New Studies on the Reactivity of Hydride-Containing Niobocene Complexes Towards Insertion and Protonation Processes

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The trihydride complex [Nb(η^5-$C_5H_4SiMe_3)_2(H)_3$] **(1)** reacts with diphenylphosphane to afford the monohydride [Nb(η^5-$C_5H_4SiMe_3)_2(H)(PHPh_2)$] **(3)**. The synthesis of complex **3** has also been achieved from the initial formation of the phosphonium salt [Nb(η^5-$C_5H_4SiMe_3)_2(H)_2(PHPh_2)$]Cl **(2)** by reaction of the trihydride complex [Nb(η^5-$C_5H_4SiMe_3)_2(H)_3$] **(1)** with chlorodiphenylphosphane, followed by deprotonation of this salt in aqueous NaOH. Protonation of complex **3** at low temperature with a slight excess of CF_3COOH or CF_3COOD leads to the η^2-dihydrogen complex [Nb(η^5-$C_5H_4SiMe_3)_2(\eta^2$-$H_2)(PHPh_2)$]CF_3CO_2 **(4)** or its monodeuterated isotopomer [Nb(η^5-$C_5H_4SiMe_3)_2(\eta^2$-HD)$(PHPh_2)$]CF_3CO_2 **(5)**. When the temperature is increased to room temperature, complexes **4** and **5** transform into the *transoid* dihydrides [Nb(η^5-$C_5H_4SiMe_3)_2(H)_2(PHPh_2)$]$CF_3CO_2$ **(6)** and [Nb(η^5-$C_5H_4SiMe_3)_2(H)_2$-$(PDPh_2)$]CF_3CO_2 **(7)**, respectively. Complex **3** undergoes an insertion of CS_2 into the niobium–hydrogen bond to give the η^1-dithioformato complex [Nb(η^5-$C_5H_4SiMe_3)_2(PHPh_2)(\eta^1$-*S*-S(S)CH)] **(8)**. This complex could be detected by NMR spectroscopy but could not be isolated due to rapid conversion into the η^2-dithioformato complex [Nb(η^5-$C_5H_4SiMe_3)_2(\eta^2$-*S*,*S*-SSCH)] **(9)** by loss of the phosphane molecule. Complex **3** also reacts with CO_2 to give the η^2-formato complex [Nb(η^5-$C_5H_4SiMe_3)_2(\eta^2$-*O*,*O*-OOCH)] **(10)**; in this case the η^1-formato complex could not be detected. The reagent $ClPPh_2$ very smoothly inserts into the Nb–H bond of the complexes [Nb(η^5-$C_5H_4SiMe_3)_2(H)(L)$] [L = $PHPh_2$, CN(xylyl), CO; xylyl = 2,6-dimethylphenyl], yielding the new ionic complexes [Nb(η^5-$C_5H_4SiMe_3)_2(PHPh_2)(L)$]Cl [L = $PHPh_2$ **(11)**, CN(xylyl) **(12)**, CO **(13)**]. All the complexes described have been characterized by analytical and spectroscopic methods.

Introduction

Hydride complexes of transition metals represent one of the most important classes of compounds due to their chemical reactivity and importance in catalysis.[1] Furthermore, the chemistry of phosphorus-substituted early transition metal complexes has also recently received a great deal of attention.[2] Several groups[3,4] have found that the trihydrides [Cp_2MH_3] (M = Nb, Ta) react with chlorophosphanes PR_2Cl to afford the phosphonium salts [Cp_2MH_2-(PR_2H)]Cl. Depending on the metal (Nb or Ta) and on the nature of the phosphane substituent, deprotonation of these salts leads to hydride(phosphane) [$Cp_2MH(PR_2H)$] or hydride(phosphide) [$Cp_2MH_2(PPh_2)$] metalloligands. As part of a study of the electronic and steric influence of trimethylsilyl-substituted cyclopentadienyl ligands on the properties of niobocene complexes, we have studied the reaction of the trihydride niobocene complex [Nb(η^5-$C_5H_4SiMe_3)_2H_3$][5] with $ClPPh_2$ and the subsequent deprotonation of the phosphonium salt obtained. We have previously prepared[6] the hydride(phosphane) niobocene complexes [Nb(η^5-C_5H_4Si-$Me_3)_2(H)(PR_3)$] by heating the trihydride complex [Nb(η^5-$C_5H_4SiMe_3)_2H_3$] (**1**) in the presence of the corresponding phosphane PR_3. We have now used this method to synthesize the monohydride phosphane complex [Nb(η^5-C_5H_4Si-$Me_3)_2(H)(PHPh_2)$] (**3**) by thermal reaction of [Nb(η^5-$C_5H_4SiMe_3)_2H_3$] (**1**) with $PHPh_2$. In addition, and in keeping with our interest in dihydrogen complexes,[6,7] we report here the results for the low temperature protonation of the new monohydride complex [Nb(η^5-$C_5H_4SiMe_3)_2(H)$-$(PHPh_2)$] (**3**) and, for the first time, the deprotonation reaction of the cationic species obtained in this kind of reaction when the temperature is increased to room temperature.

Finally, the insertion of unsaturated molecules into the metal−hydride bond is considered as a fundamental chemical step in several catalytic cycles and frequently leads to reactive intermediates.[8] In connection with our recent studies of metal-promoted activation of unsaturated molecules such as heterocumulenes,[9] carbon disulfide,[10] carbon dioxide,[11] and activated alkynes,[12] we also decided to explore the reactivity of the new hydride phosphanyl complex **3** with carbon disulfide and carbon dioxide. These reactions have permitted the isolation of dithioformato- and formato-derivatives as well as the insertion of $ClPPh_2$ into the Nb−H bond of the monohydride derivatives [Nb(η^5-$C_5H_4SiMe_3)_2(H)(L)$] [L = $PHPh_2$, CN(2,6-$Me_2C_6H_3$), CO], and this has allowed us to prepare new cationic Nb^{III} species.

Results and Discussion

Reaction of [Nb(η^5-$C_5H_4SiMe_3)_2(H)_3$] With $ClPPh_2$

The reaction of [Nb(η^5-$C_5H_4SiMe_3)_2(H)_3$] (**1**) with $ClPPh_2$ proceeds smoothly to give quantitatively the ionic

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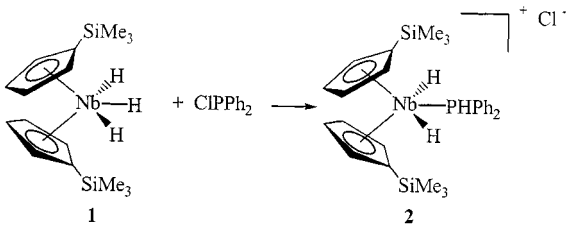
complex $[Nb(\eta^5\text{-}C_5H_4SiMe_3)_2(H)_2(PHPh_2]Cl$ (**2**) as depicted in Equation (1).

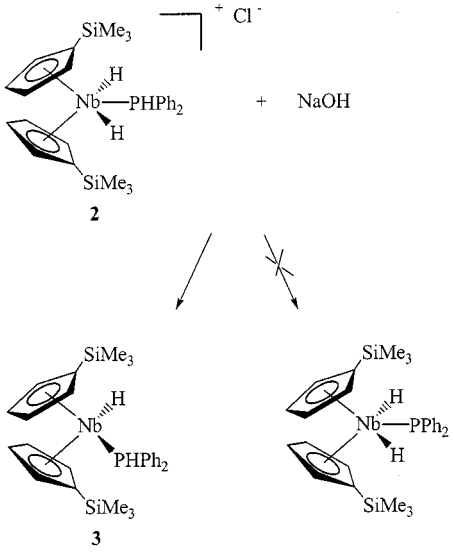


1 **2** (1)

Complex **2** immediately precipitates as grey voluminous flakes after mixing Et_2O solutions of $[Nb(\eta^5\text{-}C_5H_4SiMe_3)_2(H)_3]$ (**1**) and $ClPPh_2$ at room temperature. Even at low temperature (253 K) the rate of the reaction is very fast. The low solubility of complex **2** in hydrocarbons, ethers and aromatic solvents means that the product can be isolated very easily in an analytically pure form. However, it is sufficiently soluble in acetone to allow its NMR spectrum to be recorded. The ionic nature of complex **2** was confirmed by measurement of the molar conductivity (Λ_M = 135 $\Omega^{-1}mol^{-1}$), which is in agreement with a 1:1 electrolyte.[13] Complex **2** was formed in high yield and was characterized by ^1H and ^{31}P NMR and IR spectroscopy. In the ^1H NMR spectrum ([D$_6$]acetone) only the symmetric isomer $[Nb(\eta^5\text{-}C_5H_4SiMe_3)_2(H)_2(PHPh_2)]Cl$ was observed. The cyclopentadienyl rings are equivalent and give rise to two broad resonances (see Experimental Section) for an A_2B_2 spin system in the ^1H NMR spectrum, which indicates a symmetrical disposition at the niobium centre with a rapid rotation of the phosphane moiety around the Nb−P bond. The ^1H NMR spectrum also shows a resonance due to the hydride ligands at $\delta = -2.16$ and this value is similar to those reported for the equivalent hydride ligands in $[Nb(\eta^5\text{-}C_5H_4SiMe_3)_2(H)_2(L)]PF_6$[6a] [L = P(OR)$_3$, PMe$_2$Ph] and $[M(\eta^5\text{-}C_5H_5)_2(H)_2(PR_3)]^+$.[14] The hydride ligands are equivalent and show a single resonance that appears as a doublet due to coupling with the phosphorus atom ($^2J_{HP}$ = 78.2 Hz). The signal for the hydrogen atom of the P−H group appears as a doublet at $\delta = 6.67$ ($^1J_{HP}$ = 283 Hz). The $^3J_{HH}$ value could not be observed due to the broadness of the signals. The ^{31}P NMR spectrum shows a broad doublet at $\delta = 20$ that corresponds to a second-order spin system due to the couplings $^1J_{HP}$ and $^2J_{HP}$. The IR spectrum shows a ν(P−H) band at ca. 2293 cm^{-1}, which confirms the existence of the coordinated phosphane molecule, and also a ν(Nb−H) band of medium intensity at ca. 1703 cm^{-1} (see Experimental Section).

A characteristic feature of complex **2** is the existence of two acidic centres: the P−H and the Nb−H bonds. The reaction between complex **2** and an aqueous solution of NaOH in toluene affords only the hydride(phosphane) complex **3** in good yield (75%); the corresponding phosphido complex could not be observed (Scheme 1).

The tantalum phosphido complex $Cp_2TaH_2(PPh_2)$ has been isolated by Nikonov et al. while the homologous niobium compound $Cp_2NbH_2(PPh_2)$ was not observed.[3] The



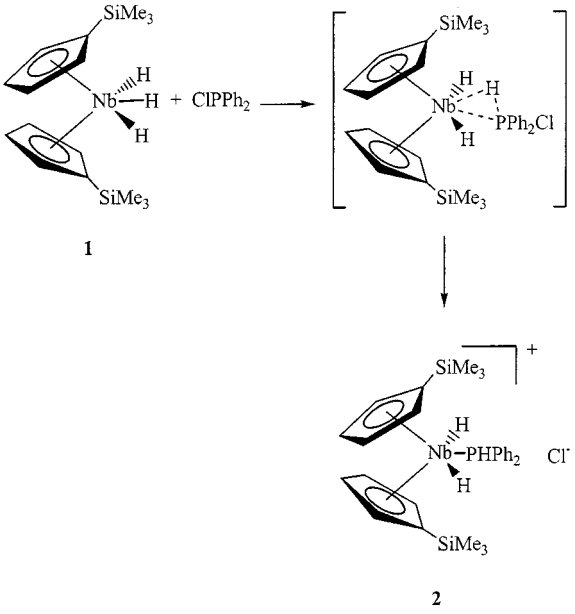
Scheme 1. Formation of **3** by reaction of **2** with NaOH

reaction was carried out in a two-phase system (water/toluene), which enabled easy extraction and isolation of the product as a red oily material. The characterization of complex **3** was performed by NMR and IR spectroscopy. The ^1H NMR spectrum shows a high-field resonance at $\delta = -7.37$ for the hydride ligand, which appears as a doublet ($^2J_{HP}$ = 29.30 Hz), whereas the P−H resonance appears as a doublet at $\delta = 6.90$ ($^1J_{HP}$ = 332 Hz). Three multiplets can also be observed that integrate for 4, 2 and 2 protons, respectively, and correspond to an AA′BB′ spin system. These signals are due to the cyclopentadienyl rings and are in accordance with an asymmetrical environment for the niobium centre (see Experimental Section). Finally, the IR spectrum shows two bands at ca. 1643 and 2281 cm^{-1}, which correspond to ν(Nb−H) and ν(P−H), respectively, and confirm the existence of the coordinated phosphane molecule.

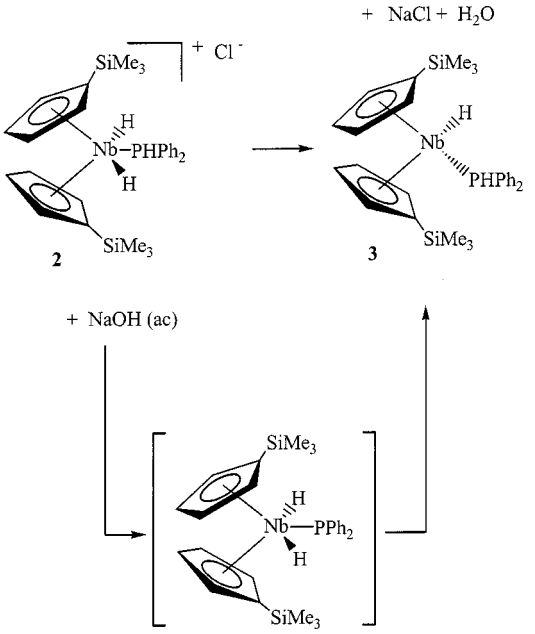
The reaction of $[Nb(\eta^5\text{-}C_5H_4SiMe_3)_2(H)_3]$ (**1**) with $ClPPh_2$ can be rationalized in terms of an insertion of the chlorophosphane into the Nb−H bond, followed by elimination of the chloride ion and rearrangement of the molecule as shown in Scheme 2. The nature of the insertion process can be considered as an interaction of the empty d-orbitals on the phosphorous with the Nb−H σ-bond, a situation that means a pentavalent phosphorus structure should be initially formed.

Deprotonation of **2** should initially occur at the more labile hydrogen atom, which is, according to the spectroscopic data, the P−H proton. This implies that deprotonation of **2** should initially produce a dihydride(phosphide) complex. However, such a complex could not be detected and probably transforms rapidly into complex **3** through a hydride shift into the vacant d-orbital at phosphorus (see Scheme 3).

Further experiments, which are described later in this paper, allowed us to confirm unequivocally that deprotonation occurs at the P−H bond. This is not unexpected



Scheme 2. Proposed reaction pathway for the formation of **2**

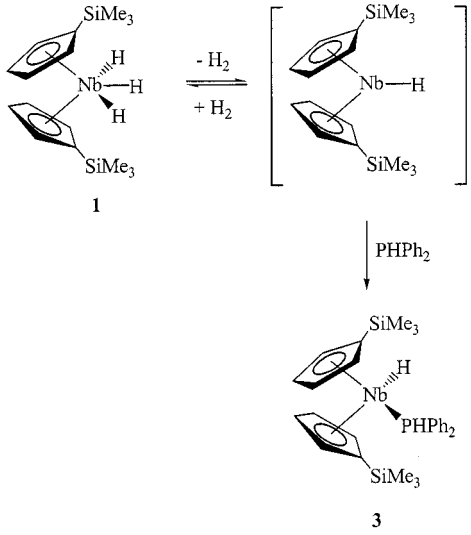


Scheme 3. Proposed reaction pathway for the deprotonation of **2**

as the P−H bond is kinetically more labile than the Nb−H bond.

Reaction of $[Nb(\eta^5\text{-}C_5H_4SiMe_3)_2(H)_3]$ With $PHPh_2$

We also prepared complex **3** in an alternative manner by reaction of $[Nb(\eta^5\text{-}C_5H_4SiMe_3)_2(H)_3]$ with $PHPh_2$. In fact, $[Nb(\eta^5\text{-}C_5H_4SiMe_3)_2(H)_3]$ (**1**) reacts slowly (3 hours) with $PHPh_2$ in THF at ca. 70 °C to afford the complex $[Nb(\eta^5\text{-}C_5H_4SiMe_3)_2(H)(PHPh_2)]$ (**3**). The initial step should be the formation of the coordinatively unsaturated 16-electron species $[Nb(\eta^5\text{-}C_5H_4SiMe_3)_2(H)]$ by thermolytic loss of H_2, followed by coordination of the phosphane ligand [Equation (2)].



(2)

The reaction is similar to that previously reported[6a,7,10] for the preparation of several families of niobocene complexes $[Nb(\eta^5\text{-}C_5H_4SiMe_3)_2(H)(L)]$ (L = π-acid ligand). Complex **3** was isolated as a spectroscopically pure, air-sensitive red oily material and the spectroscopic data are in agreement with those recorded for the complex isolated by the first method described in this paper. This one-step synthesis gives a better yield (90%) and represents a cleaner way of preparing complex **3**.

Protonation Reaction of $[Nb(\eta^5\text{-}C_5H_4SiMe_3)_2(H)(PHPh_2)]$ (3)

Complex **3** was easily protonated with CF_3COOH at low temperature to give the corresponding *cisoid* dihydrogen-containing complex **4** according to Equation (3).

$$[Cp'_2Nb(H)(PHPh_2)]\ \mathbf{(3)} + CF_3COOH \longrightarrow [Cp'_2Nb(\eta^2\text{-}H_2)(PHPh_2)]^+CF_3COO^-\ \mathbf{(4)} \quad (3)$$

When CF_3COOD is used, the monodeuterated complex **5** is obtained [Equation (4)]:

$$[Cp'_2Nb(H)(PHPh_2)]\ \mathbf{(3)} + CF_3COOD \longrightarrow [Cp'_2Nb(\eta^2\text{-}HD)(PHPh_2)]^+CF_3COO^-\ \mathbf{(5)} \quad (4)$$

These processes were carried out by adding a slight excess of CF_3COOH/D to a solution of complex **2** in $[D_6]$acetone in an NMR tube at 183 K.

The ^1H NMR spectrum of **4** at low temperature shows a dihydrogen resonance at ca. $\delta = -4.57$ that appears as a doublet due to the H-P coupling ($J_{HP} = 19.7$ Hz). The signal broadens at very low temperature but does not show decoalescence. The high-field $^1H\{^{31}P\}$ NMR spectrum of **5** at 183 K shows two triplets (1:1:1) at ca. $\delta = -4.7$ due to the existence of two different rotamers; *endo* **5a** and *exo* **5b**

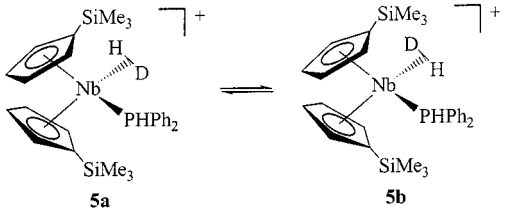


Figure 1. Rotation process of the HD coordinated molecule

(Figure 1). Both isomers show a similar J_{HD} coupling of ca. 18.20 Hz.

These rotamers exist due to the fact that the rotation of the coordinated HD molecule is frozen on the NMR time scale at this temperature.[6a,7]

When the temperature is raised, the rotamers *endo* H **5a** and *exo* H **5b** interconvert by rotation of the HD molecule. Coalescence is reached at 225 K, and at this temperature it is not possible to distinguish between the two isomers. At 263 K a single resonance (1:1:1 triplet) is observed at ca. $\delta = -4.70$ for the HD fragment (Figure 2).

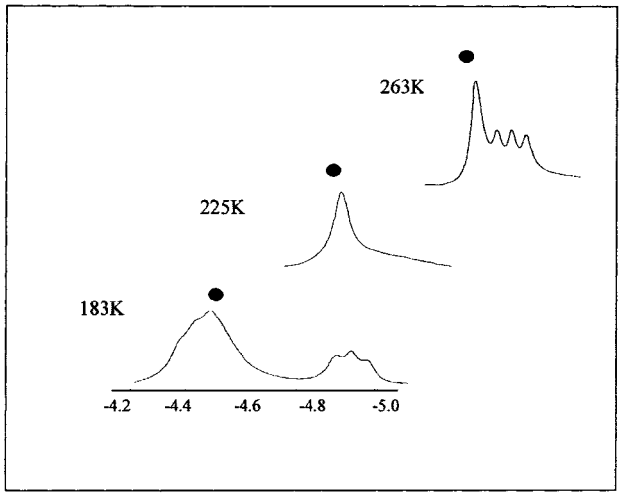
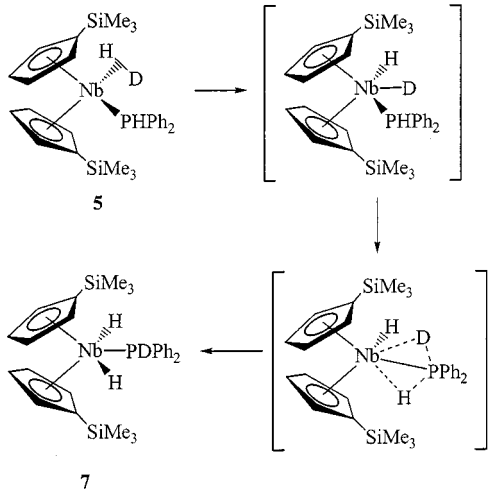


Figure 2. High-field $^1H\{^{31}P\}$ NMR spectrum (300 MHz) of **5** at variable temperature; the point denotes the presence of residual complex **4**

This phenomenon allowed the estimation of the free energy of activation of the internal rotation at the coalescence temperature ($\Delta G^{\neq} \approx 10.43$ kcal/mol K). Similar values have been observed previously for the related complexes $[Nb(\eta^5\text{-}C_5H_4SiMe_3)_2(\eta^2\text{-}HD)(PMe_2Ph)]^+$ ($\Delta G^{\ddagger} \approx 11$ kcal/mol K)[6a] and $[Nb(\eta^5\text{-}C_5H_4SiMe_3)_2(\eta^2\text{-}HD)(CNR)]^+$ ($\Delta G^{\ddagger} \approx 8-9$ kcal/mol K).[7] As a consequence of this high barrier, rotation of the HD molecule can be blocked on the NMR time scale. The value of the J_{HD} coupling constant (18.2 Hz) verifies the presence of an H−D bond and is strong evidence for the presence of a dihydrogen complex.[7] Moreover, the observation of low longitudinal-relaxation times, T_1, is very useful in providing evidence for the existence of a dihydrogen ligand. The T_1 values of the dihydrogen nuclei of **4**, $T_1(H_2)$, and the hydride ligand of complex **3**, $T_1(H)$, were determined using the method described by Crabtree et al.[15] The T_1 minima were found to be 15.8 ms at 215 K for **4** and 95 ms at 186 K for complex **3**. According to Crabtree's proposal, the H−H distance r_{H-H} in the coordinated H_2 ligand can be determined from the T_1 measurements. The observed relaxation, R_{obs}, for **4** is the sum of that due to the H−H dipole−dipole interaction (R_{H-H}) and that due to all other effects (R_O), which can be estimated using the observed relaxation for **3** [R_{obs} (3)], as a reasonable indication of the niobium and solvent contributions. From this equation we calculated $R_{H-H} = 52.68$ (μs^{-1}). Using the Morris approximation,[16] we found that $r_{H-H} = 1.16$ Å assuming rapid rotation of dihydrogen and $r_{H-H} = 0.92$ Å assuming a slow rotation. These values are in agreement with the J_{H-D} value measured for complex **5** and indicate significant stretching of the coordinated H−H bond. Similar results were found for the related compounds $[Nb(\eta^5\text{-}C_5H_4SiMe_3)_2(\eta^2\text{-}HD)(L)]^+$ [L = $P(OEt)_3$, PMe_2Ph].[6a]

After low-temperature protonation the temperature was raised to room temperature and **4** and **5** transformed into the *transoid* isomers $[Nb(\eta^5\text{-}C_5H_4SiMe_3)_2(H)_2(PHPh_2)]\text{-}CF_3CO_2$ (**6**) and $[Nb(\eta^5\text{-}C_5H_4SiMe_3)_2(H)_2(PDPh_2)]\text{-}CF_3CO_2$ (**7**), respectively, through an irreversible process. Complex **6** shows similar spectroscopic data to complex **2**, with the counterion being the only difference between the two. Complex **7** also shows very similar spectroscopic data and these are in agreement with a symmetrical disposition of the niobium centre, showing an A_2B_2 spin system in the ^1H NMR spectrum for the cyclopentadienyl ligands. Thus, the $^1H\{^{31}P\}$ NMR spectrum shows a singlet resonance at $\delta = -1.76$ due to the hydride ligands; no resonance due to a possible PH moiety is observed. Moreover, the ^{31}P NMR spectrum shows a 1:1:1 triplet resonance due to coupling with the deuterium atom ($^1J_{PD} = 34$ Hz). This signal allowed us to confirm the existence of the P−D bond for complex **7**.

The formation of complexes **6** and **7** could be considered to be the result of an oxidative addition of a coordinated dihydrogen molecule to give a *cisoid* dihydride derivative that transforms rapidly into the *transoid* isomer. According to the results obtained, the *cisoid*−*transoid* isomerization may involve the phosphorus atom, as shown in Scheme 4.



Scheme 4. Proposed reaction pathway for the formation of **7**

Isomerization of **5** may proceed by attack of the Nb−D bond at an empty d-orbital of the phosphorus atom. At the same time the P−H bond interacts with the niobium centre, thus making possible the rearrangement of the molecule to give the *transoid* derivative **7**.

When the reaction between **3** and CF_3COOH/D in acetone is performed on a Schlenk-tube scale, the only isolated products are the *transoid* dihydrides **6** and **7**. The low solubility of these complexes in hydrocarbons, ethers and aromatic solvents enabled very easy isolation of the products as colourless, analytically pure solids.

The similarity between complexes **6** and **7** and the phosphonium salt **2**, which was obtained by the reaction between trihydride **1** and $ClPPh_2$, led us to study their behaviour towards deprotonation reactions. Both complexes react with aqueous sodium hydroxide in toluene to give the previously characterized hydridophosphane **3**. This observation confirms that deprotonation of complexes **2**, **6** and **7** occurs at the P−H(P−D) bond, as discussed above.

Reaction of $[Nb(\eta^5\text{-}C_5H_4SiMe_3)_2(H)(PHPh_2)]$ (3) with CX_2 (X = S, O)

Insertion of CS_2 into the Nb−H bond of $[Nb(\eta^5\text{-}C_5H_4SiMe_3)_2(H)(PHPh_2)]$ results in the formation of an η^1-dithioformato intermediate $[Nb(\eta^5\text{-}C_5H_4SiMe_3)_2(PHPh_2)(\eta^1\text{-}S\text{-}S(S)CH)]$ (**8**), which could not be isolated but could be detected by ^1H NMR spectroscopy. This complex rapidly evolves by an elimination of phosphane (due to a substitution reaction of phosphane by the noncoordinated sulfur atom) to give an η^2-dithioformato complex $[Nb(\eta^5\text{-}C_5H_4SiMe_3)_2(\eta^2\text{-}S,S\text{-}SSCH)]$ (**9**) (Scheme 5). This complex was isolated as an air-sensitive orange solid and was previously isolated and characterized by some of us.[10]

This behaviour has previously been found in the reactions of some complexes of the type $[Nb(\eta^5\text{-}C_5H_4SiMe_3)_2(H)(L)]$ with CS_2.[10]

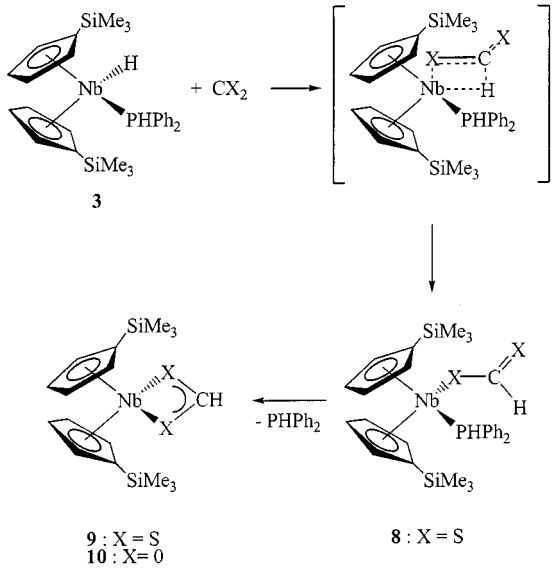
The most significant ^1H NMR spectroscopic data for **8** is the resonance at $\delta = 12.33$, which corresponds to the C−H group and appears as a doublet ($^4J_{PH} = 2$ Hz). This coupling constant confirms the presence of the coordinated phosphane. In addition, the ^1H NMR spectrum shows four multiplets for the cyclopentadienyl rings in accordance with an asymmetrical environment for the niobium centre.

The reaction of $[Nb(\eta^5\text{-}C_5H_4SiMe_3)_2(H)(PHPh_2)]$ (**3**) with CO_2 in THF under 2.5 atm. of CO_2 results in the formation of the η^2-formato complex $[Nb(\eta^5\text{-}C_5H_4SiMe_3)_2(\eta^2\text{-}O,O\text{-}OOCH)]$ (**10**) (Scheme 5) as a brown, air-sensitive oily product after appropriate workup. Complex **10** was previously prepared by some of us using different methods.[11] We have been unable to detect the η^1-formato complex due to the difficulties involved in carrying out test reactions on an NMR-tube scale. The spectroscopic data of **10** agree with those previously described.[11]

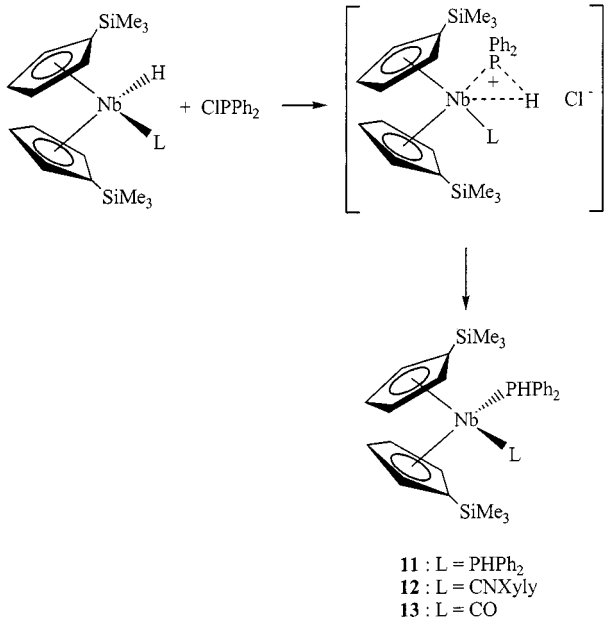
Reactivity of $[Nb(\eta^5\text{-}C_5H_4SiMe_3)_2(H)(L)]$ (L = $PHPh_2$, CN(xylyl), CO) Towards $ClPPh_2$

$ClPPh_2$ very smoothly inserts into the Nb−H bond of $[Nb(\eta^5\text{-}C_5H_4SiMe_3)_2(H)(L)]$ [L = $PHPh_2$, CN(xylyl), CO] to give the ionic phosphanyl complexes $[Nb(\eta^5\text{-}C_5H_4SiMe_3)_2(PHPh_2)(L)]Cl$ [L = $PHPh_2$ (**11**), CN(xylyl) (**12**), CO (**13**)] (Scheme 6). These reactions can be rationalized in terms of an electrophilic attack of the phosphorus atom (which contains empty d orbitals) at the Nb−H bond, forming a three-centre transition state that evolves with elimination of chloride.

Complexes **11**−**13** were formed in high yield (≈ 85%) as red solids after precipitation from Et_2O. The ^1H NMR spectrum of **11** reveals the equivalence of the cyclopentadienyl rings, with two pseudotriplets observed at $\delta = 5.36$ and $\delta = 5.50$. In contrast, an asymmetrical environment for the niobium centre is observed for complexes **12**



Scheme 5. Proposed reaction pathway for the formation of **9** and **10**



Scheme 6. Insertion process of $ClPPh_2$ into an Nb−H bond

and **13**. In addition, the ^{1}H NMR spectra of **11**−**13** show a doublet resonance for the P−H moiety ($^1J_{PH} \approx 370$ Hz). The IR spectra of **11**−**13** reveal the absence of an ν(Nb−H) band and the existence of ν(P−H) at ca. 2280 cm^{-1}.

In conclusion, several aspects of the reactivity of hydride-containing niobocene species have been considered in the work described here. In particular, the reactions of $ClPPh_2$ towards hydride-niobocene complexes [Nb(η^5-$C_5H_4SiMe_3)_2(H)_3$] (**1**) and [Nb(η^5-$C_5H_4SiMe_3)_2(H)(L)$] occur through insertion of chlorophosphane into an Nb−H bond. Furthermore, the protonation reaction of **3** at low temperature gives an η^2-dihydrogen complex, which evolves at high temperature to the corresponding *transoid* dihydride species. Further work in this field is in progress.

Experimental Section

General Remarks: All operations were performed under an inert atmosphere using standard vacuum line (Schlenk) techniques. Solvents were purified by distillation from the appropriate drying agents before use. NMR spectra were obtained on a Varian Unity FT-300 and Varian Gemini FT-200 instruments. IR spectra were recorded on a Perkin−Elmer PE 883 IR spectrophotometer. Elemental analyses were performed on a Perkin−Elmer 2400 microanalyzer. [Nb(η^5-$C_5H_4SiMe_3)_2(H)_3$] was prepared as described previously.[5]

Preparation of [Nb(η^5-$C_5H_4SiMe_3)_2(H)_2(PHPh_2)$]Cl (2): [Nb(η^5-$C_5H_4SiMe_3)_2(H)_3$] (**1**) (0.30 g, 0.80 mmol) was dissolved in 40 mL of Et_2O to form a tan solution. To this solution was added $ClPPh_2$ (180 μL, 1 mmol). A colourless precipitate formed immediately. When sedimentation was complete, the colourless solution was filtered and the residue washed twice with 10 mL of Et_2O and dried in vacuo. Complex **2** was isolated as a grey solid (yield: 90%). − IR (KBr): $\nu_{(Nb-H)} = 1703$ cm^{-1}; $\nu_{(P-H)} = 2293$ cm^{-1}. − ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.08 (s, 18 H, Si*Me*$_3$), 4.76 (m, 4 H, C_5H_4), 5.86 (m, 4 H, C_5H_4), 6.67 (d, $^1J_{PH}$ = 283 Hz, 1 H, P−*H*), −2.16 (d, $^2J_{PH}$ = 78.20 Hz, 2 H, Nb−*H*), 7.33−7.45 (m, *Ph*). − ^{13}C NMR (300 MHz, $CDCl_3$): δ = −0.2 (Si*Me*$_3$), 98.0 (*C*$_5$H$_4$, *C*$_1$), 99.9 (*C*$_5$H$_4$), 97.2 (*C*$_5$H$_4$), 131.9 (s, *Ph*, *C*$_1$), 130.9 (*Ph*), 128.9 (*Ph*). − ^{31}P NMR (300 MHz, $CDCl_3$): δ = 20.00 (d, $^1J_{PH}$ = 283 Hz, *P*−H). − $C_{28}H_{39}ClNbPSi_2$ (590.45): calcd. C 56.86, H 6.60; found C 56.20, H 6.45.

Preparation of [Nb(η^5-$C_5H_4SiMe_3)_2(H)(PHPh_2)$] (3): (a) [Nb(η^5-$C_5H_4SiMe_3)_2(H)_3$] (**1**) (0.30 g, 0.80 mmol) was dissolved in 40 mL of THF to form a tan solution. To this solution was added $PHPh_2$ (0.14 mL, 0.80 mmol) by syringe. The mixture was stirred at 343 K for 4 h. The resulting red solution was evaporated to dryness. Complex **3** was isolated as a red oily material after maintaining it under vacuum for a lengthy period (yield: 95%). − (b) [Nb(η^5-$C_5H_4SiMe_3)_2(H)_2(PHPh_2)$]Cl (**2**) (0.30 g, 0.51 mmol) in 30 mL of toluene was treated with an excess (4 mL) of 0.5 M aqueous NaOH. The mixture was vigorously stirred. Within 1 h the precipitate had dissolved and the organic phase turned dark red. The toluene solution was filtered and evaporated to dryness. Complex **3** was obtained as a red oily material (yield: 75%). − IR (CsI): $\nu_{(Nb-H)} = 1643$ cm^{-1}; $\nu_{(P-H)} = 2281$ cm^{-1}. − ^{1}H NMR (300 MHz, C_6D_6): δ = 0.26 (s, 18 H, Si*Me*$_3$), 3.63 (pst, 2 H, C_5H_4), 4.03 (pst, 2 H, C_5H_4), 4.72 (m, 4 H, C_5H_4), 6.90 (d, $^1J_{PH}$ = 322 Hz, 1 H, P−*H*), −7.37 (d, $^2J_{PH}$ = 29.30 Hz, 2 H, Nb−*H*), 7.36−7.71 (m, *Ph*), 8.12 [s, 2 H, *H*$_{para}$ (*Ph*)]. − ^{13}C NMR (300 MHz, C_6D_6): δ = 0.9 (Si*Me*$_3$), 90.6 (*C*$_5$H$_4$, *C*$_1$), 91.2 (*C*$_5$H$_4$), 89.1 (*C*$_5$H$_4$), 88.7 (*C*$_5$H$_4$), 83.4 (*C*$_5$H$_4$), 134.3 (s, *Ph*, *C*$_1$), 133.3 (*Ph*), 129.0 (*Ph*), 128.3 (*Ph*). − ^{31}P NMR (300 MHz, C_6D_6): δ = −38.20 (d, $^1J_{PH}$ = 322 Hz, *P*−H).

Protonation of [Nb(η^5-$C_5H_4SiMe_3)_2(H)(PHPh_2)$] (3): Either CF_3COOH or CF_3COOD was added to a [D$_6$]acetone solution of [Nb(η^5-$C_5H_4SiMe_3)_2(H)(PHPh_2)$] (**3**) in a 5 mm NMR tube at 183 K, to give either the dihydrogen complex [Nb(η^5-$C_5H_4SiMe_3)_2(\eta^2$-$H_2)(PHPh_2)$]CF_3CO_2 (**4**) or its isotopomer [Nb(η^5-$C_5H_4SiMe_3)_2(\eta^2$-HD)$(PHPh_2)$]CF_3CO_2 (**5**).

Preparation of [Nb(η^5-$C_5H_4SiMe_3)_2(H)_2(PHPh_2)$]$CF_3CO_2$ (6) and [Nb(η^5-$C_5H_4SiMe_3)_2(H)_2(PDPh_2)$]$CF_3CO_2$ (7): To a solution of [Nb(η^5-$C_5H_4SiMe_3)_2(H)(PHPh_2)$] (**3**) (0.30 g, 0.55 mmol) in 30 mL of THF at 183 K was added CF_3COOH or CF_3COOD (42 μL, 0.55 mmol) by syringe. The solution was allowed to reach room temperature and stirred for 2 h. The resulting solution was evaporated to dryness. Complexes **6** and **7** were obtained as colourless solids after precipitation with Et_2O (yield: 80%).

Preparation of [Nb(η^5-$C_5H_4SiMe_3)_2(\eta^2$-*S*,*S*-SSCH)] (9): To a solution of [Nb(η^5-$C_5H_4SiMe_3)_2(H)(PHPh_2)$] (**3**) (0.30 g, 0.55 mmol) in THF (40 mL) was added CS_2 (93.1 μL, 0.55 mmol) and the reaction mixture was stirred for 1 h. The resulting solution was evaporated to dryness to give a red oily material. Complex **9** was isolated as an orange solid after precipitation from hexane (yield: 95%). − ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.22 (s, 18 H, Si*Me*$_3$), 5.05 (4 H, C_5H_4), 5.44 (4 H, C_5H_4), 4.17 (s, 1 H, SSC*H*). − ^{13}C{^{1}H} NMR (300 MHz, $CDCl_3$): δ = 0.5 (Si*Me*$_3$), 98.6 (*C*$_5$H$_4$, *C*$_1$), 103.6 (*C*$_5$H$_4$), 106.9 (*C*$_5$H$_4$), 120.0 (S*C*HS). − $C_{17}H_{27}NbS_2Si_2$ (444.12): calcd. C 45.95, H 6.08; found C, 45.81, H 5.96.

Preparation of [Nb(η^5-$C_5H_4SiMe_3)_2(\eta^2$-*O*,*O*-OOCH)] (10): A THF solution of [Nb(η^5-$C_5H_4SiMe_3)_2(H)(PHPh_2)$] (**3**) (0.30 g, 0.55 mmol) was saturated with CO_2 (2.5 atm.) in a Fischer−Porter bottle for 8 h at room temperature. The solution became increasingly dark and a brown solution was finally obtained and then evaporated to dryness. Complex **10** was obtained as an oily brown material (yield: 90%). − IR (Nujol): ν_{asym} (CO_2^-) = 1638 cm^{-1}; ν_{sym} (CO_2^-) = 1545 cm^{-1}. − ^{1}H NMR (300 MHz, C_6D_6): δ = −0.04 (s, 18 H, Si*Me*$_3$), 4.14 (m, 4 H, C_5H_4), 5.68 (m, 4 H, C_5H_4), 7.47 (s, 1 H, O_2CH). ^{13}C{^{1}H} NMR (300 MHz, C_6D_6): δ = 0.1 (Si*Me*$_3$), 107.8 (*C*$_5$H$_4$, *C*$_1$), 105.0 (*C*$_5$H$_4$), 108.1 (*C*$_5$H$_4$), 184.3 (O_2CH).

Preparation of [Nb(η^5-$C_5H_4SiMe_3)_2(PHPh_2)(L)$]Cl [L = $PHPh_2$ (11), CN(xylyl) (12), CO (13)]: To a solution of [Nb(η^5-$C_5H_4SiMe_3)_2(H)(L)$] [L = $PHPh_2$, CN(xylyl), CO] (0.55 mmol) in 40 mL of Et_2O was added $ClPPh_2$ (125 μL, 0.70 mmol) by syringe. A red-orange precipitate formed immediately. When sedimentation was complete the solution was filtered and the residue washed twice with 20 mL of Et_2O and dried in vacuo. Complexes **11**, **12** and **13** were obtained as orange or red solids. − **11:** IR (KBr): $\nu_{(P-H)}$ = 2297 cm^{-1}. − ^{1}H NMR (300 MHz, [D$_6$]acetone): δ = 0.05 (s, 18 H, Si*Me*$_3$), 5.36 (m, 4 H, C_5H_4), 5.50 (m, 4 H, C_5H_4), 7.87 (d, $^1J_{HP}$ = 362 Hz, 1 H, P−*H*), 7.35−7.60 (m, *Ph*), 8.12 [s, 2 H, *H*$_{para}$ (*Ph*)]. − ^{13}C NMR (300 MHz, [D$_6$]acetone): δ = 0.1 (Si*Me*$_3$), 102.9 (*C*$_5$H$_4$, *C*$_1$), 92.5 (*C*$_5$H$_4$), 103.7 (*C*$_5$H$_4$), 135.7 (*Ph*, *C*$_1$), 133.0 (*Ph*), 129.0 (*Ph*), 128.3 (*Ph*). − ^{31}P NMR (300 MHz, [D$_6$]acetone): δ = 32.00 (d, $^1J_{HP}$ = 362 Hz, *P*−H). − $C_{40}H_{48}ClNbP_2Si_2$ (774.45): calcd. C 61.98, H 6.20; found C 62.10, H 6.18.

12: IR (KBr): $\nu_{(P-H)} = 2280$ cm^{-1}; $\nu_{(CNAr)} = 2058$ cm^{-1}. − ^{1}H NMR (300 MHz, [D$_6$]acetone): δ = 0.17 (s, 18 H, Si*Me*$_3$), 5.36 (m, 2 H, C_5H_4), 5.55 (m, 2 H, C_5H_4), 5.65 (m, 2 H, C_5H_4), 6.11 (m, 2 H, C_5H_4), 8.70 (d, $^1J_{HP}$ = 387 Hz, 1 H, P−*H*), 7.35−7.90 (m, *Ph*),

2.31 [CN(2,6-$Me_2C_6H_3$)]. – ^{13}C NMR (300 MHz, [D$_6$]acetone): δ = 0.1 (SiMe_3), 100.2 (C_5H_4, C_1), 92.3 (C_5H_4), 100.0 (C_5H_4), 100.8 (C_5H_4), 102.4 (C_5H_4), 132.5 (*Ph*, C_1), 133.0 (*Ph*), 129.0 (*Ph*), 127.6 (*Ph*), 19.4 [CN(2,6-$Me_2C_6H_3$)], 248.0 [*C*N(2,6-$Me_2C_6H_3$)]. – ^{31}P NMR (300 MHz, [D$_6$]acetone): δ = 38.50 (d, $^1J_{HP}$ = 387 Hz, *P*–H). – $C_{37}H_{46}NNbPSi_2$ (684.00): C 66.86, H 6.93; found C 66.01, H 6.95.

13: IR (KBr): $\nu_{(P-H)}$ = 2276 cm^{-1}; $\nu_{(CO)}$ = 1940 cm^{-1}. – ^{1}H NMR (300 MHz, [D$_6$]acetone): δ = 0.24 (s, 18 H, SiMe_3), 5.10 (m, 2 H, C_5H_4), 5.82 (m, 2 H, C_5H_4), 5.93 (m, 2 H, C_5H_4), 6.03 (m, 2 H, C_5H_4), 7.90 (d, $^1J_{HP}$ = 381 Hz, 1 H, P–*H*), 7.35–7.60 (m, Ph), 8.12 [s, 2 H, H_{para} (*Ph*)]. – ^{13}C NMR (300 MHz, [D$_6$]acetone): δ = –0.5 (SiMe_3), 102.9 (C_5H_4, C_1), 97.0 (C_5H_4), 98.1 (C_5H_4), 100.6 (C_5H_4), 101.8 (C_5H_4), 131.5 (*Ph*, C_1), 131.0 (*Ph*), 129.5 (*Ph*), 128.0 (*Ph*), 250 (*C*O). – ^{31}P NMR (300 MHz, [D$_6$]acetone): δ = 38.00 (d, $^1J_{HP}$ = 381 Hz, *P*–H). – $C_{29}H_{37}NbOPSi_2$ (581.16): C 62.03, H 6.60; found C 61.82, H 6.68.

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