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Niobocene hydrides with functionalised silyl ligands. Tuning of interligand hypervalent interactions (IHI) M–H → Si–X

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This paper presents syntheses and X-ray structure determinations of a variety of mono- and bis-(silyl) niobocene hydride complexes with functionalised silyl ligands. Complexes of the type [NbCp$_2$(SiR$_3$)H$_2$] (SiR$_3$ = SiMe$_2$Cl (**3**), Si(OEt)$_3$, SiMe$_2$OEt (**4**)) can be prepared conveniently by heating the precursor [NbCp$_2$H$_3$] in the presence of the corresponding silane HSiR$_3$. As the electrondonating ability of the R group increases, the corresponding mono(silyl) derivatives [NbCp$_2$(SiR$_3$)H$_2$] are either unstable (SiR$_3$ = SiMe$_3$) or do not exist at all (SiR$_3$ = SiEt$_3$, Si(OCH$_2$CH$_2$)$_3$N). The previously described bis(silyl) complex [NbCp$_2$(SiMe$_2$H)$_2$H] easily reacts with half an equivalent of iodine, giving the functionalised derivative [NbCp$_2$(SiMe$_2$I)$_2$H] (**10**). A labelling experiment for the analogous reaction with bromine establishes that an electrophile attacks the more accessible Si–H bond rather than the more electron-rich Nb–H bond. Bis(silyl) complexes [NbCp$_2$(SiMe$_2$X)$_2$H] (X = Br (**8**), I (**10**), OTfl (**11**)) can be conveniently prepared by the reaction of [NbCp$_2$(SiMe$_2$Cl)$_2$H] (**2**) with the corresponding silane XSiMe$_3$. Reactions of **2** with fluorinating reagents such as [CPh$_3$][BF$_4$], BF$_3$·OEt$_2$ and AgBF$_4$ do not work well for the synthesis of the compound [NbCp$_2$(SiMe$_2$F)$_2$H]. Nucleophilic chlorine substitution in **2** under the action of lithium amides and alkoxides does not occur, whereas reaction with soft reagents such as MeLi, LiPPh$_2$ and LiSPh leads to the corresponding derivatives [NbCp$_2$(SiMe$_3$)$_2$H] and [NbCp$_2$(SiMe$_2$EPh$_n$)$_2$H] (E = S, n = 1 (**14**); E = P, n = 2 (**15**)). Methanolysis of **10** gives high yields of the derivative [NbCp$_2$(SiMe$_2$OMe)$_2$H] (**18**). The mono(silyl) precursor [NbCp$_2$(SiMe$_2$Cl)H$_2$] (**3**) reacts with LiOEt affording a mixture of [NbCp$_2$(SiMe$_2$OEt)H$_2$] and [NbCp$_2$H$_3$]. Reaction of **3** with LiPPh$_2$ gives high yields of the compound [NbCp$_2$(SiMe$_2$PPh$_2$)H$_2$] (**17**). Reduction of **3** with LiAlH$_4$ results in the dimeric compound [NbCp$_2$H$_2$Al(μ-H)$_2$]$_2$ (**13**). Carrying out this reaction in the presence of an amine leads to the formation of the complex [NbCp$_2$(SiMe$_2$H)H$_2$]. X-Ray structure determinations were performed for the compounds (**10**), (**13**), (**17**), and (**18**). Complex (**10**) has 5 centre–6 electron interligand hypervalent interactions (IHIs) I–Si · · · H · · · Si–I; the analogous IHI O–Si · · · H · · · Si–O in **18** is significantly weaker, whereas **17** has a classical structure. Complex **13** has a cenrosymmetric dimeric structure, with two five-co-ordinate aluminium centres bridged by hydride ligands.

Introduction

Transition metal silyl complexes [L$_n$M–SiR$_3$] are of significant interest[1] as intermediates in metal mediated transformations, such as different silylation reactions[2] and dehydropolymerisation of silanes.[3] The majority of silyl complexes studied bear chemically inert alkyl and aryl substituents at silicon, whereas complexes with functionalised silyl groups are usually restricted to trichloro, trifluoro and trialkoxy derivatives.[4] However, one can expect that other functionalised silyl complexes can be valuable reagents for the synthesis of new silicon-based materials. Apart from this practical aspect we were encouraged by the discovery that transition metal silyl complexes of the type [L$_n$M(H)(SiR$_2$X)], bearing basic hydride ligands, can possess non-classical interligand hypervalent interactions (IHIs) between the hydride and functionalised silyl groups.[5] Complexes [NbCp$_2$(SiMe$_2$X)$_2$H] with X = F, Cl and Br were thoroughly studied by X-ray, neutron diffraction, NMR relaxation and DFT calculation techniques.[5a–d]

To explore further the phenomenon of IHI, we were interested in extending these studies to other functional substituents X at silicon. Synthetic approaches to complexes with functionalised silyl groups are scarce and usually not generally applicable. Here we report our search for convenient routes to the mono- and bis-(silyl) niobocene hydrides bearing SiMe$_2$X groups and present further examples of IHI in these systems. Si–H bond oxidative addition, metathetical (salt elimination) and electrophilic and nucleophilic substitution reactions at the co-ordinated silyl groups were tested and compared.

Results and discussion

1. Oxidative addition route

Oxidative addition of Si–H bonds is one of the most frequently used approaches for the synthesis of transition metal silyls and a variety of Group 5 hydridosilyl derivatives were made by thermolysis of [NbCp$_2$H$_3$] (**1**) in the presence of silanes HSiR$_3$.[6–10] However, in case of electron-donating R groups on the silicon atom the corresponding silyls are unstable. Thus heating **1** with HSiEt$_3$ results in bis(niobocene) [Nb(η^5-Cp)(μ,η^5:η^5-C$_5$H$_4$)(H)]$_2$, although intermediate complexation of the silane to niobium was inferred from a labelling experiment.[6] Our attempts to prepare [NbCp$_2$H$_2$(SiEt$_3$)] under milder conditions[5c] by addition of HSiEt$_3$ to a transient [NbCp$_2$H] generated from [NbCp$_2$(BH$_4$)] under the action of NEt$_3$ again produced only bis(niobocene). Thus we can conclude that [NbCp$_2$H$_2$(SiEt$_3$)] is intrinsically unstable towards silane elimination even at room temperature. The very similar trialkylsilane [NbCp$_2$H$_2$(SiMe$_3$)], appears to be the borderline case: it

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can be made in 35% yield by addition of silane $HSiMe_3$ to **1** at 35 °C but decomposes when excess silane is pumped off.[9] In an analogous fashion, the preparation of $[NbCp_2H_2\{Si(OCH_2CH_2)_3N\}]$ *via* addition of $HSi(OCH_2CH_2)_3N$ to **1** failed. Although the target compound $[NbCp_2H_2\{Si(OCH_2CH_2)_3N\}]$ would be closely related to the known (and stable) tris(alkoxy)-derivative $[NbCp_2H_2\{Si(OEt)_3\}]$,[5c] the essential difference between them is that the former has an intramolecular dative Si–N bond, making the silyl centre more electron-rich. Apparently, the stability of these mono(silyl) systems correlates with the electron density on the silicon atom. Thus the richer the silicon, the less stable is the complex towards silane elimination.

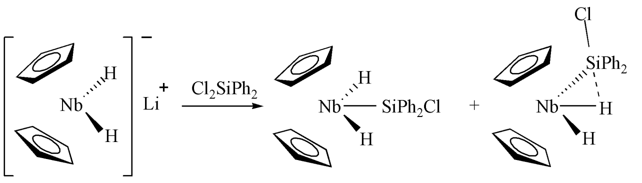
Heating the compounds **1** or $[NbCp_2H_2\{Si(OEt)_3\}]$ with $HSi(OEt)_3$ at 100 °C gives bis(niobocene) as the sole product rather than the target bis(silyl) derivative $[NbCp_2H(Si(OEt)_3)_2]$. This is in contrast to the reactivity of $[NbCp_2(SiMe_2Cl)H_2]$ (**3**) which eliminates dihydrogen under similar conditions and oxidatively adds another equivalent of silane $HSiMe_2Cl$, affording the bis(silyl) $[NbCp_2(SiMe_2Cl)_2H]$.[5c] The essential difference between $[NbCp_2H(Si(OEt)_3)_2]$ and **3** is that the latter exists as a mixture of two isomers, differing in the position of the silyl ligand, with the isomer **3b** having the silyl group in the lateral position in the niobocene bisectral plane and the two hydrides *cis* to each other. By way of contrast $[NbCp_2H(Si(OEt)_3)_2]$ exists only in the form of the central isomer in which the hydrides are separated by the silyl ligand, and the lateral isomer apparently is not available even at high temperature. Therefore, the nature of the functional substituent X at silicon plays a crucial role in this reaction. Previous DFT calculations showed that in the mono(silyl) niobocene dihydrides the interligand hypervalent interactions (IHI) of the type H ··· S–X are stronger for the lateral isomers and, in principle, can outweigh the increased steric repulsion therein.[5c] With the aim of testing the performance of the OR substituent in the $SiMe_2OR$ group we prepared the compound $[NbCp_2H_2(SiMe_2OEt)]$ (**4**) using thermolysis of **1** in the presence of $HSiMe_2OEt$ at 55 °C. Only the central isomer **4a** was observed by ^1H NMR spectroscopy, suggesting that any interligand interaction of the type H–Si ··· OEt is rather weak. Structural data for the related bis(silyl) derivative (*vide infra*) support this conclusion. As for the $Si(OEt)_3$ derivative mentioned above, refluxing **4a** in toluene in the presence of silane, gives only bis(niobocene).

Finally, we report that heating $[NbCp_2H(\eta^2\text{-}C_2H_3Ph)]$ with the silane $HSiMe_2Cl$ in addition to the previously described compound $[NbCp_2H(SiMe_2Cl)_2]$ (**2**, 60%)[5a] also affords $[NbCp_2(SiMe_2Cl)(\eta^2\text{-}C_2H_3Ph)]$ (**5**), isolated as a mixture of *exo*- and *endo*-isomers in 15% yield and characterised by NMR spectroscopy. This by-product most likely arises from styrene elimination from the starting material $[NbCp_2H(\eta^2\text{-}C_2H_3Ph)]$, as was originally postulated by Green *et al.* for the related tin chemistry,[11] and its recombination with the intermediate complex $[NbCp_2(SiMe_2Cl)]$.

2. Metathetical approach

Green and Hughes found that addition of Me_3SiCl to $[NbCp_2H_2]Li$[12] results in a slow reaction leading to a mixture of $[NbCp_2H_2(SiMe_3)]$, $[NbCp_2H(SiMe_3)_2]$ and bis(niobocene).[9] We independently observed the same result. However, we also found that reaction of $[NbCp_2H_2]Li$ with Cl_2SiPh_2 in THF gives the expected product $[NbCp_2H_2(SiPh_2Cl)]$ (**6**) isolated as a mixture of two isomers (central **6a** and lateral **6b**) albeit in a very low yield (eqn. (1)). An improved preparation of this material has been developed.[13] Surprisingly, when this reaction was attempted in hexanes, the main product in the reaction mixture was the complex $[NbCp_2H_2(SiPh_2H)]$ (**7**). This compound exhibits a hydride signal as a singlet at −4.44 ppm and a Si–H signal as a singlet at 5.93 ppm. The origin of the Si–H bond remains unknown. Unfortunately, **7** was contaminated by a significant amount of **6a**,**b** and its isolation in a pure form, by recrystallisation, failed. Apparently the presence of reactive functional substituents at silicon is not quite compatible with the highly reducing conditions of the metathetical route.

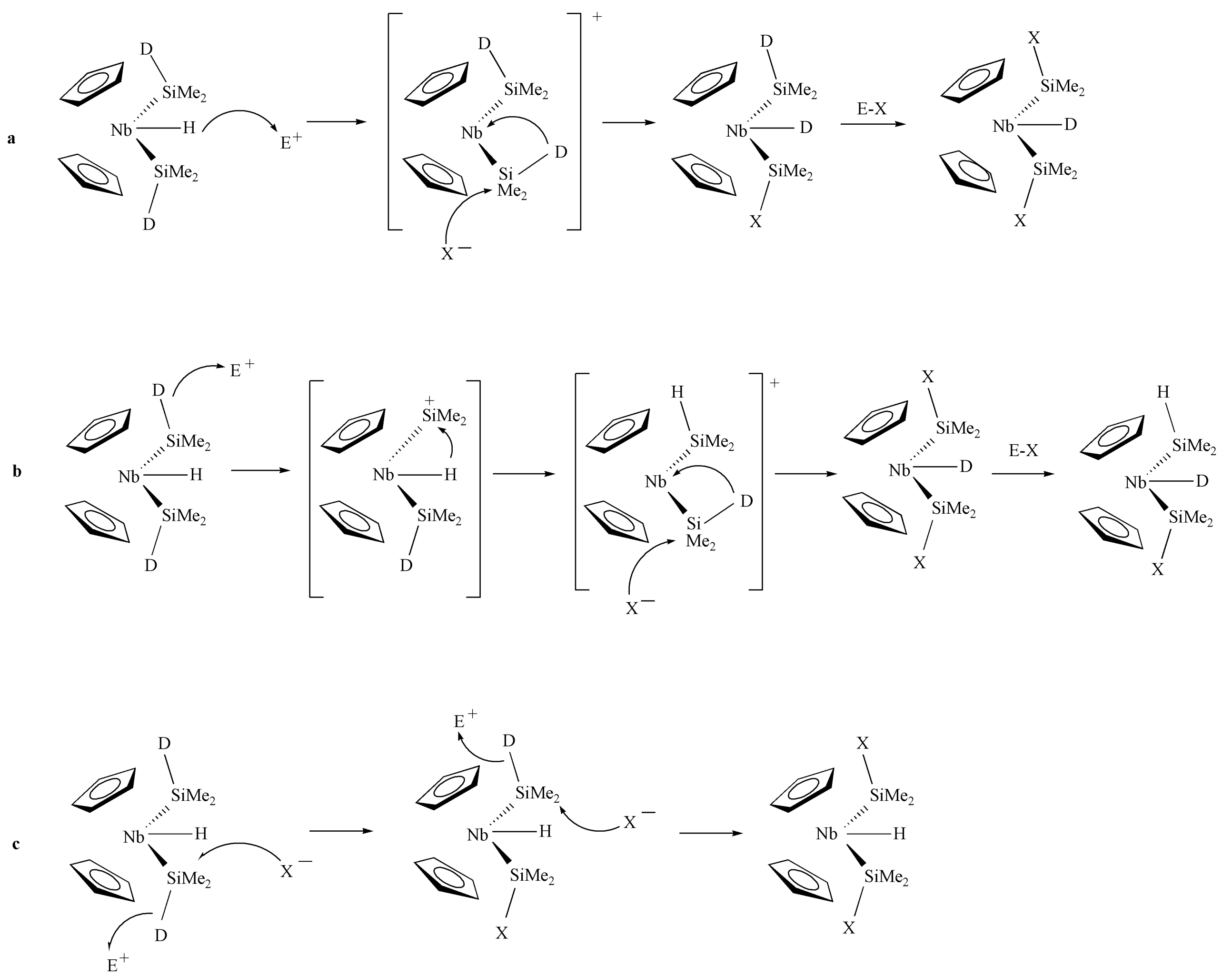
(1)



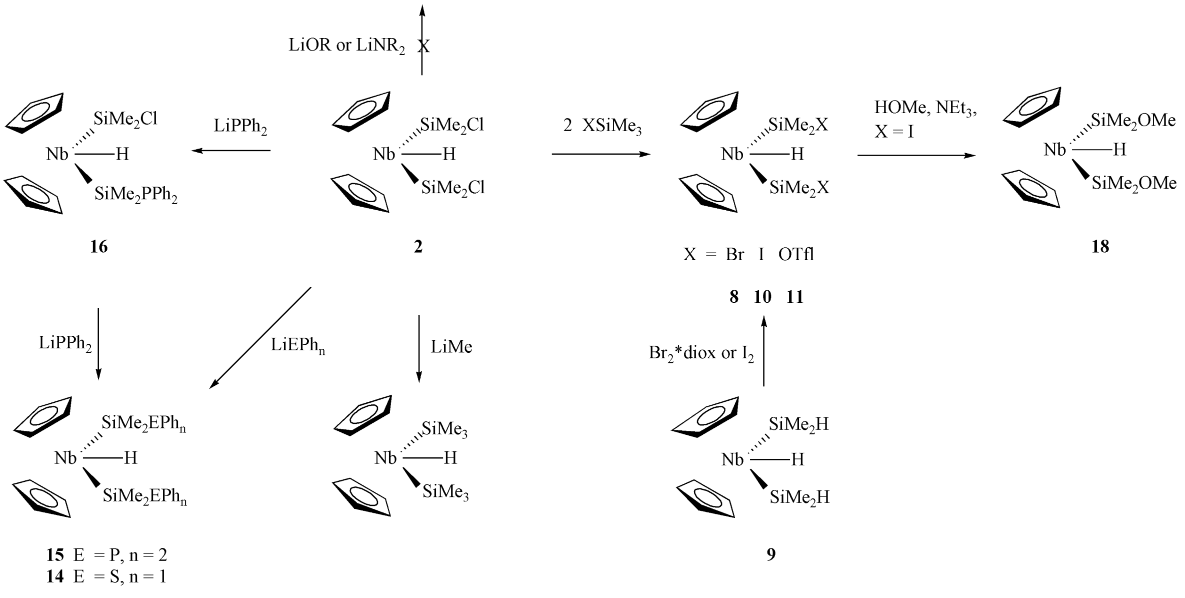
6a **6b**

3. Electrophilic functionalisation of co-ordinated silyls

An elegant way of synthesising halogenosilyl complexes by electrophilic activation of the Si–H bond in silyl derivatives was suggested by Schubert *et al.*[14] We previously used this approach for the preparation of complexes $[NbCp_2(SiXMe_2)_2H]$ (X = F, Br (**8**)) by reacting the compound $[NbCp_2(SiHMe_2)_2H]$ (**9**) with CPh_3BF_4 and $[Br_2{\cdot}diox]$ (diox = 1,4-dioxane), respectively.[5c] Using two equivs of $[Br_2{\cdot}diox]$ led then to only 25% yield of **8**. Wishing to improve the performance we analysed the mechanism of this reaction. In principle, the Si–X bond could arise either from the attack of an electrophile on the Si–H bond or on the Nb–H bond with further rearrangement. In total three routes are possible (Scheme 1). This point has been elucidated by means of labelling experiments. The labelled compound $[NbCp_2(SiDMe_2)_2H]$ ($\mathbf{9_D}$) was prepared in 90% yield analogously to **9** by the reaction of **2** with $LiAlD_4$. $\mathbf{9_D}$ is sufficiently stable for some days, but on keeping at room temperature a slow redistribution of the Nb–H and Si–D atoms occurs. After 2 weeks of reaction 33% deuterium incorporation into the hydride position was achieved. In principle, the H–D exchange could proceed *via* $HDSiMe_2$ elimination followed by oxidative addition into the Si–D bond. However, an intramolecular route cannot be excluded taking into account Berry's report that isomerisation of the lateral isomer of $[TaCp_2H_2(SiR_3)]$ into the central one occurs without silane elimination.[7b] In our experiments a reaction of the complex $\mathbf{9_D}$ with an equivalent of $[Br_2{\cdot}diox]$ gave only the compound **8** in high yield. Careful integration of the hydride region of the ^1H NMR spectrum revealed no significant deuterium incorporation. It is noteworthy that some small amount of the mono(brominated) complex $[NbCp_2(SiDMe_2)(H)(SiMe_2Br)]$ also observed in the NMR spectrum of the reaction mixture did not exhibit any Si–H hydrogen signal. Among the three mechanisms shown in Scheme 1 only route **c** does not allow any deuterium incorporation into the hydride position upon the reaction of $\mathbf{9_D}$ with $[Br_2{\cdot}diox]$. This route involves the interaction of an electrophile with the Si–D bond, affording the Si–X derivative, followed by the attack on the second Si–D bond by DX thus released, eventually giving the disubstituted product. Therefore routes **a** and **b** do not contribute significantly to the formation of **8** and all reaction steps occur at the silicon–hydrogen bond. This result is surprising, taking into account the greater basicity of the Nb–H bond, and is most likely caused by its steric protection by the two bulky silyl groups. Another conclusion of this study is that the acids HX are very effective halogenating agents in this reaction and therefore only one equivalent of halide X_2 is required. This conclusion is supported by the preparation in 70% isolated yield of the bromo derivative **8** by reacting **9** with exactly one equivalent of $[Br_2{\cdot}diox]$ and also by the synthesis of the new iodo derivative $[NbCp_2(SiIMe_2)_2H]$ (**10**). Reaction of **9** with 2 equivs of I_2 gives **10** in only 17% yield. The lower yield of **10** in comparison with **8** by using this stoichiometry is most likely caused by the greater decomposition of the product under the action of excess iodine and the more acidic HI. However, with an exact 1 : 1 stoichiometry the compound **10** was obtained in 43% isolated yield (Scheme 2). The identity of **10**



Scheme 1



Scheme 2

was established by IR and NMR spectroscopies and confirmed by X-ray diffraction study (*vide infra*).

The most convenient route to complexes **8** and **10** consists of the reaction of the readily available bis(chlorosilyl) compound $[NbCp_2H(SiClMe_2)]$ (**2**) with halogenosilanes Me_3SiX (X = Br, I) (Scheme 1). Thus, **2** reacts readily with Me_3SiI at room temperature, giving a high yield of **10**. Reaction of **2** with Me_3SiBr is slow under these conditions, affording a 10 : 1 mixture of **2** and $[NbCp_2(SiClMe_2)H(SiMe_2Br)]$ after ten days. However, heating at 80 °C for some days allows for the preparation of **8** in 70% yield (Scheme 2). The triflate derivative $[NbCp_2H(SiMe_2OTfl)_2]$ (**11**) was prepared analogously to **10** by $Me_3SiOTfl$ addition to **2** at room temperature (68% yield). No reaction, even after heating at 60 °C, was observed between **2** and Me_3SiN_3. Attempted reaction of $[NbCp_2(SiClMe_2)H_2]$ (**3**) with Me_3SiI resulted in fast decomposition.

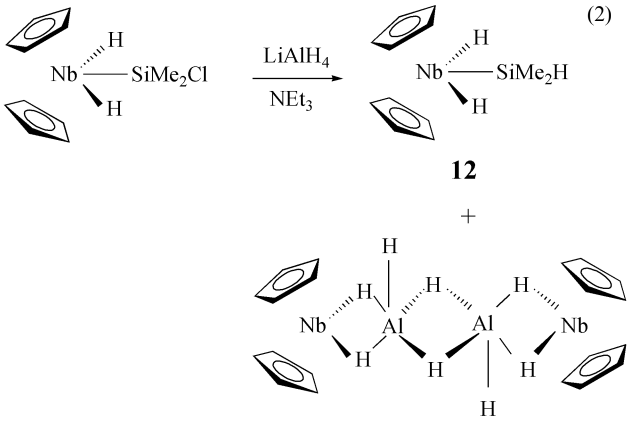
Chloride appears to be a poorer leaving group than hydride in electrophilic substitution. Thus no chloride abstraction occurs under the action of the trityl reagent $[CPh_3][BF_4]$ or $[BF_3{\cdot}OEt_2]$ on **2**. Reaction with $AgBF_4$ proceeds slowly and results in a mixture of starting compound **2**, $[NbCp_2(SiClMe_2)(H)(SiFMe_2)]$ and $[NbCp_2(H)(SiFMe)_2]$, identified by ^1H NMR spectroscopy. This reaction is much less convenient for the synthesis of $[NbCp_2(H)(SiFMe)_2]$ than the previously described reaction of **2** with $[CPh_3][BF_4]$.[5c] Fast decomposition and formation of a silver mirror is observed when the dihydride mono(silyl) **3** is mixed with $AgBF_4$.

4. Nucleophilic functionalisation of co-ordinated silyls

Bis(silyl) complex $[NbCp_2(SiMe_2Cl)_2H]$ (**2**) and mono(silyl) complex $[NbCp_2(SiMe_2Cl)H_2]$ (**3**) present themselves as "natural" precursors for nucleophilic chloride substitution by the desired functional groups X. However, their interaction with lithium alkoxy and amide reagents was not successful. No reaction of **2** with LiOMe, LiOEt, $LiNH^tBu$, LiNHPh or $LiNEt_2$ was observed. In contrast, the mono(silyl) compound **3** reacts with these reagents, giving mixtures containing noticeable amounts of the trihydride $[NbCp_2H_3]$ (**1**). Reaction of **3** with LiOEt, however, does give high yields of the desired product $[NbCp_2(SiMe_2OEt)H_2]$ along with a small amount of **1**. Formation of **1** is most likely caused by the niobocene anion $[NbCp_2H_2]^-$ rather than chloride substitution at the silicon centre. This transition metal anion displacement has precedents, for example, in the reaction of $[FeCp(CO)_2(SiHMe_2)]$ with $P(OMe)_3$.[15]

Attempted synthesis of the compound $[NbCp_2H_2(SiHMe_2)]$ (**12**) by the method used for preparing **9**, namely by chloride for hydride substitution, also met with little success. Thus, reaction of $NaBH_4$ with **3** gives $[NbCp_2H_3]$ and the known borohydride complex $[NbCp_2BH_4]$ whereas treatment with $LiAlH_4$ gives the related hydride $[Cp_2Nb(\mu\text{-}H)_2Al(\mu\text{-}H)H]_2$ (**13**). The molecular structure of the latter long-known compound[16] has been eventually established by us and is reported here. In contrast to the mononuclear boron congener, it is a hydride-bridged dimer, which accounts for its low solubility in aromatic solvents and diethyl ether. Formation of these Group 3 substituted products could be again caused by $[NbCp_2H_2]^-$ displacement reactions, or alternatively they may result from the reactions of the Nb–Si bonds of the initially formed complex **12** with the Lewis acids EH_3 (E = B, Al), emerging in the reaction mixture. The latter possibility appears to be more likely because carrying out the reaction of **3** with $LiAlH_4$ in the presence of a Lewis base NEt_3 does produce **12** as a mixture with **13** (eqn. (2)). It is interesting that **12** also emerges as the result of thermal decomposition of $[NbCp_2(SiHMe_2)_2H]$ (**9**). Partial conversion to **12** was observed after heating a C_6D_6 solution of **9** at 60 °C in a sealed NMR tube. The silane product of this formal silylene extrusion process is the disilane $(HSiMe_2)_2$ identified by its Si–H signal (septet at 3.92 ppm, $J_{H\text{–}H} = 4.2$ Hz) and Me-group signal (doublet at −0.4 ppm, $J_{H\text{–}H} = 4.2$ Hz). Longer thermolysis at 100 °C proceeds further to give eventually the bis(niobocene). Analogously, thermolysis of deuterated compound $\mathbf{9_D}$ at 100 °C for 2.5 h gives a mixture of $\mathbf{9_D}$ and $\mathbf{12_D}$, in which deuterium is distributed among the niobium and silicon positions, and partially (about 50%) deuterated disilane $(H\{D\}SiMe_2)_2$. Apparently, deuterium/proton scrambling among the Nb–H and Si–H positions in $\mathbf{9_D}$ occurs prior to disilane elimination which does not allow us to make any conclusion about the mechanism of this transformation. Unexpectedly, compound **12** is also formed by the reaction of LiI with complex $[NbCp_2(SiMe_2Cl)H_2]$ (**3**), the other product being bis(niobocene).

Chloride displacement by iodide was attempted also on **2**. Reaction with LiI in ether proceeds slowly affording a mixture of the mono(substituted) product $[NbCp_2(SiClMe_2)H(SiMe_2I)]$ and **10**. A mixture of $[NbCp_2(SiClMe_2)H(SiMe_2Br)]$ and **8** is formed after two days reaction of **2** with $MgBr_2$ in ether. No Si–H bond formation products were observed in these transformations. These alkali metal salt reactions are of no synthetic significance since a considerable decomposition accompanied by the formation of a toluene insoluble material is observed. No reaction of **2** with NaN_3 in THF occurs.



Although hard nucleophilic reagents are not effective in the chloride substitution of **2** and **3**, we found that soft reagents exhibit a better performance. Thus MeLi easily reacts with **2** giving the known compound $[NbCp_2H(SiMe_3)_2]$.[9] LiSPh (2 equivs) does not react with **2** in ether because of the relative insolubility of the lithium thiolate, but nevertheless smoothly reacts in THF giving the disubstituted compound $[NbCp_2(SiMe_2SPh)_2H]$ (**14**) in almost quantitative yield (Scheme 2). The analogous reaction with $LiPPh_2$ proceeds even in ether and affords the compound $[NbCp_2(SiMe_2PPh_2)_2H]$ (**15**). The course of this reaction was monitored by NMR spectroscopy and intermediate formation of the mono(substituted) product $[NbCp_2(SiClMe_2)H(SiMe_2PPh_2)]$ (**16**) was identified. In the ^1H NMR spectrum of the reaction mixture two different methyl groups of **16** resonate closely to the corresponding signals of **2** and **15** (singlet at 0.60 ppm and doublet at 0.47 ppm, $^3J_{H\text{–}P} = 5.0$ Hz) but the hydride signal at −4.33 ppm lies in between those of **2** and **15** (−5.15 ppm and −3.45 ppm, respectively). Unfortunately, **16** cannot be made by the reaction of exactly one equivalent of $LiPPh_2$ with **2** as a mixture of **15**, **16** and unreacted **2** is formed. The monosilyl **3** also reacts with $LiPPh_2$ giving the substituted product $[NbCp_2H_2(SiMe_2PPh_2)]$ (**17**). An X-ray quality crystal of this compound was grown and the molecular structure determination performed (*vide infra*).

We have already mentioned that complex **2** is surprisingly stable to water and alcohols.[5c] Stirring **2** in wet THF under argon requires some days until a brown precipitate of decomposition products forms. No new compound was identified in the THF soluble part by NMR. Reaction of **2** with EtOH in the presence of amine proceeds very slowly and only 15% conversion into $[NbCp_2H(SiMe_2OEt)_2]$ was observed after two weeks. Keeping the reaction mixture for longer results in a mixture of other as yet unidentified products. Complex **10**, having a much better leaving group such as iodide, is more reactive. In the presence of an amine it readily reacts with a slight excess of MeOH giving the substitution product $[NbCp_2H(SiMe_2OMe)_2]$ (**18**) in almost quantitative yield (Scheme 2). The structure of this compound was confirmed by X-ray diffraction analysis (see next section).

5. X-Ray structure determinations

The molecular structure of $[NbCp_2(SiMe_2I)_2H]$ (**10**) is shown in Fig. 1. To the best of our knowledge this is the first transition metal iodosilyl derivative characterised by X-ray structure analysis. Determination of the structure of this compound completes our study of the whole series of symmetrical halogen

Table 1 Selected molecular parameters for complexes [$NbCp_2(SiXMe_2)_2H$] (X = F, Cl (**2**), Br (**8**), I (**10**))

Compound	Nb–Si/Å	Si–X/Å	Si–Nb–Si/°	Si ··· H/Å
[$NbCp_2(SiFMe_2)_2H$]	2.618(1) 2.622(1)	1.652(3) 1.644(3)	105.57(4)	1.98
[$NbCp_2(SiClMe_2)_2H$]	2.597(1)	2.163(1)	104.27(5)	2.06
[$NbCp_2(SiBrMe_2)_2H$]	2.604(2)	2.349(2)	103.37(7)	2.05
[$NbCp_2(SiIMe_2)_2H$]	2.595(3)	2.590(3)	104.4(1)	2.07

Table 2 Comparison of the silicon–halogen bond lengths in silanes and in the niobocene silylhydrido complexes

Compound	Si–X bonds in silanes/Å	Lengthening of the Si–X bond in complexes/Å	Lengthening of the Si–X bond in complexes (%)
[$NbCp_2(SiFMe_2)_2H$]	1.550	0.102	6.6
[$NbCp_2(SiClMe_2)_2H$]	2.020	0.143	7.1
[$NbCp_2(SiClMe_2)H_2$]	2.020	0.150	7.4
[$NbCp_2(SiBrMe_2)_2H$	2.235[a]	0.114	5.1
[$NbCp_2(SiIMe_2)_2H$]	2.537[b]	0.053	2.1

[a] Si–Br bond length in Me_3SiBr;[17] average Si–Br distance for 4 structures from CCDC[18] is 2.250 Å. [b] Average for 5 structures from CCDC.[18]

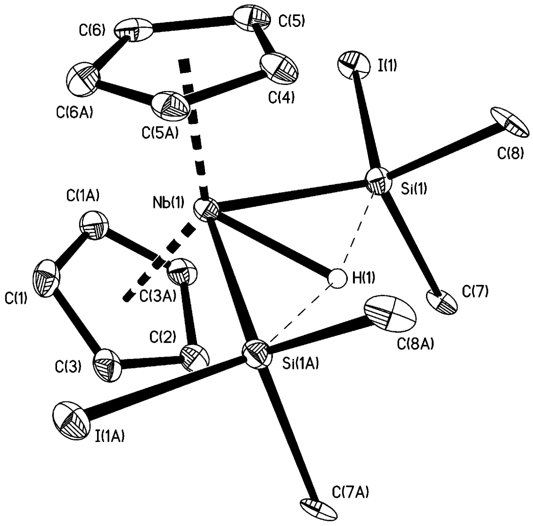


Fig. 1 Molecular structure of **10**. Hydrogen atoms apart from hydrides are omitted for clarity.

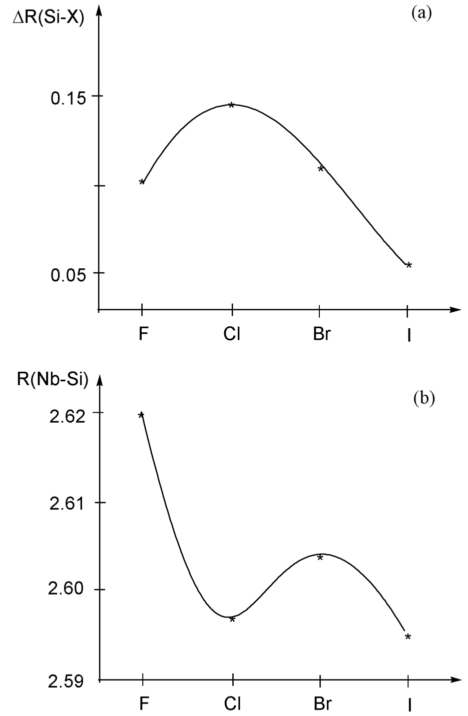


Fig. 2 Dependence of the Si–X and Nb–Si bond length on the halogen X. (a) Relative lengthening of the Si–X bond in complexes [$NbCp_2(SiMe_2X)_2H$] in comparison with silanes X–SiR_3 *versus* halogen position in the Periodic Table. (b) Nb–Si bond length in complexes [$NbCp_2(SiMe_2X)_2H$] *versus* halogen position in the Periodic Table.

substituted bis(silyl) niobocenes hydrides of the type [$NbCp_2(SiMe_2X)_2H$] (X = F, Cl, Br, I). The structures of the fluoro-, chloro- and bromo-analogues have been reported elsewhere.[5c] The most important molecular parameters for the complexes [$NbCp_2(SiMe_2X)_2H$] are collected in Table 1. The Nb–Si bond length in **10** is close to that in the chloro- and bromo-substituted analogues, whereas the Si–Nb–Si bond angle and the value of the Si–H contact does not differ much for all complexes of this series. The observed Si–I bond (2.590(3) Å) is longer than the structurally characterised Si–I bond in tetra-co-ordinate silanes (range 2.487–2.574 Å, mean 2.537 Å for five structures). The data for the Si–X bond length in complexes [$NbCp_2(SiMe_2X)_2H$] and in corresponding tetra-co-ordinate silanes are compared in Table 2. It can be seen that lengthening of the Si–X bond in silyl complexes relative to the parent silanes $XSiMe_3$ forms an inverted V-shaped function on going down the halogen group (Fig. 2a). This trend is opposite to the change of the Nb–Si bond lengths in the series X = F, Cl, Br, where the Nb–Si bond lengths form a V-shaped function with respect to the halogen position in the Periodic Table (Fig. 2b). This irregularity was discussed previously in terms of the superposition of two factors responsible for the shortening of the Nb–Si and relative lengthening of the Si–X bonds, namely due to the operation of Bent's rule and interligand hypervalent interactions (IHI).[5c] The importance and contributions of these factors to the Nb–Si and Si–X parameters change in opposite directions on going down the halogen group. Summation of two monotonic functions with opposite slopes creates this V-shaped curve (or inverted V-shaped curve in the case of the Si–X distance). The Si–I bond length follows the trend shown in Fig. 2a, while the Nb–Si bond length is less than expected (Fig. 2b). This can be due to crystal packing effects, which for the large iodine group could shorten both the Nb–Si and Si–I bonds.

The structure of the related methoxy substituted derivative **18** has several different features (Fig. 3 and Table 3), signifying a substantial decrease in interligand interactions. Compared with the halogenosilyl analogues, in this compound there is a noticeable elongation of the Nb–Si bonds to 2.624(1) and 2.629(1) Å, which are however still shorter than the range usually observed for alkyl and aryl substituted silyl derivatives of niobo- and tantalo-cenes (2.646–2.669(1) Å)[6–8,19] and close to the Ta–Si bond length in [$Cp_2Ta(SiHMe_2)_2H$] (2.624(2) and 2.633(2) Å).[20]

Table 3 Selected molecular parameters (bonds in Å, bond angles in °) for the compound $[NbCp_2(SiMe_2OMe)_2H]$ **18**

Nb(1)–Si(1)	2.6240(9)	Nb(1)–Si(2)	2.6285(9)
Si(1)–O(1)	1.696(3)	Si(2)–O(2)	1.691(2)
O(1)–C(15)	1.414(5)	O(2)–C(16)	1.419(5)
Nb(1)–H(1)	1.88(5)		
Si(1)–Nb(1)–Si(2)	108.20(3)		
Si(1)–Nb(1)–H(1)	55.4(15)	Si(2)–Nb(1)–H(1)	52.8(15)
O(1)–Si(1)–Nb(1)	109.83(9)	O(2)–Si(2)–Nb(1)	108.79(9)

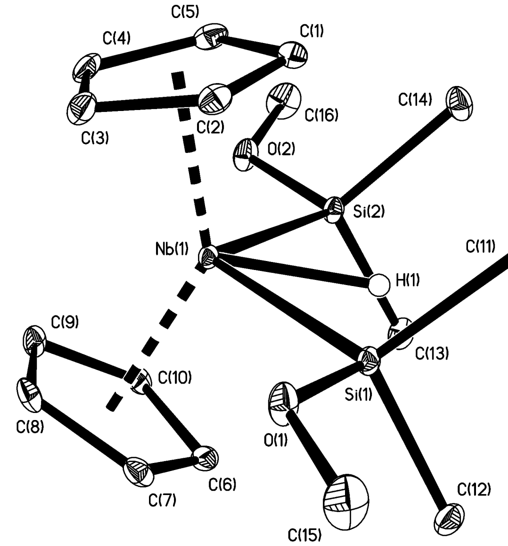


Fig. 3 Molecular structure of **18**. Hydrogen atoms apart from hydride are omitted for clarity.

Table 4 Selected molecular parameters (bonds in Å, bond angles in °) for the compound $[NbCp_2H_2(SiMe_2PPh_2)]$ (**17**)

Nb(1)–Si(1)	2.6491(4)	P(1)–Si(1)	2.3065(5)
Nb(1)–H(1′)	1.65(2)	Nb(1)–H(2′)	1.70(2)
P(1)–C(11)	1.842(2)	P(1)–C(17)	1.849(2)
H(1′)–Nb(1)–H(2′)	118.1(10)	P(1)–Si(1)–Nb(1)	111.08(2)
Si(1)–Nb(1)–H(1′)	54.1(7)	Si(1)–Nb(1)–H(2′)	64.2(7)

Table 5 Selected molecular parameters (bonds in Å, bond angles in °) for the compound $[NbCp_2(AlH_4)]_2$ (**13**)

Nb(1)–Al(1)	2.621(1)	Al(1)–Al(1′)	2.683(2)
Nb(1)–H(3)	1.59(3)	Nb(1)–H(4)	1.69(3)
Al(1)–H(1)	1.64(2)	Al(1)–H(2)	1.48(3)
Al(1)–H(3)	1.98(3)	Al(1)–H(4)	1.99(3)
Al(1)–Nb(1)–H(3)	49.0(12)	Al(1)–Nb(1)–(H)4	49.4(12)
H(3)–Nb(1)–H(4)	98.4(17)	Nb(1)–Al(1)–Al(1′)	130.66(5)
Nb(1)–Al(1)–H(1)	118.4(9)	Al(1)–Al(1′)–H(1)	40.0(8)
Nb(1)–Al(1)–H(2)	128.4(11)	Al(1′)–Al(1)–H(2)	100.6(11)
H(1)–Al(1)–H(2)	104.0(14)	Nb(1)–Al(1)–H(3)	37.2(10)
Al(1′)–Al(1)–H(3)	110.0(10)	H(1)–Al(1)–H(3)	126.6(13)
H(2)–Al(1)–H(3)	127.9(15)	Nb(1)–Al(1)–(H4)	40.0(10)
Al(1′)–Al(1)–H(4)	132.1(10)	H(1)–Al(1)–H(4)	96.5(13)
H(2)–Al(1)–H(4)	111.5(15)	H(3)–Al(1)–H(4)	77.2(14)

The increased Si–Nb–Si bond angle of 108.20(3)° lies between the values found for $[NbCp_2(SiMe_2X)_2H]$ (103–106°, see Table 1) and classical compounds $[NbCp_2(SiMe_2Ph)_2H]$ (110.81(6)°) and $[TaCp_2(SiMe_2H)_2H]$ (109.90(7)°), which also suggests diminished IHI. This conclusion allows us to understand the absence of the lateral isomer in the case of the alkoxy derivative $[NbCp_2H_2(SiMe_2OEt)]$ and suggests that the electronegativity of the functional group at silicon is not the only prerequisite for the occurrence of a strong interligand hypervalent interaction. The ability of the substituent to serve as a good leaving group is also important.[21] The Si–O bond of 1.696(3) Å in **18** is less than that in five-co-ordinate silicon compounds having an alkoxy group in the apical position (mean 1.785 Å from the range 1.656–1.855 Å for 20 structures from the CCDC).[18] However, it is still elongated in comparison with the normal silicon–oxygen covalent bond (1.640 Å, average for 1237 structures with $Si–OC(sp^3)$ bonds in tetra-coordinated organosilanes;[18] Δ = 0.056 Å, 3.4%) and the Si–O bonds in two other structurally characterised compounds with SiR_2OR fragments, namely the complexes $[Cp(CO)_2Fe\{SiMe(OMe)(C_6H_4\{CH_2NHMe_2\}\text{-}2)\}][PF_6]$ (1.671 Å)[22] and $[Ir(acac)(PCy_3)_2(\eta^2\text{-}SiPh_2OCH(OCH_3)C(CHCO_2CH_3))]$ (1.656(4) Å).[23] This elongation can be either due to the stronger electron donating ability of the $[NbCp_2]$ fragment (*i.e.* manifestation of Bent's rule) or the presence of a weak H ··· Si–O interaction, or more likely is due to the simultaneous operation of both effects.

The molecular structure of $[NbCp_2H_2(SiMe_2PPh_2)]$ (**17**) is shown in Fig. 4 and selected molecular parameters are collected in Table 4. This is a typical trisubstituted niobocene structure with a centrally positioned main-group element substituent. The phosphorus centre is pyramidal, with the sum of the bond angles being equal to 312.35°. The Nb–Si bond length (2.6491(4) Å) is normal for an organosilicon group having only electron-donor substituents at the silicon atom. The P–Si bond length of 2.3065(5) Å is close to the sum of the covalent radii (2.27 Å). In another transition metal silyl derivative with a terminal phosphido substituent at silicon, the compound $[Cp(CO)_2Fe\{SiMeBu^t(PH\{SiF(2,4,6\text{-}Pr^i_3C_6H_3)_2\})\}]$, the Si–P bond is almost the same (2.297 Å).[24] In the complex $[Cp(CO)_2W(\eta^2\text{-}SiMe_2PPh\{N(SiMe_3)_2\})]$, where the silicon-bound phosphido group is also co-ordinated to the metal *via* the phosphorus lone pair, the Si–P bond is 2.197(3) Å.[25] For comparison, in the phosphido substituted silylene complex the direct Si–P single bond is 2.294(1) Å,[26] whereas in the phosphino stabilised silylene complex the donor–acceptor Si–P bond is elongated to 2.364(1) Å.[27]

The molecular structure of the binuclear complex $[Cp_2Nb(\mu\text{-}H)_2AlH(\mu\text{-}H)]_2$ (**13**) is shown in Fig. 5 and selected molecular parameters are given in Table 5. For a long time complex **13** was believed to be monomeric in analogy with the structurally characterised complex $[NbCp_2(\mu\text{-}H)_2(BH_2)]$.[28] Its dimeric structure is unequivocally established in this study. Two aluminium hydride units are associated *via* two hydride bridges, with each unique aluminium centre being five-coordinate. The co-ordination environment of aluminium can be described as pseudo-square-pyramidal. This structural motif is abundant[29] in Group 4 metallocene chemistry[30] and in other complexes[31] but for the Group 5 metallocenes the only relevant example is the ditantalum complex $[TaCp_2(\mu\text{-}H)_2AlH(\mu\text{-}OBu)]_2$ where the two units are bridged by two OBu^n groups rather than hydrides.[32] A related alkoxy-bridged species is the compound $[Ta(dmpe)_2(\mu\text{-}H)_2Al(OC_2H_4OMe)(\mu\text{-}OC_2H_4OMe)]_2$.[33] In **13** all hydride atoms were located from difference Fourier maps and refined isotropically. The Nb–H distances are 1.59(3) and 1.69(3) Å, whereas the Al–H bond to the bridging hydrides are 1.98(3) and 1.99(3) Å to the niobium bridges and 1.64(2) Å to the aluminium bridge. In $[TiCp^*_2(\mu\text{-}H)_2AlH(\mu\text{-}H)]_2$[30b] the corresponding Al–H bond values are 1.67(1) Å (average of two distances) and 1.56(1) Å and similar parameters were observed for $[ZrCp^*_2(H)(\mu\text{-}H)_2AlH(\mu\text{-}H)]_2$[30c] (1.65(7) Å for the Al–H(Zr) bond and 1.75(6) Å for the Al–H(Al) bond). In contrast, the Al–H bond to the terminal hydride in **13** is much shorter (1.48(3) Å) and can be compared to the terminal Al–H bonds in $[TaCp_2(\mu\text{-}H)_2AlH(\mu\text{-}OBu)]_2$ (1.39 Å), $[TiCp^*_2(\mu\text{-}H)_2AlH(\mu\text{-}H)]_2$ (1.51(1) Å) and $[ZrCp^*_2(H)(\mu\text{-}H)_2AlH(\mu\text{-}H)]_2$ (1.52(6) Å). The Nb–Al contact of 2.621(1) Å is somewhat shorter than in the tantalum product (2.671(4) Å), probably due to the different substituents at the aluminium.

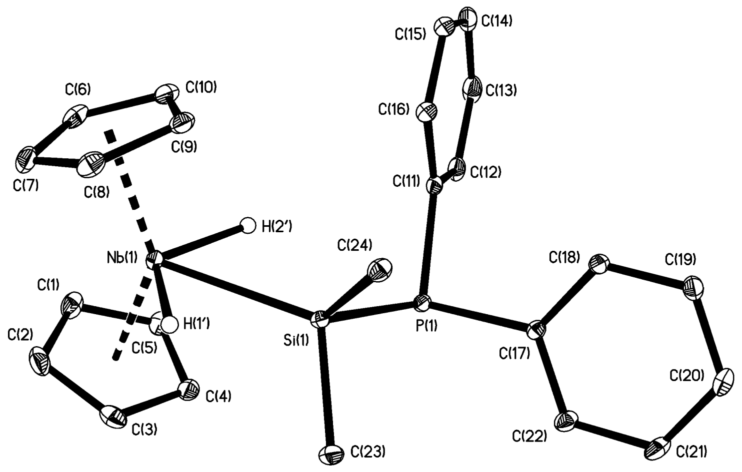


Fig. 4 Molecular structure of **17**. Hydrogen atoms apart from hydrides are omitted for clarity.

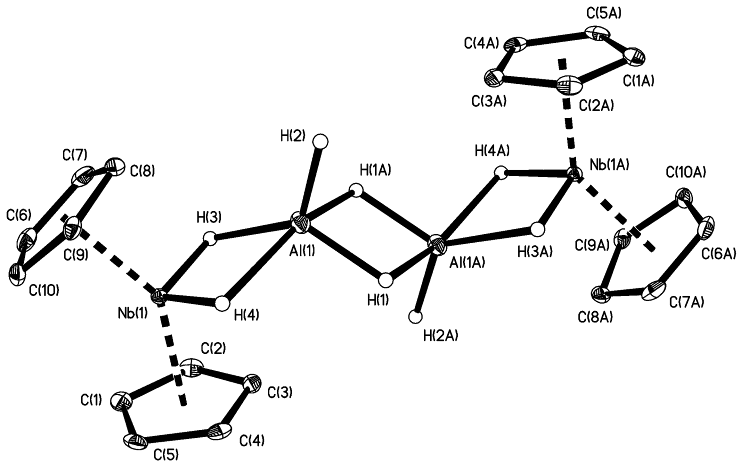


Fig. 5 Molecular structure of **13**. Hydrogen atoms apart from hydrides are omitted for clarity.

Conclusions

Transition metal complexes with functionalised silyl groups can be made by a variety of methods, the success of which depends on the choice of the functionalised substituent. The bis(silyl) niobocene complexes [$NbCp_2(SiMe_2X)_2H$] can be equally well made either by electrophilic or nucleophilic functionalisation reactions. The most efficient approach to the derivatives with X = F, Br, I is electrophilic substitution at the Si–H bond in the precursor compound [$NbCp_2(SiMe_2H)_2H$]. Complexes with X = Br, I, OTfl can also be made by chlorine substitution in [$NbCp_2(SiMe_2H)_2H$] by $XSiMe_3$. Sulfur and phosphorus substituted complexes [$NbCp_2(SiMe_2EPh_n)_2H$] (E = S, $n = 1$; E = P, $n = 2$) and also [$NbCp_2(SiMe_3)_2H$] can be made by nucleophilic chlorine displacement in the compound [$NbCp_2(SiMe_2Cl)_2H$]. We found that chlorine substitution does not work for hard nucleophiles such as amides and alkoxides. Also this reaction does not work well with alcohol for making the alkoxy derivatives [$NbCp_2(SiMe_2OR)_2H$], but analogous substitution of iodine to give [$NbCp_2(SiMe_2OMe)_2H$] readily occurs under the action of methanol. Synthesis of mono(silyl) dihydrides [$NbCp_2(SiMe_2X)H_2$] turned out to be more difficult. Attempted electrophilic substitutions lead to decomposition, whereas nucleophilic substitution can be used only for soft reagents such as phosphides, alkyls, *etc.* In this case, oxidative addition of silanes can be helpful provided the silane $HSiR_2X$ is available. For example, silyls [$NbCp_2(SiMe_2OEt)H_2$] and [$NbCp_2(Si\{OEt\}_3)H_2$] were made by this method. Approaches based on the transition metal anion [Cp_2NbH_2]$^-$ met with little success due to concurrent reactions.

Significant I–Si–H(Nb)–Si–I interligand hypervalent interactions (IHI) were found by X-ray structure determination for the iodine derivative [$NbCp_2(SiMe_2I)_2H$] but not for [$NbCp_2(SiMe_2OMe)_2H$]. The latter compound is intermediate between the non-classical halogeno-substituted complexes [$NbCp_2(SiMe_2X)_2H$] and classical alkyl substituted compounds [$NbCp_2(SiR_3)_2H$]. The phosphorus derivative [$NbCp_2(SiMe_2PPh_2)H_2$] is classical. Summarising this stage of study of IHI, we can conclude that this type of interligand interaction is more pronounced for functional substituents that are both highly electronegative and good leaving groups.

Experimental

General methods

All manipulations were carried out using conventional Schlenk high vacuum and argon techniques. Solvents were dried over sodium or sodium benzophenone ketyl and distilled into the reaction vessel by high vacuum gas phase transfer. NMR spectra were recorded on a Varian VXR-400 spectrometer (^1H, 400 MHz; ^{13}C, 100,4 MHz). IR spectra were obtained in Nujol with a FTIR Perkin-Elmer 1600 series spectrometer. Silanes were purchased from Aldrich. [Cp_2NbH_3] was prepared according to a literature method.[16]

Preparation of [$NbCp_2(C_2H_3Ph)(SiMe_2Cl)$]

A solution of [$NbCp_2H_3$] (1.67 g, 1.42 mmol) in toluene was treated with a five-fold excess styrene. Next day all volatile materials were pumped off and the residue was redissolved in 50 mL of toluene. A four-fold excess of the silane $HSiMe_2Cl$ was added and the mixture heated at 65–70 °C for 3 h. All volatiles were removed *in vacuo* and the residue extracted with ether, filtered and dried. The ^1H NMR spectrum in $CDCl_3$ showed a mixture of $[NbCp_2(SiMe_2Cl)_2H]$ and $[NbCp_2(C_2H_3Ph)(SiMe_2Cl)]$ in the ratio 5 : 2. The mixture was dissolved in ether (≈ 100 mL) and left at −25 °C. The cold solution was filtered from the precipitate and dried to give 0.97 g of a mixture of $[NbCp_2(SiMe_2Cl)_2H]$ and $[NbCp_2(C_2H_3Ph)(SiMe_2Cl)]$ in the ratio 10 : 1. Yield of the precipitate was 0.974 g. According to the ^1H NMR spectrum in $CDCl_3$ it consisted of $[NbCp_2(SiMe_2Cl)_2H]$ and $[NbCp_2(C_2H_3Ph)(SiMe_2Cl)]$ in the ratio 7 : 6. Complete isolation of $[NbCp_2(C_2H_3Ph)(SiMe_2Cl)]$ from $[NbCp_2(SiMe_2Cl)_2H]$ was not achieved. ^1H NMR (C_6D_6): 4.46 (s, 5, Cp), 4.20 (s, 5, Cp), 2.39 (pseudo-triplet, $J_{H–H}$ = 12.2 Hz, 1, PhCHCH_2), 1.08 (dd, $J_{H–H}$ = 6.8 Hz, $J_{H–H}$ = 12.6 Hz, 1, PhCHCH_2), 0.96 (s, 3, SiCH_3), 0.90 (s, 3, SiCH_3), 0.80 (dd, $J_{H–H}$ = 6.8 Hz, $J_{H–H}$ = 13.0 Hz, 1, PhCHCH_2).

Preparation of $[NbCp_2H_2(SiMe_2OEt)]$ (5)

A solution of 0.30 mL (2.18 mmol) of $HSiMe_2OEt$ in 5 mL of toluene was added to 10 mL of a toluene solution of $[NbCp_2H_3]$ (0.321 g, 1.42 mmol). The mixture was heated for 5 h at 55 °C. The solution was filtered and volatiles removed leaving a yellow product. Yield of the crude material: 0.371 g. This was recrystallised from ether giving 0.27 g (.83 mmol, 58%) of **5**. ^1H NMR (C_6D_6): 4.66 (s, 10, Cp), 3.79 (q, $J_{H–H}$ = 6.4 Hz, 2, OCH_2), 1.31 (t, $J_{H–H}$ = 6.4 Hz, 3, CH$_2$CH_3), 0.66 (s, 6, SiCH_3), −5.38 (s, 2, Nb–H). $C_{14}H_{23}NbOSi$: calcd C 51.22, H 7.06; found: C 50.89, H 7.00%.

Thermolysis of 5 with $HSiMe_2OEt$

A mixture of 0.20 g (0.61 mmol) of $[NbCp_2H_2(SiMe_2OEt)]$ and 0.23 mL (1.67 mmol) of $HSiMe_2OEt$ were refluxed in 10 mL of toluene for 3 h. The solution was filtered and volatiles removed *in vacuo*. The ^1H NMR spectrum taken from the residue revealed the formation of bis(niobocene).

Reactions of $[NbCp_2H_2(SiMe_2Cl)]$ with $LiAlH_4$

Method (a). 0.342 g (1.073 mmol) of $[NbCp_2H_2(SiMe_2Cl)]$ were treated with an excess of $LiAlH_4$ in 15 mL of ether. A red-orange solution is formed. The volatiles were removed *in vacuo*, and the residue extracted with 10 mL of toluene, filtered and dried to give a light orange powder. The NMR spectrum showed the formation of a mixture of the known compound **13**[16] (major) and $[NbCp_2H_3]$. Crystals of **13** suitable for X-ray diffraction study were obtained from a dilute pentane solution. **13**: NMR (C_6D_6): 5.4 (br s, 1, Al–H), 4.71 (s, 10, Cp), 3.6 (br s, 1, Al–H–Al), −9.79 (s, 2, Nb–H–Al). $^{13}C-\{^1H\}$ NMR (C_6D_6): 85.40 (Cp).

Method (b). 0.299 g (0.938 mmol) of $[NbCp_2H_2(SiMe_2Cl)]$ were treated with an excess of $LiAlH_4$ in a solution of 3 mL of amine NEt_3 in 15 mL of ether. A red-orange solution is formed. The volatiles were removed *in vacuo*, and the residue extracted with 10 mL of toluene, filtered and dried to give a light orange powder, which according to ^1H NMR is a mixture of **13** and $[Cp_2NbH_2(SiMe_2H)]$ (**12**) in the ratio 3 : 1. This material was treated with 10 mL of pentane. Filtration followed by volatiles removal *in vacuo* gave an orange oil of **12**. **12**: ^1H NMR (C_6D_6): 5.06 (sept, $J_{H–H}$ = 3.6 Hz, 1, Si–H), 4.58 (s, 10, Cp), 0.69 (s, $J_{H–H}$ = 3.6 Hz, 6, SiCH_3), −5.05 (s, 2, Nb–H). $^{13}C-\{^1H\}$ NMR (C_6D_6): 95.69 (Cp), 8.09 ($SiMe_2$).

The analogous tantalum compound $[NbCp_2H_2(SiMe_2H)]$ has been previously characterised.[7b]

Preparation of $[NbCp_2H_2(SiMe_2PPh_2)]$ (17)

A supension of 0.971 g (2.95 mmol) of $Ph_2PLi{\cdot}2THF$ in 30 mL of Et_2O was added to 0.664 g (2.08 mmol) of $[NbCp_2H_2(SiMe_2Cl)]$ in 20 mL of Et_2O. The mixture was stirred overnight. Filtration and solvent removal gave a brown oily compound. This was redissolved in 40 mL of ether and cooled to −30 °C. Light beige crystals were formed over 2 days. The cold solution was filtered and the residue dried. Yield: 0.406 g (0.867 mmol, 42%). IR (Nujol): $\nu_{Nb–H}$ = 1751 cm^{-1}. ^1H NMR (C_6D_6): 7.83 (t, $J_{H–H}$ = 6.9 Hz, 4, Ph), 7.06 (m, Ph), 4.49 (s, 10, Cp), 0.61 (d, $J_{P–H}$ = 6.0 Hz, 6, Me), −4.44 (s, 2, Nb–H). $^{13}C-\{^1H\}$ NMR (C_6D_6): 135.0 (d, $J_{C–P}$ = 22.1 Hz, Ph), 126.5 (Ph), 88.0 (Cp), 9.4 (d, $J_{C–P}$ = 20.1 Hz, Me). $^{31}P-\{^1H\}$ NMR (C_6D_6): −27.3. $C_{24}H_{28}NbPSi$: calcd C 59.23, H 6.02; found: C 58.79, H 5.83%.

Preparation of $[NbCp_2H(SiMe_2Br)_2]$ (8)

Improved method (a). 0.31 g (1.23 mmol) of $[Br_2{\cdot}diox]$ in 25 mL of ether was added to 0.42 g (1. 23 mmol) of $[NbCp_2H(SiMe_2D)_2]$. A light crimson solution and a precipitate are formed. The mixture was stirred overnight at room temperature. The solution was filtered and stripped of volatiles. Yield: 0.43 g (0.86 mmol, 70%).

New method (b). 0.296 g (0.72 mmol) of $[NbCp_2H(SiMe_2Cl)_2]$ and 1.5 mL of $BrSiMe_3$ were heated at 80 °C in 10 mL of toluene for 1 week. The solution was filtered and stripped of volatiles. The residue was recrystallised from ether to give 0.260 g (0.52 mmol, 72%). ^1H NMR (C_6D_6): 4.70 (s, 10, Cp), 0.71 (s, 12, SiCH_3), −5.16 (s, 1, Nb–H). $^{13}C-\{^1H\}$ NMR (C_6D_6): 93.76 (Cp), 14.06 ($SiMe_2$). For full characterization data see ref. 5*c*.

Preparation of $[NbCp_2H(SiMe_2I)_2]$ (10)

Method (a). Iodine (0.813 g, 3.20 mmol) was added to 0.55 g (1.61 mmol) of $[NbCp_2H(SiMe_2H)_2]$ in 30 mL of ether. A purple solution and a dark red precipitate developed. The solution was filtered and the precipitate dried *in vacuo*. Yield: 0.474 g. Volatiles were removed *in vacuo* from the solution, leaving a red substance. This was recrystallised from ether. Yield: 0.16 g (0.269 mmol, 17%).

Method (b). 1.1 mL (8.1 mmol) of $ISiMe_3$ was added to 30 mL of a toluene solution of 1.15 g (2.8 mmol) of $[NbCp_2H(SiMe_2Cl)_2]$. The mixture was stirred for 4 days at room temperature. The solution was filtered and stripped of volatiles. Yield: 1.13 g (1.90 mmol, 68%). IR (Nujol): $\nu_{Nb–H}$ = 1713 cm^{-1}. ^1H NMR (C_6D_6): 4.71 (s, 10, Cp), 0.870 (s, 12, SiCH_3), −4.91 (s, 1, Nb–H). $^{13}C-\{^1H\}$ NMR (C_6D_6): 95.69 (Cp), 14.65 ($SiMe_2$). $C_{14}H_{23}NbSi_2I_2$: calcd C 28.30, H 3.90; found C 28.02, H 3.75%.

Preparation of $[NbCp_2H(SiMe_2OMe)_2]$ (18)

0.06 mL (1.48 mmol) of HOMe and 1 mL of NEt_3 were added by microsyringe to 30 mL of an ether suspension of 0.316 g (0.53 mmol) of $[NbCp_2NbH(SiMe_2I)_2]$. The mixture was stirred for 2 days at room temperature. The solution was filtered, the residue washed with 10 mL of ether and the volatiles were removed from the combined fractions. The yield was quantitative. IR (Nujol): $\nu_{Nb–H}$ = 1735 cm^{-1}. ^1H NMR (C_6D_6): 4.60 (s, 10, Cp), 3.42 (s, 6, OCH_3), 0.50 (s, 12, SiCH_3), −4.49 (s, 1, Nb–H). $^{13}C-\{^1H\}$ NMR (C_6D_6): 89.08 (Cp), 50.86 (OMe), 8.44 ($SiMe_2$). $C_{16}H_{29}NbO_2Si_2$: calcd C 47.75; H 7.26; found C 47.43, H 7.10%.

Preparation of $[NbCp_2H(SiMe_2OTfl)_2]$ (11)

0.6 mL (3.31 mmol) of $Me_3SiOTfl$ was added to 20 mL of an ether solution of 0.44 g (1.06 mmol) of $[NbCp_2H(SiMe_2Cl)_2]$. The mixture was stirred for 24 h at room temperature. The

Table 6 Crystal data and structure refinement for **10**, **18**, **17** and **13**

	10	**18**	**17**	**13**
Empirical formula	$C_{16}H_{23}NbI_2Si_2$	$C_{16}H_{29}NbO_2Si_2$	$C_{24}H_{28}NbPSi$	$C_{10}H_{14}AlNb$
Formula weight	594.21	402.48	468.43	254.10
Crystal size/mm	0.44 × 0.36 × 0.26	0.66 × 0.18 × 0.08	0.44 × 0.42 × 0.20	0.30 × 0.10 × 0.10
Crystal system, space group	Tetragonal, *I*4/*m*	Triclinic, $P\bar{1}$	Monoclinic, $P2_1/c$	Monoclinic, $P2_1/c$
a/Å	18.996(3)	7.7729(1)	13.3692(2)	5.894(2)
b/Å	18.996(3)	10.5018(2)	12.8331(1)	12.499(2)
c/Å	13.031(3)	13.0324(2)	12.6511(2)	14.256(4)
α/°	90	70.100(1)	90	90.00
β/°	90	72.739(1)	92.848(1)	101.01(2)
γ/°	90	73.936(1)	90	90.00
V/Å^3	4702.2(1)	936.79(3)	2167.85(5)	1031.0(5)
Z	8	2	4	4
μ/mm^{-1}	3.230	0.772	0.691	1.196
T/K	173(2)	153.0(2)	153.0(2)	150.0(2)
Reflections collected	1417	6066	5007	2138
Independent reflections	1122	3648	4991	2031
Goodness-of-fit on F^2	1.115	1.111	1.091	1.152
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0560$, $wR_2 = 0.1658$	$R_1 = 0.0361$, $wR_2 = 0.0843$	$R_1 = 0.0209$, $wR_2 = 0.0497$	$R_1 = 0.0251$, $wR_2 = 0.0491$
R indices (all data)	$R_1 = 0.0736$, $wR_2 = 0.1758$	$R_1 = 0.0442$, $wR_2 = 0.0959$	$R_1 = 0.0256$, $wR_2 = 0.0552$	$R_1 = 0.0342$, $wR_2 = 0.0541$

solution was cooled to −26 °C for some days. Tiny yellow crystals were formed. The solution was slowly concentrated while cold and filtered. Yield: 0.48 g (0.75 mmol, 71%). ^{1}H NMR (C_6D_6): 4.70 (s, 10, Cp), 0.33 (s, 12, $SiCH_3$), −6.76 (s, 1, Nb–H). ^{13}C-{^{1}H} NMR (C_6D_6): 91.88 (Cp), 11.02 ($SiMe_2$). $C_{16}H_{23}F_6NbO_6Si_2S_2$: calcd C 30.10, H 3.63, found C 29.79, H 3.31%.

Reaction of [$NbCp_2H(SiMe_2Cl)_2$] with $MgBr_2$

Fresh $MgBr_2$ was prepared by reaction of 0.22 g (9.05 mmol) of magnesium with dibromethane. $MgBr_2$ was suspended in 25 mL of THF and added to 20 mL of a THF solution of [$NbCp_2H(SiMe_2Cl)_2$] (0.628 g, 1.53 mmol). The mixture was stirred for 2 days at room temperature to give a light green solution. THF was removed *in vacuo* and the residue extracted with 25 mL of toluene. The solution was filtered and stripped of volatiles. Yield: 0.71 g. The ^{1}H NMR spectrum revealed a mixture of [$NbCp_2H(SiMe_2Cl)_2$], [$NbCp_2H(SiMe_2Br)(SiMe_2Cl)$] and [$NbCp_2H(SiMe_2Br)_2$]. NMR data for [$NbCp_2H(SiMe_2Br)(SiMe_2Cl)$]: ^{1}H NMR ($C_6D_6$): 4.69 (s, 10, Cp), 0.74 (s, 12, $BrSiCH_3$), 0.58 (s, 12, $ClSiCH_3$). ^{13}C-{^{1}H} NMR (C_6D_6): 93.11 (Cp).

Preparation of [$NbCp_2H(SiMe_2SPh)_2$] (14)

2.61 mmol of PhSLi, prepared by the reaction of PhSH with MeLi, in 10 mL of THF was added to 15 ml of a THF solution of 0.536 g (1.30 mmol) of [$NbCp_2H(SiMe_2Cl)_2$]. The mixture was stirred for 5 days affording a crimson solution. Volatiles were removed *in vacuo* and the residue extracted with 35 mL of ether. Filtration and solvent removal gave 0.689 g of crude product which contained **14** as the only Cp-containing compound. In addition to signals of **14** in the ^{1}H NMR spectrum this compound also displays THF signals (3.50 and 1.26 ppm) probably due to an admixture of (LiCl)·*x*THF. An analytically pure white microcrystalline material was obtained by cooling a saturated ether solution at −30 °C. IR (Nujol): $\nu_{Nb–H}$ = 1725 cm^{-1}. ^{1}H NMR (C_6D_6): 7.59 (d, $J_{H–H}$ = 1.8 Hz, 4, Ph), 7.08 (m, Ph), 4.85 (s, 10, Cp), 0.46 (s, 12, $SiCH_3$), −4.29 (s, 1, Nb–H). ^{13}C-{^{1}H} NMR (C_6D_6): 135.88, 135.01, 120.46 (Ph), 91.85(Cp), 9.60 ($SiMe_2$). $C_{26}H_{33}NbSi_2S_2$: calcd C 55.89, H 5.95; found C 55.50, H 5.80%.

Preparation of [$NbCp_2H(SiMe_2PPh_2)_2$] (15)

A suspension of 0.818 g (2.43 mmol) of Ph_2PLi·2THF in 30 mL of Et_2O was added to 0.500 g (1.22 mmol) of [$NbCp_2H(SiMe_2Cl)_2$]. The mixture was stirred for 2 days. Filtration and solvent removal gave a brown oily compound. This was dissolved in ether and cooled to −30 °C. Light beige crystals were formed over 2 days. The cold solution was filtered and the residue dried. Yield: 0.12 g. IR (Nujol): $\nu_{Nb–H}$ = 1759 cm^{-1}. ^{1}H NMR (C_6D_6): 7.76 (t, $J_{H–H}$ = 7.0 Hz, 8, Ph), 7.52 (m, Ph), 7.03 (m, Ph), 4.59 (s, 10, Cp), 0.49 (d, $^3J_{P–H}$ = 5.0 Hz, 12, $SiCH_3$), −3.33 (s, 1, Nb–H). ^{13}C-{^{1}H} NMR (C_6D_6): 90.3 (Cp), 7.2 (d, $^2J_{P–C}$ = 14.7 Hz, $SiMe_2$). ^{31}P-{^{1}H} NMR (C_6D_6): −27.2 (s). Satisfactory elemental analysis could not be obtained.

Crystal structure determinations

Pink crystals of [$NbCp_2H(SiMe_2I)_2$] (**10**), orange crystals of [$NbCp_2H_2Al(\mu$-$H)_2]_2$ (**13**), beige crystals of [$NbCp_2H_2(SiMe_2PPh_2)$] (**17**) and colourless crystals of [$NbCp_2H(SiMe_2OMe)_2$] (**12**) were grown from ether by cooling the solutions to −25 to −30 °C. The crystals were covered by polyperfluoro oil. Crystals of **13**, **17**, and **18** were mounted directly on the Bruker Smart three-circle diffractometer with CCD area detector at −120 °C (−123 °C for **13**) and a crystal of **10** was mounted on an Enraf-Nonius CAD-4 diffractometer at −100 °C. The crystallographic data and characteristics of structure solution and refinement are given in Table 6. The structure factor amplitudes for all independent reflections were obtained after the Lorentz and polarization corrections. An empirical absorption correction based on measurements of several equivalent reflections was applied for **10** and **13**. The structures were solved by heavy-atom methods[34] and refined by full-matrix least squares procedures, using $\omega(|F_o^2| - |F_c^2|)^2$ as the refined function.[34] All hydrogen atoms were found from the difference map. In the final cycles of refinement, all the non-hydrogen atoms were refined with anisotropic temperature parameters. The hydride ligands were refined isotropically, other hydrogen atoms were refined using the riding scheme. The largest residuals in the final difference Fourier maps were small (1.086 and −0.768 e Å^{-3} for **10**, 0.563 and −0.472 e Å^{-3} for **13**, 0.374 and −0.329 e Å^{-3} for **17**, 0.559 and −0.915 e Å^{-3} for **18**), location and magnitude of the residual electron density was of no chemical significance. The largest residuals in the final difference Fourier maps of [$NbCp_2H(SiMe_2I)_2$] were more significant and could be rationalised either as some partial co-crystallisation of an ether molecule or polyiodide.

CCDC reference numbers 175461–175464.

See http://www.rsc.org/suppdata/dt/b1/b110998g/ for crystallographic data in CIF or other electronic format.

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