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Tantalizing Chemistry of the Half-Sandwich Silylhydride Complexes of Niobium: Identification of Likely Intermediates on the Way to Agostic Complexes

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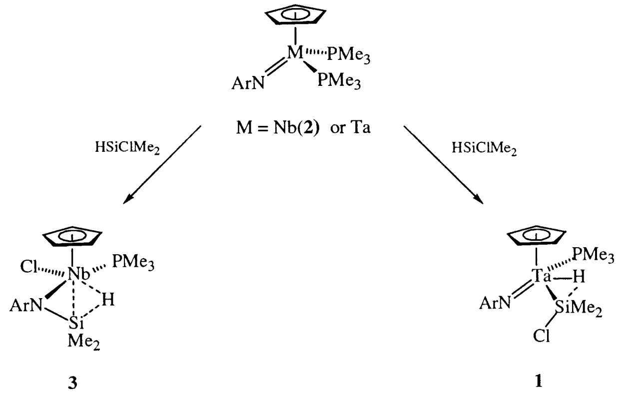
Reactions of the compound [NbCp(ArN)(PMe$_3$)$_2$] with chlorosilanes HSiRR′Cl give a series of silyl complexes [NbCp(ArN)(PMe$_3$)(H)(SiRR′Cl)] and [NbCp(ArN)(PMe$_3$)(Cl)(SiRR′H)] which are likely intermediates to the agostic complexes [NbCp(ArN(RR′$_2$Si–H···))(PMe$_3$)(Cl)].

Silane σ-complexes have been known for more than 30 years and are now well-studied.[1] Agostic Si−H−M interactions were first reported about 10 years ago.[2−4] Recently, new types of nonclassical complexes have been discovered,[5] some of which were found to have *interligand hypervalent interactions* (IHI).[6,7] Examining the latter type of bonding we observed that Cp(ArN)Ta(PMe$_3$)$_2$ (Ar = 2,6-diisopropylphenyl) reacts with HSiMe$_2$Cl giving the compound Cp(ArN)Ta(PMe$_3$)(H)(SiMe$_2$Cl) (**1**) with IHI, whereas its niobium analogue, Cp(ArN)Nb(PMe$_3$)$_2$ (**2**), affords the first stretched β-agostic Si−H···M complex Cp(ArNMe$_2$Si−H···)Nb(PMe$_3$)(Cl) (**3**) (Scheme 1).[7] Whether this reaction proceeds via silane addition across the Nb═N bond or via oxidative addition to the metal to give a tantalum-like structure Cp(ArN)Nb(PMe$_3$)(H)(SiMe$_2$Cl) with subsequent rearrangement was not clear at that time. Our further studies in this field showed that, first, simple variation of the silane dramatically changes the type of product to the tantalum-like complex Cp(ArN)Nb(PMe$_3$)(H)(SiR$_3$) and, second, unprecedented intramolecular exchange of hydrogen and chlorine atoms between the silicon and niobium sites is

Scheme 1



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(8) Crystal data for **4**: $C_{29}H_{33}ClNSiPNb$, orthorhombic, $Pna2_1$, $a = 21.030(4)$ Å, $b = 8.730(2)$ Å, $c = 36.900(7)$ Å, $V = 6775(2)$ Å^3, $T = 150$ K, $Z = 4$, μ(Mo Kα) = 0.54 mm^{-1}. A total of 12578 reflections were measured (9549 observed). R1 = 0.054, wR2 = 0.1275, and GOF = 1.041.

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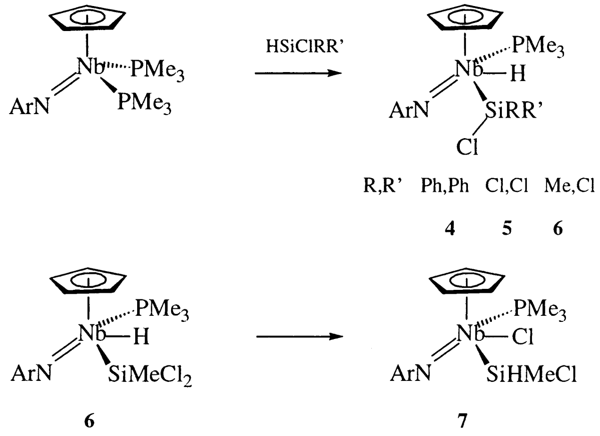
Scheme 2



possible. These findings underpin a likely mechanistic pathway to β-agostic species.

By reacting the precursor **2** with $HSiPh_2Cl$ instead of $HSiMe_2Cl$ we unexpectedly obtained the silylhydrido complex $Cp(ArN)Nb(PMe_3)(H)(SiPh_2Cl)$ (**4**) similar to the tantalum compound **1** (Scheme 2). Complex **4** has the hydride signal as a doublet at 2.86 ppm ($J_{P-H} = 63.5$ Hz) and two doublets for the nonequivalent Me groups of the Ar ligand, which is typical for complexes of the types Cp(RN)Nb(X)(Y) and $Cp(RN)Nb(PR'_3)(X)(Y)$. The Nb−H bond stretching can be seen in the IR spectrum as a band at 1616 cm^{-1}. The connectivity of **4** was further supported by X-ray study.[8] A similar product $Cp(ArN)Nb(PMe_3)(H)(SiCl_3)$ (**5**) is formed when **2** reacts with $HSiCl_3$.

An orthorhombic crystal of **4** has two independent molecules in the unit cell. The molecular structure of one of them is shown in Figure 1. These two molecules have somewhat different Nb−Si bond lengths of 2.587(2) and 2.577(2) Å, which can be attributed to crystal packing effects. These values are comparable with the Ta−Si bond of 2.574(2) Å in the related complex $Cp(ArN)Ta(PMe_3)(H)(SiMe_2Cl)$ (**1**) and with the Nb−Si bonds in the isolobal niobocenes $Cp_2Nb(SiMe_2Cl)H_2$ (2.579(2) Å) and $Cp_2Nb(SiMe_2Cl)_2H$ (2.597(1) Å). Short M−Si bonds and long Si−Cl bonds (range 2.163−2.177(2) Å) in the latter three compounds have been previously attributed to the presence of interligand hypervalent interactions (IHIs) M−H···Si−Cl.[6,7] Whereas the Nb−Si bond lengths in the two independent molecules of **4** fall well within the range of distances found for complexes with IHI, the Si−Cl bond lengths observed for **4** are shorter (2.146(2) and 2.153(3) Å), signifying diminished interligand interactions. Nevertheless, these Si−Cl bonds are still at the upper end of values found for classical complexes $LnM(SiR_2Cl)$ (R = alkyl, aryl, 2.094−2.149 Å),[9] among which the longest Si−Cl distance of 2.149(2) Å is found in $WCp_2(SiMe_3)(SiPr^i{}_2Cl)$, which, in its turn, may be affected by the increased bulkiness of the isopropyl group.[9d] These data establish that some weak Si−H interactions in **4** may still be present, although they are significantly reduced in comparison with the related Nb and Ta compounds. The reason for this may lie in the different electronegativities of niobium and tantalum and in the different electron releasing abilities of the Cp_2 and Cp/ArN/PMe_3 ligand sets. Tantalum is known to stabilize higher oxidation states better than niobium and thus, probably, is a better electron donor, making the hydride in **1** more basic. However, one should not also exclude the possibility of a hyperconjugation between the π-system of the phenyl rings and the (Si−Cl)* antibonding orbital, which can also reduce interaction of this orbital with the Nb−H bonding orbital, resulting in diminished IHI.

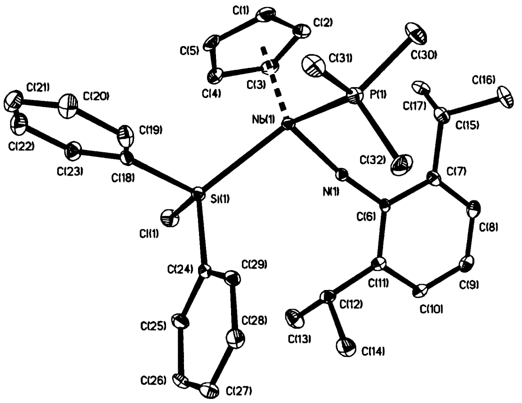


Figure 1. Molecular structure of **4**. Selected bond lengths (Å) and angles (deg) for molecule **A**: Nb1−P1 2.545(2), Nb1−Si1 2.587(2), Si1−Cl1 2.146(2), Nb1−N1 1.811(5), P1 −Nb1−Si1 117.13(6). For molecule **B**: Nb2−P2 2.537(2), Nb2−Si2 2.577(2), Si2−Cl2 2.153(3), P2−Nb2−Si2 116.52(6).

Reaction of **2** with $HSiMeCl_2$ during 30 min followed by a quick workup affords a high yield of the complex $NbCp(ArN)(PMe_3)(H)(SiMeCl_2)$ (**6**), which also has a "tantalum-like" structure (Scheme 2). In addition to the Nb−H hydride signal at 2.51 ppm ($^2J_{P-H} = 70.2$ Hz) in the ^1H NMR spectrum, it exhibits the Nb−H band at 1620 cm^{-1} in the IR spectrum. When isolated, this complex is stable at room temperature at least for some weeks. When this reaction was carried out in the NMR tube, complex **6** was observed as the sole product in 15 min after mixing the reagents. However, after about 30 min its transformation into another product **7** was noticed, which was complete in few hours. This reaction was performed on the Schlenk tube scale by stirring the reagents overnight, and complex **7** was obtained in 63% isolated yield. Its ^1H NMR spectrum pattern is similar to that of **6** apart from the absence of the Nb−H resonance and appearance of a quartet at 6.24 ppm ($^3J_{H-H} = 3.3$ Hz), integrated as 1 and coupled to the Si−Me resonance (doublet at 1.23 ppm). The IR spectrum of **7** no longer shows the Nb−H band, but a new band at 2142 cm^{-1} in the typical Si−H region appears. The ^{29}Si NMR spectrum confirmed the presence of a direct Si−H bond (J(Si−H) = 207 Hz). The elemental analysis of **6** and **7** shows that their composition is the same. All together these data establish that **7** has the structure $Cp(ArN)Nb(PMe_3)(Cl)(SiMeClH)$, i.e., an unexpected hydride for chloride exchange took place. This reactivity contrasts to what is found for Rh and Ir complexes, for which migration of chlorides from the metal to silyls

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occurs.[10] This difference can be attributed to the high halophilicity of the early transition metals such as niobium. We also found that **7** is stable in the presence of $MeSiCl_3$ but decomposes to unknown products when $HSiMeCl_2$ is added and reacts with PMe_3 to give $Cp(PMe_3)_3NbCl_2$. Although the nature of the rearrangement of **6** into **7** is not clear at the moment, it is apparently assisted by the ingredients of the reaction mixture. Interestingly, the related compounds **4** and **5** do not show this type of transformation in the mother liquor, most likely due to different electronic and steric properties of the substituents at the silicon center.

Finally, when the silane HSiMePhCl, "intermediate" in its properties to $HSiMe_2Cl$ and $HSiPh_2Cl$, was reacted with **2**, a mixture of all possible structural types ("tantalum-like" **4**−**6**, agostic **3**, rearranged **7**), identified by their characteristic Nb−H and Si−H signals, was formed. Therefore, it is reasonable to assume that a possible pathway for the formation of agostic species $Cp(ArNMe_2Si{-}H\cdots)Nb(PMe_3)(Cl)$ (**3**) in the reaction of **2** with $HSiMe_2Cl$ includes, as the first step, formation of the complex $Cp(ArN)Nb(PMe_3)(H)(SiMe_2Cl)$ of the type **4**−**6** followed by its quick rearrangement into $Cp(ArN)Nb(PMe_3)(Cl)(SiMe_2H)$, an analogue of **7**. Migration of the $SiMe_2H$ group onto the imido group completes the reaction sequences. Such a migration of the silyl group is precedented.[11] Apparently, the particular choice of substituents at the silicon in **4**, **5**, and **7** freezes each stage of this unusual reaction.

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Supporting Information Available: Preparation and characterization details for new compounds and X-ray data (CIF) for **4**. This material is available free of charge via the Internet at http://pubs.acs.org.

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