Silylimido Complexes of Niobium and Tantalum at the Limit of π-Bond Saturation

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Dedicated to Professor Ernst-G. Jäger on the occasion of his 65th birthday

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Convenient strategies towards the synthesis of silylimido niobium and -tantalum complexes of the metallocene and half-sandwich type are reported. Bent metallocenes [(η^5-C_5H_5)$_2$M($NSiMe_3$)Cl] (M = Nb: **1a**; Ta: **1b**) and [(η^5-C_5H_5)$_2$M($NSiMe_3$)(η^1-C_5H_5)] (M = Nb: **2a**; Ta: **2b**) are synthesized by reaction of [M($NSiMe_3$)Cl_3(py)$_2$] with 2 or 3 equiv. NaCp, respectively. Half-sandwich type silylimido complexes [(η^5-C_5Me_5)M($NSiMe_3$)Cl_2] (M = Nb: **3a**; Ta: **3b**) cannot selectively be obtained from the (pyridine)(silylimido) precursor complexes. However, their synthesis is accomplished by reaction of [(η^5-C_5Me_5)MCl_4] with LiN($SiMe_3$)$_2$. On the other hand pyridine silylimido complexes are perfect starting materials for the synthesis of the related hydridotris(pyrazolyl)borato complexes [Tp*M($NSiMe_3$)Cl_2] [M = Nb: **4a**; Ta: **4b**; Tp* = κ^3-HB(3,5-Me_2pz)$_3$]. A comparative study of the σ,π-donor capability of isoelectronically related *tert*-butyl- and trimethylsilylimido ligands in complexes [(η^5-C_5H_5)$_2$Ta(NR)(η^1-C_5H_5)] (R = $SiMe_3$: **2b**; *t*Bu: **2c**) is presented. With respect to solid-state structural investigations and solution variable-temperature NMR-spectroscopic studies on the dynamic exchange process of η^5- and η^1-bonded cyclopentadienyl rings in **2b**,**c**, *tert*-butlyimido ligands are better donors than silylimido ligands, and both are better donors towards a d^0 metal center than an η^5-C_5H_5 ligand.

Introduction

The last two decades have witnessed an increasing interest in the organometallic chemistry of transition metal complexes containing imido ligands $[NR]^{2-}$.[1] Half-sandwich imido complexes of group-5 metals containing the fragment [(η^5-$C_5R'_5$)M(NR)] have been investigated in their relationship with bent metallocenes of group-4 metals.[2] The concept of the cyclopentadienyl imido ligand analogy[3] was introduced to explain the surprising similarities in structural features and reactivity of both complex classes and led to new catalytic systems.[4] Variation of the ancillary substituent R at the imido function $[NR]^{2-}$ offers a tool for the fine tuning of the steric demand and electronic properties of these ligands. In previous studies we and others have established the chemistry of organoimido complexes (R = alkyl, aryl) of type [(η^5-$C_5R'_5$)M(NR)X_2],[2,5] [(η^5-$C_5R'_5$)$_2$M(NR)X][5a,5k,6] and [Tp*M(NR)Cl_2][7,22] (M = Nb, Ta, X = anionic ligand). Less reports are available, by far, for corresponding silylimido complexes of niobium and tantalum:[8] the key compounds are [M($NSiMe_3$)Cl_3(py)$_2$] reported by Doherty et al.[9], [Nb{(η^5-C_5H_4)CMe_2(η^5-C_5H_4)}($NSiMe_3$)Cl], a representative of a silylimido *ansa*-metallocene complex reported by Green and co-workers[10] and [Cp*Ta(NSi*t*Bu_3)Cl_2], which was synthesized and tested by Stryker et al.[4b] as an interesting catalyst for olefin polymerization reactions. Our interest in developing silylimido compounds stems from their potential to act as precursors for heterobimetallic complexes containing bridging nitrido ligands.[11] We believe that electronic saturation of all empty d orbitals of a d^0-metal center by interaction with a set of strong σ- and, especially, π-donor ligands might be a good strategy in order to direct the attack of a nucleophile, for example fluoride or chloride, towards the silicon atom of the silylimido ligand instead of the d^0-metal center. We anticipate that π-bond saturation of a Lewis-acidic metal center might increase the selectivity in condensation reactions with other reactive metal compounds. Therefore we set out to systematically synthesize a series of new silylimido complexes of half-sandwich, bent metallocene and tris(pyrazolyl)borate types. Furthermore we intended to receive experimental data from crystal structure analyses and variable-temperature NMR-spectroscopic studies in order to compare the donor capability of *tert*-butyl- and silylimido ligands in isoelectronically related compounds.

Results and Discussion

Preparative Studies

The starting compounds [M($NSiMe_3$)Cl_3(py)$_2$] (M = Nb, Ta) are readily prepared from the metal pentachlorides and (Me_3Si)$_2$NH.[9] All our attempts to synthesize half-sandwich complexes by treatment of these pyridine complex precursors with an equimolar amount of NaCp or LiCp* in THF or toluene failed. This is in contrast to the results of Otero et al. who recently described that [(η^5-C_5H_5)Nb(N*t*Bu)Cl_2] can be obtained in 80% yield by reaction of [Nb(N*t*Bu)Cl_3(py)$_2$] with NaCp in THF[12]. In agree-

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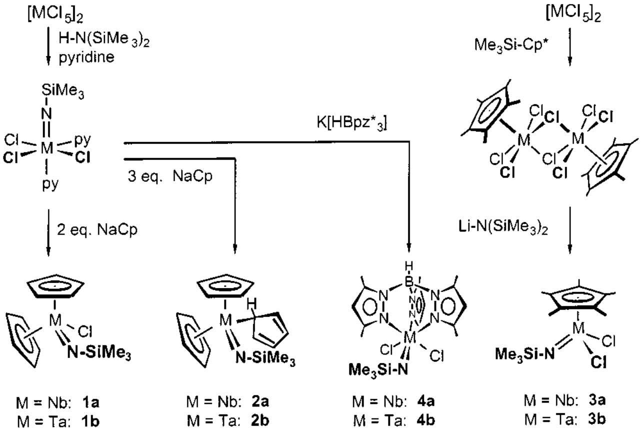
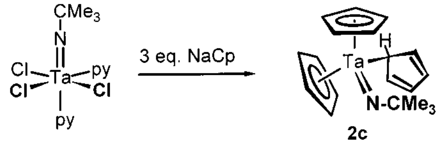
ment with our report on this class of cyclopentadienyl imido complexes[5a] the selectivity of the reaction is increased, when 2 equiv. of NaCp are treated with the pyridine silylimido precursors. We were able to synthesize the corresponding bent metallocenes [(η^5-C_5H_5)$_2$M(NSiMe$_3$)Cl] (M = Nb: **1a**; Ta: **1b**), which were isolated as yellow powders in good yields (Scheme 1). The cyclopentadienyl protons in silylimido complex **1a** (δ = 6.14) are less shielded compared to the corresponding (*tert*-butylimido)niobium complex (δ = 5.74)[5a]. A similar trend is found for the silylimido tantalum complex **1b** and its *tert*-butylimido derivative. This is the first experimental evidence, that the donor strength of NCMe$_3$ is superior to that of NSiMe$_3$.



Scheme 1

In previous work Green and co-workers examined the reaction of [(η^5-C_5H_5)Nb(N*t*Bu)Cl$_2$] with NaCp in THF at room temperature leading to the blue d^0-metal compound [(η^5-C_5H_5)$_2$Nb(N*t*Bu)(η^1-C_5H_5)]. The latter was structurally characterized and the dynamic exchange between σ- and π-bonded cyclopentadienyl rings was examined.[13] We prepared the corresponding silylimido niobium and -tantalum complexes [(η^5-C_5H_5)$_2$M(NSiMe$_3$)(η^1-C_5H_5)] (M = Nb: **2a**; Ta: **2b**) by reaction of [M(NSiMe$_3$)Cl$_3$(py)$_2$] (M = Nb, Ta) with 10 equiv. of NaCp. The large excess is needed for complete conversion to the highly π-bond-saturated products. Their variable-temperature NMR-spectroscopic study is described below.

In order to have two isoelectronically and structurally related complexes for a comparative study of the σ,π-donor capability of NCMe$_3$ vs. NSiMe$_3$ ligands, the alkylimido complex [(η^5-C_5H_5)$_2$Ta(N*t*Bu)(η^1-C_5H_5)] (**2c**) was synthesized by reaction of [(η^5-C_5H_5)$_2$Ta(N*t*Bu)Cl][5a] with 1 equiv. of NaCp or by reaction of [Ta(N*t*Bu)Cl$_3$(py)$_2$] with 3 equiv. of NaCp in THF.



2c

Finally we intended to obtain hitherto unknown silylimido complexes of the half-sandwich type [(η^5-C_5Me_5)M(NSiMe$_3$)Cl$_2$] (M = Nb: **3a**; Ta: **3b**) as well as their related tris(pyrazolyl)borato derivatives [Tp*M(NSiMe$_3$)Cl$_2$] [M = Nb: **4a**; Ta: **4b**; Tp* = κ^3-HB(3,5-Me$_2$pz)$_3$]. It was found that a silylimido ligand may be introduced to preformed half-sandwich complexes [(η^5-C_5Me_5)MCl$_4$][14] (M = Nb, Ta). By applying ultrasound the reaction of [(η^5-C_5H_5)MCl$_4$] (M = Nb, Ta) with LiN(SiMe$_3$)$_2$ in toluene (40 °C) leads to the pale yellow condensation products **3a** and **3b**. Bis(trimethylsilyl)amido complex intermediates[15] were not observed spectroscopically under these conditions.

EHMO calculations support the statement that the monoanionic 6-electron donor ligands Tp and Tp* [Tp = κ^3-HBpz$_3$; Tp* = κ^3-HB(3,5-Me$_2$pz)$_3$] possess similar σ,2π-bonding interactions with metal d orbitals as an η^5-cyclopentadienyl group.[16] Therefore these ligands can be envisaged as cyclopentadienyl ligand equivalents with a very high steric demand.[17] According to our procedure developed for the synthesis of [Tp*M(N*t*Bu)Cl$_2$] (M = Nb, Ta)[7] we treated [M(NSiMe$_3$)Cl$_3$(py)$_2$] (M = Nb, Ta)[9] with 1 equiv. of KTp* in THF and isolated [Tp*M(NSiMe$_3$)Cl$_2$] (M = Nb: **4a**, Ta: **4b**) in good yields. The 2:1 ratio of chemically equivalent ^{1}H and ^{13}C nuclei of the Tp* ligand reflects the C_s symmetry of complexes **4a** and **4b**. Because of the quadrupole moment of the ^{93}Nb nucleus (I = 9/2, 100%) ^{29}Si NMR signals of all niobium complexes described in this paper are too broad to be detected under standard conditions. The corresponding silylimido tantalum complexes reveal ^{29}Si NMR signals in the range of δ_{Si} = −4.9 (**2b**), −2.4 (**3b**), −2.3 (**1b**) and −1.5 (**4b**). As expected, by increasing the strength and number of σ,π-donor ligands the ^{29}Si nucleus becomes more shielded. In oscillators with a linear M=N−Si backbone the ν(M=N) and ν(N−Si) vibrational modes are probably coupled.[18] Therefore in most literature reports, assignments of the stretching modes ν(M=N−Si) of imido niobium or -tantalum complexes are not reported. By synthesis of the analogous *tert*-butyl- and silylimido complexes and by comparing their IR absorptions in the region 900−1300 cm^{-1} we were able to assign the stretching frequencies ν_{sym}(M=N−E) (E = C, Si). Vibrational absorptions are shifted towards lower wavenumbers due to the higher atomic mass of silicon versus carbon. Because of the coupling of vibrational modes IR data seems to be too insignificant to compare the donor strength via bond orders of the silyl- and *tert*-butylimido ligands.

Molecular Structures

In order to evaluate the σ,π-donor strength of the two imido ligands, NCMe$_3$ and NSiMe$_3$, single crystals of two isoelectronically related complexes [(η^5-C_5H_5)$_2$Ta(NEMe$_3$)(η^1-C_5H_5)] (E = Si **2b**; C **2c**) were grown. Yellow needles of **2b** crystallized from a saturated hexane solution at −30 °C whereas cubic crystals of **2c** were obtained from acetonitrile. The results of the X-ray analyses are shown in Figure 1 and Figure 2.

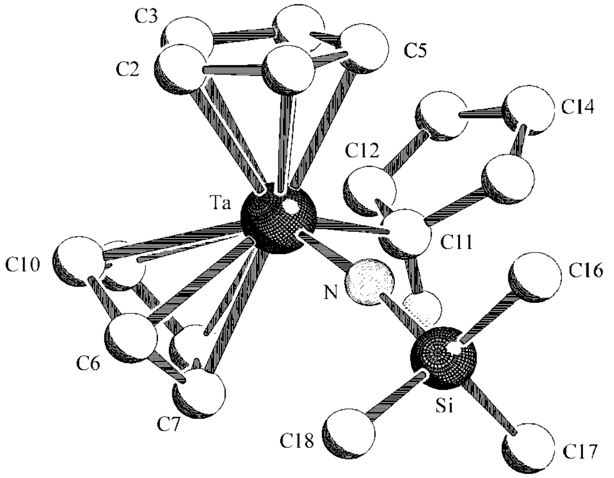


Figure 1. Molecular structure of **2b**; selected bond lengths [Å] and angles [°]: Ta−N(1) 1.796(7), Ta−C(11) 2.291(8), N(1)−Si 1.701(8), Ta−X(1) 2.168, Ta−X(2) 2.185, Ta−C(1) 2.449(9), Ta−C(2) 2.461(10), Ta−C(3) 2.523(9), Ta−C(4) 2.500(9), Ta−C(5) 2.438(9), Ta−C(6) 2.410(9), Ta−C(7) 2.457(9), Ta−C(8) 2.530(9), Ta−C(9) 2.547(10), Ta−C(10) 2.485(10), Ta−C(11) 229.1(8); Ta−N(1)−Si 171.9(5), X(1)−Ta−X(2) 125.9, X(1)−Ta−N(1) 111.7, X(1)−Ta−C(11) 117.0, X(2)−Ta−N(1) 111.3, X(2)−Ta−C(11) 102.8; X(1) is the centroid of the ring C(1)−C(5); X(2) is the centroid of the ring C(6)−C(10)

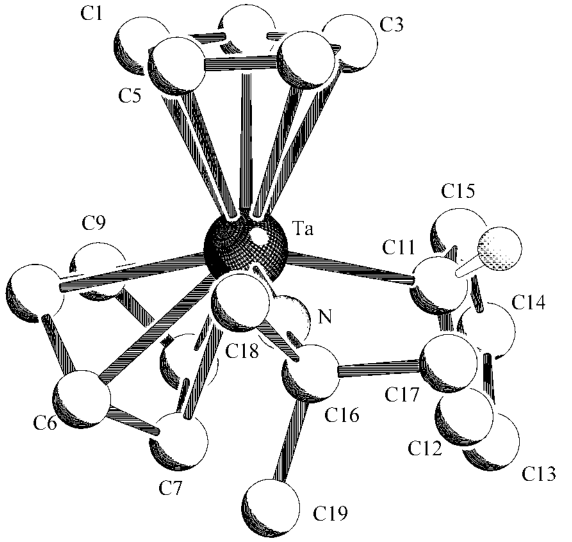


Figure 2. Molecular structure of **2c**; selected bond lengths [Å] and angles [°]: Ta−N(1) 1.761(5), Ta−C(11) 2.308(6), N(1)−C(16) 1.450(9), Ta−X(1) 2.199, Ta−X(2) 2.192, Ta−C(1) 2.510(7), Ta−C(2) 2.573(7), Ta−C(3) 2.525(6), Ta−C(4) 2.474(8), Ta−C(5) 2.417(8), Ta−C(6) 2.444(6), Ta−C(7) 2.447(7), Ta−C(8) 2.518(7), Ta−C(9) 2.570(7), Ta−C(10) 2.483(7), Ta−C(11) 2.308(6), Ta−N(1)−C(16) 175.2(5), X(1)−Ta−X(2) 124.2, X(1)−Ta−N(1) 113.1, X(1)−Ta−C(11) 102.3, X(2)−Ta−N(1) 112.3, X(2)−Ta−C(11) 107.2; X(1) is the centroid of the ring C(1)−C(5); X(2) is the centroid of the ring C(6)−C(10)

Both complexes **2b** and **2c** reveal a pseudotetrahedral coordination sphere at the tantalum atom defined by the centroids of two η^5-bonded cyclopentadienyl ligands X(1) and X(2), C(11) of the η^1-bonded cyclopentadienyl ring and the nitrogen atom N(1) of the imido ligand. They crystallize in different conformers with respect to the rotation about the Ta−C(11) bond. It is evident that the silylimido ligand, being less basic and also sterically less demanding than its carbon counterpart, forms a longer bond to the metal center: Ta−N(1)SiMe$_3$ 179.6(7) pm versus Ta−N(1)*t*Bu 176.1(5) pm. This is in agreement with the view that the dianion [NSiMe$_3$]$^{2-}$ is a weaker donor than [NCMe$_3$]$^{2-}$. The shorter Ta−N(1) bond of *tert*-butylimido complex **2c** corresponds with a longer distance Ta−C(11) 230.8(6) pm and longer distances of the tantalum atom to the centroids Ta−X(1) 219.9 and Ta−X(2) 219.2 pm of both η^5-C$_5$H$_5$ rings, whereas a longer Ta−N(2) bond of the silylimido complex **2b** corresponds with shorter distances Ta−C(11) 229.1(8), Ta−X(1) 216.8 and Ta−X(2) 218.5 pm. Steric ligand repulsion, but also the stronger σ,π-donor capability of the more π-basic alkylimido ligand, seem to be responsible for this trend. Due to the strong *trans* influence of the imido ligands Ta−C, the distances of the η^5-C$_5$H$_5$ ligands are not equivalent, the ones *trans* to Ta−N are longer. This is a typical structural feature of the imido half-sandwich complexes.[19] The angle between the ring centroids X(1)−Ta−X(2) of **2c** (124.2°) and **2b** (125.9°) are significantly smaller than in other bent tantalocenes.[6] This is probably due to steric repulsion. In both compounds **2b** and **2c** four ligands, with a potential for one σ- and two π-bonds and a maximum electron count of 6, are competing for π-interactions with a limited set of empty metal s, p and d orbitals. Orbital-symmetry restrictions are limiting the number of π-type interactions in a tetrahedral transition metal complex to five: two strong π-bonds are generated by the *e* set and three weaker π-bonds by the t_2 set of metal orbitals.[20] Four σ- and five π-bonding electron pairs would also be in agreement with the 18 valence electrons rule. If in a π-bond-saturated pseudo-tetrahedral molecule more than five orbitals of π-symmetry (p orbitals at N atoms or e_1-group orbitals of η^5-C$_5$H$_5$ rings) are available at the 4 ligands, electron density essentially remains in nonbonding orbitals (lone pairs) centered at the ligands, and only the strongest π-interactions dominate the π-bond regime.[21] Our structural data indicates that both dianionic [NR]$^{2-}$ ligands (R = SiMe$_3$, CMe$_3$) possess a stronger π-donor capability towards the relatively hard d^0-metal center than the more polarizable, softer and sterically more demanding ligand [C$_5$H$_5$]$^-$ that is released into a σ-bonding mode.

In π-bond-saturated complexes **2b**,**c** the Ta−N bond order, based on its length, is about 2. With respect to orbital symmetry and electron count considerations a higher Ta−N bond order is expected for the octahedral complex **4b**. In order to check this proposal, colorless cubic crystals of **4b** were grown from acetonitrile and submitted for an X-ray structural analysis. The molecular structure of **4b** is presented in Figure 3.

The tantalum center is octahedrally coordinated by three *fac*-binding nitrogen atoms of the Tp* ligand, by two chlorine atoms and one nitrogen atom of the silylimido ligand. The tantalum−imido bond Ta−N(1) 176.7(6) pm in **4b** is short compared with Ta−N(1) 179.6(7) pm in **2b**. This is in agreement with the assumption, that the silylimido ligand

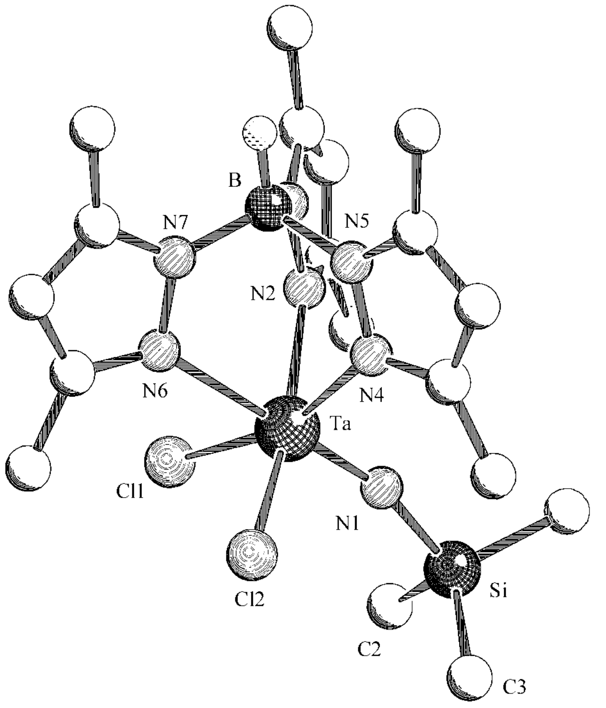


Figure 3. Molecular structure of **3b**; selected bond lengths [Å] and angles [°]: Ta−N(1) 1.767(6), Ta−N(2) 2.176(6), Ta−N(4) 2.201(6), Ta−N(6) 2.387(6), Ta−Cl(1) 2.373(2), Ta−Cl(2) 2.367(2), Si−N(1) 1.742(6), B−N(3) 1.550(11), B−N(5) 1.527(11), B−N(7) 1.515(12); Ta−N(1)−Si 164.8(4), N(1)−Ta−N(2) 97.9(3), N(1)−Ta−N(4) 97.8(3), N(1)−Ta−N(6) 179.5(3), N(1)−Ta−Cl(1) 96.8(2), N(1)−Ta−Cl(2) 96.29(19)

of [Tp*Ta($NSiMe_3$)Cl_2] is more involved in π-bonding to the metal center than **2b**. The higher Ta−N bond order is a consequence of the lower π-bond saturation due to a weaker set of donor ligands in **4b**. It is worth noting that a shorter Ta−N bond corresponds with a longer N−Si bond: N(1)−Si 174.2(6) pm in **4b** vs. N(1)−Si 170.1(8) pm in **2b**. This is a result of an unequal competition of the electrophilic centers, the d^0-metal atom and the $SiMe_3$ substituent, for the electron density at the nitrogen atom of the nitrido bridge. The Ta−N−Si axis 164.8(4)° of **4b** deviates considerably from linearity, presumably a result of the steric requirement imposed by the bulky trimethylsilyl group and the Tp* ligand. Deviations from M−N−C linearity in the range 160−180° are not specific for the evaluation of bond orders.[21] There is no correlation of bond order and angle; e.g. the more π-saturated **2b** has a lower Ta−N bond order but a higher angle Ta−N(1)−Si(1) 171.9(5)°. The strong *trans* influence of the imido ligand is evident in the longer tantalum−pyrazol distance Ta−N(6) 238.7(6) pm *trans* to the imido ligand when compared with the *cis*-bonded pyrazol groups Ta−N(2) 217.6(6) pm and Ta−N(4) 220.1(6) pm. This is in agreement with other structurally characterized tris(pyrazolyl)borato complexes [Tp*Ta(NDip)Cl_2][22] and [Tp*Mo(N*t*Bu)$_2$Cl].[7]

Variable-Temperature NMR-Spectroscopic Studies

In solutions of π-bond-saturated complexes with σ- and π-bonded enyl ligands of the same type, ligand fluxionality is expected. The potential of the electronically flexible imido ligand to act as either a 4- or 6-electron donor $[NR]^{2-}$ should support the fluxional rearrangement of the σ- and π-bonded cyclopentadienyl ligands by lowering the energy barriers between the η^1-, η^3- and η^5-coordination modes. In agreement with the experiments of Green et al. on the related complex [(η^5-C_5H_5)$_2$Nb($NCMe_3$)(η^1-C_5H_5)][13] variable-temperature ^{1}H-NMR spectroscopic studies, which are shown in Figure 4 and Figure 5, reveal the dynamic behavior of the cyclopentadienyl ligands in complexes **2b** and **2c**.

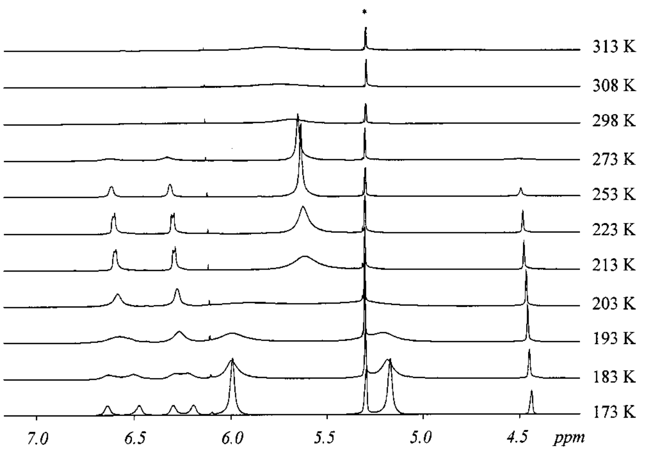


Figure 4. Variable-temperature ^{1}H NMR spectra of [(η^5-C_5H_5)$_2$Ta($NSiMe_3$)(η^1-C_5H_5)] (**2b**) (400 MHz, CD_2Cl_2), showing the dynamic behavior of the C_5H_5 ligand; the asterisk denotes the solvent resonance

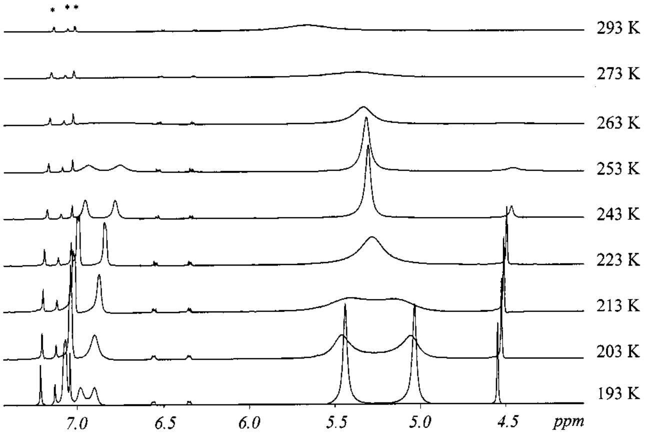
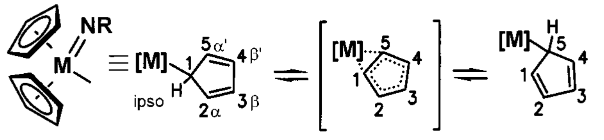
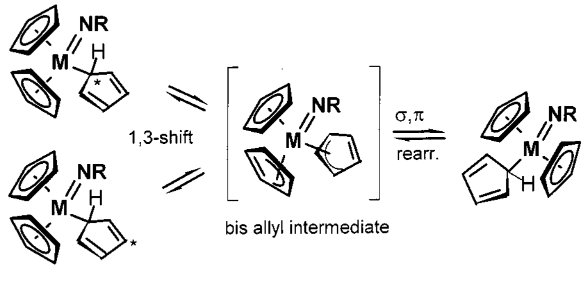


Figure 5. Variable-temperature ^{1}H NMR spectra of [(η^5-C_5H_5)$_2$Ta(N*t*Bu)(η^1-C_5H_5)] (**2c**) (400 MHz, [D_8]toluene), showing the dynamic behavior of the C_5H_5 ligand; the asterisks denote the solvent resonances

Three fluxional processes shown in Scheme 2 and Scheme 3 are observed for **2b** and **2c**: The rotation of the σ-C_5H_5 ligand about the Ta−C_{ipso} bond, the metallotropic migration of the tantalum center between the σ-C_5H_5 ring carbon atoms, and the σ,π-exchange of the cyclopentadienyl ligands.



Scheme 2. 1,2-Metallotropic rearrangement by 1,5-sigmatropic shift of [M] (M = Nb, Ta)



Scheme 3. 1,3-Shift of [M] and σ,π-rearrangement via the allyl intermediate (M = Nb, Ta)

In the slow-exchange-limiting ^{1}H NMR spectrum of **2b** at 173 K two resonances of the η^5-C_5H_5 ligands at $\delta = 6.02$ and 5.20 and five resonances of the σ-C_5H_5 ligand at $\delta =$ 6.66, 6.50, 6.32, 6.22, 4.46 are separated. This is consistent with a hindered rotation about the Ta−C_{ipso} bond on the NMR time scale. The same separation is observed for *tert*-butylimido complex **2c** but at a higher coalescence temperature. Upon raising the temperature a pairwise coalescence of the signals of both η^5-C_5H_5 ligands and of the σ-C_5H_5 olefinic protons H_α, $H_{\alpha'}$, H_β, $H_{\beta'}$ is observed, while H_{ipso} remains unchanged, as expected for a system with free rotation about the Ta−C_{ipso} bond. Experimental data of dynamic exchange processes and their coalescence temperatures for complexes **2b** and **2c** are listed in Table 1. The assignment of H_α and $H_{\alpha'}$ is based on the assumption that due to their closer position to the tantalum center, their chemical shift difference will be larger than between H_β and $H_{\beta'}$.

There is a trend in that the three exchange processes originating from a hindered rotation about the Ta−C_{ipso} bond, have higher coalescence temperatures for *tert*-butylimido complex **2c** than for the silylimido complex **2b**. This is probably due to the higher degree of RN→M π-donation and to the greater steric demand of the *tert*-butylimido versus silylimido ligand. The free activation enthalpy of rotation about the Ta−C_{ipso} bond reveals $\Delta G^{\neq}(T_C)$ values in the range 37.5−40.6 kJmol^{-1} (**2b**) and 40.7−41.9 kJmol^{-1} (**2c**) depending on the type of exchanging nuclei chosen for this estimation (Table 1). These barriers are slightly lower than 43.4 kJ mol^{-1} reported by Green for the sterically slightly more hindered complex [(η^5-C_5H_5)$_2$Nb(NCMe$_3$)-(η^1-C_5H_5)].[13] It is evident that in the sterically less hindered silylimido complex **2b**, rotation is less hindered. On the other hand, the lower coalescence temperatures for the σ,π-exchange of silylimido complex **2b** suggests that the stronger donor [NCMe$_3$]$^{2-}$ promotes the ring slippage into an η^3- and finally the η^1-cyclopentadienyl bonding mode more readily than the weaker donor [NSiMe$_3$]$^{2-}$. In our complexes the migration of the tantalum atom between the carbon atoms of σ-C_5H_5 could occur by either a metallotropic 1,3-shift via such η^3-allyl intermediates or by a concerted 1,2-shift, a process that could also be envisaged as a symmetry-allowed 1,5-sigmatropic rearrangement. According to Cotton et al. a 1,2-shift mechanism will lead to a faster initial broadening of the resonances assigned to the H_α and $H_{\alpha'}$ resonances relative to the *ipso* hydrogen atom, while initial broadening of the resonances assigned to H_β and $H_{\beta'}$ would be indicative of a 1,3-shift mechanism. In agreement with our variable-temperature NMR spectra we favor the 1,2-shift mechanism. We are facing the same problem discussed for [(η^5-C_5H_5)$_2$Nb(NCMe$_3$)(η^1-C_5H_5)][13] since we are not able to fully resolve the coupled fluxional processes associated with the Ta−C_{ipso} rotation on our NMR time scale in order to obtain quantitative results of the rate constants of the metallotropic migration.

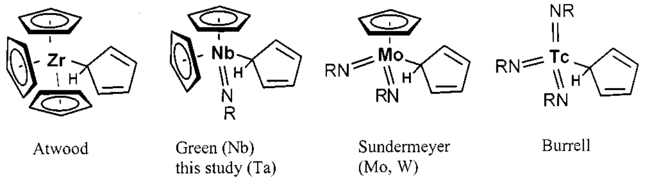
Conclusion

A series of new silylimido niobium and -tantalum complexes of half-sandwich and metallocene type has been synthesized. To the best of our knowledge the donor strength of isoelectronically related trimethylsilyl- and *tert*-butylimido complexes has not been evaluated by experimental methods before. M−N bond lengths and, in a less pronounced manner, dynamic exchange of η^1- and η^5-coordinated cyclopentadienyl ligands in isoelectronic compounds of the formula [(η^5-C_5H_5)$_2$M(NEMe$_3$)(η^1-C_5H_5)] (M = Nb, Ta; E = C, Si) indicate that *tert*-butylimido ligands are stronger donors than their silylimido counterparts. This might have been expected from the standpoint of N-basicity or proton affinity of the corresponding amines that is, to a certain extent, reflecting the donor strength of the ligand.

Table 1. Coalescence temperatures T_c, rate constants k and free activation enthalpies $\Delta G^0(T_C)$ for the Ta−C_{ipso} bond rotation process in **2b** and **2c**

Exchanging nuclei	[(η^5-C_5H_5)$_2$Ta(NSiMe$_3$)(η^1-C_5H_5)] **2b**				[(η^5-C_5H_5)$_2$Ta(N*t*Bu)(η^1-C_5H_5)] **2c**			
	Δν [Hz]	T_c [K]	k [s^{-1}]	ΔG [kJmol^{-1}]	Δν [Hz]	T_c [K]	k [s^{-1}]	ΔG [kJmol^{-1}]
H_β, $H_{\beta'}$	40.0	193	177.7	38.3	32.0	203	142.2	40.7
H_α, $H_{\alpha'}$	64.0	193	284.3	37.5	64.0	213	284.3	41.6
η^5,η^5-C_5H_5	328.1	223	1457.7	40.6	164.1	223	729.1	41.9
η^5,η^1-C_5H_5	–	293±5	–	–		273±5	–	–

By this study we extend the series of isolobal, highly π-bond-saturated organometallic complexes of group-4 −7 metals with a set of competing cyclopentadienyl and imido ligands. The isolobal relationship among the complexes shown in Scheme 4 is based on the cyclopentadienyl imido ligand analogy.[3]



Scheme 4. Isolobally related π-bond-saturated molecules based on the cyclopentadienyl-imido ligand analogy; references: Atwood,[23] Green,[13] Sundermeyer,[24] Burrell[25]

Experimental Section

Materials and Methods: All manipulations were performed under dry argon 4.8. Solvents were rigorously dried, distilled and stored over 3 Å and 4 Å molecular sieves before use. All air-sensitive compounds were stored in glove boxes MB 150B-G-II and Lab Master 130 (MBraun) under nitrogen. − Melting points (uncorrected) were determined with a melting point apparatus Büchi-SMP 20. − The ^{1}H, ^{13}C and ^{29}Si NMR spectra were recorded with a Bruker ARX200, a Bruker AMX300 and a Bruker DRX400 at 25 °C if not indicated otherwise. All ^{13}C NMR spectra are proton-decoupled. The signals of solvents were used as internal standards for the ^{1}H and ^{13}C NMR spectra: CD_2Cl_2 (δ = 5.32; 54.2), $CDCl_3$ (δ = 7.24; 77.0), C_6D_6 (δ = 7.15; 128.0) and C_7D_8 (δ = 2.03; 20.4). Tetramethylsilane served as an external standard for the ^{29}Si NMR spectra. − The IR spectra were recorded with a Nicolet 510 M FT spectrometer. All solids were recorded as Nujol mulls between KBr plates. − Elemental analyses were performed in the microanalytical laboratories of the Chemistry Department at Marburg University. − EI mass spectra were recorded with a Varian MAT CH7 (70 eV) and APCI mass spectra were recorded with a Hewlett Packard HP 5989 B spectrometer. − The X-ray structure analyses were performed with an Enraf Nonius CAD4 diffractometer. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-132475 (**2b**), -132476 (**2c**), and -132477 (**4b**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK [Fax: (internat.) + 44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk]. Starting materials: Niobium and tantalum pentachloride were products of H. C. Starck GmbH & Co. KG. The following compounds were prepared as described in the literature: $Na(C_5H_5)$,[26] $Li(C_5Me_5)$,[27] $Me_3Si(C_5Me_5)$,[28] $LiN(SiMe_3)_2$,[29] KTp*,[30] $[(\eta^5\text{-}C_5Me_5)MCl_4]$,[14] $[M(NSiMe_3)Cl_3(py)_2]$ (M = Nb, Ta)[9].

$[(\eta^5\text{-}C_5H_5)_2Nb(NSiMe_3)Cl]$ (1a): A mixture of $[Nb(NSiMe_3)Cl_3(py)_2]$ (250 mg, 0.56 mmol) and NaC_5H_5 (104 mg, 1.18 mmol) was dissolved in 20 mL of THF at −78 °C. After 1 h, the temperature was allowed to reach 25 °C and the color of the mixture turned from yellow to brown. After 2 h of stirring, the volatiles were removed in vacuo. The brown residue was extracted into 25 mL of toluene and the solution was filtered. Part of the solvent of the filtrate was evaporated to leave 10 mL, which was layered with 7 mL of hexane and stored at −30 °C to afford **1a** as a yellow powder. Yield: 65 mg (0.19 mmol, 30%); m.p. 156 °C. − ^{1}H NMR (300 MHz, C_6D_6): δ = 0.02 [s, 9 H, $Si(CH_3)_3$], 5.81 (s, 10 H, C_5H_5). − ^{1}H NMR (200 MHz, $CDCl_3$): δ = − 0.03 [s, 9 H, $Si(CH_3)_3$], 6.14 (s, 10 H, C_5H_5). − ^{13}C NMR (75 MHz, C_6D_6): δ = 0.5 [s, $Si(CH_3)_3$], 112.5 (s, C_5H_5). − IR (Nujol): ṽ = 3086 vw, 1634 vw ν(C=C), 1377 s, 1262 m, 1246 s, 1078 vs ν(Nb=N−Si), 1067 vs, 951 w, 835 vs, 812 vs, 793 vs, 748 m, 687 w, 633 w cm^{-1}. − $C_{13}H_{19}ClNNbSi$ (345.75): calcd. C 45.16, H 5.54, N 4.05; found C 44.36, H 5.60, N 3.74. − EI-MS (70 eV, EI): *m/z* (%) = 346 (74) [M$^+$], 311 (12) [M$^+$ − Cl]. − APCI-MS (CH_3CN): *m/z* (%) = 346 (100) [M$^+$].

$[(\eta^5\text{-}C_5H_5)_2Ta(NSiMe_3)Cl]$ (1b): A mixture of $[Ta(NSiMe_3)Cl_3(py)_2]$ (250 mg, 0.47 mmol) and NaC_5H_5 (87 mg, 0.99 mmol) was dissolved in 25 mL of THF at −78 °C. After 2 h, the temperature was allowed to reach 25 °C and the color of the mixture turned brown. After 2 h of stirring, the volatiles were removed in vacuo. The brown residue was extracted into 30 mL of *n*-hexane, the solution was filtered and reduced in volume. **1b** was obtained at −30 °C as a yellow powder. Yield: 100 mg (0.23 mmol, 45%); m.p. 145 °C. − ^{1}H NMR (200 MHz, C_6D_6): δ = − 0.09 [s, 9 H, $Si(CH_3)_3$], 5.78 (s, 10 H, C_5H_5). − ^{1}H NMR (300 MHz, $CDCl_3$): δ = − 0.06 [s, 9 H, $Si(CH_3)_3$], 6.13 (s, 10 H, C_5H_5). − ^{13}C NMR (75 MHz, $CDCl_3$): δ = 1.5 [s, $Si(CH_3)_3$], 111.4 (s, C_5H_5). − ^{29}Si NMR (78 MHz, C_6D_6): δ = −2.3 [s, $Si(CH_3)_3$]. − IR (Nujol): ṽ = 3137 vw, 3122 w, 3082 w, 1638 vw, 1611 m ν(C=C), 1528 m, 1456 vs, 1435 vs, 1395 w, 1377 s, 1368 s, 1261 s, 1244 s, 1113 vs ν(Ta=N−Si), 1080 vs, 1026 vs, 920 m, 855 br, 801 br, 745 vs, 706 vs, 631 vs, 606 m cm^{-1}. − $C_{13}H_{19}ClNSiTa$ (433.79): calcd. C 35.99, H 4.41, N 3.23; found C 35.99, H 4.98, N 3.01. − EI-MS (70 eV): *m/z* (%) = 433 (55) [M$^+$], 418 (100) [M$^+$ − CH_3].

$[(\eta^5\text{-}C_5H_5)_2Nb(NSiMe_3)(\sigma\text{-}C_5H_5)]$ (2a): A mixture of $[Nb(NSiMe_3)Cl_3(py)_2]$ (300 mg, 0.68 mmol) and an excess of NaC_5H_5 (595 mg, 6.75 mmol) was dissolved in 25 mL of THF at −78 °C. After 2 h, the temperature was allowed to reach 25 °C. After 2 h of stirring at 25 °C, the volatiles of the light-brown reaction mixture were removed completely and the residue was extracted into 30 mL of *n*-hexane. The solution was filtered and reduced in volume to 7 mL and stored for 1 week at −30 °C to give **2a** as a yellow, microcrystalline solid. Yield: 100 mg (0.27 mmol, 30%); m.p. 132 °C. − ^{1}H NMR (400 MHz, CD_2Cl_2, 298 K): δ = 0.01 [s, 9 H, $NSi(CH_3)_3$], 5.64 (br. s, 10 H, $\eta^5\text{-}C_5H_5$), 6.27 (br. s, 5 H, $\eta^1\text{-}C_5H_5$). − ^{1}H NMR (400 MHz, CD_2Cl_2, 173 K): δ = −0.11 [s, 9 H, $NSi(CH_3)_3$], 5.09 (br. s, 5 H, $\eta^5\text{-}C_5H_5$), 5.14 (br. s, 1 H, C-H_{ipso}), 5.99 (br. s, 5 H, $\eta^5\text{-}C_5H_5$), 6.26 (m, br, 2 H, C-$H_{\beta,\beta'}$), 6.49 and 6.61 (m, 2 H, C-$H_{\alpha,\alpha'}$). − ^{13}C NMR (75 MHz, CD_2Cl_2, 298 K): δ = 1.5 [s, $NSi(CH_3)_3$], 111.0 (s, $\eta^5\text{-}C_5H_5$), 132.9 (br. s, $C_{\beta,\beta'}$), 133.9 (br. s, $C_{\alpha,\alpha'}$), C_{ipso} is not observed. − ^{13}C NMR (100 MHz, CD_2Cl_2, 173 K): δ = 0.3 [s, $NSi(CH_3)_3$], 55.5 (s, C_{ipso}), 109.0 and 110.7 (br. s, $\eta^5\text{-}C_5H_5$), 121.15 and 119.4 (br. s, $C_{\beta,\beta'}$), 136.3 and 141.0 (br. s, $C_{\alpha,\alpha'}$). − IR (Nujol): ṽ = 3102 m, 3079 m, 3065 w, 1624 vw, 1607 m ν(C=C), 1383 s, 1366 m, 1300 w, 1262 vs, 1244 vs, 1128 vw, 1080 vs ν(Nb=N−Si), 1030 vs, 972 m, 909 vw, 883 s, 835 vs, 801 vs, 752 s, 737 vs, 714 s, 693 w, 685 w, 633 m, 625 m, 611 vw cm^{-1}. − $C_{18}H_{24}NNbSi$ (375.39): calcd. C 57.59, H 6.44, N 3.73; found C 57.22, H 6.23, N 3.44. − EI-MS (70 eV): *m/z* (%) = 375 (26) [M$^+$], 310 (37) [M$^+$ − C_5H_5].

$[(\eta^5\text{-}C_5H_5)_2Ta(NSiMe_3)(\sigma\text{-}C_5H_5)]$ (2b): **2b** was prepared analogously to **2a** by treating $[Ta(NSiMe_3)Cl_3(py)_2]$ (300 mg, 0.56 mmol) with NaC_5H_5 (496 mg, 5.63 mmol). The reaction time was 20 h at 25 °C. Yellow needles of **2b** were obtained from *n*-hexane at −30 °C. Yield: 100 mg (0.216 mmol, 38%); m.p. 135 °C. − ^{1}H NMR (400 MHz, CD_2Cl_2, 298 K): δ = −0.01 [s, 9 H, $NSi(CH_3)_3$], 5.71

(br. s, 10 H, η^5-C_5H_5), 5.91 (br. s, 5 H, η^1-C_5H_5). – ^{1}H NMR (400 MHz, CD_2Cl_2, 173 K): δ = –0.13 [s, 9 H, NSi(CH_3)$_3$], 4.46 (br. s, 1 H, C-H_{ipso}), 5.20 (br. s, 5 H, η^5-C_5H_5), 6.02 (br. s, 5 H, η^5-C_5H_5), 6.22 and 6.32 (m, br, 2 H, C-$H_{\beta,\beta'}$), 6.50 and 6.66 (m, 2 H, C-$H_{\alpha,\alpha'}$). – ^{13}C NMR (100 MHz, CD_2Cl_2, 233 K): δ = 1.3 [s, NSi(CH_3)$_3$], 57.2 (s, C_{ipso}), 108.8 (s, η^5-C_5H_5), 122.4 (br. s, $C_{\beta,\beta'}$), 141.4 (br. s, $C_{\alpha,\alpha'}$). – ^{13}C NMR (100 MHz, CD_2Cl_2, 173 K): δ = 0.7 [s, NSi(CH_3)$_3$], 56.3 (s, C_{ipso}), 106.6 and 107.7 (br. s, η^5-C_5H_5), 120.8 and 122.5 (br. s, $C_{\beta,\beta'}$), 138.1 and 143.5 (br. s, $C_{\alpha,\alpha'}$) – ^{29}Si NMR (78 MHz, C_6D_6): δ = –4.9 [s, Si(CH_3)$_3$]. – IR (Nujol): ṽ = 3103 vw, 3080 w, 3064 vw, 1634 w ν(C=C), 1441 vw, 1398 m, 1261 s, 1244 vs, 1117 vs ν(Ta=N–Si), 1086 s, 1023 vs, 969 m, 910 m, 818 vs, br, 742 vs, 714 m, 630 m cm^{-1} – $C_{18}H_{24}ClNSiTa$ (463.43): calcd. C 46.65, H 5.22, N 3.02; found C 46.18, H 5.72, N 3.01 – EI-MS (70 eV): *m*/*z* (%) = 463 (78) [M$^+$], 398 (60) [M$^+$ – C_5H_5], 383 (100) [M$^+$ – C_5H_5–CH_3].

X-ray Structure Analysis of 2b:[31] $C_{18}H_{24}NSiTa$, M_r = 463.43, tetragonal, space group $P4_2/n$ (no. 105), $a = b$ = 19.978(1), c = 8.868(1) Å, V = 3539.7(4) Å^3, Z = 8, $\rho_{calcd.}$ = 1.739 g cm^{-3}, λ(Mo-K_α) = 0.71073 Å, μ = 6.272 mm^{-1}, T = 203(2) K. A pale yellow crystal 0.60 × 0.20 × 0.20 mm was used to record 2791 intensities to θ = 24.96°, of which 2637 ($R_{int.}$ = 0.0788) were unique and 2229 were observed [$I > 2\sigma(I)$]. An empirical absorption correction was applied on the basis of ψ-scans, with the transmission minimum at 36.7%. The structure was solved by direct methods (SHELXS-97) and subjected to full-matrix least-squares refinement on F^2 (SHELXL-97). All non-hydrogen atoms were refined anisotropically; H atoms were geometrically positioned (riding model) with a 1.5-fold isotropic U value of the equivalent U value of the corresponding C atom. Refinement proceeded with 198 parameters to R = 0.0509; wR_2 = 0.1485 for all data, GooF = 1.045; w^{-1} = [$\sigma^2(F_o^2)$ + $(0.1114P)^2$ + 8.3375P] where P = [F_o^2 + $2F_c^2$]/3; maximum/minimum residual electron densities 2.356/–1.213 e/Å^3.

[(η^5-C_5H_5)$_2$Ta(N*t*Bu)(σ-C_5H_5)] (2c): [Ta(N*t*Bu)Cl_3(py)$_2$] (300 mg, 0.58 mmol) and 3.5 equiv. of NaC_5H_5 (181 mg, 2.03 mmol) were dissolved in 30 mL of THF at –78 °C. The stirred mixture was allowed to reach 25 °C within 2 h and stirred for another 20 h at this temperature. Volatiles were removed in vacuo, the product extracted into 30 mL of *n*-hexane and insoluble material was removed by decanting the solution after centrifugation. After reducing the volume of the solvent, cubic crystals of **2c** crystallized at –30 °C. Yield: 180 mg, (0.40 mmol, 70%); m.p. 125 °C. – ^{1}H NMR (400 MHz, C_7D_8, 263 K): δ = 0.97 [s, 9 H, NC(CH_3)$_3$], 4.38 (br. s, 1 H, C-H_{ipso}), 5.24 (s, 10 H, η^5-C_5H_5), 6.65 (br. s, 4 H, C-$H_{\alpha,\alpha',\beta,\beta'}$). – ^{1}H NMR (400 MHz, C_7D_8, 193 K): δ = 1.00 [s, 9 H, NC(CH_3)$_3$], 4.45 (br. s, 1 H, C-H_{ipso}), 4.93 (br. s, 5 H, η^5-C_5H_5), 5.34 (br. s, 5 H, η^5-C_5H_5), 6.80 and 6.88 (s, 2 H, C-$H_{\beta,\beta'}$), 6.94 and 7.10 (s, 2 H, C-$H_{\alpha,\alpha'}$). – ^{13}C NMR (75 MHz, C_6D_6, 298 K): δ = 32.3 [s, NC(CH_3)$_3$], 66.1 [s, NC(CH_3)$_3$], 107.0–117.6 (br. s, η^5-C_5H_5 and η^1-C_5H_5). – IR (Nujol): ṽ = 3104 vw, 3082 w, 3069 vw, 1630 vw, 1611 m, ν(C=C), 1541 vw, 1524 vw, 1449 vs, 1439 vs, 1385 s, 1366 m, 1352 vs, 1262 vs, br, 1211 vs ν(Ta=N–C), 1086 vs, br, 1025 vs, br, 970 vs, 899 vs, 792 vs, br, 739 vs, 714 s, 631 s, 544 m, 527 vs cm^{-1} – $C_{19}H_{24}NTa$ (447.36): calcd. C 51.01, H 5.41, N 3.13; found C 50.94, H 5.39, N 3.12 – EI-MS (70 eV): *m*/*z* (%) = 447.0 (17) [M$^+$], 382 (5) [M$^+$ – C_5H_5], 367 (60) [M$^+$ – C_5H_5–CH_3].

X-ray Structure Analysis of 2c:[31] $C_{19}H_{24}NTa$, M_r = 447.36, tetragonal, space group $I4_1/amd$ (no. 141), $a = b$ = 19.7571(8), c = 8.6796(8) Å, V = 3388.0(4) Å^3, Z = 8, $\rho_{calcd.}$ = 1.754 g cm^{-3}, λ(Mo-K_α) = 0.71073 Å, μ = 6.482 mm^{-1}, T = 197(2) K. A yellow cubic crystal 0.30 × 0.20 × 0.20 mm was used to record 3627 intensities to θ = 26.26°, of which 3426 ($R_{int.}$ = 0.0432) were unique and 2903 were observed [$I > 2\sigma(I)$]. An empirical absorption correction was applied on the basis of ψ-scans, with the transmission minimum at 24.7%. The structure was solved by direct methods (SHELXS-97) and subjected to full-matrix least-squares refinement on F^2 (SHELXL-97). All non-hydrogen atoms were refined anisotropically; H atoms were geometrically positioned (riding model) with a 1.5-fold isotropic U value of the equivalent U value of the corresponding C atom. Refinement proceeded with 183 parameters to R = 0.0464; wR_2 = 0.1236 for all data, GooF = 1.098; w^{-1} = [$\sigma^2(F_o^2)$ + $(0.1776P)^2$ + 64.5121P] where P = [F_o^2 + $2F_c^2$]/3; maximum/minimum residual electron densities 1.055/–3.939e/Å^3.

[(η^5-C_5Me_5)Nb($NSiMe_3$)Cl_2] (3a): [(η^5-C_5Me_5)$NbCl_4$] (250 mg, 0.68 mmol) and LiN($SiMe_3$)$_2$ (124 mg, 0.74 mmol) were suspended in 30 mL of toluene at room temperature. The color immediately changed from yellow to green. The suspension was treated with ultrasound (40 h/40 °C water bath). LiCl and other insoluble material were removed by centrifugation. The solvent was completely removed in vacuo and the yellow residue dissolved in 10 mL of *n*-hexane. At –30 °C the crystalline product **3a** precipitated. Yield: 85 mg (0.22 mmol, 30%); m.p. 165 °C. – ^{1}H NMR (300 MHz, C_6D_6): δ = 0.18 [s, 9 H, NSi(CH_3)$_3$], 1.93 [s, 15 H, C_5(CH_3)$_5$]. – ^{13}C NMR (75 MHz, C_6D_6): δ = 1.9 [s, Si(CH_3)$_3$], 12.7 [s, C_5(CH_3)$_5$], 120.6 [s, C_5(CH_3)$_5$]. – IR (Nujol): ṽ = 3148 m, br, 1618 w ν(C=C), 1306 w, 1262 vs, 1093 vs, br ν(Nb=N–Si), 1020 vs, 974 w, 918 w, 876 w, 845 m, 801 s, 723 m, 588 w cm^{-1} – $C_{13}H_{24}Cl_2NNbSi$ (386.24): calcd. C 40.42, H 6.26, N 3.63; found C 40.97, H 5.47, N 4.41 – EI-MS (70 eV): *m*/*z* (%) = 355 (2) [M$^+$ – 2CH_3] – APCI-MS (CH_3CN): *m*/*z* (%) = 387 (8) [M$^+$], 315 (100) [M$^+$ – 2Cl].

[(η^5-C_5Me_5)Ta($NSiMe_3$)Cl_2] (3b): 3b was synthesized analogously to **3a** from [(η^5-C_5Me_5)$TaCl_4$] (250 mg, 0.55 mmol) and LiN($SiMe_3$)$_2$ (101 mg, 0.60 mmol). Yellow microcrystalline **3b** precipitated from *n*-hexane at –30 °C. Yield: 100 mg (40 mg, 0.08 mmol) of **3b**; m.p. 202 °C. – ^{1}H NMR (300 MHz, C_6D_6): δ = 0.18 [s, 9 H, NSi(CH_3)$_3$], 1.93 [s, 15 H, C_5(CH_3)$_5$]. – ^{13}C NMR (75 MHz, C_6D_6): δ = 2.4 [s, NSi(CH_3)$_3$], 11.7 [s, C_5(CH_3)$_5$], 121.9 [s, C_5(CH_3)$_5$] – ^{29}Si NMR (78 MHz, C_6D_6): δ = –2.4 [s, NSi(CH_3)$_3$]. – IR (Nujol): ṽ = 3110 m, br, 3050 m, br, 1617 w ν(C=C), 1262 vs, 1080 vs, br ν(Ta=N–Si), 1022 vs, br, 862 s, 799 vs, br, 702 s, 687 s, 662 s, 631 m, 588 w cm^{-1} – $C_{13}H_{24}Cl_2NSiTa$ (474.28): calcd. C 32.92, H 5.10, N 2.95; found C 34.93, H 5.58, N 2.94 – EI-MS (70 eV): *m*/*z* (%) = 439 (2) [M$^+$ – Cl], 330 (100) [M$^+$ – Cl–Me_3SiCl].

[Tp*Nb($NSiMe_3$)Cl_2] (4a): To 300 mg (0.68 mmol) of [Nb($NSiMe_3$)Cl_3(py)$_2$] and 231 mg (0.69 mmol) of KTp* was added 30 mL of THF at –78 °C. After warming up (1 h) the solution, it was stirred for 1 d at 25 °C and the solvent completely removed in vacuo. The residue was extracted into 30 mL of toluene, and KCl and other insoluble side products were separated by filtration. Toluene was removed in vacuo and the residue crystallized from MeCN at –30 °C to give yellow cubic crystals of **4a**. Yield: 315 mg (0.58 mmol, 85%); m.p. 296 °C. – ^{1}H NMR (300 MHz, C_6D_6): δ = 0.40 [s, 9 H, NSi(CH_3)$_3$], 1.87 [s, 6 H, pz_A-C(5)–CH_3], 2.09 [s, 3 H, pz_B-C(5)–CH_3], 2.64 [s, 6 H, pz_A-C(3)–CH_3], 2.87 [s, 3 H, pz_B-C(3)–CH_3], 5.31 [s, 2H pz_A, C(4)-H], 5.54 [s, 1 H, pz_B-C(4)-H]. – ^{13}C NMR (75 MHz, C_6D_6): δ = 1.4 [s, NSi(CH_3)$_3$], 12.2 [s, pz_B-C(5)-CH_3], 12.5 [s, pz_A-C(5)-CH_3], 15.0 [s, pz_B-C(3)-CH_3], 16.6 [s, pz_B-C(3)-CH_3], 107.1 [s, pz_A, C(4)], 107.6 [s, pz_B, C(4)], 142.9 [s, pz_A, C(3)], 145.8 [s, pz_B, C(3)], 152.7 [s, pz_A, C(5)], 153.8 [s, pz_B, C(5)]. – IR (Nujol): ṽ = 3339 m ν(C–H_{pz}), 3288 m, br, 3130 m, 2733 w, 2542 vs ν(B–H), 2362 w, 2212 w, 1572 s, 1541 vs ν(C–N_{pz}), 1524 m, 1381 vs, 1366 vs, 1252 vs, 1202 vs, 1090 vs, br ν(Nb=

N−Si), 1043 vs, 982 s, 941 s, 841 vs,br, 799 vs, br, 777 s, 694 s, 662 s, 596 vw, 522 m, 478 s cm^{-1} − $C_{18}H_{31}BCl_2NNbSi$ (548.21): calcd. C 39.44, H 5.70, N 17.89; found C 39.27, H 5.80, N 17.47 − EI-MS (70 eV): *m*/*z* (%) = 547 (19) [M$^+$], 532 (13) [M$^+$ − CH_3], 511 (100) [M$^+$ − Cl].

[Tp*Ta(NSiMe$_3$)Cl$_2$] (4b): 4b was synthesized analogously to **4a** from [Ta(NSiMe$_3$)Cl$_3$(py)$_2$] (300 mg, 0.56 mmol) and KTp* (193 mg, 0.57 mmol). Colorless cubic crystals were obtained at −30 °C from MeCN. Yield: 250 mg (0.39 mmol, 70%); m.p. 310 °C. − ^{1}H NMR (300 MHz, C_6D_6): δ = 0.44 [s, 9 H, NSi(C*H*$_3$)$_3$], 1.83 [s, 6 H, pz$_A$-C(5)−C*H*$_3$], 2.05 [s, 3 H, pz$_B$-C(5)−C*H*$_3$], 2.70 [s, 6 H, pz$_A$-C(3)−C*H*$_3$], 2.86 [s, 3 H, pz$_B$-C(3)−C*H*$_3$], 5.29 [s, 2H pz$_A$, C(4)-*H*], 5.65 [s, 1 H, pz$_B$-C(4)-*H*]. − ^{13}C NMR (75 MHz, C_6D_6): δ = 1.5 [s, NSi(*C*H$_3$)$_3$], 12.2 [s, pz$_B$-C(5)-*C*H$_3$], 12.4 [s, pz$_A$-C(5)-*C*H$_3$], 15.3 [s, pz$_B$-C(3)-*C*H$_3$], 17.0 [s, pz$_B$-C(3)-*C*H$_3$], 107.6 [s, pz$_A$, *C*(4)], 108.0 [s, pz$_B$, *C*(4)], 143.7 [s, pz$_B$, *C*(3)], 146.0 [s, pz$_A$, *C*(3)], 153.9 [s, pz$_A$, *C*(5)], 154.4 [s, pz$_B$, *C*(5)] − ^{29}Si NMR (78 MHz, C_6D_6): δ = −1.5 [s, N*Si*(CH$_3$)$_3$]. − IR (Nujol): $\tilde{\nu}$ = 3288 m ν(C−H$_{pz}$), 3130 m, br, 2544 vs ν(B−H), 2362 vw, 2226 w, 1574 m, 1545 vs ν(C−N$_{pz}$), 1451 vs, 1414 vs, 1383 vs, 1366 vs, 1250 vs, 1215 m, 1202 vs, 1123 vs, br, 1074 vs ν(Ta=N−Si), 1044 vs, 982 m, 941 s, 847 vs, br, 801 vs, br, 694 m, 662 m cm^{-1} − $C_{18}H_{31}BCl_2NSiTa$ (636.25): C 33.98, H 4.91, N 15.41; found C 33.75, H 5.02, N 15.33 − EI-MS (70 eV): *m*/*z* (%) = 635 (61) [M$^+$], 620 (100) [M$^+$ − CH_3].

X-ray Structure Analysis of 4b:[31] $C_{22}H_{31}BCl_2N_9SiTa$, M_r = 447.36, triclinic, space group $P\bar{1}$ (no. 2), a = 10.075(2), b = 10.256(2), c = 15.635(4) Å, α = 79.29(2), β = 80.17(2), γ = 82.30(2)°, V = 1555.5(4) Å^3, Z = 2, $\rho_{calcd.}$ = 1.521 g cm^{-3}, λ(Mo-K_α) = 0.71073 Å, μ = 3.771 mm^{-1}, T = 193(2) K. A yellow cubic crystal 0.40 × 0.20 × 0.10 mm was used to record 6115 intensities to θ = 24.97°, of which 5449 ($R_{int.}$ = 0.0595) were unique and 2229 were observed [$I > 2\sigma(I)$]. An empirical absorption correction was applied on the basis of ψ-scans, with the transmission minimum at 70.4%. Structure solution and refinement: The structure was solved by direct methods (SHELXS-97) and subjected to full-matrix least-squares refinement on F^2 (SHELXL-97). All non-hydrogen atoms were refined anisotropically; H atoms were geometrically positioned (riding model) with a 1.5-fold isotropic U value of the equivalent U value of the corresponding C atom. Refinement proceeded with 198 parameters to R = 0.0493; wR_2 = 0.1043 for all data, GooF = 1.002, $w^{-1} = [\sigma^2(F_o^2) + (0.0522P)^2]$ where $P = [F_o^2 + 2F_c^2]/3$; maximum/minimum residual electron densities 1.075/−1.530 e/Å^3.

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