

Preliminary communication

 First amido-functionalized niobium and tantalum complexes of the *ansa*-structural type: synthesis and photochemical Si-N bond cleavage ☆

 Wolfgang A. Herrmann *, Walter Baratta ¹

Anorganisch-chemisches Institut der Technischen Universität München, Lichtenbergstraße 4, D-85747 Garching, Germany

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Abstract

Niobium(V) and tantalum(V) amides $[(\eta^5\text{-C}_5\text{H}_4\text{-Si}(\text{CH}_3)_2\text{-NR})\text{M}[\text{N}(\text{CH}_3)_2]_3]$ ($\text{R} = \text{C}_6\text{H}_5$) containing chelate-type C, N-Ligands are available in 45% ($\text{M} = \text{Nb}$) and 60% ($\text{M} = \text{Ta}$) isolated yield, respectively, from the homoleptic amides $\text{M}[\text{N}(\text{CH}_3)_2]_5$ and the N-functionalized cyclopentadiene $\text{C}_5\text{H}_5\text{-Si}(\text{CH}_3)_2\text{-NHR}$ by double amine elimination. The niobium and tantalum derivatives undergo an unprecedented photo-induced rearrangement at room temperature, yielding the imido complexes $[(\eta^5\text{-C}_5\text{H}_4\text{-Si}(\text{CH}_3)_2\text{-N}(\text{CH}_3)_2)\text{M}(=\text{NR})[\text{N}(\text{CH}_3)_2]_2]$ as a result of Si-N bond cleavage.

Keywords: Niobium; Tantalum; Amino-functionalized cyclopentadienyl; Amide; Rearrangement; Si-N Bond cleavage

1. Introduction

There is extensive literature available on Group IV transition metal coordination chemistry with π -bonded *ansa* ligands. It is the stereorrigidity that makes metallocenes of C_2 -symmetry suitable for the stereospecific α -olefin polymerization [1]. It is an emerging concept that the C_s -symmetrical half-sandwich *ansa*-derivatives catalyze again, in the presence of alumoxanes, the syndiospecific polymerization of propylene [2]. By way of contrast, very little is known about the chemistry of *ansa*-metallocenes of transition metals other than those of the titanium group [3]. It was only recently that Group V metal systems such as vanadium/alkylaluminum, $(\text{HBPz}_3)\text{V}(=\text{N}^t\text{Bu})\text{Cl}_2/\text{methylalumoxane}$ and $(\eta^5\text{-C}_5\text{H}_5)\text{M}(\eta^4\text{-diene})(\text{CH}_3)_2/\text{methylalumoxane}$ ($\text{M} = \text{Nb, Ta}$) were discovered as catalytic precursors for the polymerization of ethylene [4,5,6]. Although monocyclopentadienyl compounds CpMCl_4 **A** and $\text{CpMCl}_2(=\text{NR})$ **B** ($\text{M} = \text{Nb}$ and Ta) have been known [7,8], their amide (NR_2^-) congeners, e.g. compounds

C, are relatively rare indeed [9]. We now describe the first example of *ansa*-complexes **D** of niobium and tantalum.

2. Results and discussion

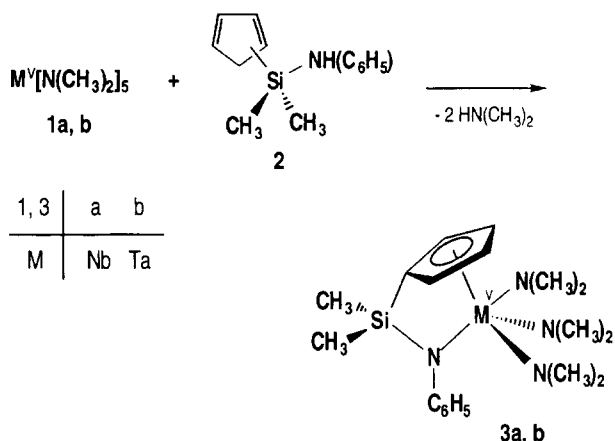
The homoleptic niobium(V) and tantalum(V) amides $\text{Nb}[\text{N}(\text{CH}_3)_2]_5$ **1a** and $\text{Ta}[\text{N}(\text{CH}_3)_2]_5$ **1b**, respectively, were treated with equimolar amounts of the protic ligand **2**. The new *ansa*-type complexes **3a,b** form quantitatively, as monitored by the ^1H NMR spectra, and were isolated as orange and yellow solids in 45% and 60% yield, respectively (Scheme 1). They are extremely water-sensitive: colorless, insoluble products form when moisture is added to samples **3a,b**.

The ^1H -, ^{13}C - and ^{29}Si NMR spectra are very similar; the three amido ligands are equivalent at 20°C on the NMR time scale. The ^1H NMR low-temperature spectra of **3b** in d_8 -toluene reveal a dynamic process, compatible with a pseudorotation of the three $\text{N}(\text{CH}_3)_2$ groups on the metal center [10]. Upon cooling, the resonance at $\delta = 2.97$ ppm (20°C: $\Delta\nu_{1/2} = 5$ Hz) of the amido ligands broadens (−60°C: $\Delta\nu_{1/2} = 80$ Hz), while the other signals do not change substantially. The ^1H NMR spectrum at −90°C shows two resonances ($\delta = 3.07$, 2.60 ppm) in a 2:1 ratio, suggesting the presence of two nonequivalent groups of $\text{N}(\text{CH}_3)_2$ ligands. Flux-

☆ Dedicated to Professor Henri Brunner on the occasion of his 60th birthday.

* Corresponding author.

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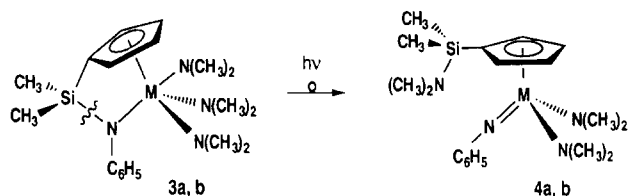


Scheme 1. Conditions: M = Nb, toluene, 1 h at -78°C , 2 h from -78°C to 25°C , 2 h at 25°C ; M = Ta, toluene, 0.5 h at 70°C , 1 h at 90°C .

ional behavior without bond breaking is quite common for the pentacoordinate compounds of the Group V main elements. Stereochemically non-rigid trigonal bipyramidal phosphorus compounds have been well studied, and it was shown that pseudorotation can be inhibited in the presence of suitable bridging groups [11]. The ^{29}Si NMR spectra of **3a,b** show single resonances at $\delta = -20.1$ (M = Nb) and -23.5 ppm (M = Ta). These data are similar to those of the compounds $[(\eta^5\text{-C}_5\text{H}_4)\text{-Si}(\text{CH}_3)_2\text{-(NC}_6\text{H}_5)]\text{M}[\text{N}(\text{CH}_3)_2]_2$ ($\delta = -20.3$ ppm, M = Zr [12]; $\delta = -20.6$ ppm, M = Mo [13]) but quite different from those of the three isomers of the free ligand **2** at $\delta = 2.4$, 1.1 and -0.7 ppm [2e]. The spectra thus suggest the presence of an *ansa*-ligand, and a C_2 symmetry is assigned to the two complexes.

The presence of a bridged ligand, as in the case of $[(\eta^5\text{-C}_5\text{H}_4)\text{-Si}(\text{CH}_3)_2\text{-(NC}_6\text{H}_5)]\text{Mo}[\text{N}(\text{CH}_3)_2]_2$, stabilizes complexes towards redox reactions [13]. In fact the expected formation of $(\eta^5\text{-C}_5\text{H}_5)\text{Nb}[\text{N}(\text{CH}_3)_2]_4$ was not observed: **1a** reacts with cyclopentadiene in *n*-pentane at low temperature and a purple suspension containing different products is formed [14].

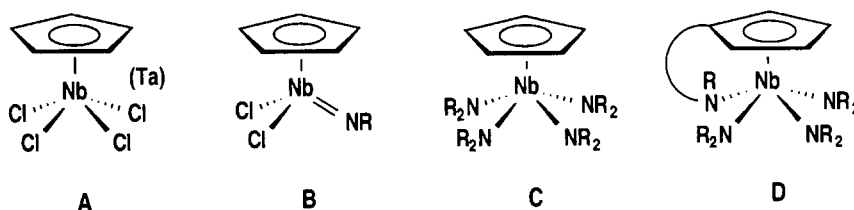
The reactivity of the starting amides $\text{M}[\text{N}(\text{CH}_3)_2]_5$ **1a,b** is quite different: protonation of **1a** with the aminosilane **2** occurs in toluene at temperatures below 0°C while **1b** reacts only at temperatures above 60°C . An interesting and, to our knowledge, unprecedented isomerization occurs with the complexes **3a,b** by irradiation at ambient temperature. The new *imido* com-



Scheme 2. Conditions: M = Nb, toluene, mercury lamp, 12 h, 20°C ; M = Ta, toluene, mercury lamp, 10 h, 20°C .

plexes **4a,b**—characterized by NMR spectroscopy, mass spectrometry and elemental analysis—form quantitatively according to Scheme 2.

Visible light entails cleavage of the Si–N bond of the niobium complex **3a** to form **4a** in solution and in the solid state [15]. By way of contrast, no isomerization of the tantalum congener **3b** was observed even after several months under the same conditions. The absorption electronic spectra of **3a,b** are similar and exhibit two bands and one shoulder with the absorptions of the Ta complex shifted to shorter wavelengths as compared with the Nb congener (242, 292, 440 (sh) nm, for Nb; 234, 268, 370 (sh) nm for Ta). The ^1H NMR of **4a,b** show two resonances for the $\text{N}(\text{CH}_3)_2$ groups ($\delta = 3.21$, 2.35 ppm and $\delta = 3.25$, 2.34 ppm for M = Nb, Ta, respectively in C_6D_6) in a 2:1 ratio. The first resonances are near to those of the $\text{N}(\text{CH}_3)_2$ groups of the amido/imido complexes $(\eta^5\text{-C}_5\text{H}_5)\text{M}[\text{N}(2,6\text{-iPr}_2\text{C}_6\text{H}_3)]_2[\text{N}(\text{CH}_3)_2]_2$ [16] ($\delta = 3.22$ and 3.24 ppm for M = Nb, Ta in C_6D_6), the second resonances are close to that of the amido group of the compound $(\text{CH}_3)_3\text{SiN}(\text{CH}_3)_2$ ($\delta = 2.38$ ppm, C_6D_6). The ^{13}C NMR spectra of **4a,b** exhibit two resonances for the $\text{N}(\text{CH}_3)_2$ groups ($\delta = 52.2$, 38.1 and $\delta = 51.7$, 38.1 ppm for M = Nb, Ta, in C_6D_6) in a 2:1 ratio. Again, the first signals are near to the resonances of the $\text{N}(\text{CH}_3)_2$ groups of $(\eta^5\text{-C}_5\text{H}_5)\text{M}[\text{N}(2,6\text{-iPr}_2\text{C}_6\text{H}_3)]_2[\text{N}(\text{CH}_3)_2]_2$ ($\delta = 52.1$ and 51.4 ppm for M = Nb, Ta, in C_6D_6), the latter signals being close to that of the amido group of $(\text{CH}_3)_3\text{SiN}(\text{CH}_3)_2$ ($\delta = 37.9$ ppm, C_6D_6). The ^{13}C NMR resonances of the $\text{Si}(\text{CH}_3)_2$ fragments of **4a,b** ($\delta = -1.5$ and -1.6 ppm for M = Nb and Ta) are shifted upfield as compared to those of the *ansa*-complexes **3a,b** ($\delta = 1.6$ and 1.4 ppm for M = Nb and Ta) and are near to that of the methyl group of $(\text{CH}_3)_3\text{SiN}(\text{CH}_3)_2$ ($\delta = -1.3$ ppm, C_6D_6) [17]. The ^{13}C NMR resonances of the *ipso* carbon atoms of the



Formulae A–D

phenyl rings of **4a,b** ($\delta = 156.8$ and 158.1 ppm, for $M = Nb$ and Ta) compare well with those of the related imido cyclopentadienyl complexes $[\eta^5\text{-C}_5\text{H}_4\text{Si}(\text{CH}_3)_3]_2\text{Nb}(\text{NC}_6\text{H}_5)\text{Cl}$, $[\eta^5\text{-C}_5(\text{CH}_3)_5]_2\text{Ta}(\text{NC}_6\text{H}_5)\text{H}$ and $(\eta^5\text{-C}_5\text{H}_4\text{CH}_3)_2\text{Mo}(\text{NC}_6\text{H}_5)$ ($\delta = 159.9$; 160.9 and 160.2 ppm, respectively) [18,19,20]. It is interesting to note that the ^{13}C NMR resonances of the *ipso* and *ortho* carbons of the phenyl rings of the complexes **4a,b** are shifted downfield with $\Delta\delta = 9.6$, 9.3 ppm ($M = Nb$) and $\Delta\delta = 10.9$, 10.2 ppm ($M = Ta$) as compared to the signals of the free amine $\text{C}_6\text{H}_5\text{NH}_2$. These values are bigger with respect to those of the imido *ansa*-complexes **3a,b**, $\Delta\delta = 5.3$, 6.8 ppm ($M = Nb$) and $\Delta\delta = 4.3$, 7.5 ppm ($M = Ta$), but quite near to those of the imido complexes $(\eta^5\text{-C}_5\text{H}_5)\text{M}[\text{N}(2,6\text{-}^i\text{Pr}_2\text{C}_6\text{H}_3)]\text{N}(\text{CH}_3)_2$, $\Delta\delta = 12.1$, 10.8 ppm ($M = Nb$) and $\Delta\delta = 12.0$, 11.0 ppm ($M = Ta$) to referred to the free amine $(2,6\text{-}^i\text{Pr}_2\text{C}_6\text{H}_3)\text{NH}_2$ [21]. Finally, the ^{29}Si NMR spectra of **4a,b** show one resonance at $\delta = -2.9$ ppm in C_6D_6 , cf. $(\text{C}_5\text{H}_5)\text{Si}(\text{CH}_3)_2\text{NHC}(\text{CH}_3)_3$ $\delta = -1.8/-3.3/-4.2$ ppm [2e]. The *ansa*-structure has thus been lost during the isomerization. The CI mass spectrum of **4a,b** exhibits the molecular peaks with the strongest peaks at $m/z = 394.2$ and 482.6 amu, corresponding to $[\text{4a}^+ - \text{N}(\text{CH}_3)_2]$ and $[\text{4b}^+ + \text{H} - \text{N}(\text{CH}_3)_2]$, respectively.

Cleavage of the bridging ligands of *ansa*-metallocenes was reported recently: polymers containing skeletal iron atoms were obtained from ring-tilted *ansa*-ferrocenophanes of the type $[(\text{C}_5\text{H}_4)_2(\text{ER}_z)_x]\text{Fe}$ ($E = \text{Si}, \text{Ge}, \text{P}$) through a thermal disruption of a C–E bond [22]. Steric congestion is frequently a critical factor in promoting multiple bond formation, and the “ α -hydrogen abstraction” is a well known reaction to prepare alkylidene and imido metal complexes [23]. The imido compound $\text{Ta}[\text{NC}(\text{CH}_3)_3][\text{N}(\text{CH}_3)_2]_3$ form from the homoleptic amide and $(\text{CH}_3)_3\text{C-NH}_2$ through an α -hydrogen abstraction [24]. More interesting is the formation of the imido complex $[\eta^5\text{-C}_5(\text{CH}_3)_5]\text{Ta}(\text{CH}_3)_2[\text{N}(\text{CH}_3)]$ and methane from $[\eta^5\text{-C}_5(\text{CH}_3)_5]\text{Ta}(\text{CH}_3)_3\text{Cl}$ and $\text{LiNH}(\text{CH}_3)$ [25]. This reaction probably involves the (thermally unstable) complex $[\eta^5\text{-C}_5(\text{CH}_3)_5]\text{Ta}(\text{CH}_3)_3[\text{NH}(\text{CH}_3)]$ quite similar to $[\eta^5\text{-C}_5(\text{CH}_3)_5]\text{Ta}(\text{CH}_3)_3[\text{N}(\text{CH}_3)_2]$, isolated and stable at $T < 0^\circ\text{C}$, that evolves to the imino complex $[\eta^5\text{-C}_5(\text{CH}_3)_5]\text{Ta}(\text{CH}_3)_2[\text{CH}_2\text{N}(\text{CH}_3)]$. In the present case, we tentatively assign the isomerization **3a,b** $\rightarrow$ **4a,b** to an “ α -silicon abstraction” as a result of steric crowding between the π -cyclopentadienyl and the four amido ligands. Although the cleavage of silyl leaving groups with concomitant formation of strong covalent bonds (e.g., Si–O, Si–Cl) was applied to synthesize imido complexes from metal oxides or metal halides [26], a light-induced rearrangement with formation of an imido ligand has not yet been reported. The thermal stability of the photolysis products **4a,b** ought to be attributed to the presence of an imido ligand ($=\text{NC}_6\text{H}_5$)—a well-

known feature of high oxidation-state organometallics [23c,27].

3. Experimental section

All operations were carried out in dry oxygen-free solvents (< 3 ppm H_2O , Karl Fischer titration control) and in a dry argon atmosphere (Schlenk tube and Glove-box techniques). Photochemical experiments were performed with a high-pressure Hanau TQ 150 mercury lamp, surrounded by a water-cooled immersion well. The metal amides $\text{Nb}[\text{N}(\text{CH}_3)_2]_5$ and $\text{Ta}[\text{N}(\text{CH}_3)_2]_5$ were prepared as reported in the literature [28,29] and used as freshly sublimed materials. The ligand **2** was synthesized from two equivalents of aniline and one equivalent of $(\text{C}_5\text{H}_5)\text{Si}(\text{CH}_3)_2\text{Cl}$ [2e]; the latter compound was obtained from dichlorodimethylsilane and lithium cyclopentadienyl [30]. Elemental analyses were carried out at the microanalytical laboratory of the authors' institute. NMR spectra were measured with a JEOL-JMN-GX 400 spectrometer; UV–vis spectra were performed on a Hewlett Packard 8452A spectrophotometer. Mass spectra (CI) were measured with a Varian-MAT 90 spectrometer.

3.1. *Tris(dimethylamido)[η^1 : η^5 -{(N-phenylamido)dimethyl-silyl}cyclopentadienyl] niobium(V) 3a*

To a solution of $\text{Nb}[\text{N}(\text{CH}_3)_2]_5$ **1a** (509 mg, 1.62 mmol) in 10 ml of toluene, a solution of the ligand **2** (350 mg, 1.63 mmol) in 20 ml of toluene was added dropwise at -78°C . The mixture was stirred in the dark at -78°C for 1 h and was allowed to attain room temperature within 2 h. After 2 h at room temperature, the solution was gently heated at 50°C for 30 min, and toluene was evaporated in vacuo. The orange oily residue becomes solid on standing under reduced pressure for 1 h. The solid was dissolved in a minimum amount of *n*-pentane (3 ml) and re-precipitated by keeping it at -78°C . **3a** was filtered and dried under reduced pressure (320 mg, 45% yield). The dark-orange waxy product is best stored at -78°C . Anal. Found (Calc.) for $\text{C}_{19}\text{H}_{33}\text{N}_4\text{NbSi}$: C 51.90 (52.04); H 7.53 (7.59); N 12.41 (12.78); Si 6.33 (6.41). Spectroscopic data: ^1H NMR (400 MHz, C_6D_6 , 25°C , TMS): $\delta = 0.66$ (s, 6 H; $\text{Si}(\text{CH}_3)_2$), 2.86 (s, 18 H; $\text{N}(\text{CH}_3)_2$), 6.25 (m, 2 H; C_5H_4), 6.88 (t, 1 H; $^3J(\text{H}, \text{H}) = 7.9$ Hz, *p*- C_6H_5), 6.92 (m, 2 H; C_5H_4), 6.93 (d, 2 H; $^3J(\text{H}, \text{H}) = 8.0$ Hz, *o*- C_6H_5), 7.25 (t, 2 H; $^3J(\text{H}, \text{H}) = 7.9$ Hz, *m*- C_6H_5). $^{13}\text{C}\{^1\text{H}\}$ NMR (100.4 MHz, C_6D_6 , 25°C , TMS): $\delta = 1.6$ ($\text{Si}(\text{CH}_3)_2$), 47.8 ($\text{N}(\text{CH}_3)_2$), 93.9 (*ipso*- C_5H_4), 119.2 (C_5H_4), 119.9 (*p*- C_6H_5), 121.8 (*o*- C_6H_5), 125.0 (C_5H_4), 129.1 (*m*- C_6H_5), 152.5 (*ipso*- C_6H_5). ^{29}Si NMR (DEPT, 79.5 MHz, C_6D_6 , 25°C , TMS): $\delta = -20.1$ ($\text{Si}(\text{CH}_3)_2$). UV–vis (Heptane, 25°C): $\lambda = 242$, 292 and

440 (sh) nm. MS (CI): $m/z(\%) = 439.1$ (31) [$M^+ + H$], 394.1 (63) [$M^+ - N(CH_3)_2$].

3.2. *Tris(dimethylamido)[η^5 -(*N*-phenylamido)dimethyl-silyl]cyclopentadienyl] tantalum(V) 3b*

To a solution of $Ta[N(CH_3)_2]_5$ **1b** (205 mg, 0.511 mmol) in 10 ml of toluene, a solution of the ligand **2** (110 mg, 0.511 mmol) in 15 ml of toluene was added dropwise at -30°C . The mixture was allowed to attain room temperature. The solution was heated at 70°C for 30 min and at 90 – 95°C for 1 h. The solvent was evaporated in vacuo. The yellow–orange oily residue becomes solid on standing under reduced pressure for 1 h. The solid was dissolved in a minimum amount of *n*-pentane (2 ml) and separated from solution on cooling to -7°C . The yellow product was filtered and dried under reduced pressure (160 mg, 60% yield). Anal. Found (Calc.) for $C_{19}H_{33}N_4TaSi$: C 43.16 (43.34); H 6.40 (6.32); N 10.35 (10.64); Si 5.60 (5.33). Spectroscopic data: ^1H NMR (400 MHz, C_6D_6 , 25°C , TMS): $\delta = 0.62$ (s, 6 H; $Si(CH_3)_2$), 3.01 (s, 18 H; $N(CH_3)_2$), 6.33 (m, 2 H; C_5H_4), 6.87 (t, 1 H; $^3J(H, H) = 7.2$ Hz, *p*- C_6H_5), 6.91 (m, 2 H; C_5H_4), 6.95 (d, 2 H; $^3J(H, H) = 8.5$ Hz, *o*- C_6H_5), 7.27 (t, 2 H; $^3J(H, H) = 7.9$ Hz, *m*- C_6H_5). $^{13}\text{C}\{^1\text{H}\}$ NMR (100.4 MHz, C_6D_6 , 25°C , TMS): $\delta = 1.4$ ($Si(CH_3)_2$), 46.3 ($N(CH_3)_2$), 94.0 (*ipso*- C_5H_4), 119.4 (C_5H_4), 120.2 (*p*- C_6H_5), 122.5 (*o*- C_6H_5), 126.4 (C_5H_4), 129.2 (*m*- C_6H_5), 151.5 (*ipso*- C_6H_5). ^{29}Si NMR (DEPT, 79.5 MHz, C_6D_6 , 25°C , TMS): $\delta = -23.5$ ($Si(CH_3)_2$). UV–vis (Heptane, 25°C): $\lambda = 234$, 268 and 370 (sh) nm. MS (CI): $m/z(\%) = 527.6$ (13) [$M^+ + H$], 482.4 (72) [$M^+ - N(CH_3)_2$].

3.3. *Bis(dimethylamido)(N-phenylimido)[η^5 -(dimethylamido)(dimethyl-silyl)]cyclopentadienyl]niobium(V) 4a*

3a (128 mg, 0.292 mmol) was dissolved in 4 ml of toluene (20 ml Schlenk tube). The solution was kept at the distance of approximately 3 cm from the mercury lamp while it was stirred and irradiated for 12 h at 20°C . During this period the color of the solution changed from orange to red–brown. The solvent was evaporated in vacuo and the resulting brown oil **4a** was dried under reduced pressure (122 mg, 95% yield). Anal. Found (Calc.) for $C_{19}H_{33}N_4NbSi$: C 51.74 (52.04); H 7.43 (7.59); N 12.14 (12.78); Si 6.66 (6.41). Spectroscopic data: ^1H NMR (400 MHz, C_6D_6 , 25°C , TMS): $\delta = 0.23$ (s, 6 H; $Si(CH_3)_2$), 2.35 (s, 6 H; $SiN(CH_3)_2$), 3.21 (s, 12 H; $N(CH_3)_2$), 6.09 (t, 2 H; $^3J(H, H) = 2.4$ Hz, C_5H_4), 6.39 (t, 2 H; $^3J(H, H) = 2.4$ Hz, C_5H_4), 6.83 (t, 1 H; $^3J(H, H) = 8.0$ Hz, *p*- C_6H_5), 7.04 (d, 2 H; $^3J(H, H) = 8.0$ Hz, *o*- C_6H_5), 7.11 (t, 2 H; $^3J(H, H) = 7.3$ Hz, *m*- C_6H_5). $^{13}\text{C}\{^1\text{H}\}$ NMR (100.4 MHz, C_6D_6 , 25°C , TMS): $\delta = -1.5$ ($Si(CH_3)_2$), 38.1

($SiN(CH_3)_2$), 52.2 ($N(CH_3)_2$), 111.4 (C_5H_4), 114.5 (C_5H_4), 115.0 (*ipso*- C_5H_4), 122.8 (*p*- C_6H_5), 124.3 (*o*- C_6H_5), 128.6 (*m*- C_6H_5), 156.8 (*ipso*- C_6H_5). ^{29}Si NMR (DEPT, 79.5 MHz, C_6D_6 , 25°C , TMS): $\delta = -2.9$ ($Si(CH_3)_2$). MS (CI): $m/z(\%) = 437.3$ (3) [$M^+ - H$], 394.2 (100) [$M^+ - N(CH_3)_2$].

3.4. *Bis(dimethylamido)(N-phenylimido)[η^5 -(dimethylamido)(dimethyl-silyl)]cyclopentadienyl]tantalum(V) 4b*

This synthesis was carried out as described above for the niobium congener. **3b** (180 mg, 0.342 mmol) was dissolved in 4 ml of toluene and the solution was irradiated for 10 h at 20°C . During this period the color of the solution changed from yellow to brown. The solvent was evaporated in vacuo and the resulting yellow–brown oil **4b** was dried under reduced pressure (171 mg, 95% yield). Anal. Found (Calc.) for $C_{19}H_{33}N_4TaSi$: C 41.65 (43.34); H 6.04 (6.32); N 10.21 (10.64). Spectroscopic data: ^1H NMR (400 MHz, C_6D_6 , 25°C , TMS): $\delta = 0.24$ (s, 6 H; $Si(CH_3)_2$), 2.34 (s, 6 H; $SiN(CH_3)_2$), 3.25 (s, 12 H; $N(CH_3)_2$), 6.05 (t, 2 H; $^3J(H, H) = 2.5$ Hz, C_5H_4), 6.39 (t, 2 H; $^3J(H, H) = 2.4$ Hz, C_5H_4), 6.81 (t, 1 H; $^3J(H, H) = 7.3$ Hz, *p*- C_6H_5), 6.96 (d, 2 H; $^3J(H, H) = 7.3$ Hz, *o*- C_6H_5), 7.19 (t, 2 H; $^3J(H, H) = 7.5$ Hz, *m*- C_6H_5). $^{13}\text{C}\{^1\text{H}\}$ NMR (100.4 MHz, C_6D_6 , 25°C , TMS): $\delta = -1.6$ ($Si(CH_3)_2$), 38.1 ($SiN(CH_3)_2$), 51.7 ($N(CH_3)_2$), 111.7 (C_5H_4), 114.4 (C_5H_4), 115.3 (*ipso*- C_5H_4), 121.8 (*p*- C_6H_5), 125.2 (*o*- C_6H_5), 128.4 (*m*- C_6H_5), 158.1 (*ipso*- C_6H_5). ^{29}Si NMR (DEPT, 79.5 MHz, C_6D_6 , 25°C , TMS): $\delta = -2.9$ ($Si(CH_3)_2$). MS (CI): $m/z(\%) = 526.7$ (1) [M^+], 482.6 (100) [$M^+ + H - N(CH_3)_2$], 481.6 (80) [$M^+ - N(CH_3)_2$].

References and Notes

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