 1.26 (s, 9H, CMe$_3$), 1.40 (br s, 4H, β-CH$_2$, THF), 1.80 (s, 6H, C$_5$CH$_3$), 2.04 (s, 6H, C5CH$_3$), 2.29 (s, 2H, CH$_2$), 2.32 (s, 3H, C$_6$H$_3$CH$_3$), 3.62 (s, 3H, OCH$_3$), 3.87 (br s, 4H, α-CH$_2$, THF), 6.41 (s, 1H, C$_6$H$_3$), 6.90 (d, $^3J_{HH} = 6.5$ Hz, 1H, C$_6$H$_3$), 7.45 (d, $^3J_{HH} = 6.5$ Hz, 1H, C$_6$H$_3$). $^{13}C\{^1H\}$ NMR (C_6D_6, 60 °C): δ 8.8 (SiCH$_3$), 11.1, 11.8 (C$_5$(CH$_3$)$_4$), 18.4 (CH$_2$SiN), 21.8 (C$_6$H$_3$CH$_3$), 25.1 (β-CH$_2$, THF), 34.7 (C(CH$_3$)$_3$), 54.6 (C(CH$_3$)$_3$), 55.3 (OCH$_3$), 71.4 (α-CH$_2$, THF), 106.7 (C$_6$H$_3$), 114.6 (C$_5$(CH$_3$)$_4$), 116.7 (C$_5$(CH$_3$)$_4$), 123.6, 123.8, 135.6 (C$_6$H$_3$), 138.7 (C$_6$H$_3$), 165.3 (d, $^1J_{YC} = 38.9$ Hz, 1-C$_6$H$_3$), 168.4 (C$_6$H$_3$). Anal. Calc. for C$_{28}$H$_{46}$NO$_2$SiY: C, 61.63; H, 8.50; N, 2.57. Found: C, 61.01; H, 8.75; N, 2.81%.

4.4. $[Y(\eta^5:\eta^1-C_5Me_4CH_2SiMe_2N^tBu)\{2-C_6H_4(Me-5)OMe\}(THF)]$ (4)

A 20-fold excess of 4-methylanisole (2.44 g, 20.0 mmol) was added at room temperature to a solution of $[Y(\eta^5:\eta^1-C_5Me_4CH_2SiMe_2N^tBu)(CH_2SiMe_3)(THF)]$ (**1**) (0.51 g, 1.0 mmol) in benzene (4 ml), and the mixture was stirred for 12 h at room temperature. All volatiles were removed in vacuo and hexane was added to the residue. The solution was cooled at $-30\,^{\circ}C$, and after removal of the supernatant, **4** was obtained as a colorless powder; yield: 0.35 g (65%). ^1H NMR (C_6D_6): δ 0.53 (br s, 6H, SiCH$_3$), 1.25 (br, β-CH$_2$, THF), 1.27 (s, 9H, CMe$_3$), 1.71 (br s, 3H, C$_5$CH$_3$), 2.07 (br s, 3H, C$_5$CH$_3$), 2.12 (br s, 3H, C$_5$CH$_3$), 2.24 (br s, 3H, C$_5$CH$_3$), 2.31 (br s, 2H, CH$_2$), 2.40 (s, 3H, PhCH$_3$), 3.52 (s, 3H, OCH$_3$), 3.83 (br s, 4H, α-CH$_2$, THF), 6.45 (d, $^3J_{HH} =$

8.8 Hz, 1H, C$_6$H$_3$), 6.99 (dd, $J_{HH} = 8.8$ Hz and 1.8 Hz, 1H, C$_6$H$_3$), 7.47 (br s, 1H, C$_6$H$_3$). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 8.5, 9.1 (br s, SiCH$_3$), 11.2 (C$_5$(CH$_3$)$_4$), 11.9 (br s, C$_5$(CH$_3$)$_4$), 18.2 (CH$_2$SiN), 21.4 (C$_6$H$_3$CH$_3$), 24.9 (β-CH$_2$, THF), 34.5 (C(CH$_3$)$_3$), 54.6 (C(CH$_3$)$_3$), 55.5 (OCH$_3$), 71.6 (α-CH$_2$, THF), 105.1 (C$_6$H$_3$), 114.1, 115.2, 115.4, 117.7 (br s, C$_5$(CH$_3$)$_4$), 123.7 (C$_6$H$_3$), 126.8 (C$_5$(CH$_3$)$_4$), 130.5 (C$_6$H$_3$), 139.5 (C$_6$H$_3$), 165.9 (d, $^2J_{YC} = 2.5$ Hz, C$_6$H$_3$), 169.6 (d, $^1J_{YC} = 38.6$ Hz, C$_6$H$_3$). ^1H NMR (C_6D_6, 60 °C): δ 0.50 (s, 6H, SiCH$_3$), 1.27 (s, 9H, CMe$_3$), 1.35 (br s, 4H, β-CH$_2$, THF), 1.82 (s, 6H, C$_5$CH$_3$), 2.12 (s, 6H, C$_5$CH$_3$), 2.27 (s, 2H, CH$_2$), 2.36 (s, 3H, PhCH$_3$), 3.58 (s, 3H, OCH$_3$), 3.89 (br s, 4H, α-CH$_2$, THF), 6.54 (d, $^3J_{HH} = 7.2$ Hz, 1H, C$_6$H$_3$), 6.70 (dd, $J_{HH} = 7.9$ Hz and 1.5 Hz, 1H, C$_6$H$_3$), 7.43 (br s, 1H, C$_6$H$_3$). $^{13}C\{^1H\}$ NMR (C_6D_6, 60 °C): δ 8.3 (SiCH$_3$), 10.6, 11.3 (C$_5$(CH$_3$)$_4$), 17.8 (CH$_2$SiN), 20.7 (C$_6$H$_3$CH$_3$), 24.5 (β-CH$_2$, THF), 34.1 (C(CH$_3$)$_3$), 54.1 (C(CH$_3$)$_3$), 55.0 (OCH$_3$), 71.1 (α-CH$_2$, THF), 104.7 (C$_6$H$_3$), 114.1 (C$_5$(CH$_3$)$_4$), 116.1 (C$_5$(CH$_3$)$_4$), 123.3 (C$_6$H$_3$), 126.3 (C$_5$(CH$_3$)$_4$ attached to CH$_2$), 130.1 (C$_6$H$_3$), 139.0 (C$_6$H$_3$), 165.5 (d, $^2J_{YC} = 2.4$ Hz, C$_6$H$_3$), 169.2 (d, $^1J_{YC} = 38.6$ Hz, C$_6$H$_3$). Anal. Calc. for C$_{28}$H$_{46}$NO$_2$SiY: C, 61.63; H, 8.50; N, 2.57. Found: C, 60.80; H, 8.25; N, 2.41%.

4.5. $[Y(\eta^5:\eta^1-C_5Me_4CH_2SiMe_2N^tBu)(2-C_6H_4OEt)(THF)]$ (5)

A 20-fold excess of phenetole (2.44 g, 20.0 mmol) was added at room temperature to a solution of $[Y(\eta^5:\eta^1-C_5Me_4CH_2SiMe_2N^tBu)(CH_2SiMe_3)(THF)]$ (**1**) (0.51 g, 1.0 mmol) in benzene (4 ml), and the mixture was stirred for 24 h at room temperature. The volatiles were removed in vacuo and hexane was added to the residue. The solution was cooled to $-30\,^{\circ}C$, and after removal of the supernatant, **5** was obtained as yellowish powder; yield: 0.170 g (31%). ^1H NMR (C_6D_6): δ 0.53 (s, 6H, SiCH$_3$), 1.17 (t, $J_{HH} = 7.2$ Hz, 3H, CH$_2$CH$_3$), 1.28 (br, 4H, β-CH$_2$, THF), 1.31 (s, 9H, CMe$_3$), 1.80 (br s, 6H, C$_5$CH$_3$), 2.16 (br s, 6H, C$_5$CH$_3$), 2.29 (s, 2H, CH$_2$), 3.83 (br, 4H, α-CH$_2$, THF), 4.10 (q, $^3J_{HH} = 7.2$ Hz, 2H, OCH$_2$), 6.51 (d, $^3J_{HH} = 7.2$ Hz, 1H, C$_6$H$_4$), 7.11–7.18 (m, 2H, C$_6$H$_4$), 7.65 (d, $^3J_{HH} = 5.7$ Hz, 1H, C$_6$H$_4$). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 8.8 (SiCH$_3$), 11.1, 11.9 (C$_5$(CH$_3$)$_4$), 14.3 (CH$_2$CH$_3$), 18.2 (CH$_2$SiN), 24.9 (β-CH$_2$, THF), 34.4 (SiCH$_3$), 54.7 (C(CH$_3$)$_3$), 63.4 (OCH$_2$), 71.5 (α-CH$_2$, THF), 107.1 (C$_6$H$_4$), 114.4 (C$_5$(CH$_3$)$_4$), 116.2 (C$_5$(CH$_3$)$_4$), 122.4 (C$_6$H$_4$), 126.3 (C$_5$(CH$_3$)$_4$ attached to CH$_2$), 129.7 (C$_6$H$_4$), 139.3 (C$_6$H$_4$), 165.6 (d, $^2J_{YC} = 2.2$ Hz, 2-C$_6$H$_4$), 170.3 (d, $^1J_{YC} = 37.9$ Hz, 1-C$_6$H$_4$). Anal. Calc. for C$_{28}$H$_{46}$NO$_2$SiY: C, 61.63; H, 8.50; N, 2.57. Found: C, 60.17; H, 8.13; N, 2.22%.

4.6. $[Y(\eta^5:\eta^1-C_5Me_4CH_2SiMe_2N^tBu)$ $\{CH_2C_6H_4(OCH_3)-2\}(THF)]$ (6)

A 20-fold excess of 2-methylanisole (2.44 g, 20.0 mmol) was added at room temperature to a solution of $[Y(\eta^5:\eta^1-C_5Me_4CH_2SiMe_2N^tBu)(CH_2SiMe_3)(THF)]$ (1) (0.51 g, 1.0 mmol) in benzene (4 ml), and the mixture was stirred for 24 h at room temperature. All volatiles were removed in vacuo and pentane was added to the residue. The mixture was cooled to $-70\,°C$ and the supernatant was removed to give 6 as a yellow oil which was contaminated with 2-methylanisole; yield: 0.43 g (79%). ^1H NMR (C_6D_6): δ 0.50 (s, 6H, SiCH$_3$), 1.24 (s, 9H, CMe$_3$), 1.25 (br, 4H, β-CH$_2$, THF), 1.36 (s, 2H, CH_2C$_6$H$_4$), 1.87 (s, 6H, C$_5$CH_3), 2.03 (s, 6H, C$_5$CH_3), 2.18 (s, 2H, CH$_2$Si), 3.59 (br, 4H, α-CH$_2$, THF), 3.63 (s, 3H, OCH$_3$), 6.52 (d, $^3J_{HH} = 7.2$ Hz, 1H, C$_6$H$_4$), 6.70 (dd, $^3J_{HH} = 7.2$ Hz, 1H, C$_6$H$_4$), 6.95 (dd, $^3J_{HH} = 7.2$ Hz, 1H, C$_6$H$_4$), 7.13 (d, $^3J_{HH} = 7.2$ Hz, 1H, C$_6$H$_4$). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 9.0 (SiCH$_3$), 10.9, 11.9 (C$_5$(CH$_3$)$_4$), 18.2 (CH_2SiN), 24.8 (β-CH$_2$, THF), 34.9 (C(CH$_3$)$_3$), 41.9 ($^1J_{YC} = 37.3$ Hz, YCH_2), 53.6 (C(CH$_3$)$_3$), 58.8 (OCH$_3$), 71.7 (α-CH$_2$, THF), 111.2 (C$_6$H$_4$), 114.9 (C$_5$(CH$_3$)$_4$), 116.4 (C$_5$(CH$_3$)$_4$), 118.4 (C$_6$H$_4$), 123.6, 124.4 (C$_6$H$_4$), 126.6 (C_5(CH$_3$)$_4$ attached to CH$_2$), 144.8, 154.7 (C$_6$H$_3$).

4.7. X-ray crystal structure analysis and determination of the structure of 2

Colorless crystals of $[Y(\eta^5:\eta^1-C_5Me_4CH_2Si-Me_2N^tBu)(2-C_6H_4OMe)(THF)]$ (2), $C_{27}H_{44}NO_2SiY$, 531.65 g mol^{-1}, were obtained from a hexane solution at $-30\,°C$. For a needle of dimensions $0.135 \times 0.090 \times 0.085$ mm^3, monoclinic, $P2_1$, $a = 9.862(1)$ Å, $b = 13.607(2)$ Å, $c = 10.222(1)$ Å, $\beta = 95.153(3)°$, $V = 1366.2(3)$ Å^3, $Z = 2$, $\rho_{calc} = 1.292$ g cm^{-3}, $\mu = 2.201$ mm^{-1}, F(0 0 0) = 564, the data set was obtained with a Bruker AXS diffractometer at $-90\,°C$ in the ω-scan mode up to $2\theta_{max} = 56.5°$ (Mo–K$_\alpha$ radiation). 8560 reflections were collected, 5471 were unique [$R_{int} = 0.0346$] of which 4423 were observed [$I > 2\sigma(I)$]. The data correction was carried out using the program system SAINT [13a]. The structure was solved by Patterson and Fourier methods using the program SHELXS-86 [13b], the refinement was carried out using the program SHELXL-97 based on F^2 [13c]. Anisotropic thermal parameters were refined for the non-hydrogen atoms. All hydrogen atoms could be located in Fourier difference maps and were refined in their positions with isotropic thermal parameters. $R_1 = 0.039$, $wR_2 = 0.069$ (observed data), goodness-of-fit on $F^2 = 0.915$; residual electron density (max/min) $0.637/-0.535$ e Å^{-3}.

5. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 202192 for compound 2. 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; e-mail deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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