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Journal of Organometallic Chemistry 610 (2000) 42–48

Journal of Organometallic Chemistry

A study of *ortho*- and *para*-siloxyanilines for the synthesis of mono-, bi-, and tetra-nuclear early transition metal–imido complexes

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Received 17 April 2000; accepted 27 June 2000

Abstract

The siloxyanilines *o*-$Me_3SiOC_6H_4NH_2$ (**1**) and *p*-$RMe_2SiOC_6H_4NH_2$ (R = H (**2**); R = Me (**3**)), and their N-silylated derivatives *p*-$Me_3SiOC_6H_4NHSiMe_3$ (**4**) and *p*-$Me_3SiOC_6H_4N(SiMe_3)_2$ (**5**) have been prepared from *ortho*- or *para*-aminophenol and used in the synthesis of imido complexes. Thus, binuclear $[\{Ti(\eta^5\text{-}C_5H_5)Cl\}\{\mu\text{-}NC_6H_4(p\text{-}OSiMe_3)\}]_2$ (**6**) and mononuclear $[TiCl_2\{NC_6H_4(p\text{-}OSiMe_3)\}(py)_3]$ (**7**) imido complexes have been obtained from the reaction of **3** and $[Ti(\eta^5\text{-}C_5H_5)Cl_3]$ or $[TiCl_2(N^tBu)(py)_3]$, respectively. In contrast, the reaction of **1** with $TiCl_4$ and ^{t}Bupy affords the titanocycle $[TiCl_2\{OC_6H_4(o\text{-}NH)\text{–}N,O\}(^tBupy)_2]$ (**8**). Compound **5** has also been used to prepare the niobium imide complex $[NbCl_3\{NC_6H_4(p\text{-}OSiMe_3)\}(MeCN)_2]$ (**9**), by its reaction with $NbCl_5$ in CH_3CN. These findings have been applied to the synthesis of polynuclear systems. Thus, chlorocarbosilane $Si[CH_2CH_2CH_2Si(Me)_2Cl]_4$ (CS–Cl) has been functionalized with the *ortho*- and *para*-aminophenoxy groups to give **10** and **11**, respectively. The use of **11** has allowed the formation of the tetranuclear compound **12**. Attempts to synthesize terminal imido titanium complexes from **10** and $TiCl_4$ in the presence of ^{t}Bupy and Et_3N, give complex **8** and carbosilane CS–Cl. © 2000 Elsevier Science S.A. All rights reserved.

Keywords: Imido complexes; Cyclopentadienyl complexes; Transition metal dendrimers; Titanium; Niobium

1. Introduction

Due to the relevance of imido complexes in transition metal chemistry, a large variety of synthetic methodologies have been developed [1a,2]. Among the main features of the imido ligand are its electronic flexibility, which allows a chemical behavior ranging from remarkable stability to extreme reactivity, its variety of coordination modes, and its capability to stabilize high oxidation states [1,2]. We are looking for NR complexes of early transition metals in which the R group is linked to a silyl group. Our interest in such imido ligands is because their synthesis might be extended to support transition metal complexes on carbosilane dendrimers through imido links [3]. For instance, reports published up to date on titanium dendrimers are limited to alkoxo or cyclopentadienyl anchoring ligands [4,5].

Here, we present work carried out on the synthesis of imido complexes of titanium and niobium containing siloxy-substituted phenylimido ligands. The siloxyaniline *p*-$Me_3SiOC_6H_4NH_2$ (**3**) and its N-silyl substituted *p*-$Me_3SiOC_6H_4N(SiMe_3)_2$ (**5**) have been useful as precursors for the synthesis of terminal and bridging imido complexes. In the last part of this article we describe the synthesis of the tetranuclear titanium complex **12**, a non-branched model of a dendrimer.

2. Results and discussion

NMR and analytical data for **1**–**12** are given in Section 4. Only selected data will be presented for this discussion.

The lithium aminophenoxides **Ia**–**b** (Scheme 1) have been obtained by deprotonation of the hydroxyl group in *ortho*- or *para*-aminophenol with one equivalent of Li^{n}Bu in THF. They can be isolated as white solids,

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PII: S0022-328X(00)00391-0

although they have been used in situ through this work. Reaction of **I** and one equivalent of $SiMe_2RCl$ (R = H, Me) has allowed the synthesis of the oily siloxyanilines *o*-$Me_3SiOC_6H_4NH_2$ (**1**), *p*-$HMe_2SiOC_6H_4NH_2$ (**2**), and *p*-$Me_3SiOC_6H_4NH_2$ (**3**) in good yields (> 80% relative to aminophenol).

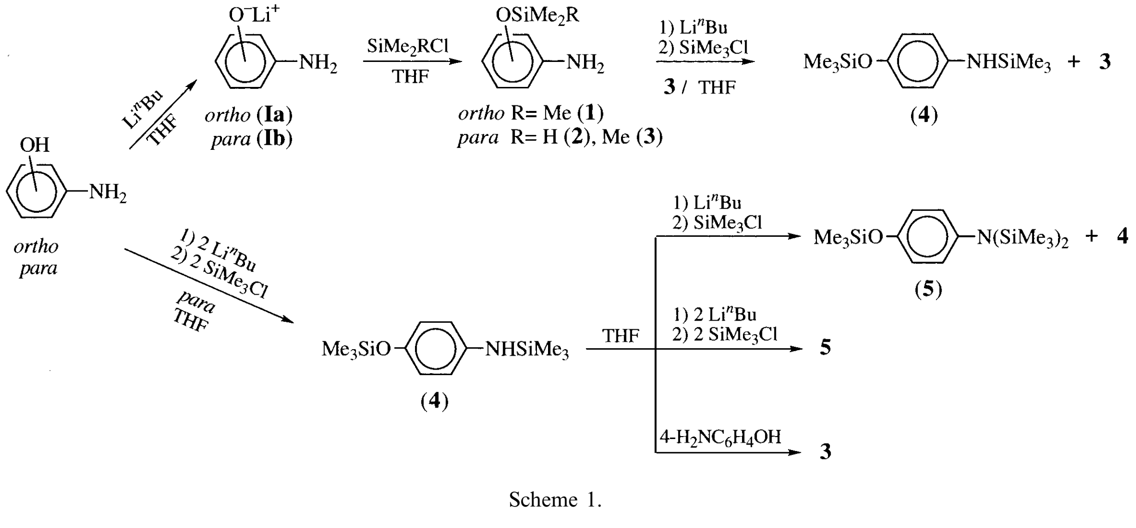
The regioselectivity of the silylation process on the oxygen of aminophenols must be understood as a result of the much higher Brönsted acidity of the hydroxy compared with the amino group ($pK_a \sim 10$ and ~ 27 for phenol and aniline, respectively [6]). Thus, any eventual lithium amide formation during the course of the deprotonation reaction must shift the proton transfer equilibrium from HOC_6H_4NHLi to the side of $LiOC_6H_4NH_2$ ($K_{eq} \sim 10^{17}$). Moreover, in an experiment carried out in a NMR-tube scale, the mixture of *p*-$Me_3SiOC_6H_4NHSiMe_3$ (**4**, vide infra) with *p*-$HOC_6H_4NH_2$, one to one in THF, followed by replacement of the solvent by $CDCl_3$, gives 4-$Me_3SiOC_6H_4NH_2$ (**3**) as the only product detected by ^{1}H-NMR (Scheme 1)

Stepwise reaction of **3** through the sequence (i) one equivalent of Li^nBu (ii) one equivalent of $SiMe_3Cl$ in THF, has led to mixtures of *p*-$Me_3SiOC_6H_4NHSiMe_3$ (**4**) and the starting material **3** (Scheme 1). Instead, **4** is readily synthesized free of **3** by addition of two equivalents of Li^nBu and $SiMe_3Cl$ to *p*-aminophenol. Similarly, further N-silylation of compound **4** in THF with only one equivalent of Li^nBu and $SiMe_3Cl$ has given mixtures of *p*-$Me_3SiOC_6H_4N(SiMe_3)_2$ (**5**) and **4** (Scheme 1). Although both compounds are separated by fractional distillation, pure compound **5** has been obtained by reaction of **4** with two equivalents of Li^nBu and $SiMe_3Cl$. The different results using one or two equivalents of $Li^nBu/SiMe_3Cl$ for the synthesis of **4** and **5**, are most likely due to nucleophilic attack of Li^nBu to the Si–O bond competing with deprotonation of the amino group. Since trimethylsilyl ethers are easily cleaved by nucleophiles, the effect of two equivalents of butyllithium on compounds **3** and **4** must be the formation of *p*-$LiOC_6H_4N(H)Li$ and *p*-$LiOC_6H_4N(SiMe_3)Li$, respectively. Thereafter, the addition of $SiMe_3Cl$ must proceed with silylation back on the oxygen atom and silylation on the nitrogen as well, leading to the target compounds **4** and **5**. Both compounds are oils and have been found to be moisture sensitive, as samples exposed to air slowly undergo hydrolysis of the N–Si bonds to produce compound **3** (^{1}H-NMR evidence).

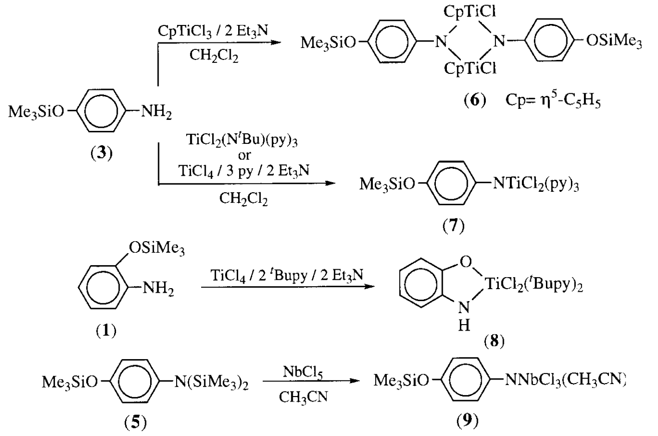
The ^{1}H-NMR spectra of **1**–**5** show resonances due to the aromatic ring consistent with the AA′BB′ (*para*) or ABCD (*ortho*) spin systems. In addition, a broad singlet (δ 3.2–3.9) is recorded for the NH_x protons in **1**–**4**, and a heptet (δ 4.88) for the $SiMe_2H$ proton in **2**. Also, a SiMe resonance for **1**–**3** and two for **4**–**5** are observed in ^{1}H- and ^{29}Si-NMR; ^{1}H integration confirms the progressive proton substitution by $SiMe_3$ groups at the nitrogen atom, on going from **3** to **5**.

Many procedures have been described for the synthesis of early transition metal–imido complexes [1a,2]. Among them, deprotonation of primary amines and exchange reactions of alkylimido ligands and arylamines have been found to be straightforward synthetic methods [7]. Siloxyanilines **1** and **3** have been tested as potential precursors of TiN compounds using both methods.

The reaction of **3** with $[Ti(\eta^5\text{-}C_5H_5)Cl_3]$ in CH_2Cl_2, in the presence of two equivalents of Et_3N as an auxiliary base, yields the imido binuclear complex $[\{Ti(\eta^5\text{-}C_5H_5)Cl\}\{\mu\text{-}NC_6H_4(p\text{-}OSiMe_3)\}]_2$ (**6**) (Scheme 2). This compound is obtained as a dark violet solid moderately moisture stable, although it readily decomposes into wet solvents. Due to the high oxophilic character of Ti(IV) species, the high yield of its preparation (ca. 90%) reveals an effective oxygen-protection by the $SiMe_3$ group in compound **3**. The NMR data of complex **6** show equivalent cyclopentadienyl, phenyl and



Scheme 1.



Scheme 2.

SiMe$_3$ groups, quite in agreement with either a mononuclear or a symmetric binuclear structure. A binuclear arrangement with imido bridges is assumed by comparison with the proposed or determined structures for other analogues [8], such as [Ti(η^5-C$_5$H$_5$)Cl]$_2$(μ-NPh)$_2$] [8a], and accordingly with the observation of a MS peak corresponding to a dimeric molecule (see Section 4). On the other hand, cyclopentadienyl mononuclear compounds with terminal imido groups have only been observed in complexes of general formula [TiCp(NR)ClL] (Cp = generic cyclopentadienyl ring, L = py, ^{t}Bupy; py = pyridine, ^{t}Bupy = 4-*tert*-butylpyridine), which contain coordinated pyridine ligands [9]. Our attempts to obtain mononuclear complexes adding py or ^{t}Bupy in the synthetic procedure of complex **6** were unsuccessful as no other organometallic compound than **6**, free of any L ligand, was detected. This result is in agreement with the observed tendency of mono- or non-substituted cyclopentadienyl complexes [TiCp(NR)ClL] to lose the L ligand affording dimers [9b].

Complex **7** has been obtained as a very moisture sensitive brownish–yellow solid by exchange of the *tert*-butylimido group in [TiCl$_2$(N^{t}Bu)(py)$_3$] by the siloxyaniline **3** or, alternatively, by deprotonation of **3** with TiCl$_4$, pyridine and two equivalents of Et$_3$N in CH$_2$Cl$_2$ (Scheme 2). Pure **7** can be isolated by simple removal of the solvent and of the ^{t}BuNH$_2$ byproduct in the first case, whereas attempts to isolate neat samples from the deprotonation reaction failed. The pyridine ligands appear in the ^{1}H-NMR spectrum of **7** as two groups of resonances in a 2:1 ratio, with those of the single pyridine ligand occurring at higher fields and being somewhat broadened. This is the same spectroscopic behavior found in other [TiCl$_2$(NR)(py)$_3$] complexes [7a] and corresponds to a *trans* arrangement of the chloride and mer of the pyridine ligands with a labile py *trans* to the imido group.

The synthesis of imido derivatives from the *ortho* substituted arylamine **1** was unsuccessful under the same conditions. Thus, the reaction of **1** with TiCl$_4$ in the presence of two equivalents of ^{t}Bupy and two equivalents of Et$_3$N in CH$_2$Cl$_2$, gives the titanocycle [TiCl$_2${OC$_6$H$_4$(*o*-NH)–N,O}(^{t}Bupy)$_2$] (**8**), obtained as a moisture sensitive dark violet microcrystalline solid. The presence of the amido group is confirmed by a low field resonance (δ 11.16) in the ^{1}H-NMR spectrum. Both ^{t}Bupy ligands are equivalent suggesting a *trans* arrangement in the octahedral titanium environment. The fairly similar compound [TiCl$_2${OC$_6$H$_4$(*o*-NH)–N,O}(py)$_2$] is detected by ^{1}H-NMR [10] in the reaction of **1** and [TiCl$_2$(N^{t}Bu)(py)$_3$], although attempts to isolated pure samples failed. During the course of these reactions, the *ortho* position of the trimethylsiloxy group clearly facilitates the Si–O bond cleavage, most likely assisted by SiMe$_3$Cl elimination. This finding suggests that reaction of siloxyanilines and TiCl$_4$ proceeds through amido intermediates that evolve to the imido compound **7** or to the titanocycle **8**, depending on the *para* or *ortho* position of the OSiMe$_3$ group.

Cleavage of N–Si bond in *N*-silylamines or *N*-silylanilines, accompanied by formation of strong Si–halide bond, has also been reported as an effective synthetic method for introducing imido ligands in early transition metal complexes [1b,11]. Accordingly, compound **5** reacts with NbCl$_5$ in CH$_3$CN at room temperature affording the siloxyarylimide [NbCl$_3${NC$_6$H$_4$(*p*-OSiMe$_3$)}(MeCN)$_2$] (**9**), which is isolated as a moisture sensitive orange–red solid (Scheme 2). Analytical and spectroscopic data are consistent with the structure proposed for **9** and show the presence of two equivalent CH$_3$CN ligands coordinated to the metal center in an octahedral environment, suggesting a *trans* arrangement of them and therefore mer of the chlorides. When the ^{1}H-NMR spectrum of **9** is registered in CD$_3$CN, only free CH$_3$CN is observed, indicating exchange between free and coordinated acetonitrile.

The reactions described above for the synthesis of terminal-imido complexes can be useful for the synthesis of periphery-metallated carbosilane structures starting from aniline-functionalized cores as **10** or **11** (Scheme 3). These are easily prepared as yellow oils by reaction of the chloro terminated derivative CS–Cl [12] with phenoxides **Ia** or **Ib**, respectively. Both compounds have been characterized by ^{1}H- and ^{13}C{^{1}H}-NMR, and **11** by ^{29}Si{^{1}H}-NMR, elemental analysis and MALDI-TOF MS as well (see Section 4). Chemical shifts observed for the –SiMe$_2$OC$_6$H$_4$NH$_2$ moieties in **10** and **11** are similar to those for **1** and **3**, respectively.

Attemps to synthesize terminal arylimido titanium complexes from **10** and **11** have yielded comparable results with those described above for **1** and **3**. Thus, the reaction of **10** with TiCl$_4$ in the presence of ^{t}Bupy and Et_3N in CH_2Cl_2, gives complex **8** (Scheme 3), together with the recovery of the chlorocarbosilane CS–Cl. Again, the *ortho* position of the siloxy group facilitates the Si–O bond cleavage to afford the metallocycle **8**. Instead, the tetranuclear titanium compound **12** can be prepared from the *para*-substituted isomer **11** (Scheme 3). Although complex **12** is obtained from the reaction of **11** with either, four equivalents of $[TiCl_2(N^tBu)(py)_3]$ in CH_2Cl_2 at room temperature, or a mixture of $TiCl_4$, pyridine and Et_3N in CH_2Cl_2, the former procedure is cleaner, as observed in the related synthesis of **7** from **3**. The product is isolated as a moisture sensitive dark-brown solid. Interestingly, its NMR data show free and coordinated pyridine ligands (ratio 1:2) in solution even after several washings of the solid in pentane. However, analytical and spectroscopic data of samples dried in vacuo at 50°C for several hours are consistent with the presence of only two py ligands per titanium, *cis* to the imido group and *trans* each other (see Section 4). Five-coordinated titanium complexes of this type (i.e. $[TiCl_2(NR)(py)_2]$) have been reported by Mountford and co-workers [9], and their formation explained as a consequence of the *trans*-labilizing ability of the imido group. Therefore, it is most likely that the crude solid obtained in the preparation of **12** holds a titanium environment with a loosely coordinated *trans*-py, which remains after washings with pentane. This pyridine ligand must be readily liberated in solution or removed upon warming under vacuum due to a marked *trans*-labilitation effect in compound **12**.

3. Conclusions

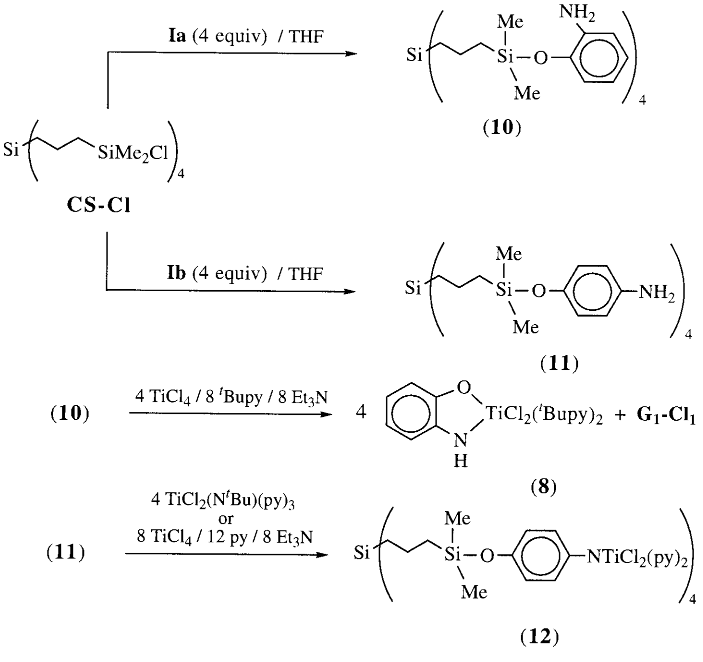
ortho- and *para*-Siloxyanilines **1** and **3**, and the N-disilylated derivative of the latter (**5**) have been studied as potential ligands for the synthesis of early transition metal–imido complexes. The *para* compounds are useful in this regard (e.g. compounds **7** and **9**), while the *ortho* one undergoes desilylation of the oxygen leading to the formation of the metallocycle **8**. Similar results are observed in attempts toward the synthesis of polynuclear arylimido–titanium complexes using aniline derivatives as anchoring ligands. Thus, the aniline-functionalized carbosilane **11** has allowed the isolation of tetranuclear titanium compound **12**, in which the metal moieties are linked to the framework by terminal imido ligands.

As stated in the introduction, the work initiated here is directed toward the support of early transition metal moieties to the periphery of carbosilane dendrimers through imido ligands. However, several issues must be worked out first such as poor moisture stability and low yield found for compound **12**. As a future work, a study comprising *para*-silylanilines, instead of siloxyanilines, is underway.

4. Experimental

4.1. General methods

All operations were performed under an argon atmosphere using Schlenk or dry-box techniques. Unless



Scheme 3.

otherwise stated, reagents were obtained from commercial sources and used as received. Solvents were previously dried and purified as described elsewhere [13]. [Ti(η^5-C_5H_5)Cl_3] [14], [$TiCl_2$(N^tBu)$(py)_3$] [7a] and carbosilane Si[$CH_2CH_2CH_2Si(Me)_2Cl$]$_4$ (CS–Cl, see Scheme 3) [12] were prepared according to literature procedures. NMR spectra were recorded on Varian Unity 500+, Varian Unity VR-300 or Varian Unity 200 NMR spectrometers. Chemical shifts (δ) are reported in ppm referenced to TMS for ^1H, ^{13}C and ^{29}Si. Elemental analyses were performed by the Microanalytical Laboratories of the Universidad de Alcalá on a Heraeus CHN-O-Rapid mycroanalyzer, and MALDI-TOF MS were performed by the Analytical Services of the Universidad Autónoma de Madrid.

4.2. Preparation of siloxyanilines $RMe_2SiOC_6H_4NH_2$ (*1–3*)

The synthesis of the siloxyanilines (**1**–**3**) and intermediates (**Ia** and **Ib**) are exemplified by the preparation of *p*-$Me_3SiOC_6H_4NH_2$ (**3**).

Li^nBu (28.7 ml, 1.6 M in hexane, 45.9 mmol) was slowly added, from a funnel equipped with a bubbler, to a solution of *p*-$HOC_6H_4NH_2$ (5.00 g, 45.8 mmol) in THF (50 ml) at room temperature (r.t.). After the addition was completed, the reaction mixture was stirred for 4 h. Then, the solvent was removed under reduced pressure and the remaining solid washed with hexane (2 × 30 ml) to afford the lithium phenoxide derivative **Ib** as a white powder. $SiMe_3Cl$ (5.8 ml, 45.9 mmol) was added to a solution of **Ib** in THF (50 ml) at r.t. and the mixture was stirred overnight. The volatile products were removed in vacuo and the residue extracted into CH_2Cl_2. Compound **3** (6.84 g, 82%) was isolated as an orange oil by evaporation of the filtrates in vacuo to dryness.

1: Anal. Calc. for $C_9H_{15}NOSi$: C, 59.62; H, 8.34; N, 7.73. Found: C, 58.81; H, 8.64; N, 7.42%. ^1H-NMR ($CDCl_3$): δ 6.8–6.6 (m, 4H, C_6H_4), 3.89 (br s, 2H, NH_2), 0.30 (s, 9H, $SiMe_3$). $^{13}C\{^1H\}$-NMR ($CDCl_3$): δ 142.8 (*ipso*-C_6H_4), 138.0 (*ipso*-C_6H_4), 121.9 (C_6H_4), 118.5 (C_6H_4, two resonances overlapping), 115.7 (C_6H_4), 0.4 ($SiMe_3$). $^{29}Si\{^1H\}$-NMR ($CDCl_3$): δ 16.7.

2: ^1H-NMR ($CDCl_3$): δ 6.71 and 6.57 (AA′ and BB′ parts of an AA′BB′ spin system, 4H, C_6H_4), 4.88 (sept, 1H, $J = 18$ Hz, SiH), 3.42 (br s, 2H, NH_2), 0.31 (d, 6H, $J = 18$ Hz, $SiMe_2$). $^{13}C\{^1H\}$-NMR ($CDCl_3$): δ 147.8 (*ipso*-C_6H_4), 140.6 (*ipso*-C_6H_4), 119.9 (C_6H_4), 116.2 (C_6H_4), −1.5 ($SiMe_2$).

3: Anal. Calc. for $C_9H_{15}NOSi$: C, 59.62; H, 8.34; N, 7.73. Found: C, 60.22; H, 8.16; N, 7.87%. ^1H-NMR ($CDCl_3$): δ 6.65 and 6.58 (AA′ and BB′ parts of an AA′BB′ spin system, 4H, C_6H_4), 3.77 (br s, 2H, NH_2), 0.20 (s, 9H, $SiMe_3$). $^{13}C\{^1H\}$-NMR ($CDCl_3$): δ 147.8 (*ipso*-C_6H_4), 139.9 (*ipso*-C_6H_4), 120.6 (C_6H_4), 116.5 (C_6H_4), 0.0 ($SiMe_3$). $^{29}Si\{^1H\}$-NMR ($CDCl_3$): δ 15.4.

4.3. Preparation of *p*-$Me_3SiOC_6H_4NHSiMe_3$ (*4*)

Li^nBu (34.4 ml, 1.6 M in hexane, 55.0 mmol) was slowly added, from a funnel equipped with a bubbler, to a solution of 4-$HOC_6H_4NH_2$ (3.00 g, 27.5 mmol). After stirring for 4 h in THF (50 ml) at r.t., $SiMe_3Cl$ (7.0 ml, 55.3 mmol) in THF (50 ml) was added at −78°C, and the reaction mixture was allowed to warm up to r.t. Then, the solvent was removed under vacuum, and the residue extracted into hexane. Compound **4** (5.00 g, 72%) was obtained as a yellow–orange oil by evaporation of the hexane solution to dryness. Anal. Calc. for $C_{12}H_{23}NOSi_2$: C, 56.86; H, 9.15; N, 5.53. Found: C, 56.21; H, 9.11; N, 5.78%. ^1H-NMR ($CDCl_3$): δ 6.63 and 6.50 (AA′ and BB′ parts of an AA′BB′ spin system, 4H, C_6H_4), 3.19 (br s, 1H, NH), 0.23 (s, 9H, $SiMe_3$), 0.21 (s, 9H, $SiMe_3$). $^{13}C\{^1H\}$-NMR ($CDCl_3$): δ 146.8 (*ipso*-C_6H_4), 141.5 (*ipso*-C_6H_4), 120.7 (C_6H_4), 116.8 (C_6H_4), 0.2 ($SiMe_3$), 0.1 ($SiMe_3$). $^{29}Si\{^1H\}$-NMR ($CDCl_3$): δ 15.0 ($OSiMe_3$), 2.2 ($NSiMe_3$).

4.4. Preparation of *p*-$Me_3SiOC_6H_4N(SiMe_3)_2$ (*5*)

Compound **4** was prepared as described above from *p*-$HOC_6H_4NH_2$ (3.00 g, 27.5 mmol) and reacted in situ with two additional equivalents of Li^nBu (34.4 ml, 1.6 M in hexane, 55.0 mmol) in THF for 4 h. Then, $SiMe_3Cl$ (7.0 ml, 55.0 mmol) was syringed to the reaction mixture at 0°C, and the yellow solution with white precipitate stirred overnight at r.t. The volatile products were removed under reduced pressure and the residue extracted into pentane. Compound **5** was obtained spectroscopically pure as a dark orange oil by evaporation of the solvent. Fractional distillation of this crude oil (60–65°C, 10–3 mmHg) afforded analytically pure **5** as a pale-yellow oil (7.92 g, 88%). Anal. Calc. for $C_{15}H_{31}NOSi_3$: C, 55.32; H, 9.59; N, 4.30. Found: C, 55.16; H, 9.45; N, 4.37%. ^1H-NMR ($CDCl_3$): δ 6.72 and 6.65 (AA′ and BB′ parts of an AA′BB′ spin system, 4H, C_6H_4), 0.23 (s, 9H, $OSiMe_3$), 0.03 (s, 18H, $NSiMe_3$). $^{13}C\{^1H\}$-NMR ($CDCl_3$): δ 151.3 (*ipso*-C_6H_4), 141.3 (*ipso*-C_6H_4), 130.8 (C_6H_4), 119.8 (C_6H_4), 2.0 ($NSiMe_3$), 0.2 ($OSiMe_3$). $^{29}Si\{^1H\}$-NMR ($CDCl_3$): δ 19.4 ($OSiMe_3$), 4.7 ($NSiMe_3$).

4.5. Preparation of [{Ti(η^5-C_5H_5)Cl}{μ-NC_6H_4(p-$OSiMe_3$)}]$_2$ (*6*)

A solution of **3** (0.50 g, 2.8 mmol) in CH_2Cl_2 (20 ml) was added dropwise to a mixture of Ti(η^5-C_5H_5)Cl_3 (0.60 g, 2.7 mmol), pyridine (py) (0.23 ml, 2.8 mmol) and Et_3N (0.77 ml, 5.5 mmol) in CH_2Cl_2 (20 ml) at r.t. The solution turned to dark violet and was stirred for 24 h. Then, the volatile products were evaporated under vacuum and the residue was extracted into toluene (2 × 20 ml). The solution was filtered to remove the

Et_3NHCl byproduct and evaporated to dryness. The resulting solid was recrystallized from toluene leading to complex **6** (0.80 g, 89%) as a microcrystalline dark violet solid. Anal. Calc. for $C_{28}H_{36}Cl_2N_2O_2Si_2Ti_2$: C, 51.31; H, 5.54; N, 4.27. Found: C, 50.89; H, 5.44; N, 3.86%. ^1H-NMR ($CDCl_3$): δ 6.68 and 6.55 (AA′ and BB′ parts of an AA′BB′ spin system, 4H, C_6H_4), 6.27 (s, 5H, C_5H_5), 0.25 (s, 9H, $SiMe_3$). $^{13}C\{^1H\}$-NMR ($CDCl_3$): δ 152.9 (*ipso*-C_6H_4), 149.3 (*ipso*-C_6H_4), 122.8 (C_6H_4), 119.8 (C_6H_4), 117.6 (C_5H_5), 0.2 ($SiMe_3$). $^{29}Si\{^1H\}$-NMR ($CDCl_3$): δ 12.2 ($SiMe_3$). MS (70 eV, EI): *m*/*z*: 654 [M^+].

4.6. Preparation of [$TiCl_2\{NC_6H_4(p\text{-}OSiMe_3)\}(py)_3$] (7)

A solution of **3** (1.37 g, 7.56 mmol) in CH_2Cl_2 (25 ml) was added to another solution of [$TiCl_2(N^tBu)(py)_3$] (3.22 g, 7.56 mmol) in CH_2Cl_2 (25 ml) at r.t. The solution turned to a darker red color and was stirred overnight. After removal of the volatile products, the resulting solid was washed with hexane (2 × 25 ml) and dried in vacuo. Complex **7** (3.12 g, 77%) was thus obtained as a brown–yellow powder. Anal. Calc. for $C_{24}H_{28}N_4OSiCl_2Ti$: C, 53.84; H, 5.27; N, 10.46. Found: C, 53.46; H, 5.32; N, 10.52%. ^1H-NMR ($CDCl_3$): δ 9.07 (d, 4H, *ortho*-H of *cis*-py), 8.75 (br s, 2H, *ortho*-H of *trans*-py), 7.76 (t, 2H, *para*-H of *cis*-py), 7.65 (br t, 1H, *para*-H of *trans*-py), 7.31 (t, 4H, meta-H of *cis*-py), 7.19 (br t, 2H, meta-H of *trans*-py), 6.80 and 6.45 (AA′ and BB′ parts of an AA′BB′ spin system, 4H, C_6H_4), 0.15 (s, 9H, $SiMe_3$). $^{13}C\{^1H\}$-NMR ($CDCl_3$): δ 151.4 (*ortho*-C of *cis*-py), 150.6 (*ortho*-C of *trans*-py), 138.6 (*para*-C of *cis*-py), 136.8 (*para*-C of -*trans*-py), 124.7 (C_6H_4), 124.2 (meta-C of *cis*-py), 123.7 (meta-C of *trans*-py), 119.2 (C_6H_4), 0.2 ($SiMe_3$). $^{29}Si\{^1H\}$-NMR ($CDCl_3$): $SiMe_3$ not observed after 72 h at 99 Hz.

4.7. Preparation of [$TiCl_2\{OC_6H_4(o\text{-}NH)\text{–}N,O\}(^tBupy)_2$] (8)

$TiCl_4$ (0.6 ml, 5.5 mmol) was added to a mixture of **1** (1.00 g, 5.5 mmol), Et_3N (1.6 ml, 11.5 mmol), and 4-*tert*-butylpyridine (^{t}Bupy) (1.7 ml, 11.5 mmol) in CH_2Cl_2 (30 ml) at r.t. With the addition, the solution warmed and changed to a dark violet color. Then, the stirring was kept 48 h, the volatile products were removed under reduced pressure and the residue was washed with diethyl ether (20 ml) and extracted into toluene. After partial solvent evaporation, complex **8** (2.05 g, 75%) precipitated at − 20°C as a shiny dark violet microcrystalline solid. Anal. Calc. for $C_{24}H_{31}N_3OCl_2Ti$: C, 58.08; H, 6.30; N, 8.47. Found: C, 57.45; H, 6.43; N, 7.97%. ^1H-NMR ($CDCl_3$): δ 11.16 (br s, 1H, NH), 9.15 (d, 4H, ^{t}Bupy), 7.50 (d, 4H, ^{t}Bupy), 6.60, 6.50, 6.17, and 5.78 (ABCD system, 4 H, C_6H_4), 1.35 (s, 18 H, ^{t}Bupy). $^{13}C\{^1H\}$-NMR ($CDCl_3$): δ 164.4 (*ipso*-^{t}Bupy), 156.4 (*ipso*-C_6H_4), 149.1 (^{t}Bupy), 147.6 (*ipso*-C_6H_4), 123.9 (C_6H_4), 123.8 (C_6H_4), 121.7 (^{t}Bupy), 111.7 (C_6H_4), 111.4 (C_6H_4) , 35.3 (^{t}Bupy-quaternary), 30.3 (^{t}Bupy), *ipso*-C_6H_4 not observed.

4.8. Preparation of [$NbCl_3\{NC_6H_4(p\text{-}OSiMe_3)\}(MeCN)_2$] (9)

A solution of $NbCl_5$ (1.012 g, 3.75 mmol) in acetonitrile (20 ml) was added to **5** (1.22 g, 3.75 mmol) in acetonitrile (20 ml) at r.t. The solution quickly changed to a red color and was stirred for 24 h. Evaporation of the solvent afforded crude material as a foamy red solid, which was washed with hexane (2 × 20 ml), and dried under vacuum to give **9** (1.51 g, 87%). Anal. Calc. for $C_{13}H_{19}$ Cl_3N_3NbOSi: C, 33.90; H, 4.16; N, 9.12 Found: C, 33.80; H, 4.04; N, 8.71%. ^1H-NMR ($CDCl_3$): δ 7.26 and 6.71 (AA′ and BB′ parts of an AA′BB′ spin system, 4H, C_6H_4), 2.15 (br s, 6H, MeCN), 0.23 (s, 9H, $SiMe_3$). $^{13}C\{^1H\}$-NMR (CD_3CN): δ 155.4 (*ipso*-C_6H_4, other C-*ipso* not observed), 127.5 (C_6H_4), 120.8 (C_6H_4), 1.6 (CH_3CN, signal for quaternary carbon of coordinated CH_3CN obscured by CD_3CN at 118.20 ppm), 0.0 ($SiMe_3$).

4.9. Preparation of [$Si\{CH_2CH_2CH_2SiMe_2OC_6H_4(o\text{-}NH_2)\}_4$] (**10**)

The same procedure described below for **11** was followed to synthesize the *ortho*-substituted **10**, starting from **Ia** (13.7 mmol) and CS–Cl (1.96 g, 3.43 mmol). Compound **10** (1.90 g, 64%) was obtained as a spectroscopically pure yellow oil, but satisfactory microanalysis failed likely due to residual LiCl. ^1H-NMR ($CDCl_3$): δ 6.8–6.5 (m, 4H, C_6H_4), 3.62 (br s, 2H, NH_2), 1.40 (m, 2H, $CH_2CH_2CH_2$), 0.81 (m, 2H, outermost $SiCH_2$), 0.56 (m, 2H, innermost $SiCH_2$), 0.23 (s, 6H, $SiMe_2$). $^{13}C\{^1H\}$-NMR ($CDCl_3$): δ 142.7 (*ipso*-C_6H_4), 138.1 (*ipso*-C_6H_4), 121.9 (C_6H_4), 118.4 (C_6H_4), 118.3 (C_6H_4), 115.6 (C_6H_4), 21.7 (CH_2), 17.8 (CH_2), 17.0 (CH_2), − 1.1 ($SiMe_2$).

4.10. Preparation of [$Si\{CH_2CH_2CH_2SiMe_2OC_6H_4(p\text{-}NH_2)\}_4$] (**11**)

Lithium phenoxide derivative **Ib** (16.8 mmol) was prepared as described above and reacted in situ with chlorocarbosilane CS–Cl (2.40 g, 4.20 mmol) in THF (50 ml) at r.t. The resulting yellow solution was stirred overnight, the solvent removed under vacuum, and the residue extracted into CH_2Cl_2 (2 × 25 ml). Compound **11** (3.28 g, 91%) was obtained as a pale yellow oil by evaporation of the solvent in vacuo to dryness. Anal. Calc. for $C_{44}H_{72}N_4O_4Si_5$: C, 61.34; H, 8.42; N, 6.50. Found: C, 60.98; H, 8.88; N, 5.90%. MS (MADI-TOF): *m*/*z* 883.3, Calc. [MNa^+]: 883.4. ^1H-NMR ($CDCl_3$): δ

6.64 and 6.55 (AA′ and BB′ parts of an AA′BB′ spin system, 4H, C_6H_4), 3.42 (br s, 2H, NH_2), 1.39 (m, 2H, $CH_2CH_2CH_2$), 0.76 (m, 2H, outermost $SiCH_2$), 0.59 (m, 2H, innermost $SiCH_2$), 0.19 (s, 6H, $SiMe_2$). $^{13}C\{^1H\}$-NMR ($CDCl_3$): δ 147.2 (*ipso*-C_6H_4), 140.3 (*ipso*-C_6H_4), 120.3 (C_6H_4), 116.0 (C_6H_4), 21.1 (CH_2), 17.5 (CH_2), 16.7 (CH_2), −1.5 ($SiMe_2$). $^{29}Si\{^1H\}$-NMR ($CDCl_3$): δ 14.9 ($SiMe_2$), 1.0 (Si-core).

4.11. Preparation of *$[Si\{CH_2CH_2CH_2SiMe_2OC_6H_4[p\text{-}NTiCl_2(py)_2]\}_4]$* ***(12)***

A solution of **11** (0.82 g, 0.95 mmol) in CH_2Cl_2 (15 ml) was added to another solution of $TiCl_2(N^tBu)(py)_3$ (1.62 g, 3.80 mmol) in CH_2Cl_2 (15 ml) at r.t. The solution turned to a darker red color and was stirred overnight. After removal of the volatile products, the resulting solid was washed with pentane (2 × 15 ml), dried in vacuo at 50°C, and extracted into toluene. After partial solvent evaporation, compound **12** (1.07 g, 51%) precipitated at −20°C as a dark brown solid. Anal. Calc. for $C_{84}H_{104}N_{12}O_4Si_5Cl_8Ti_4$: C, 51.44; H, 5.34; N, 8.57. Found: C, 50.97; H, 5.68; N, 8.93%. ^1H-NMR ($CDCl_3$): δ 9.07 (br s, 2H, *ortho*-py), 7.65 (t, 2H, *para*-py), 7.31 (m, 1H, meta-py), 6.79 and 6.44 (AA′ and BB′ parts of an AA′BB′ spin system, 4H, C_6H_4), 1.38 (m, 2H, $CH_2CH_2CH_2$), 0.70 (m, 2H, $SiCH_2$), 0.54 (m, 2H, $SiCH_2$), 0.11 (s, 6H, $SiMe_2$). $^{13}C\{^1H\}$-NMR ($CDCl_3$): δ 151.3 (*ortho*-py), 138.8 (*para*-py), 124.7 (C_6H_4), 124.2 (meta-py), 119.3 (C_6H_4), 21.4 (CH_2), 17.7 (CH_2), 17.0 (CH_2), −1.3 ($SiMe_2$), *ipso*-C_6H_4 not observed.

Acknowledgements

We gratefully acknowledge financial support from the Dirección General de Enseñanza Superior e Investigación Científica del Ministerio de Educación y Cultura (ref. PB97-0765), the University of Alcalá (ref. no. E020/98 and E040/99) and The Royal Society of Chemistry of UK (ref. SSL/vca).

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[10] $[TiCl_2\{OC_6H_4(2\text{-}NH)\text{-}N,O\}(py)_2]$ ^1H-NMR ($CDCl_3$): δ 11.22 (br s, 1 H, NH), 9.29 (d, 4H, *ortho*-H of py), 7.94 (t, 2H, *para*-H of py), 7.54 (t, 4H, meta-H of py), 6.53 (2 t overlapping, 2H, C_6H_4), 6.15 (d, 1 H, C_6H_4), 5.76 (d, 1 H, C_6H_4).

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