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Studies on the reactivity of Nb(η^5-$C_5H_4SiMe_3$)$_2$(X)(L), X = H,Cl; L = CNXylyl, CNCy, CO and Nb(η^5-$C_5H_4SiMe_3$)$_2$(H)$_3$ complexes toward the Lewis acids B(C_6F_5)$_3$ and BF_3

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Abstract

The reaction of the electron-rich, coordinatively saturated, niobocene–hydride or –halide complexes Nb(η^5-$C_5H_4SiMe_3$)$_2$(X)(L), X = H or Cl, L = 2,6-dimethylphenylisocyanide (CNXylyl), cyclohexylisocyanide (CNCy) and carbonyl (CO), with the strong Lewis acid (B(C_6F_5)$_3$) gives the zwitterionic compounds [(η^5-$C_5H_4SiMe_3$)$_2$(CNXylyl)Nb(μ-X)(B(C_6F_5)$_3$)] (**1**), [(η^5-$C_5H_4SiMe_3$)$_2$(CNCy)Nb(μ-X)(B(C_6F_5)$_3$)] (**2**), [(η^5-$C_5H_4SiMe_3$)$_2$(CO)Nb(μ-X) (B(C_6F_5)$_3$)] (**3**), respectively, where the complexes possess a bridging hydride or halide group. Similarly, the starting niobocene-hydride species react with BF_3 to afford the corresponding zwitterionic complexes containing a bridging hydride ligand, namely [(η^5-$C_5H_4SiMe_3$)$_2$(CNXylyl)Nb(μ-H)(BF_3)] (**4**), [(η^5-$C_5H_4SiMe_3$)$_2$(CNCy)Nb(μ-H)(BF_3)] (**5**), [(η^5-$C_5H_4SiMe_3$)$_2$(CO)Nb(μ-H)(BF_3)] (**6**). The reaction of the hydride containing compounds **1**–**3** with the appropriate ligand L (1:1 molar ratio for **1** and **2**) in toluene at room temperature leads to the ionic compounds [(η^5-$C_5H_4SiMe_3$)$_2$Nb(CNXylyl)$_2$][(HB(C_6F_5)$_3$)] (**7**), [(η^5-$C_5H_4SiMe_3$)$_2$Nb(CNCy)$_2$][(HB(C_6F_5)$_3$)] (**8**), and [(η^5-$C_5H_4SiMe_3$)$_2$Nb(CO)$_2$][(HB(C_6F_5)$_3$)] (**9**), which contain two coordinated L ligands and a noncoordinated [(HB(C_6F_5)$_3$)]$^-$ counteranion. Analogous complexes were not observed in the same reaction for **4**–**6**. Finally, the compound [Nb(η^5-$C_5H_4SiMe_3$)$_2$(H)$_3$] reacts in acetone with (B(C_6F_5)$_3$) in a clean reaction to give the ionic compound [(η^5-$C_5H_4SiMe_3$)$_2$Nb][((CH_3)$_2$CHO)B(C_6F_5)$_3$)] (**10**), which contains the isopropoxide borate ion [((CH_3)$_2$CHO)B(C_6F_5)$_3$)]$^-$ as the counteranion. © 2000 Elsevier Science S.A. All rights reserved.

Keywords: Metallocenes; Niobocene; Boranes; Halides; Hydrides

1. Introduction

The chemistry of electrophilic cationic complexes such as [Cp_2MR]$^+$ (M = Ti, Zr, Hf) and other related compounds has received much attention in recent years. This is due to the fact that the title complexes have been implicated in a number of important processes, such as alkene polymerization [1] and insertion reactions of unsaturated molecules [2]. In contrast, these aspects of Group 4 metallocenes have no parallels in the analogous Group 5 metal species because little is known of their electrophilic cationic metallocene complexes [3]. Furthermore, hydride complexes of transition metals represent one of the most important classes of compounds because of their chemical reactivity and importance in catalysis [4]. In this field, the study of the reactivity of several families of transition metal hydrides toward Lewis acid reagents, such as ZnR_2, AlR_3 and BR_3, has been thoroughly considered [5]. Particularly, the behavior of metallocene–hydride complexes of group 5 metals with different classes of Lewis acid metals fragments was studied in the last 25 years, giving rise to the isolation of several di- and polynuclear complexes [6]. Recently, as part of our strategy to study the reactivity of hydride-niobocene complexes, namely Nb(η^5-$C_5H_4SiMe_3$)$_2$(H)(L), L = CO, P(OR)$_3$, we have

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studied their behavior with different Lewis acidic coinage cations, and different families of polynuclear systems associating transition-metal polyhydrides and a coinage cation, such as $[(Nb(\eta^5\text{-}C_5H_4SiMe_3)_2(P(OR)_3)(\mu\text{-}H)(AuPPh_3))PF_6]$ (R = Me, Et, Ph) [7], $[(Nb(\eta^5\text{-}C_5H_4SiMe_3)_2(CO)(\mu\text{-}H)(AuPPh_3))PF_6]$ [8], $[(Nb(\eta^5\text{-}C_5H_4SiMe_3)_2(CO)(\mu\text{-}H))_2M)PF_6]$ (M = Cu, Ag, Au) [8], $[(Nb(\eta^5\text{-}C_5H_4RR')_2(H)_3)_2M)A]$ (R = R′ = H, R = H, R′ = $SiMe_3$, R = R′ = $SiMe_3$; M = Cu, Ag, Au, A = PF_6^-, BF_4^-) [9], were isolated. In order to follow exploring this chemistry, we have decided to study the reactivity of hydride– and halide–niobocene complexes, $Nb(\eta^5\text{-}C_5H_4SiMe_3)_2(X)(L)$ (X = H, Cl; L = CO, isocyanide) and $[Nb(\eta^5\text{-}C_5H_4SiMe_3)_2(H)_3]$, toward the Lewis acid $B(C_6F_5)_3$ and BF_3 and this paper will focus on the synthesis and structural details of new zwitterionic complexes containing a bridging hydride or halide $[(\eta^5\text{-}C_5H_4SiMe_3)_2(L)Nb(\mu\text{-}X)(BY_3)]$ and new cationic d^2 complexes, $[(\eta^5\text{-}C_5H_4SiMe_3)_2Nb(L)_2][XB(C_6F_5)_3)]$ and $[(\eta^5\text{-}C_5H_4SiMe_3)_2Nb][(CH_3)_2CHO)B(C_6F_5)_3)]$.

2. Results and discussion

The reaction of one equivalent of the niobocene complexes $Nb(\eta^5\text{-}C_5H_4SiMe_3)_2(X)(L)$, (L = 2,6-dimethylphenylisocyanide (CNXylyl), cyclohexylisocyanide (CNCy) and carbonyl (CO)), with one equivalent of $(B(C_6F_5)_3)$ in toluene at low temperature (−78°C) resulted in the formation of a deep red or green solution from which air-sensitive solids, corresponding to the zwitterionic compounds $[(\eta^5\text{-}C_5H_4SiMe_3)_2(L)Nb(\mu\text{-}X)(B(C_6F_5)_3)]$ (**1**–**3**), which were isolated after the appropriate work up (Eq. (1)).

$$Nb(\eta^5\text{-}C_5H_4SiMe_3)_2(X)(L) + B(C_6F_5)_3 \rightarrow [(\eta^5\text{-}C_5H_4SiMe_3)_2(L)Nb(\mu\text{-}X)B(C_6F_5)_3] \quad (1)$$

1a: X = H, L = CNXylyl; **1b**: X = Cl, L = CNXylyl; **2a**: X = H, L = CNCy; **2b**: X = Cl, L = CNCy; **3a**: X = H, L = CO; **3b**:X = Cl, L = CO.

The complexes are partially soluble in toluene and alkenes and soluble in donor solvents, such as acetone or THF, in which they decompose slowly. Similarly, the reaction of the same starting hydride–niobocene complexes with one equivalent of $BF_3{\cdot}Et_2O$ in toluene at low temperature (−78°C) gave the appropriate zwitterionic complexes $[(\eta^5\text{-}C_5H_4SiMe_3)_2(L)Nb(\mu\text{-}H)(BF_3)]$ (**4a**–**6a**) (Eq. (2)), which were isolated as air-sensitive solids after the appropriate work up.

$$Nb(\eta^5\text{-}C_5H_4SiMe_3)_2(H)(L) + BF_3{\cdot}Et_2O \rightarrow [(\eta^5\text{-}C_5H_4SiMe_3)_2(L)Nb(\mu\text{-}H)BF_3) + Et_2O \quad (2)$$

4a: X = H, L = CNXylyl; **5a**: X = H, L = CNCy; **6a**: X = H, L = CO.

These compounds show similar solubilities to the previously described complexes **1**–**3**. Attempts to prepare suitable crystals of **1**–**6** for X-ray crystal structure determinations were unsuccessful.

We have also studied the behavior of the zwitterionic species **1**–**6** toward the addition of π-acid ligands. In fact, the reaction of **1a**–**3a** and **3b** with L (in a 1:1 molar ratio for isocyanides and an excess for CO) in toluene at room temperature (r.t.) for 48 h resulted in the slow precipitation of the ion pairs, $[(\eta^5\text{-}C_5H_4SiMe_3)_2Nb(L)_2][XB(C_6F_5)_3]$ (**7**–**9**) (Eq. (3)), which were isolated as red–orange solids.

$$[(\eta^5\text{-}C_5H_4SiMe_3)_2(L)Nb(\mu\text{-}X)B(C_6F_5)_3] + L \rightarrow [(\eta^5\text{-}C_5H_4SiMe_3)_2Nb(L)_2][XB(C_6F_5)_3] \quad (3)$$

7a: X = H, L = CNXylyl; **8a**: X = H, L = CNCy; **9a**: X = H, L = CO; **9b**: X = Cl, L = CO.

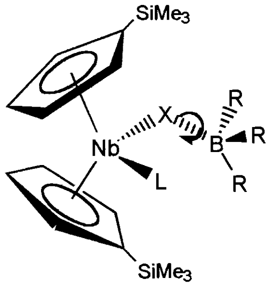
Complexes **7**–**9** are considerably more stable than **1**–**3** in donor solvents such as acetone or THF, but even in these cases it was not possible to isolate suitable crystals for X-ray crystal structure determinations. The same process for **1b**, **2b** and **4**–**6** gave rise to decomposition products. It is probable that in these reactions it is not possible to stabilize the expected ion pairs $[(\eta^5\text{-}C_5H_4SiMe_3)_2Nb(L)_2][HBF_3]$ for **4**–**6**, because the corresponding counter-anion $[HBF_3]^-$ is unstable [10]. Finally, we considered here the reaction of **1a**–**3a** and **3b** with π-acid ligands, L′, different to that present in the appropriate starting complex, giving rise to the formation of the corresponding ion pair $[(\eta^5\text{-}C_5H_4SiMe_3)_2Nb(L)(L')][XB(C_6F_5)_3]$, although these compounds were not isolated as pure samples due to the fact that they tend to disproportionate easily to give the symmetrical species $[(\eta^5\text{-}C_5H_4SiMe_3)_2Nb(L)_2][XB(C_6F_5)_3]$ and $[(\eta^5\text{-}C_5H_4SiMe_3)_2Nb(L')_2][XB(C_6F_5)_3]$.

The reactivity of $[Nb(\eta^5\text{-}C_5H_4SiMe_3)_2(H)_3]$ towards $B(C_6F_5)_3$ has also been considered. The trihydride species reacts with $B(C_6F_5)_3$ in acetone at −78°C, in a 1:1 molar ratio, to give the ion pair $[(\eta^5\text{-}C_5H_4SiMe_3)_2Nb][((CH_3)_2CHO)B(C_6F_5)_3]$ **10** (Eq. (4)), which was isolated as a yellowish–white solid after the appropriate work up.

$$[Nb(\eta^5\text{-}C_5H_4SiMe_3)_2(H)_3] + B(C_6F_5)_3 \xrightarrow[-H_2]{CH_3COCH_3} [(\eta^5\text{-}C_5H_4SiMe_3)_2Nb][(CH_3)_2CHO)B(C_6F_5)_3] \quad (4)$$

The same process in a non-coordinative solvent, such as toluene, afforded a mixture of intractable products that were not characterized. Complex **10** is soluble in acetone and THF, partially soluble in toluene, and insoluble in alkanes. It was stable for several days in solution or in the solid state under an inert atmosphere and was crystallized from acetone. However, unfortunately the crystals obtained in this way were not suitable for study by means of X-ray crystal diffractometric methods.

The new families of niobocene complexes were characterized by spectroscopic methods. The IR spectra of complexes **1**–**9** exhibit the characteristic band of the ancillary ligand L, ν_{CO} for CO at ca. 1900 cm^{-1} or ν_{CN} for RNC at ca. 2100 cm^{-1}, which are typical of a terminal ligand and indicate that no interactions between this ligand and the Lewis acid $B(C_6F_5)_3$ take place. The absence of the band corresponding to ν(Nb–H) in the spectra of complexes **1a**–**6a** and the presence of a band at ca. 2260 cm^{-1} are noteworthy, and these can be ascribed to ν(Nb–H–B); in the spectra of complexes **7a**–**9a** the ν(B–H) of the $[HB(C_6F_5)_3]^-$ appears as a band at ca. 2400 cm^{-1} [11]. The NMR spectra of **1**–**9** also provide informative data. Firstly, the ^{1}H-NMR spectra of **1a**–**6a** do not exhibit the expected resonance for the bridging hydride, and this is probably due to both its coupling with the ^{11}B atom and the high quadrupolar moments of the ^{93}Nb and ^{11}B nuclei. However, their ^{11}B-NMR spectra show a doublet at ca. -20 ppm, $^1J_{(B-H)} = 85$ Hz, by virtue of coupling between the boron atom and the proposed bridging hydride atom. This value is intermediate between that corresponding to a genuine bridging B–H ($^1J_{(B-H)} \approx 60$ Hz) and a terminal B–H ($^1J_{(B-H)} \approx 100$ Hz) bond [12]. Although the ^{1}H-NMR spectra of the ion pairs **7a**–**9a** and **9b** do not exhibit the expected resonance of the $[HB(C_6F_5)_3]^-$ anion, again probably due to the effects discussed above, their ^{11}B-NMR spectra display the corresponding resonance as a broad doublet at ca. -20 ppm ($^1J_{(B-H)} = 95$ Hz) [11c]. Three characteristic resonances for the C_6F_5 groups of the $B(C_6F_5)_3$ moieties [13] in complexes **1**–**3** and **7**–**9** and only one resonance for the BF_3 group in complexes **4a**–**6a** were observed in the ^{19}F-NMR spectra, indicating that in complexes containing a bridging hydride or halide Nb–X–B (X = H, Cl) a free rotation around the X–B bond occurs (see below) making the C_6F_5 and F groups equivalent. In accordance with the data reported, we propose the structural disposition depicted in Fig. 1 for the different classes of zwitterionic compounds. The formation of the hydride-containing complexes can be considered as the result of an electrophilic attack of the Lewis acid $B(C_6F_5)_3$ or BF_3 on the Nb–H bond, to give a well known three-center two-electron Nb–H–B bond [6b].



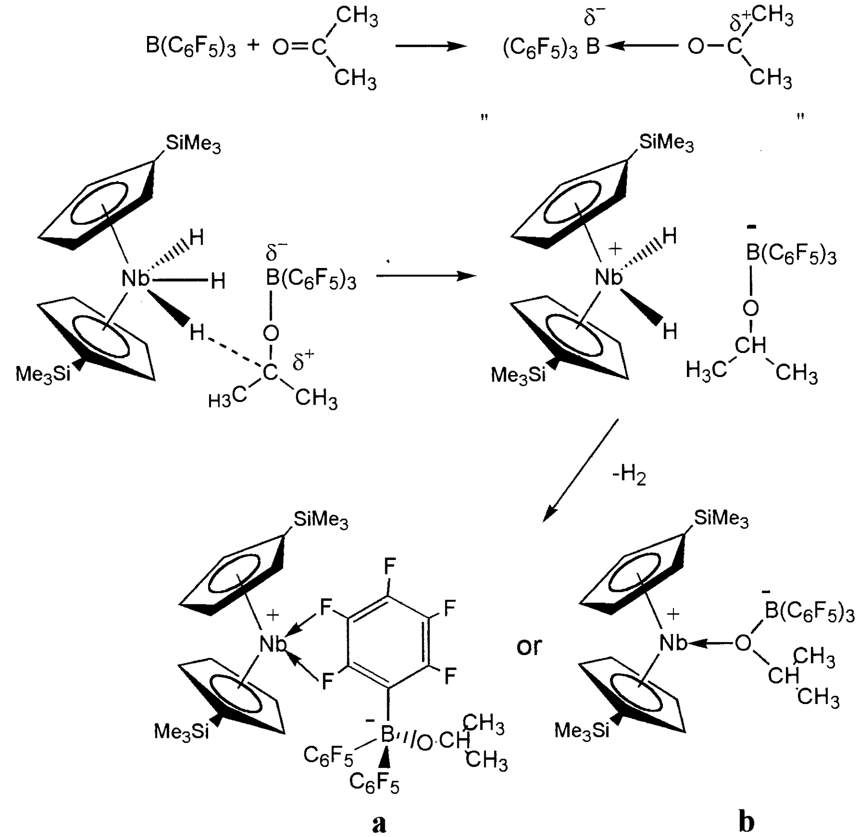
L=CNXylyl, CNCy, CO
X=H,Cl
R=C_6F_5, F

Fig. 1. Proposed structure for niobocene complexes containing a bridging hydride or halide.

A comparable situation, where the bridging chloride ligand would act as a Lewis base toward the Lewis acid $B(C_6F_5)_3$ could be considered for complexes **1b**–**3b**. Spectroscopic data will also be considered for complex **10**. The ^{1}H-NMR and ^{11}B-NMR spectra, respectively, exhibit the characteristic resonances for an isopropoxide group and a single signal. In addition, the ^{19}F-NMR spectrum displays the three characteristic resonances of the C_6F_5 group, indicating that the three groups are equivalent even when the spectrum was recorded at -90°C. The formation of **10** can be envisaged on the basis of the steps outlined in Scheme 1.

The first step would correspond to the formation of a typical adduct between both $B(C_6F_5)_3$ and acetone [14]. After this, an interaction between this adduct, through the electron deficient carbon atom, and an Nb–H bond would take place to give an ion pair, which would evolve with the elimination of H_2 to give rise to the final product **10.** One question to be considered is the exact nature of the interaction between the proposed anion $[((CH_3)_2CHO)B(C_6F_5)_3]^-$ with the proposed highly electron deficient niobocene species $[(\eta^5\text{-}C_5H_4SiMe_3)_2Nb]^+$. Two possibilities have been depicted in Scheme 1. The first implies an interaction through two fluorine atoms of one C_6F_5 group, a possibility that has previously been described in some cationic zirconocene complexes [15]. In the second possibility, such an interaction would take place alternatively through the oxygen atom of the isopropoxide group. In light of the ^{19}F-NMR spectrum recorded at low temperature (-90°C), where the three C_6F_5 groups are equivalent (see above), we are tempted to propose the second interaction as the more probable, although the first type of interaction cannot be definitively ruled out.

In conclusion, a study into the reaction of electron-rich, coordinatively saturated niobocene complexes with two strong Lewis acids, namely $B(C_6F_5)_3$ and BF_3, has been undertaken, and new families of zwitterionic complexes resulting from the interaction of these acids with the Nb–X bonds and ion pairs have been isolated and characterized. Finally, an interesting reaction between a trihydride niobocene and $B(C_6F_5)_3$ has also been considered, giving rise to an ion pair in which the presence of a highly electron poor $[(\eta^5\text{-}C_5H_4SiMe_3)_2Nb]^+$ moiety is proposed.



Scheme 1. Proposed reaction pathway for the formation of complex **10**.

3. Experimental

3.1. General

All reactions were performed using standard Schlenk-tube techniques in an atmosphere of dry nitrogen. Solvents were distilled from appropriate drying agents and degassed before use.

The following compounds: Nb(η^5-$C_5H_4SiMe_3)_2$(H)-(CNXylyl), Nb(η^5-$C_5H_4SiMe_3)_2$(H)(CNCy), Nb-(η^5-$C_5H_4SiMe_3)_2$(H)(CO), Nb(η^5-$C_5H_4SiMe_3)_2$(Cl)-(CNXylyl), Nb(η^5-$C_5H_4SiMe_3)_2$(Cl)(CNCy), Nb(η^5-$C_5H_4SiMe_3)_2$(Cl)(CO), [Nb(η^5-$C_5H_4SiMe_3)_2(H)_3$] and $B(C_6F_5)_3$ were prepared as described earlier [13,16–20]. CNXylyl, CNCy, CO and $BF_3{\cdot}OEt_2$ were used as received (Aldrich). IR spectra were recorded on a Perkin–Elmer PE 883 IR spectrophotometer. ^{1}H-, ^{13}C-, ^{11}B- and ^{19}F-NMR spectra were recorded using a Varian FT-300 spectrometer at 300, 75, 96 and 282 MHz, respectively. ^{1}H and ^{13}C chemical shifts were determined by reference to the residual deuterated solvent signal and those of ^{11}B and ^{19}F with respect to $\delta = 0$ for $BF_3{\cdot}OEt_2$ and $CFCl_3$, respectively. Microanalyses were carried out using a Perkin–Elmer 2400 CHN analyzer.

3.2. Preparation of complexes **1–3**

The strong Lewis acid $B(C_6F_5)_3$ (0.30 g, 0.59 mmol) was added to a solution of [Nb(η^5-$C_5H_4SiMe_3)_2$(H)-(CNXylyl)] (0.29 g, 0.59 mmol) in toluene (ca. 50 ml) at −78°C. The resulting mixture was stirred for 10 min and then allowed to warm up to r.t. After that time a deep red solution had formed and this was stirred for 2 h. The solvent was removed under vacuum to give a deep red oily solid, which was washed with ca. 10 ml of hexane to yield the deep red solid [(η^5-$C_5H_4SiMe_3)_2$-(CNXylyl)Nb(μ-H)$B(C_6F_5)_3$] (**1a**) (0.43 g, 72%). Complexes **2a**–**3a** were prepared in a similar manner to **1a**. Yields of 70 and 69% were obtained for **2a** and **3a**, respectively.

The method of preparation for the complexes **1b**–**3b** was similar to **1a** and gave green solids. Yields of around 70% were found in all cases.

3.2.1. Complex **1a**

IR (nujol) ν_{CN} 2058 cm^{-1}, $\nu_{(Nb-H-B)}$ 2280 cm^{-1}, 1657, 1525, 1467, 1096, 980 cm^{-1} $B(C_6F_5)_3$, 1260 cm^{-1} $SiMe_3$. ^{1}H-NMR (acetone-d_6, in ppm): $\delta = 0.12$ (s, 18 H, SiMe_3), 5.58 (2 H), 5.78 (2 H), 5.83 (2 H), 6.32 (2 H) (m, C_5H_4), 2.48 (s, 6 H, *Me*CNR), 7.21 (m, 3 H, C_6H_3CNR). ^{13}C{^{1}H}-NMR (acetone-d_6, in ppm): $\delta =$ −0.1 (SiMe_3), 99.8, 102.1 (C_1), 103.7, 104.5, 112.1

(C_5H_4), 18.5 (MeCNR), 228.6 (CNR), 139.0, 142.0, 147.0, 150.0 B(C_6F_5)$_3$. ^{19}F-NMR (acetone-d_6, in ppm): $\delta = -129.8$ (br.s. 6 F, o-F), -161.70 (t, 3 F, $^3J_{FF} = 18$ Hz, p-F), -164.0 (br. s. 6 F, m-F) B(C_6F_5)$_3$ ^{11}B{^{1}H}-NMR (acetone-d_6, in ppm): $\delta = -19.8$ B(C_6F_5)$_3$. Anal. Calc. for $C_{43}H_{36}BF_{15}NNbSi_2$: C, 50.98; H, 3.55; N, 1.48. Found: C, 50.71; H, 3.25; N, 1.28%.

3.2.2. Complex **2a**

IR (nujol) ν_{CN} 2280 cm^{-1}, $\nu_{(Nb-H-B)}$ 2290 cm^{-1}, 1657, 1525, 1467, 1096, 980 cm^{-1} B(C_6F_5)$_3$, 1253 cm^{-1} SiMe$_3$. ^{1}H-NMR (acetone-d_6, in ppm): $\delta = 0.11$ (s, 18 H, SiMe_3), 5.32 (2 H), 5.55 (2 H), 5.67 (2 H), 6.12 (2 H) (m, C_5H_4), 1.5 (m, CNCy). ^{13}C{^{1}H}-NMR (acetone-d_6, in ppm): $\delta = 1.0$ (SiMe_3), 99.9, 96.8 (C_1), 103.9, 104.3, 110.8 (C_5H_4), 68.4 (CNC_6H_{11}), 225.7 (CNC_6H_{11}), 135.0, 140.0, 147.0, 152.0 B(C_6F_5)$_3$. ^{19}F-NMR (acetone-d_6, in ppm): $\delta = -129.7$ (br. s. 6 F, o-F), -161.8 (t, 3 F, $^3J_{FF} = 18$ Hz, p-F), -164.5 (br. s. 6 F, m-F) B(C_6F_5)$_3$. ^{11}B{^{1}H}-NMR (acetone-d_6, in ppm): $\delta = -20.3$ B(C_6F_5)$_3$. Anal. Calc. for $C_{41}H_{38}BF_{15}NNbSi_2$: C, 49.75; H, 3.88; N, 1.41. Found: C, 48.52; H, 3.23; N, 1.32%.

3.2.3. Complex **3a**

IR (nujol) ν_{CO} 1920 cm^{-1}, $\nu_{(Nb-H-B)}$ 2285 cm^{-1}, 1657, 1525, 1467, 1096, 980 cm^{-1} B(C_6F_5)$_3$, 1249 cm^{-1} SiMe$_3$. ^{1}H-NMR (acetone-d_6, in ppm): $\delta = 0.23$ (s, 18 H, SiMe_3), 5.20 (2 H), 5.59 (2 H), 5.62 (2 H), 6.00 (2 H) (m, C_5H_4). ^{13}C{^{1}H}-NMR (acetone-d_6, in ppm): $\delta =$ 0.53 (SiMe_3), 98.56, 100.91 (C_1), 102.54, 105.98, 110.75 (C_5H_4), 252.00 (CO), 136.00, 141.00, 147.00, 150.00 B(C_6F_5)$_3$. ^{19}F-NMR (acetone-d_6, in ppm): $\delta = -129.90$ (br.s. 6 F, o-F), -161.70 (t, 3 F, $^3J_{FF} = 18.30$ Hz, p-F), -164.53 (br. s. 6 F, m-F) B(C_6F_5)$_3$. ^{11}B{^{1}H}-NMR (acetone-d_6, in ppm): $\delta = -20.20$ B(C_6F_5)$_3$. Anal. Calc. for $C_{35}H_{27}BF_{15}NbOSi_2$: C, 46.25; H, 2.97. Found: C, 45.81; H, 2.35%.

3.2.4. Complex **1b**

IR (nujol) ν_{CN} 2204 cm^{-1}, 1644, 1515, 1466, 1093, 975 cm^{-1} B(C_6F_5)$_3$, 1252 cm^{-1} SiMe$_3$. ^{1}H-NMR (acetone-d_6, in ppm): $\delta = 0.12$ (s, 18 H, SiMe_3), 5.59 (2 H), 5.78 (2 H), 5.87 (2 H), 6.34 (2 H) (m, C_5H_4), 2.48 (s, 6 H, MeCNR), 7.15 (m, 3 H, C_6H_3CNR). ^{13}C{^{1}H}-NMR (acetone-d_6, in ppm): $\delta = -0.1$ (SiMe_3), 99.0, 99.8 (C_1), 103.7, 104.5, 112.1 (C_5H_4), 19.2 (MeCNR), 134.9, 137.4, 139.7, 142.2 B(C_6F_5)$_3$. ^{19}F-NMR (acetone-d_6, in ppm): $\delta = -131.5$ (br. s. 6 F, o-F), -158.5 (t, 3 F, $^3J_{FF} = 18$ Hz, p-F), -163.2 (br. s. 6 F, m-F) B(C_6F_5)$_3$. ^{11}B{^{1}H}-NMR (acetone-d_6, in ppm): $\delta = 1.0$ B(C_6F_5)$_3$. Anal. Calc. for $C_{43}H_{35}BClF_{15}NNbSi_2$: C, 49.36; H, 3.35; N, 1.34. Found: C, 50.01; H, 3.25; N, 1.28%.

3.2.5. Complex **2b**

IR (nujol) ν_{CN} 2171 cm^{-1}, 1646, 1518, 1471, 1088, 980 cm^{-1} B(C_6F_5)$_3$, 1254 cm^{-1} SiMe$_3$. ^{1}H-NMR (acetone-d_6, in ppm): $\delta = 0.12$ (s, 18 H, SiMe_3), 5.34 (2 H), 5.54 (2 H), 5.64 (2 H), 6.12 (2 H) (m, C_5H_4), 4.50 (m, CNCy), 1.30–1.85 (m, CNCy). ^{13}C{^{1}H}-NMR (acetone-d_6, in ppm): $\delta = 0.0$ (SiMe_3), 95.2 (C_1), 99.5, 103.5, 103.9, 110.5 (C_5H_4), 57.2 (CNC_6H_{11}), 134.6, 139.5, 146.4, 150.9 B(C_6F_5)$_3$. ^{19}F-NMR (acetone-d_6, in ppm):$\delta = -131.4$ (br.s. 6 F, o-F), -157.5 (t, 3 F, $^3J_{FF} = 19$ Hz, p-F), -162.8 (br. s. 6 F, m-F) B(C_6F_5)$_3$. ^{11}B{^{1}H}-NMR (acetone-d_6, in ppm): $\delta = 1.2$ B(C_6F_5)$_3$. Anal. Calc. for $C_{41}H_{37}BClF_{15}NNbSi_2$: C, 49.36; H, 3.35; N, 1.34. Found: C, 48.52; H, 3.23; N, 1.32%.

3.2.6. Complex **3b**

IR (nujol) ν_{CO} 1946 cm^{-1}, 1645, 1517, 1471, 1090, 977 cm^{-1} B(C_6F_5)$_3$, 1285 cm^{-1} SiMe$_3$. ^{1}H-NMR (acetone-d_6, in ppm): $\delta = 0.21$ (s, 18 H, SiMe_3), 5.71 (2 H), 5.92 (2 H), 5.95 (2 H), 6.28 (2 H) (m, C_5H_4). ^{13}C{^{1}H}-NMR (acetone-d_6, in ppm): $\delta = 0.1$ (SiMe_3), 97.9 (C_1), 99.1, 104.6, 106.9, 110.2 (C_5H_4), 250.0 (CO), 135.0, 139.9, 146.3, 151.1 B(C_6F_5)$_3$. ^{19}F-NMR (acetone-d_6, in ppm): $\delta = -131.4$ (br. s. 6 F, o-F), -157.4 (t, 3 F, $^3J_{FF} = 18$ Hz, p-F), -162.8 (br. s. 6 F, m-F) B(C_6F_5)$_3$. ^{11}B{^{1}H}-NMR (acetone-d_6, in ppm): $\delta = 1.3$ B(C_6F_5)$_3$. Anal. Calc. for $C_{35}H_{26}BClF_{15}NbOSi_2$: C, 44.57; H, 2.76. Found: C, 45.31; H, 2.88%.

3.3. Preparation of complexes **4a–6a**

To a solution of [Nb(η^5-$C_5H_4SiMe_3$)$_2$(H)(CNXylyl)] (0.28 g, 0.57 mmol) in toluene (ca. 40 ml) was added $BF_3\cdot Et_2O$ (90 µl, 0.57 mmol) by a microsyringe at −78°C. The resulting mixture was stirred for 10 min and then allowed to warm up to r.t. After that time a deep red solution had formed and this was stirred for 2 h. The solvent was removed in vacuo to give a deep red oily solid, which was washed with ca. 10 ml of cool hexane to yield the deep red solid **4a** (0.25 g, 78%). Complexes **5a** and **6a** were prepared in a similar manner to **4a**. Yields of 72 and 75% were found for **5a** and **6a**, respectively.

3.3.1. Complex **4a**

IR (nujol) ν_{CN} 2084 cm^{-1}, ν_{B-F}(BF_3) 1050 cm^{-1}, 1262 cm^{-1} SiMe$_3$. ^{1}H-NMR (acetone-d_6, in ppm): $\delta =$ 0.12 (s, 18 H, SiMe_3), 5.57 (2 H), 5.77 (2 H), 5.86 (2 H), 6.32 (2 H) (m, C_5H_4), 2.49 (MeCNR), 7.20 (m, 3 H, C_6H_3CNR). ^{13}C{^{1}H}-NMR (acetone-d_6, in ppm): $\delta =$ 0.4 (SiMe_3), 100.2, 102.2 (C_1), 104.1, 105.0, 112.5 (C_5H_4), 19.6 (MeCNR), 235.0 (CNR). ^{19}F-NMR (acetone-d_6, in ppm): $\delta = -147.1$ BF_3. ^{11}B{^{1}H}-NMR (acetone-d_6, in ppm): $\delta = 4.9$ BF$_3$. Anal. Calc. for $C_{25}H_{35}BF_3NNbSi_2$: C, 51.61; H, 3.51; N, 1.36. Found: C, 50.89; H, 3.98; N, 1.42%.

3.3.2. Complex **5a**

IR (nujol) ν_{CN} 2270 cm^{-1}, ν_{B-F}(BF$_3$) 1048 cm^{-1}, 1258 cm^{-1} SiMe$_3$. ^{1}H-NMR (acetone-d_6, in ppm): $\delta =$ 0.11 (s, 18 H, SiMe_3), 5.30 (2 H), 5.53 (2 H), 5.66 (2 H), 6.12 (2 H) (m, C$_5H_4$), 1.6 (m, CNCy). ^{13}C{^{1}H}-NMR (acetone-d_6, in ppm): $\delta = 0.6$ (SiMe_3), 100.3, 101.4 (C$_1$), 103.6, 105.6, 110.9 (C_5H$_4$), 70.0 (CNCy), 238.0 (CNCy). ^{19}F-NMR (acetone-d_6, in ppm): $\delta = -147.5$ BF$_3$. ^{11}B{^{1}H}-NMR (acetone-d_6, in ppm): $\delta = 4.5$ BF$_3$. Anal. Calc. for C$_{23}$H$_{38}$BF$_3$NNbSi$_2$: C, 50.64; H, 6.97; N, 2.57. Found: C, 50.21; H, 7.22; N, 2.89%.

3.3.3. Complex **6a**

IR (nujol) ν_{CO} 1920 cm^{-1}, ν_{B-F}(BF$_3$) 1052 cm^{-1}, 1250 cm^{-1} SiMe$_3$. ^{1}H-NMR (acetone-d_6, in ppm): $\delta =$ 0.25 (s, 18 H, SiMe_3), 5.21 (2 H), 5.52 (2 H), 5.61 (2 H), 5.96 (2 H) (m, C$_5H_4$). ^{13}C{^{1}H}-NMR (acetone-d_6, in ppm): $\delta = -0.18$ (SiMe_3), 90.5, 93.5 (C$_1$), 96.8, 100.8, 101.5 (C_5H$_4$), 252.8 (CO). ^{19}F-NMR (acetone-d_6, in ppm): $\delta = -147.7$ BF$_3$. ^{11}B{^{1}H}-NMR (acetone-d_6, in ppm): $\delta = 2.2$ BF$_3$. Anal. Calc. for C$_{27}$H$_{27}$BF$_3$NbOSi$_2$: C, 43.97; H, 2.87. Found: C, 42.51; H, 5.51%.

3.4. Preparation of complexes **7**–**9**

To a solution of [(η^5-C$_5$H$_4$SiMe$_3$)$_2$(CNXylyl)Nb(μ-H)(B(C$_6$F$_5$)$_3$)] (**1a**) (0.60 g, 0.59 mmol) in toluene (ca. 50 ml) at r.t., was added CNXylyl (0.08 g, 0.59 mmol). The resulting mixture was stirred for 2 days. The color of the solution changed from deep red to orange–red and the precipitation of an orange–red solid was observed. This solid was filtered off and washed with ca. 10 ml of hexane to yield the complex [Nb(η^5-C$_5$H$_4$SiMe$_3$)$_2$(CNXylyl)$_2$][HB(C$_6$F$_5$)$_3$] (**7a**) (0.46 g, 68%). Complexes **8a**, **9a** and **9b** were prepared in a similar manner to **7a**. For complexes, **9a** and **9b** the corresponding solutions of **3a** and **3b** were saturated with CO. Yields into the range of 65–70% were found for **8a**, **9a** and **9b**.

3.4.1. Complex **7a**

IR (nujol) ν_{CN} 2124 cm^{-1}, ν_{B-H} 2381 cm^{-1}, 1640, 1511, 1463, 1089, 976 cm^{-1} B(C$_6$F$_5$)$_3$, 1251 cm^{-1} SiMe$_3$. ^{1}H-NMR (acetone-d_6, in ppm): $\delta = 0.25$ (s, 18 H, SiMe_3), 5.74 (4 H), 5.99 (4 H) (pst, C$_5H_4$), 2.46 ((s, 6H, MeCNR), 7.24 (m, 3 H, C$_6H_3$CNR). ^{13}C{^{1}H}-NMR (acetone-d_6, in ppm): $\delta = 0.0$ (SiMe_3), 97.2, 98.1 (C$_1$), 102.2 (C_5H$_4$), 19.1 (MeCNR), 226.1 (CNR), 135.0, 139.0, 147.0, 151.0 B(C_6F$_5$)$_3$. ^{19}F-NMR (acetone-d_6, in ppm): $\delta = -131.4$ (br.s. 6 F, o-F), -157.4 (t, 3 F, $^3J_{FF} = 18$ Hz, p-F), -162.8 (br. s. 6 F, m-F) B(C$_6F_5$)$_3$. ^{11}B{^{1}H}-NMR (acetone-d_6, in ppm): $\delta = -20.4$ B(C$_6$F$_5$)$_3$. Anal. Calc. for C$_{52}$H$_{45}$BF$_{15}$N$_2$NbSi$_2$: C, 54.64; H, 3.97; N, 2.45. Found: C, 55.21; H, 3.71; N, 2.89%.

3.4.2. Complex **8a**

IR (nujol) ν_{CN} 2100 cm^{-1}, ν_{B-H} 2389 cm^{-1}, 1640, 1511, 1463, 1089, 976 cm^{-1} B(C$_6$F$_5$)$_3$, 1254 cm^{-1} SiMe$_3$. ^{1}H-NMR (acetone-d_6, in ppm): $\delta = 0.23$ (s, 18 H, SiMe_3), 5.62 (4 H), 5.89 (4 H) (pst, C$_5H_4$), 1.60 (m, CNCy). ^{13}C{^{1}H}-NMR (acetone-d_6, in ppm): $\delta = 0.8$ (SiMe_3), 98.2, 97.2 (C$_1$), 102.3 (C_5H$_4$), 69.0 (CNCy), 230.0 (CNCy), 135.0, 139.0, 147.0, 151.0 B(C_6F$_5$)$_3$. ^{19}F-NMR (acetone-d_6, in ppm): $\delta = -129.6$ (br.s. 6 F, o-F), -162.0 (t, 3 F, $^3J_{FF} = 18$ Hz, p-F), -164.6 (br. s. 6 F, m-F) B(C$_6$F$_5$)$_3$. ^{11}B{^{1}H}-NMR (acetone-d_6, in ppm): $\delta = -20.4$ B(C$_6$F$_5$)$_3$. Anal. Calc. for C$_{48}$H$_{11}$BF$_{15}$N$_2$NbSi$_2$: C, 52.45; H, 4.46; N, 2.55. Found: C, 52.10; H, 4.59; N, 2.89%.

3.4.3. Complex **9a**

IR (nujol) ν_{CO} 1935 cm^{-1}, ν_{B-H} 2410 cm^{-1}, 1641, 1510, 1493, 1096, 978 cm^{-1} B(C$_6$F$_5$)$_3$, 1247 cm^{-1} SiMe$_3$. ^{1}H-NMR (acetone-d_6, in ppm): $\delta = 0.22$ (s, 18 H, SiMe_3), 5.21 (2 H), 5.52 (2 H), 5.71 (4 H), 5.98 (4 H) (spt, C$_5H_4$). ^{13}C{^{1}H}-NMR (acetone-d_6, in ppm): $\delta =$ 0.5 (SiMe_3), 98.5, 99.0 (C$_1$), 102.0 (C_5H$_4$), 248.0 (CO), 135.0, 139.0, 141.0, 151.0 B(C_6F$_5$)$_3$. ^{19}F-NMR (acetone-d_6, in ppm): $\delta = -129.7$ (br. s. 6 F, o-F), -162.0 (t, 3 F, $^3J_{FF} = 18$ Hz, p-F), -164.5 (br. s. 6 F, m-F) B(C$_6F_5$)$_3$. ^{11}B{^{1}H}-NMR (acetone-d_6, in ppm): $\delta =$ -20.4 B(C$_6$F$_5$)$_3$. Anal. Calc. for C$_{36}$H$_{27}$BF$_{15}$NbO$_2$Si$_2$: C, 46.15; H, 2.88. Found: C, 46.32; H, 2.61%.

3.4.4. Complex **9b**

IR (nujol) ν_{CO} 2057 cm^{-1}, 1645, 1519, 1471, 1082, 980 cm^{-1} B(C$_6$F$_5$)$_3$, 1258 cm^{-1} SiMe$_3$. ^{1}H-NMR (acetone-d_6, in ppm): $\delta = 0.32$ (s, 18 H, SiMe_3), 6.16 (4 H), 6.23 (4 H), (pst, C$_5H_4$). ^{13}C{^{1}H}-NMR (acetone-d_6, in ppm): $\delta = 0.5$ (SiMe_3), 98.5, 99.0 (C$_1$), 102.0 (C_5H$_4$), 248.0 (CO), 135.7, 140.1, 146.6, 151.3 B(C_6F$_5$)$_3$. ^{19}F-NMR (acetone-d_6, in ppm): $\delta = -129.7$ (br. s. 6 F, o-F), -162.0 (t, 3 F, $^3J_{FF} = 19$ Hz, p-F), -164.5 (br. s. 6 F, m-F) B(C$_6$F$_5$)$_3$. ^{11}B{^{1}H}-NMR (acetone-d_6, in ppm): $\delta = 1.0$ B(C$_6$F$_5$)$_3$. Anal. Calc. for C$_{36}$H$_{26}$BClF$_{15}$NbO$_2$Si$_2$: C, 44.52; H, 2.68. Found: C, 45.02; H, 2.88%.

3.5. Preparation of complex **10**

To a solution of [Nb(η^5-C$_5$H$_4$SiMe$_3$)$_2$(H)$_3$] (0.30 g, 0.81 mmol) in acetone (ca. 50 ml) at −78°C, was added (0.41 g, 0.81 mmol) of B(C$_6$F$_5$)$_3$. The resulting mixture was stirred for 15 min during which time it was allowed to warm up to r.t. The solution was stirred at r.t. for a further 2 h. The final color of the solution was yellow. The solvent was removed in vacuo to give a yellowish–white solid, which was washed with ca. 10 ml of pentane to yield the complex [(η^5-C$_5$H$_4$SiMe$_3$)$_2$Nb]-[(CH$_3$)$_2$CHO)B(C$_6$F$_5$)$_3$] (**10**) (0.61 g, 80%).

3.5.1. *Complex* **10**

IR (nujol) 1640, 1511, 1463, 1045, 976 cm^{-1} $B(C_6F_5)_3$, 1250 cm^{-1} $SiMe_3$. ^1H-NMR (acetone-d_6, in ppm): $\delta = 0.31$ (s, 18 H, SiMe_3), 5.46 (2 H), 5.60 (2 H), 6.66 (2 H), 6.76 (2 H) (m, C_5H_4), 1.15 [d, 6 H, $^3J_{HH} = 6$ Hz, $(CH_3)_2CH$], 3.90 [m, 1H, $(CH_3)_2CH$]. $^{13}C\{^1H\}$-NMR (acetone-d_6, in ppm): $\delta = -0.2$ (SiMe_3), 109.9, 110.7, 117.6, 118.4, 122.4 (C_1) (C_5H_4), 248.0 (*C*O), 25.0 [$(CH_3)_2CH$], 88.0 [$(CH_3)_2CH$], 135.0, 139.0, 141.0, 151.0 $B(C_6F_5)_3$. ^{19}F-NMR (acetone-d_6, in ppm): $\delta = -128.9$ (br. s. 6 F, *o*-F), -157.5 (t, 3 F, $^3J_{FF} = 18$ Hz, *p*-F), -162.2 (br. s. 6 F, *m*-F) $B(C_6F_5)_3$. $^{11}B\{^1H\}$-NMR (acetone-d_6, in ppm): $\delta = -5.2$ $B(C_6F_5)_3$. Anal. Calc. for $C_{37}H_{35}BF_{15}NbOSi_2$: C, 44.30; H, 3.90. Found: C, 44.50; H, 3.71%.

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