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Cyclopentadienyl-Silyl-Amido Niobium Complexes Prepared by a Transmetalation Reaction Using $Ti\{\eta^5-C_5H_4SiMe_2-\eta-N(CH_2)_2NRR'\}Cl_2$[†]

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Reaction of $Ti\{\eta^5-C_5H_4SiMe_2-\eta-N(CH_2)_2NRR'\}Cl_2$ with $Nb(\eta^5-C_5H_4SiMe_2Cl)Cl_4$ affords the tethered heterodinuclear complexes $TiCl_2\{\eta^5-C_5H_4SiMe_2-\eta-N(CH_2)_2-\kappa-NRR'\}Nb(\eta^5-C_5H_4SiMe_2Cl)Cl_4$, which are thermally unstable in solution and evolve to render an equimolar mixture of $Ti(\eta^5-C_5H_4SiMe_2Cl)Cl_3$ and the corresponding cyclopentadienyl-amido niobium compounds, $Nb\{\eta^5-C_5H_4SiMe_2-\eta-N(CH_2)_2NRR'\}Cl_3$. These compounds are straightforwardly obtained from the reaction of $Nb(\eta^5-C_5H_4SiMe_2Cl)Cl_4$ with 1 equiv of the appropriate diamine, $NH_2(CH_2)_n-NRR'$, in the presence of 2 equiv of NEt_3, in high yield. In this reaction, the presence of the functional pendant chain plays a central role not only in determining the course of the reaction but also in stabilizing the final product, from both an electronic and a steric point of view. The molecular structure of $Nb\{\eta^5-C_5H_4SiMe_2-\eta-N(CH_2)_3-\eta-NH_2\}Cl_3$ has been determined by X-ray diffraction methods.

The preparation of bimetallic compounds has received a great deal of interest,[1] as they allow the option of cooperative interactions between the two metal centers, which may result in unique reactivity when compared with their mononuclear analogues.[2,3] Group 4 bimetallic complexes have featured interesting structures[4] and small-molecule reactivity.[5]

While cyclopentadienyl-silyl-amido complexes of group 4 metals have been extensively studied as alternatives to the classical dicyclopentadienyl MCp_2X_2 catalyst systems,[6−8] stable and well-characterized constrained-geometry compounds of the group 5 metals remain very elusive.[9,10] This effect probably arises from a lack of suitable synthetic approachs[11] to produce the labile cyclopentadienyl-silyl-amido-Nb system.[9]

We have recently reported the synthesis of the tethered dinuclear cyclopentadienyl-silyl-amido titanium complex $Ti\{\eta^5-C_5H_4SiMe_2-\eta-N(CH_2)-\}Cl_2$[12] by reaction of $Ti\{\eta^5-C_5H_4SiMe_2-\eta-N(CH_2)_2NH_2\}Cl_2$ (**1a**) with $Ti\{\eta^5-C_5H_4SiMe_2Cl\}Cl_3$.[13] The ability of complex **1a** to react as an organic amine made it an attractive candidate for the production of heterobimetallic complexes.[14] Consequently, we decided to explore the use

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[†] Dedicated to Professor Victor Riera on the occasion of his 70th birthday

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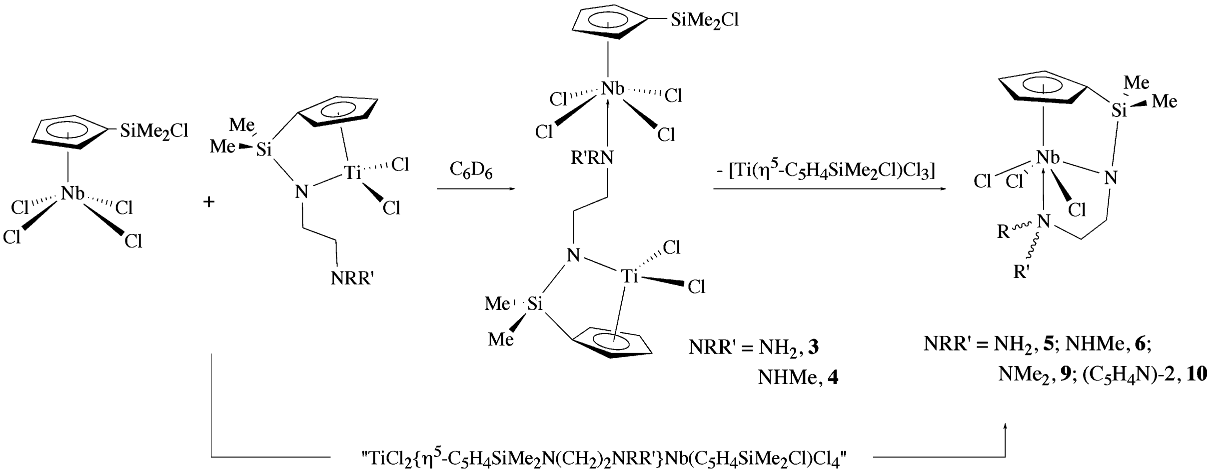
Scheme 1



of complexes **1** as precursors for tethered heterobimetallic cyclopentadienyl-silyl-amido titanium-niobium complexes.

Herein we describe the synthesis and characterization of new heterobimetallic titanium-niobium complexes, $TiCl_2\{\eta^5\text{-}C_5H_4SiMe_2\text{-}\eta\text{-}N(CH_2)_2\text{-}\kappa\text{-}NRR'\}Nb(\eta^5\text{-}C_5H_4SiMe_2Cl)Cl_4$ (NRR′ = NH_2; NHMe), and their thermal decomposition products, which are the new cyclopentadienyl-silyl-amido niobium compounds with a pendant amino group, $Nb\{\eta^5\text{-}C_5H_4SiMe_2\text{-}\eta\text{-}N(CH_2)_2NRR'\}Cl_3$ (NRR′ = NH_2; NHMe). Moreover, we report a suitable and facile synthetic method to generate such a family of stable niobium constrained-geometry derivatives in high yield. The structure of $Nb\{\eta^5\text{-}C_5H_4SiMe_2\text{-}\eta\text{-}N(CH_2)_3\text{-}\eta\text{-}NH_2\}Cl_3$ is reported.

Reactions of $Ti\{\eta^5\text{-}C_5H_4SiMe_2\text{-}\eta\text{-}N(CH_2)_2NHR'\}Cl_2$ (R′ = H, **1a**; Me, **1b**) with the chlorosilyl-substituted cyclopentadienyl niobium compound $Nb(\eta^5\text{-}C_5H_4SiMe_2Cl)Cl_4$[15] (**2**) in deuterated solvents were conducted in Teflon-valved NMR tubes and investigated by NMR spectroscopy. Complexes **1** react with an equimolar amount of $Nb(\eta^5\text{-}C_5H_4SiMe_2Cl)Cl_4$ at room temperature to afford the heterobimetallic derivatives $TiCl_2\{\eta^5\text{-}C_5H_4SiMe_2\text{-}\eta\text{-}N(CH_2)_2\text{-}\kappa\text{-}NHR'\}Nb(\eta^5\text{-}C_5H_4SiMe_2Cl)Cl_4$ (R′ = H, **3**; Me, **4**), by coordination of the amino nitrogen to the niobium atom in the position *trans* to the cyclopentadienyl group (Scheme 1).[16] These complexes are formed almost quantitatively, as judged by NMR spectroscopy, although the lack of thermal stability in solution prevents their isolation; consequently they have been characterized only spectroscopically.

The NMR features of **3** and **4** are consistent with the proposed heterodinuclear structure. The ^1H NMR spectra show two sets of signals for $C_5H_4SiMe_2Cl$ and $C_5H_4SiMe_2N$ moieties along with AA′BB′KK′ and AA′BB′K spin systems for the methylene and amino protons, respectively, for **3** and **4**. The pronounced downfield shift of the amino protons, with respect to those found in complexes **1a** and **1b** (δ 4.30 and 3.94),[12,17] indicates that the NHR′ group is fairly strongly coordinated to the niobium atom. The most striking feature of the $^{13}C\{^1H\}$ NMR spectra is the significant upfield shift observed for the cyclopentadienyl *ipso*-carbon ($\delta \approx 109$) that confirms the cyclopentadienyl-amido disposition around the titanium atom.[18]

When a solution of **3** or **4** in $CDCl_3$ or C_6D_6 is left at room temperature, these compounds evolve cleanly (**4** faster than **3**) to give an equimolar mixture of $Ti(\eta^5\text{-}C_5H_4SiMe_2Cl)Cl_3$ and new cyclopentadienyl-amido niobium compounds, $Nb\{\eta^5\text{-}C_5H_4SiMe_2\text{-}\eta\text{-}N(CH_2)_2NHR'\}Cl_3$ (R′ = H, **5**; Me, **6**) (Scheme 1). To the best of our knowledge, these complexes are the first example of stable constrained-geometry niobium compounds with a pendant amino functionality.

Formation of **5** and **6**, from the heterobimetallic compounds **3** and **4**, globally entails the transfer of the $N(CH_2)_2NHR'$ moiety from titanium to niobium. Such transformations may be proposed to occur through direct exchange of ligands or via the aminolysis of Nb−Cl and Si−Cl bonds with subsequent cleavage of the Si−N and Ti−N bonds by the HCl evolved in the first step of this process.[12,20]

To distinguish between these two possibilities, the reaction of **2** with cyclopentadienyl-amido titanium complexes containing a nonprotic pendant amino functionality was explored. Thus, reaction of $Nb(\eta^5\text{-}C_5H_4SiMe_2Cl)Cl_4$ with 1 equiv of $Ti\{\eta^5\text{-}C_5H_4SiMe_2\text{-}\eta\text{-}N(CH_2)_2NRR'\}Cl_2$ [NRR′ = NMe_2, **7**; (C_5H_4N)-2, **8**][21] at room temperature immediately gives the corresponding cyclopentadienyl-amido niobium compounds, $Nb\{\eta^5\text{-}C_5H_4SiMe_2\text{-}\eta\text{-}N(CH_2)_2NRR'\}Cl_3$ [NRR′ = NMe_2, **9**; (C_5H_4N)-2, **10**] (Scheme 1). Although the expected intermediate

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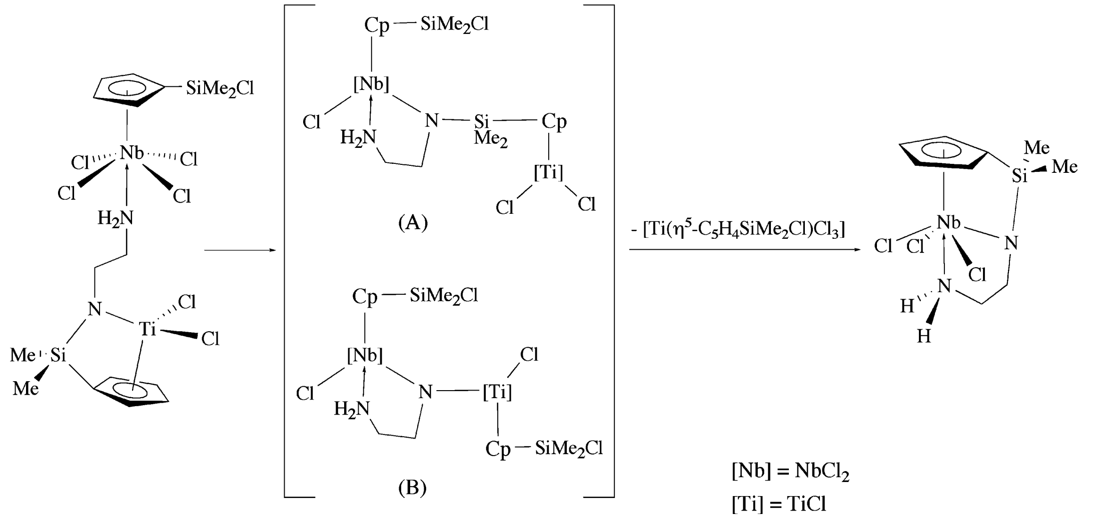
[21] Both compounds were synthesized in excellent yield (>85%) following aminolysis methodology, reaction of $[Ti(\eta^5\text{-}C_5H_4SiMe_2Cl)Cl_3]$ with the appropriate diamine in the presence of 2 equiv of NEt_3. Nevertheless, complex **7** was previously prepared by Okuda in a different synthetic route. Okuda, J.; du Plooy, K. E.; S.; Massa, W.; Kang, H. C.; Rose, U. *Chem. Ber.* **1996**, *129*, 275.

Scheme 2



adduct is not now observed, this result suggests that the reaction proceeds through a transmetalation route.

Further evidence for the direct transfer pathway is the regiospecific formation of **6** from **4** since an aminolysis process in which the MeN−H is involved should yield the formation of niobium amido derivatives featuring a Nb−NMe bond.

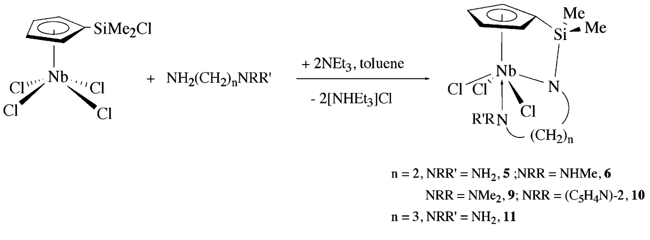
To gain insight into this process, the transformation of **3** into **5** was monitored by ^{1}H NMR spectroscopy over a period of time. Spectroscopic analysis reveals, along with the signals corresponding to the starting material and the final products, a new set of resonances assignable to a reaction intermediate.[22] Although the nature of this intermediate cannot be unambiguously established from the spectroscopic study, the NMR data do provide relevant information. Thus, a broad resonance observed at δ 5.20 arising from the two protons of the amino group indicates that this pendant group remains unperturbed and coordinated to niobium. The formation of this intermediate species indicates that the reaction proceeds in a sequential manner. Taking into account the length of the side chain, the process presumably implies, in the first step, exchange of a Nb−Cl bond. Preferential intramolecular transmetalation should give an amido intermediate[23] (A, Scheme 2), with subsequent exchange between [Ti]Si−N and [Nb]Si−Cl bonds to afford the constrained-geometry niobium complex. Alternatively, a preferential dehalosilylation reaction should give rise to a bridged imido compound[24] (B, Scheme 2), which could then be converted into the final complex through chlorination of the Ti−N bond by reaction with Si−Cl bond.[25]

Although the cyclopentadienyl-amido niobium compounds are formed almost quantitatively, the difficulty of isolating them from the reaction mixture as analytically pure samples results in modest yields. In view of such a result and taking into account the interest in this type of niobium complex, we sought a more convenient alternative synthetic route. In a procedure analogous to that used to synthesize the titanium congeners,[12] aminolysis afforded the cyclopentadienyl-amido niobium compounds, Nb{η^5-$C_5H_4SiMe_2$-η-N$(CH_2)_n$-η-NRR′}Cl_3 ($n = 2$, NRR′ = NH_2, **5**; NHMe, **6**; NMe_2, **9**; (C_5H_4N)-2, **10**; $n = 3$, NRR′ = NH_2, **11**) by reaction of Nb(η^5-$C_5H_4SiMe_2Cl$)Cl_4 with 1 equiv of the corresponding organic diamine, $NH_2(CH_2)_n$NRR′ ($n = 2$, NRR′ = NH_2; NHMe; NMe_2; (C_5H_4N)-2; $n = 3$, NRR′ = NH_2), in the presence of 2 equiv of NEt_3 (Scheme 3).

The formation of these constrained-geometry complexes contrasts with the result achieved when a parallel reaction is performed using a primary amine, in which the most thermodynamically stable imido derivative Nb(η^5-$C_5H_4SiMe_2Cl$)(NR)Cl_2 is formed,[10] signifying the importance of the pendant donor chain in reactions of this type.[19] Furthermore, in contrast to the characteristic lability found in the few examples of constrained-geometry niobium compounds reported,[9] a remarkable characteristic of these complexes is their notable photo and thermal stability. We therefore propose that the presence of the amino group plays a critical role not only in determining the course of the reaction but also in stabilizing these complexes, from both an electronic and a steric point of view.

The NMR features of these complexes support the proposed structure. In contrast with the ^{1}H NMR spectra of **5**, **9**, **10**, and **11**, which are consistent with the presence of a mirror plane, the spectrum of **6**, [Nb{η^5-$C_5H_4SiMe_2$-η-N$(CH_2)_2$-η-NHMe}Cl_3], is in agreement with a chiral species, as evidenced by the two multiplets for each pair of diastereotopic methylene and

Scheme 3



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[22] ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ 0.71, 0.88 (s, 2 × 6H, $SiMe_2$), 3.36, 4.30 (m, 2 × 2H, CH_2), 5.20 (brs, 2H, NH_2), 6.67, 6.82, 7.26, 7.40 (brm, 4 × 2H, C_5H_4).

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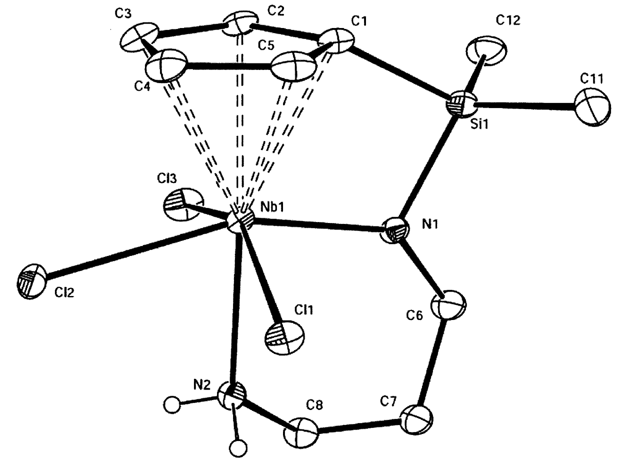

Figure 1. ORTEP representation of the molecular structure of **11** together with the atomic numbering system. Thermal ellipsoids are drawn at the 30% probability level. Selected bond lengths (Å) and angles (deg): Nb(1)−N(1) 2.005(2), Nb(1)−N(2) 2.282(2), Nb(1)−Cl(1) 2.5005(7), Nb(1)−Cl(2) 2.5493(8), Nb(1)−Cl(3) 2.4798(8), Nb(1)−Cg 2.1468, Si(1)−N(1) 1.766(2), Cg(1)−Nb(1)−N(1) 100.98.

ring protons, and methyl groups on silicon. This spectroscopic behavior undoubtedly indicates that the amino functionality is fairly rigidly coordinated to the niobium atom since such bonding disposition prevents racemization at the amino nitrogen. Furthermore, the pronounced downfield shift of both the amino protons (δ 4.68), for **5** and **11**, and the *ortho* proton of the pyridyl group (δ 10.09), in the case of **10**, is also in agreement with such a bonding interaction. On the other hand, the $^{13}C\{H\}$ and ^{29}Si NMR spectra confirm the constrained geometry for these complexes, as evidenced by the upfield shift observed for both the cyclopentadienyl *ipso*-carbon and the silicon with respect to the rest of the ring carbon resonances and the silicon resonances found for chlorosilyl-substituted cyclopentadienyl niobium compounds,[15] respectively.

The molecular structure of compound **11** was verified by X-ray diffraction studies on a single crystal (Figure 1). The coordination geometry around the niobium center can be described as pseudo-octahedral, where the equatorial plane is defined by the amido nitrogen and the three chlorine atoms, while the apical positions are occupied by the cyclopentadienyl ring and the amino nitrogen. Although analogous constrained structures are known for titanium,[12] no examples have been found in the literature for niobium.

The Cg(1)−Nb(1)−N(1) (Cg = centroid of the Cp ring) bond angle of 100.98° is similar to that found in the constrained-geometry compound [Nb(η^5-$C_5H_4SiMe_2$-η^1-NAr)(NAr)Cl], being more acute than those reported for unbridged amido ligands (106.60−116.67° range).[26] As in group 4 metal constrained-geometry cyclopentadienylsilyl-η-amido complexes, the Nb(1), Si(1), N(1), and C(6) atoms are coplanar,[12] confirming a trigonal planar environment for the amido nitrogen; however the Nb−N(1) distance (2.005(2) Å) is longer than those reported for nonbridged amido niobium derivatives, indicating lower π-bonding contribution.[26] In the structure, the coordination of the NH_2 group is clearly shown, the Nb−N(2) distance being 2.282(2) Å, within the single-bond range (1.95−2.35 Å).

In conclusion, a suitable and straightforward synthetic route to prepare and isolate constrained-geometry derivatives of niobium in high yield is described. The presence of the pendant amino group is electronically and sterically necessary for the formation and stabilization of such complexes. Furthermore, the synthesis of new types of tethered heterobimetallic titanium-niobium complexes, $TiCl_2\{\eta^5$-$C_5H_4SiMe_2$-η-$N(CH_2)_2$-κ-$NRR'\}Nb(\eta^5$-$C_5H_4SiMe_2Cl)Cl_4$ (NRR′ = NH_2; NHMe), and their thermal decomposition products is reported.

Experimental Section

Synthesis of $TiCl_2\{\eta^5$-$C_5H_4SiMe_2$-η-$N(CH_2)_2$-κ-$NH_2\}Nb(\eta^5$-$C_5H_4SiMe_2Cl)Cl_4$ (3). A C_6D_6 solution (0.3 mL) of $Ti\{\eta^5$-$C_5H_4SiMe_2N(CH_2)_2$-η-$NH_2\}Cl_2$ (0.03 g, 0.1 mmol) was added to a C_6D_6 solution (0.3 mL) of $Nb(\eta^5$-$C_5H_4SiMe_2Cl)Cl_3$ (0.04 g, 0.1 mmol) at room temperature. The color of the reaction mixture instantaneously darkened. The reaction mixture was analyzed by NMR spectroscopy, and product formation was essentially quantitative. ^1H NMR (300 MHz, C_6D_6): δ 0.16 (s, 6H, $SiMe_2N$), 0.75 (s, 6H, $SiMe_2Cl$) 3.48, 4.05 (t, J = 11,68 Hz, 2H, m, 2H, $NCH_2CH_2NH_2$), 5.16 (brs, 2H, NH_2), 6.09, 6.34, 6.65 (m, 2 × 2H, m, 4H, C_5H_4). $^{13}C\{^1H\}$ NMR (75 MHz, C_6D_6): δ − 2.6 ($SiMe_2N$), 2.7 ($SiMe_2Cl$), 47.7 (CH_2NH_2), 57.9 ($TiNCH_2$), 109.3 (C_5H_4N−C*ipso*), 124.3, 126.5, 132.0, 132.4, 135.1 (C_5H_4).

Synthesis of $TiCl_2\{\eta^5$-$C_5H_4SiMe_2$-η-$N(CH_2)_2$-κ-$NHMe\}Nb(\eta^5$-$C_5H_4SiMe_2Cl)Cl_4$ (4). A method similar to that used for **3** was adopted by using $Ti\{\eta^5$-$C_5H_4SiMe_2N(CH_2)_2$-η-$NHMe\}Cl_2$, **1b** (0.02 g, 0.064 mmol), instead of **1a**. The reaction mixture was analyzed by NMR spectroscopy, and product formation was essentially quantitative. ^1H NMR (300 MHz, C_6D_6): δ 0.79 (s, 6H, $SiMe_2N$), 0.92 (s, 6H, $SiMe_2Cl$), 2.96 (brs, 3H, NMe), 3.15, 3.26 (brm, 2 × 2H, NCH_2CH_2NH), 5.27 (brm, 1H, NH), 5.89, 6.20, 6.39, 6.97 (m, 4 × 2H, C_5H_4).

Synthesis of $Nb\{\eta^5$-$C_5H_4SiMe_2$-η-$N(CH_2)_2$-η-$NH_2\}Cl_3$ (5). Method a: A toluene solution (20 mL) of $Ti\{\eta^5$-$C_5H_4SiMe_2$-η-$N(CH_2)_2NH_2\}Cl_2$ (0.56 g, 1.87 mmol) was added to a toluene solution (20 mL) of $Nb(\eta^5$-$C_5H_4SiMe_2Cl)Cl_3$ (0.73 g, 1.87 mmol) at room temperature. The reaction mixture was stirred for 48 h, when the toluene was removed under vacuum and the resulting solid washed with *n*-hexane (5 × 10 mL). The yellow residue was characterized as **5** (0.1 g, 0.27 mmol, 15%). Anal. Calcd for $C_9H_{16}Cl_3N_2NbSi$: C, 28.47; H, 4.25; N, 7.37. Found: C, 28.83; H, 4.35; N, 7.16. ^1H NMR (300 MHz, $CDCl_3$): δ 0.52 (s, 6H, $SiMe_2$), 3.68 (m, 2H, CH_2NH_2), 4.04 (s, 2H, $NbNCH_2$), 5.12 (brs, 2H, NH_2), 6.96, 7.02 (m, 2 × 2H, C_5H_4). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ −4.4 ($SiMe_2$), 45.7 (CH_2NH_2), 60.0 ($NbNCH_2$), 102.8 (C_5H_4-*ipso*), 125.3, 128.4 (C_5H_4). ^{29}Si NMR (59.5 MHz, $CDCl_3$): −8.5 (*Si*Me_2).

Method b: A toluene solution (10 mL) of $NH_2(CH_2)_2NH_2$ (0.08 mL, 1.19 mmol) and NEt_3 (0.32 mL, 2.3 mmol) was added to a dark red solution of $Nb(\eta^5$-$C_5H_4SiMe_2Cl)Cl_3$ (0.45 g, 1.14 mmol) in toluene (20 mL). The color of the reaction mixture immediately changed to green. The reaction mixture was stirred for 3 h. The solid formed was collected by filtration and toluene removed under vacuum. The residue was extracted into toluene (2 × 10 mL), and the resulting solution was concentrated (10 mL) and cooled to − 20 °C to afford **5** in 86% yield (0.37 g, 0.98 mmol).

Synthesis of $Nb\{\eta^5$-$C_5H_4SiMe_2$-η-$N(CH_2)_2$-η-$NHMe\}Cl_3$ (6). Method a: A method similar to method a used for **5** was adopted by using 0.50 g (1.60 mmol) of $Ti\{\eta^5$-$C_5H_4SiMe_2$-η-$N(CH_2)_2NHMe\}Cl_2$ in place of **1a**. Yield: 10% (0.06 g, 0.16 mmol). Anal. Calcd for $C_{10}H_{18}Cl_3N_2NbSi$: C, 30.51; H, 4.61; N, 7.11. Found: C, 31.1; H, 4.9; N, 7.01. ^1H NMR (300 MHz, C_6D_6): δ 0.00, 0.40 (s, 2 × 3H, $SiMe_2$), 2.49, 2.90, 3.12, 3.20 (m, 4 × 1H, CH_2), 2.93 (d, ^3J = 5.97 Hz, 3H, NMe), 5.28 (brm,

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[26] (a) Humphries, M. J.; Green, M. L. H.; Douthwaite, R. E.; Rees, L. H. *J. Chem. Soc., Dalton. Trans.* **2000**, 4555.

1H, NH), 6.63, 6.67, 6.81 (m, 1H, 2H, 1H, C_5H_4). $^{13}C\{^1H\}$ NMR (75 MHz, C_6D_6): δ −5.4, −4.3 ($SiMe_2$), 40.7 (CH_2NH_2), 55.1 (NMe), 55.3 ($NbNCH_2$), 102.9 (C_5H_4-*ipso*), 124.0, 127.1, 127.8, 128.4 (C_5H_4). ^{29}Si NMR (59.6 MHz, $CDCl_3$): −8.4 (*Si*Me_2).

Method b: A method similar to method b used for **5** was adopted by using 0.15 mL (1.70 mmol) of *N*-methylethylenediamine in place of ethylenediamine. Yield: 83% (0.55 g, 1.40 mmol).

Synthesis of Nb{η^5-$C_5H_4SiMe_2$-η-N$(CH_2)_2$-η-NMe_2}Cl_3 (9). Method a: A method similar to method a used for **5** was adopted by using 0.70 g (2.13 mmol) of Ti{η^5-$C_5H_4SiMe_2N$-$(CH_2)_2$-η-NMe_2}Cl_2 in place of **1a**. Yield: 8% (0.07 g, 0.17 mmol). Anal. Calcd for $C_{11}H_{20}Cl_3N_2NbSi$: C, 32.41; H, 4.95; N, 6.87. Found: C, 32.36; H, 4.99; N, 7.0. ^1H NMR (300 MHz, $CDCl_3$): δ 0.53 (s, 6H, $SiMe_2$), 3.07 (s, 6H, NMe_2), 3.30, 3.93 (t, ^3J = 5.7 Hz, 2 × 2H, C*H_2*), 6.92, 7.03 (m, 2 × 2H, C_5H_4). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ −4.5 ($SiMe_2$), 52.9 (NMe_2), 55.3, 62.8 (CH_2), 103.4 (C_5H_4-*ipso*), 125.1, 130.9 (C_5H_4). ^{29}Si NMR (59.6 MHz, $CDCl_3$): −9.3 (*Si*Me_2).

Method b: A method similar to method b used for **5** was adopted by using 0.37 mL (3.37 mmol) of *N,N′*-dimethylethylenediamine in place of ethylenediamine. Yield: 77% (1.06 g, 2.60 mmol).

Synthesis of Nb{η^5-$C_5H_4SiMe_2$-η-N$(CH_2)_2$-η-(C_5H_4N)-2}Cl_3 (10). Method a: A method similar to method a used for **5** was adopted by using 0.56 g (1.55 mmol) of Ti{η^5-$C_5H_4SiMe_2$-η-N$(CH_2)_2(C_5H_4N)$-2}Cl_2 in place of **1a**. Yield: 23% (0.16 g, 0.35 mmol). Anal. Calcd for $C_{14}H_{18}Cl_3N_2NbSi$: C, 38.07; H, 4.11; N, 6.34. Found: C, 38.67; H, 4.60; N, 6.68. ^1H NMR (300 MHz, $CDCl_3$): δ 0.58 (s, 6H, $SiMe_2$), 3.60, 3.82 (m, 2 × 2H, C*H_2*), 7.13, 7.14 (m, 2 × 2H, C_5H_4), 7.22 (m, 1H, 6-C_5H_4N), 7.27 (m, 1H, 5-C_5H_4N), 7.72 (m, 1H, 4-C_5H_4N), 10.09 (m, 1H, 3-C_5H_4N). $^{13}C\{^1H\}$ NMR (75 MHz, C_6D_6): δ −4.2 ($SiMe_2$), 36.5, 53.1 (CH_2), 109.7 (C_5H_4-*ipso*), 127.7, 129.0 (C_5H_4), 121.8, 125.2, 139.1, 155.8, 160.7 (C_5H_4N). ^{29}Si NMR (59.6 MHz, $CDCl_3$): −10.3 (*Si*Me_2).

Method b: A method similar to method b used for **5** was adopted by using 0.20 mL (1.59 mmol) of (2-pyridyl)ethylamine in place of ethylenediamine. Yield: 15% (0.10 g, 0.23 mmol).

Synthesis of Nb{η^5-$C_5H_4SiMe_2$-η-N$(CH_2)_3$-η-NH_2}Cl_3 (11). A method similar to method b used for **5** was adopted by using 0.11 mL (1.31 mmol) of propylenediamine in place of ethylenediamine. Yield: 78% (0.40 g, 1.02 mmol). Anal. Calcd for $C_{15}H_{20}Cl_3N_2NbSi$: C, 30.51; H, 4.61; N, 7.12. Found: C, 30.13; H, 4.77; N, 7.34. ^1H NMR (300 MHz, C_6D_6): δ −0.03 (s, 6H, $SiMe_2$), 1.34, 2.51, 2.97 (m, 3 × 2H, C*H_2*), 4.58 (brs, 2H, NH_2), 6.69, 6.84 (m, 2 × 2H, C_5H_4). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ −5.3 ($SiMe_2$), 26.9, 40.1, 55.1 (CH_2), 107.3 (C_5H_4-*ipso*), 126.2, 127.9 (C_5H_4).

X-ray Crystallography. Crystal data for **11**: ($C_{10}H_{18}Cl_3N_2$-NbSi), M_r = 393.61, monoclinic, space group $P2_1/n$, a = 14.3848(15) Å, b = 7.5381(7) Å, c = 15.2675(13) Å, β = 110.582(10)°, V = 1549.8(3) Å^3, Z = 4, ρ_{calcd} = 1.687 g cm^{-3}, $F(000)$ = 792, Mo Kα radiation (λ = 0.71073 Å), μ = 1.352 mm^{-1}. Yellow crystal (0.21 × 0.14 × 0.11 mm). Data collection was performed at 200(2) K on a Nonius KappaCCD single-crystal diffractometer. Crystal structure was solved by direct methods and refined using full-matrix least squares on F^2.[27] All non-hydrogen atoms were anisotropically refined. Hydrogen atoms were geometrically placed and left riding on their parent atoms, except for H(21) and H(22), whose positions and thermal parameters were refined independently. The final cycle of full matrix least-squares refinement based on 3547 reflections and 162 parameters converged to a final values of $R_1(F^2 > 2\sigma(F^2)) = 0.0326$, $wR_2(F^2 > 2\sigma(F^2)) = 0.0633$, $R_1(F^2)$ = 0.0568, $wR_2(F^2)$ = 0.0687. Final difference Fourier maps showed no peaks higher than 0. 453 nor deeper than −0.651 e Å^{-3}.

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Supporting Information Available: Crystallographic data for **11** in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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[27] Sheldrick, G. M. *SHELXL-97*; University of Göttingen: Göttingen, 1997.