

# Heterocycle-containing niobocene derivatives from hydride–niobocene complexes

## X-ray molecular structure of $[\text{Cp}'_2\text{Nb}(\text{CNXylyl})_2][\text{I}_3]$ and $[\text{Cp}'_2\text{Nb}(\text{H})(\text{P}(\text{OMe})_3)] \cdot (\text{bzta})'\text{-NH}_2$ [ $(\text{bzta})'\text{-NH}_2 = 2\text{-amino-6-}$ $\text{methylbenzothiazole}$ ]

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### Abstract

The reaction under thermal conditions of  $[\text{Cp}'_2\text{Nb}(\text{H})_3]$  (**1**),  $\text{Cp}' = \eta^5\text{-C}_5\text{H}_4\text{SiMe}_3$ , with benzothiazole heterocycles, namely 2-aminobenzothiazole,  $\text{bzta-NH}_2$ , 2-hydroxybenzothiazole,  $\text{bzta-OH}$ , 2-mercaptobenzothiazole,  $\text{bzta-SH}$ , benzoxazole, namely 2-mercaptobenzoxazole,  $\text{bzoa-SH}$ , and triazines, namely 1,3,5-triaminetriazine, 1,3,5-trihydroxytriazine, 1,3,5-trimercaptotriazine,  $(\text{C}_3\text{N}_3)\text{-1,3,5-(XH)}_3$ ,  $\text{X} = \text{NH}$ ,  $\text{O}$ ,  $\text{S}$ , yields a new family of niobocene complexes  $[\text{Cp}'_2\text{Nb}(\kappa^2\text{-X,S-Xbzta})]$ ,  $\text{X} = \text{NH}$  (**2**),  $\text{O}$  (**3**),  $\text{S}$  (**4**),  $[\text{Cp}'_2\text{Nb}(\kappa^2\text{-S,N-Sbzoa})]$  (**5**) and  $[(\text{Cp}'_2\text{Nb})_3(\kappa^2\text{-X,N-X}_3\text{C}_3\text{N}_3)]$ ,  $\text{X} = \text{NH}$  (**6**),  $\text{X} = \text{O}$  (**7**),  $\text{X} = \text{S}$  (**8**). In the same way, the thermal treatment of complex  $[\text{Cp}'_2\text{Nb}(\text{H})(\text{CNXylyl})]$  (**9**),  $\text{Xylyl} = \text{C}_6\text{H}_4\text{-2,6-Me}_2$ , with  $\text{bzta-SH}$ ,  $\text{bzoa-SH}$  and  $(\text{C}_3\text{H}_3)\text{-1,3,5-(SH)}$  affords the complexes  $[\text{Cp}'_2\text{Nb}(\kappa^1\text{-S-Sbzta})(\text{CNXylyl})]$  (**10**),  $[\text{Cp}'_2\text{Nb}(\kappa^1\text{-S-Sbzoa})(\text{CNXylyl})]$  (**11**) and  $[(\text{Cp}'_2\text{Nb}(\text{CNXylyl}))_3(\kappa^1\text{-S-S}_3\text{C}_3\text{N}_3)]$  (**12**). The reaction of compound **10** with an excess of  $\text{MeI}$  in toluene at room temperature leads to the ionic compound  $[\text{Cp}'_2\text{Nb}(\text{CNXylyl})_2][\text{I}_3]$  (**15**), which contains two coordinated  $\text{CNXylyl}$  ligands and a non-coordinated  $\text{I}_3^-$  counteranion. All complexes were characterized by spectroscopic methods and the molecular structure of  $[\text{Cp}'_2\text{Nb}(\text{CNXylyl})_2][\text{I}_3]$  (**15**) and  $[\text{Cp}'_2\text{Nb}(\text{H})(\text{P}(\text{OMe})_3)] \cdot (\text{bzta})'\text{-NH}_2$  (**14**), an adduct of the heterocycle with the hydride–niobocene, have been determined by X-ray molecular studies.

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**Keywords:** Niobium; Hydride; Niobocene; Heterocycles

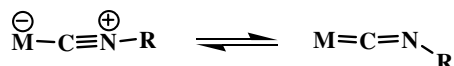
### 1. Introduction

Hydride-containing niobocene complexes are well known and they have long been of interest for both their high reactivity and their spectroscopic properties [1]. In particular, the chemistry of the trihydride complex  $[\text{Cp}'_2\text{Nb}(\text{H})_3]$  has been investigated in great detail and is itself a source of new hydride–niobocene complexes; of

these systems one of the most important families is the  $18\text{e}^-$  complexes  $[\text{Cp}'_2\text{Nb}(\text{H})\text{L}]$  ( $\text{L} = \pi\text{-acid ligand}$ ) [2]. In recent years we have focused some of our attention on the chemistry of the hydride–isocyanide niobocenes [3] in reactions such as insertion processes with heterocumulene molecules [4] and alkynes [5] as well as the synthesis of dihydrogen complexes through protonation processes [2]; in particular, this is an area in which numerous molecular structures are still not known and it is not possible to discern between the two possible resonance forms of the coordinated isocyanide, i.e., either the isocyanide or carbene coordination mode [6] (Scheme 1).

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Scheme 1.

Furthermore, in the field of early transition organometallic chemistry, previous efforts have been directed at studying the reactivity of amino-, hydroxy- or mercapto-containing heterocycles towards different types of derivatives of these elements. It is well known that some of these molecules are components in many bioactive molecules [7] and compounds of thionates and the related thiazoles are of great interest due to their numerous commercial applications, including their use as biocides and in the environmental control of toxic metals [8]. For example, some aminopyridinato-containing complexes of groups 4 and 5 have been described [9].

Some of us have previously described examples of pyrimidinethiolate-containing zirconocenes [10], oxy and thiolate pyrimidine-containing Ti and Zr species [11], mercapto-containing Zr complexes [12] and, more recently, a series of thiolate, amido, and oxy heterocyclic-containing niobocene complexes [13]. As a continuation of our interest in the chemistry of hydride–niobocenes, we report here the reactivity of  $[\text{Cp}'_2\text{Nb}(\text{H})_3]$  and  $[\text{Cp}'_2\text{Nb}(\text{H})(\text{CNXylyl})]$  towards new types of heterocycles functionalized with hydroxy, mercapto or amino groups.

## 2. Results and discussion

Following our interest in the study of the reactivity of the trihydride complex  $[\text{Cp}'_2\text{Nb}(\text{H})_3]$  (**1**), we decided to

carry out the reaction of this complex with new types of heterocycles, such as benzothiazole (a), benzoxazole (b) and triazine (c), bearing hydroxy, amino or mercapto functional groups (see Chart 1). The standard reaction procedure involved heating a stirred thf solution of **1** with the corresponding heterocycle in the appropriate molar ratio. This method allowed the isolation of the different families of oxy-, amido- and mercapto-containing niobocene complexes (Scheme 2).

Complexes **2–8** were isolated as air-sensitive oily (**2–5**) or solid (**6–8**) materials that are soluble in most common organic solvents such as toluene, hexane, thf and acetone.

All the complexes described in this work were spectroscopically characterized. In the  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra of complexes **2–8** each cyclopentadienyl ring exhibits four and five resonances, respectively, which indicates the presence of an asymmetrical environment for the niobium centre. In this respect the metallacycle formed by the niobium atom and the two atoms of the bidentate ligand is proposed to be practically coplanar and would lie in the equatorial plane that bisects the dihedral angle formed by cyclopentadienyl rings. In addition, the NMR spectra exhibit the resonances for the benzothiazole, benzoxazole and triazine moieties, respectively (see Section 4). On the basis of the spectroscopic data, two possible structural dispositions can be proposed for complexes **2–5**, as depicted in Fig. 1, with a  $\kappa^2\text{-X,N}$  (b) or  $\kappa^2\text{-X,S}$  (a) coordination mode.

However, in the IR spectra the position of the band corresponding to  $\nu(\text{C}=\text{N})$  of the heterocycles appears at ca.  $1590\text{ cm}^{-1}$  for **2–4** and this value is near to that found in the free ligands. On the basis of this observation, coordina-

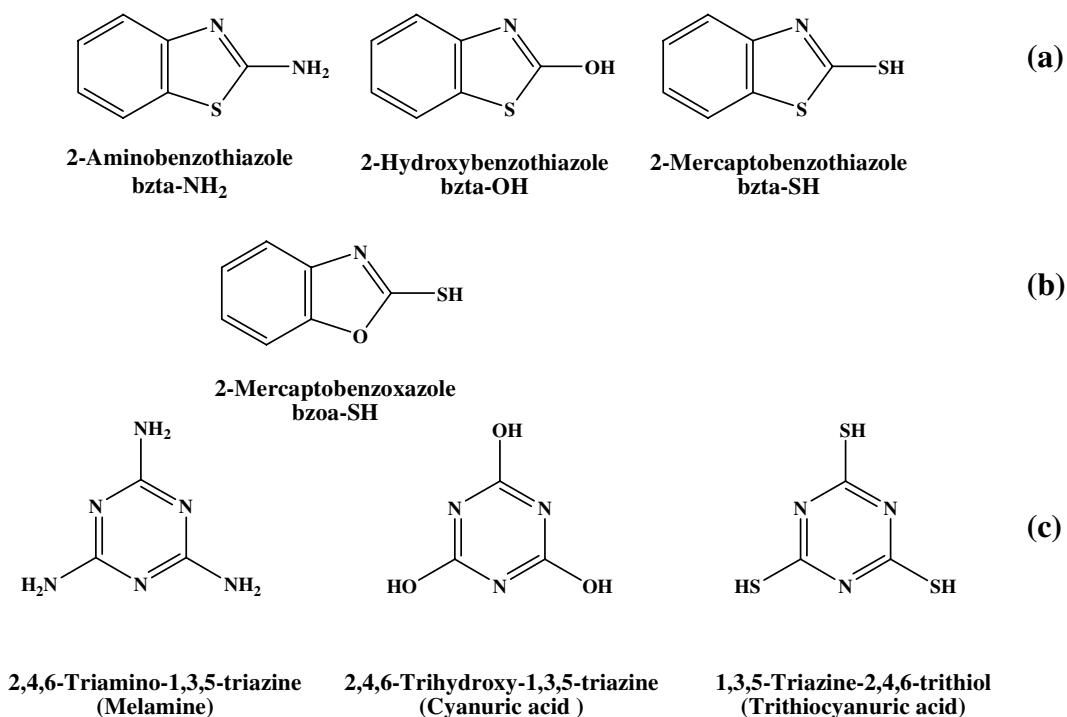
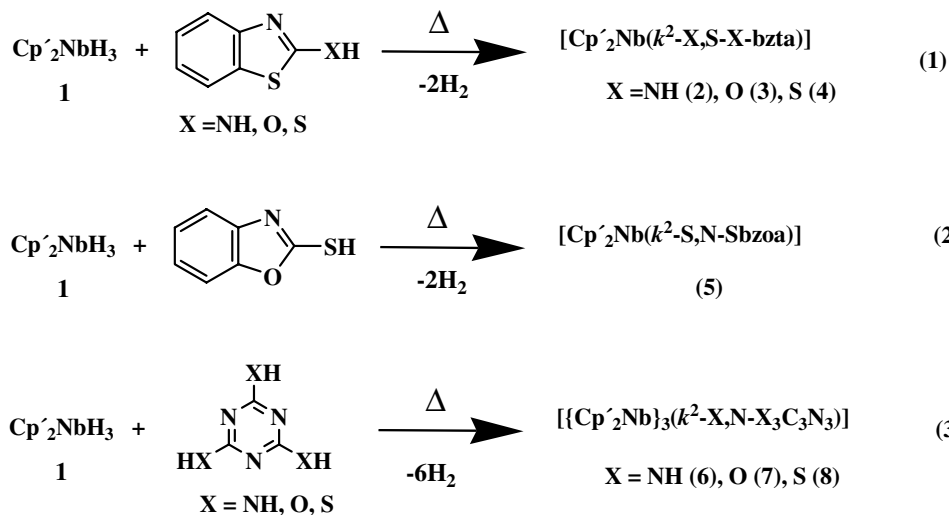
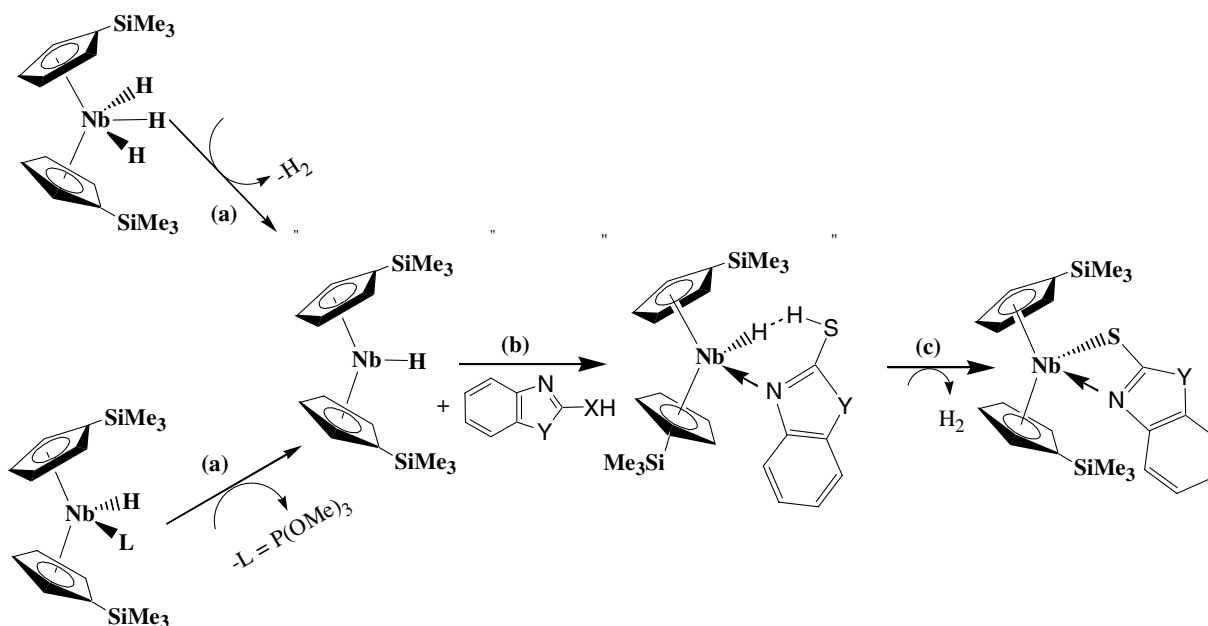


Chart 1. Heterocycles utilized in this study.



Scheme 2. Synthesis of complexes 2–8.



Scheme 3. Proposed reaction pathway for the formation of complexes 2–5.

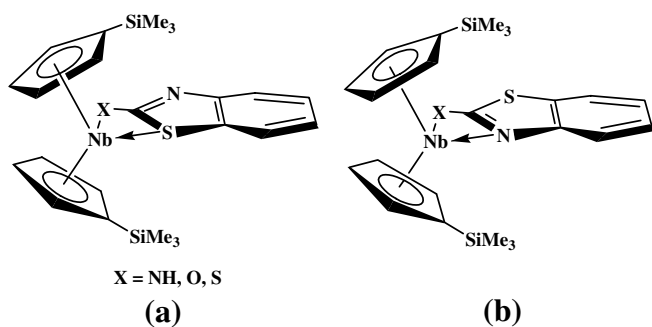


Fig. 1. Proposed structures for complexes 2–4.

tion mode (a) is proposed as the most probable. In the same way, an analogous structural disposition may be proposed for complex 5, with the benzoxazolone ligand bonded

with either  $\kappa^2\text{-S,N}$  (b) or  $\kappa^2\text{-S,O}$  (a) coordination modes. In the IR spectrum of 5 the  $\nu(\text{C}=\text{N})$  band appears at  $1580\text{ cm}^{-1}$  and this is significantly shifted with respect to  $\nu(\text{C}=\text{N})$  of the free heterocycle (at  $1620\text{ cm}^{-1}$ ). On this basis a  $\kappa^2\text{-S,N}$  coordination is proposed to be present in this complex.

For complexes 6–8 a trinuclear niobium species based on a bidentate coordination fashion,  $\text{Nb}(\kappa^2\text{-X,N})$ , can be considered for the appropriate triazine ligand (see Fig. 2).

These trinuclear complexes were isolated as the only products even when niobocene:triazine molar ratios lower than 3:1 were employed, indicating that the formation of the trinuclear species is thermodynamically favoured.

The isolation of complexes 2–8 can be understood in terms of the pathway depicted in Scheme 3. Step (a) corresponds to the elimination of  $\text{H}_2$  to give a very reactive

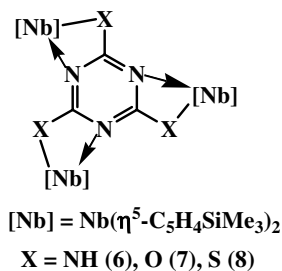
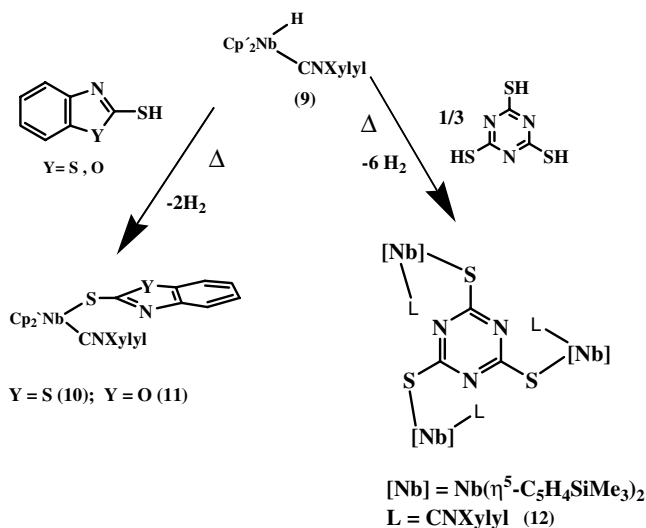


Fig. 2. Proposed structures for complexes 6–8.



Scheme 4. Reactions for the formation of complexes 10–12.

16-electron monohydride niobocene intermediate, which has previously been proposed by us in several processes [14]. Coordination of the corresponding heterocycle to this

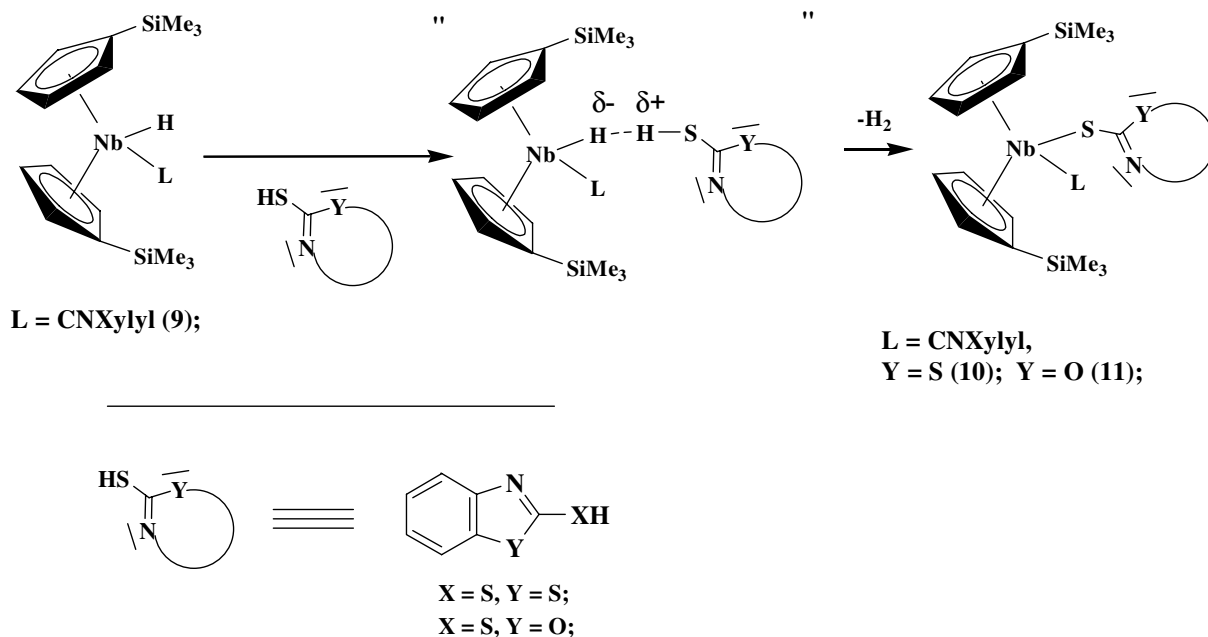
unsaturated species would give an 18-electron hydride-heterocycle intermediate by coordination through the nitrogen atoms – as proposed in step (b) for complexes 2–4. (In the case of complex 5 the coordination of the heterocycle must be through the oxygen atom.) Finally, elimination of a molecule of  $\text{H}_2$  by intramolecular interaction of the hydride ligand and the hydrogen atom of the XH moiety of the heterocycle would give the final complex containing a bidentate ligand, step (c).

However, other plausible alternative pathways, e.g. through an initial  $\text{Nb-H} \cdots \text{HX-R}$  (heterocycle) interaction [15], can not definitively be ruled out.

In order to study the stability of the resulting four-membered metallacycle proposed in the structures of complexes 2–8, different unsuccessful insertion processes were carried out with different types of unsaturated molecules, namely  $\text{CO}$ ,  $\text{CS}_2$ , isocyanides and activated alkynes. This behaviour is consistent with the lack of fluxionality in solution, which was demonstrated for these molecules by means of variable-temperature  $^1\text{H}$  NMR studies.

Furthermore, in relation to our interest in studying new isocyanide-niobocene systems we carried out reactivity studies on the 18-electron  $d^2$  niobocene complex  $[\text{Cp}'_2\text{Nb}(\text{H})(\text{CNXylyl})]$  (9) towards some of the aforementioned heterocycles (see Scheme 4). In fact, reactions of 9 with bzta-SH, bzoa-SH or  $(\text{C}_3\text{N}_3)\text{-1,3,5-(SH)}_3$  in thf in the appropriate molar ratios led to the isolation of new complexes 10–12 after the appropriate work-up procedure.

Complexes 10–12 were isolated as air-sensitive oily (10–11) or solid (12) products and they were soluble in most common organic solvents such as toluene, hexane, thf and acetone.



Scheme 5. Proposed reaction pathway for the formation of complexes 10–11.

In accordance with the lack of symmetry in the proposed structures, the  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra of these complexes exhibit four (or three) and five resonances for each cyclopentadienyl ring, respectively. The carbon resonances for the CNXylyl ligand in **10–12** appear at  $\delta$  215.2, 206.2 and 209.8, respectively. In these complexes a  $\kappa^1\text{-S}$  coordination mode for the heterocyclic ligand is proposed.

The formation of complexes **10–12** can be understood in terms of an acid–base process where in a first step a Nb–H bond interacts with the H–S moiety of the benzothiazole, benzoxazole or triazine. This is followed by the elimination of  $\text{H}_2$  and the subsequent formation of the corresponding thiolate-containing complexes (see Scheme 5). It is noteworthy that under our experimental conditions a possible final step corresponding to the de-coordination of the appropriate auxiliary ligand, namely CNXylyl, and the formation of a chelate  $\kappa^2\text{-S,X}$ -heterocyclic-containing niobocene was not observed. This behaviour is in accordance with the previously observed high stability of the Nb–CNR bonds in this class of 18-electron  $d^2$  niobocene species [16].

Furthermore, it has been observed that the heterocycles-containing amino or hydroxy functionality, namely bzta- $\text{NH}_2$  and  $(\text{C}_3\text{N}_3)\text{-1,3,5-(NH}_2)_3$ , bzta-OH, bzta- $\text{NH}_2$  and  $(\text{C}_3\text{N}_3)\text{-1,3,5-(OH)}_3$ , do not react with complex **9** even at  $100^\circ\text{C}$ . This behaviour is probably due to the lower acidity of the  $\text{NH}_2$  or OH group in comparison to the SH group in bzta-SH and  $(\text{C}_3\text{N}_3)\text{-1,3,5-(SH)}_3$ . However, when  $[\text{Cp}'_2\text{Nb(H)(P(OMe)}_3)]$  (**13**) is reacted with bzta-SH, bzta-OH, bzta- $\text{NH}_2$ , bzoa-SH,  $(\text{C}_3\text{N}_3)\text{-1,3,5-(SH)}_3$ ,  $(\text{C}_3\text{N}_3)\text{-1,3,5-(OH)}_3$  or  $(\text{C}_3\text{N}_3)\text{-1,3,5-(NH}_2)_3$  in toluene at  $100^\circ\text{C}$ , the reaction gave complexes **2–8** by elimination of hydrogen and  $\text{P(OMe)}_3$ . This behaviour can be explained in terms of prior coordination of the heterocyclic ligand to the unsaturated niobium intermediate obtained by the thermal elimination of the  $\text{P(OMe)}_3$  followed by hydrogen elimination (see Scheme 3); this proposal is consistent with

the lower stability of the Nb– $\text{P(OMe)}_3$  bond in comparison to the Nb–CNR one.

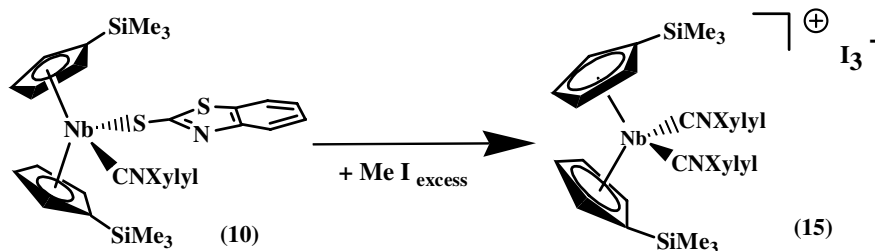
In a parallel experiment, complex  $[\text{Cp}'_2\text{Nb(H)(P(OMe)}_3)]$  (**13**) was treated with 2-amino-6-methylbenzothiazole, (bzta)'- $\text{NH}_2$ , in a 1:1 molar ratio at  $65^\circ\text{C}$  during 36 h. However, under these conditions a reaction did not take place. When the solution in toluene was kept at room temperature during two weeks a red microcrystalline material was obtained and this corresponds to the adduct  $[\text{Cp}'_2\text{Nb(H)(P(OMe)}_3)] \cdot (\text{bzta})'\text{NH}_2$  (**14**) (see X-ray diffraction study).

In addition, further reaction of  $\text{CH}_3\text{I}$  with **10** gave the cationic bis(isocyanide)niobocene triiodide complex  $[\text{Cp}'_2\text{Nb(CNXylyl)}_2][\text{I}_3]$  (**15**) (Scheme 6) rather than the expected niobocene-containing N-alkylated or S-alkylated ligand [17] (Scheme 7).

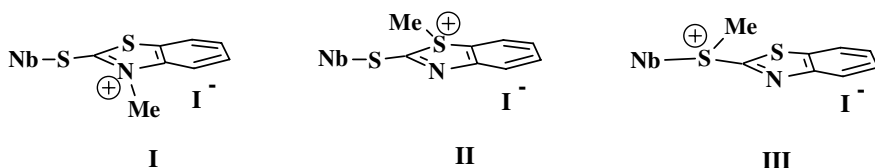
Complex **15** was isolated as an air-sensitive red solid and is soluble in organic solvents such as toluene, thf and acetone. This complex contains the same cation as the complex  $[\text{Cp}'_2\text{Nb(CNXylyl)}_2][\text{HB(C}_6\text{F}_5)_3]$  reported by some of us [13] in an acid–base process involving **9** with  $\text{B(C}_6\text{F}_5)_3$  in the presence of CNXylyl. The geometry proposed for the structure of **15** (see Scheme 6) is consistent with the  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra of this complex. The spectra exhibit two and three resonances for each cyclopentadienyl ring, respectively. The carbon resonance for the CNXylyl ligand appears at  $\delta$  226.1. Furthermore, signals corresponding to the heterocyclic ligand are absent from the spectra, indicating the loss of this unit during the process. Suitable crystals of **15** for an X-ray crystal structure study were obtained.

### 2.1. X-ray diffraction study of $[\text{Cp}'_2\text{Nb(CNXylyl)}_2][\text{I}_3]$ (**15**)

The molecular structure of complex **15** was determined by X-ray diffraction. The ORTEP diagram is shown in



Scheme 6. Reaction process for the formation of complex **15**.



Scheme 7. Potential alkylation products from complex **10** using MeI.

Fig. 3. To the best of our knowledge, the number of isocyanideniobocene complexes characterized by X-ray crystallography is not very large [18]. Selected bond distances and bond angles are listed in Table 1.

There are two molecules in the asymmetric unit cell and the structure consists of monomeric cations  $[\text{Cp}'_2\text{Nb}(\text{CNXyly})_2]^+$  and H-bonded  $\text{I}_3^-$  anions. The cation structure is typical of bent metallocenes. The niobium atom is coordinated to both cyclopentadienyl rings in a  $\eta^5$ -mode

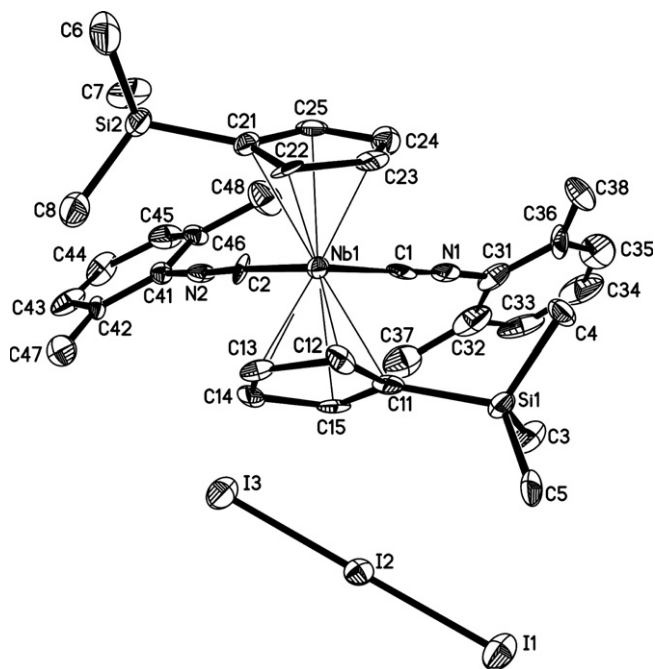


Fig. 3. Molecular structure and atom-labelling scheme for complex **15**, with thermal ellipsoids at 20% probability. Hydrogen atoms are omitted for clarity.

Table 1  
Bond lengths (Å) and angles (°) for **15**

Bond lengths		
Nb(1)–C(1)	2.11(3)	2.16(2)
Nb(1)–C(2)	2.10(2)	2.08(2)
Nb(1)–Cent(1)	2.072(2)	2.043(2)
Nb(1)–Cent(2)	2.072(2)	2.067(2)
N(1)–C(1)	1.17(3)	1.14(3)
N(1)–C(31)	1.41(3)	1.46(3)
N(2)–C(2)	1.17(2)	1.19(2)
N(2)–C(41)	1.44(2)	1.36(2)
I(1)–I(2)	2.916(3)	2.851(3)
I(2)–I(3)	2.908(3)	2.980(3)
Angles		
C(1)–Nb(1)–C(2)	83.5(9)	83.2(8)
Cent(1)–Nb(1)–Cent(2)	138.5(9)	137.5(9)
Nb(1)–C(1)–N(1)	179(2)	177(2)
C(1)–N(1)–C(31)	176(3)	176(3)
Nb(1)–C(2)–N(2)	177(2)	178(2)
C(2)–N(2)–C(41)	172(2)	174(2)
I(1)–I(2)–I(3)	179.4(1)	175.6(1)

Cent(1) is the centroid of C(11)–C(15) and Cent(2) is the centroid of C(21)–C(25).

and the two isocyanide ligands occupy the other two coordination sites in a distorted tetrahedral geometry. The orientation of the two Cp' rings is intermediate between eclipsed and staggered positions, with Si(1)–Cent(1)–Cent(2)–Si(2) angles of 168.1° and 174.6°, respectively. The values of the Cent(1)–Nb(1)–Cent(2) angles of 138.5(9)° and 137.5(9)° are typical of these bent niobocene derivatives. The C–N bond lengths of 1.17(3) and 1.17(2) Å for molecule 1 and 1.14(3) and 1.19(2) Å for molecule 2 are consistent with the presence of a carbon–nitrogen triple bond [19]. The C(1)–N(1)–C(31) angles of 176(3)° and C(2)–N(2)–C(41) angles of 172(2) and 174(2)° for molecules 1 and 2, respectively, clearly indicate the linearity of the isocyanide ligand. These values confirm the back donation of the niobium(III)  $d^2$  centre to the isocyanide ligand, with a triple bond remaining between the C and N but, in these cases, the contribution of the carbene form in the interaction with the niobium centre is small (see Scheme 1). The results of this analysis are in agreement with the IR data in solution (see Section 4).

The triiodide anion bond distances are practically equivalent, with values between 2.851(3) and 2.980(3) Å, and the angles between the three iodide atoms of 179.4(1) and 175.6(1)°, respectively, are in agreement with a linear disposition.

The crystal is stabilized by weak hydrogen bonding interactions between the triiodide anions and niobocene cations (Table 2, Fig. 4).

## 2.2. X-ray diffraction study of $[\text{Cp}'_2\text{Nb}(\text{H})(\text{P}(\text{OMe})_3)] \cdot (\text{bzta})'-\text{NH}_2$ (**14**)

The molecular structure of **14** was determined by X-ray diffraction. A few X-ray molecular structures of hydride–niobocene complexes have been reported [5,20] although this is the first X-ray study on a hydride–phosphite niobocene complex. The molecular structure and atomic numbering scheme are shown in Fig. 5. Selected bond lengths and angles for **14** are given in Table 3.

The complex crystallizes in the triclinic space group  $P\bar{1}$ , with a complex molecule,  $[\text{Cp}'_2\text{Nb}(\text{H})(\text{P}(\text{OMe})_3)]$  and a non-coordinated molecule of  $(\text{bzta})'-\text{NH}_2$  in the asymmetric unit cell. The solid-state molecular structure essentially consists of two niobium centres held by (amine)N–H $\cdots$ O and (amine)N–H $\cdots$ (heterocyclic)N hydrogen bonds (see Supplementary Material).

The niobium atom is coordinated to both cyclopentadienyl rings in a  $\eta^5$ -mode, to the P of the  $\text{P}(\text{OMe})_3$  and to the hydride in a distorted tetrahedral geometry. The Nb(1)–H(1) bond distance of 1.63(6) Å is normal for the hydride–niobium bond [21] and the Nb(1)–P(1) bond distance of 2.491(2) Å is shorter than the phosphide–niobium bond distances [22].

The two Cp' rings show an eclipsed orientation, with a Si(1)–Cent(1)–Cent(2)–Si(2) angle of 70.6(1)°. The value of the Cent(1)–Nb(1)–Cent(2) angle is 143.28(4)°, which

Table 2  
Hydrogen bonds for compound **15**

D–H···A	$d(\text{D–H})$ (Å)	$d(\text{D···A})$ (Å)	$\angle\text{DHA}$ (°)	$d(\text{D···A})$ (Å)	Symmetry <sup>a</sup>
C(47A)–H(47E)···I(1)	0.96	3.17	145.9	4.00(2)	$x, y, z$
C(12A)–H(12A)···I(2A)	0.93	3.21	138.3	3.95(2)	$x, y, z$
C(25A)–H(25A)···I(2A)	0.93	3.21	135.5	3.93(2)	$x, y, z$
C(22)–H(22)···I(3A)	0.93	3.22	143.7	4.01(2)	$x, y - 1, z$
C(35A)–H(35A)···I(3A)	0.93	3.11	139.0	3.86(3)	$1 - x, 1 - y, 1 - z$

<sup>a</sup> Symmetry operation for A.

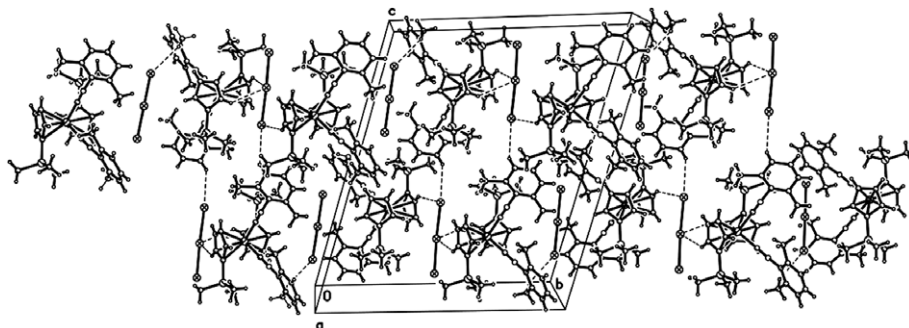


Fig. 4. Packing plot of **15**. The triiodide anion is hydrogen bonded to niobocene complex (dotted lines).

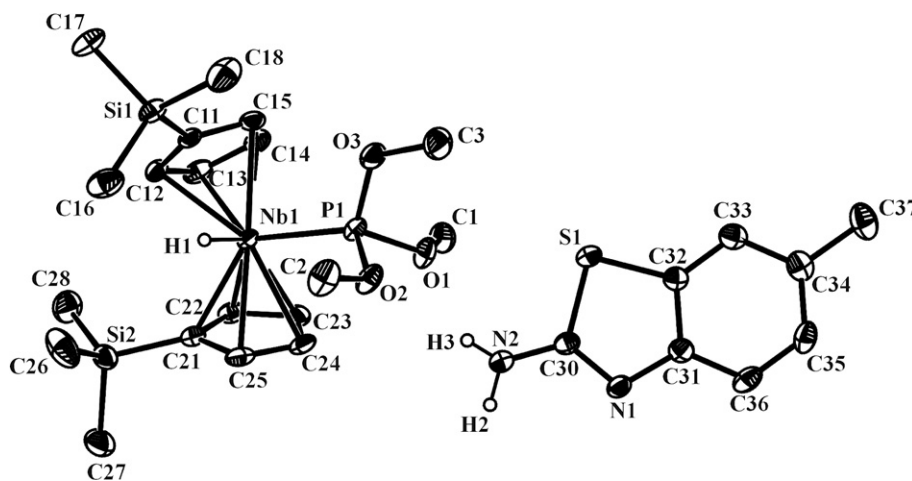


Fig. 5. Molecular structure and atom-labelling scheme for complex **14**, with thermal ellipsoids at 30% probability. Hydrogen atoms are omitted for clarity.

is typical of bent niobocene derivatives, and the dihedral angle between the two Cp' rings is  $43.0(3)^\circ$ .

Although it is quite difficult to crystallize this class of hydride–niobocene complex, in our example the interactions between the (bzta)'-NH<sub>2</sub> molecule and the hydride–niobocene complex probably contribute to stabilize the crystal. As a result, the formation of a dimer can be observed in the structure as a consequence of several intermolecular hydrogen bonding interactions (Fig. 6).

The amine group shows a bifurcated hydrogen bond with two oxygen atoms from the phosphite (N2–H3···O1 and N2–H3···O2). This kind of interaction has only been reported once before [23]. Furthermore, there is another hydrogen bond between two heterocyclic molecules

through the other hydrogen of the amino group (N2–H2···N1) (Table 4).

### 3. Conclusions

We have studied the reactivity of the niobocene trihydride **1** towards bzta-SH, bzta-NH<sub>2</sub>, bzta-OH, bzoa-SH and triazines, (C<sub>3</sub>N<sub>3</sub>)-1,3,5-(XH)<sub>3</sub>, X = NH, O, S, to produce new families of heterocycle-containing niobocene derivatives **2–8**. We have also prepared new niobocene complexes **10**, **11** and **12**, which contain isocyanide as an ancillary ligand and the appropriate heterocycle, starting from the hydride–isocyanide niobocene **9** and bzta-SH, bzoa-SH or (C<sub>3</sub>N<sub>3</sub>)-1,3,5-(SH)<sub>3</sub>. The X-ray molecular

Table 3  
Bond lengths (Å) and angles (°) for **14**

Bond lengths	
Nb(1)–P(1)	2.491(2)
Nb(1)–H(1)	1.63(6)
Nb(1)–Cent(1)	2.053(1)
Nb(1)–Cent(2)	2.046(1)
P(1)–O(3)	1.595(5)
P(1)–O(2)	1.618(4)
P(1)–O(1)	1.619(4)
O(1)–C(1)	1.423(8)
O(2)–C(2)	1.434(8)
O(3)–C(3)	1.458(8)
S(1)–C(32)	1.737(6)
S(1)–C(30)	1.756(6)
N(1)–C(30)	1.311(7)
N(1)–C(31)	1.390(8)
N(2)–C(30)	1.321(8)
Angles	
Cent(1)–Nb(1)–Cent(2)	143.28(4)
Cent(1)–Nb(1)–P(1)	110.73(5)
Cent(2)–Nb(1)–P(1)	101.48(5)
O(3)–P(1)–O(2)	102.1(3)
O(3)–P(1)–O(1)	103.1(3)
O(2)–P(1)–O(1)	89.1(2)
O(3)–P(1)–Nb(1)	116.6(2)
O(2)–P(1)–Nb(1)	118.3(2)
O(1)–P(1)–Nb(1)	122.9(2)
C(1)–O(1)–P(1)	123.4(4)
C(2)–O(2)–P(1)	120.1(4)
C(3)–O(3)–P(1)	120.8(4)
C(32)–S(1)–C(30)	89.4(3)
C(30)–N(1)–C(31)	109.8(5)

Cent(1) is the centroid of C(11)–C(15) and Cent(2) is the centroid of C(21)–C(25).

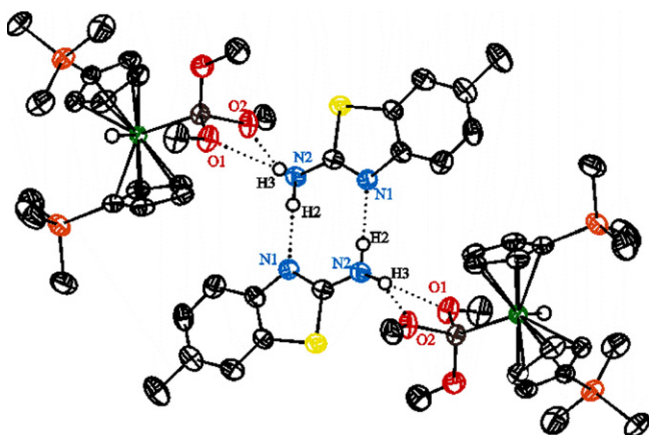


Fig. 6. Two asymmetric units of **14** (H-bonded) are shown. Only hydrogen atoms involved in hydrogen bonding are drawn.

Table 4  
Hydrogen bonds for compound **14**

N–H <sup>⋯</sup> A	d(N–H) (Å)	d(H <sup>⋯</sup> A) (Å)	∠NHA (°)	d(N <sup>⋯</sup> A) (Å)	Symmetry <sup>a</sup>
N(2)–H(2)⋯N(1)	0.91 (2)	2.07 (4)	176.9 (2)	2.97 (2)	–x, –y, 1 – z
N(2)–H(3)⋯O(1)	0.73 (3)	2.47 (1)	140.5 (1)	3.07 (3)	x – 1, y, z
N(2)–H(3)⋯O(2)	0.73 (3)	2.36 (1)	159.5 (1)	3.05 (1)	x – 1, y, z

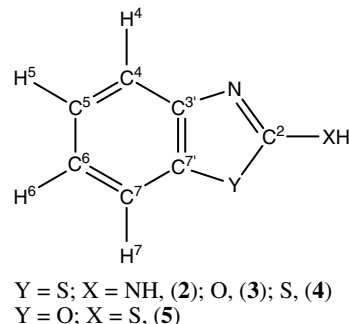
<sup>a</sup> Symmetry operation for A.

structures of two complexes (**14** and **15**) were determined, with **15** being a representative member of a small family of early transition metallocenes bearing an isocyanide ancillary ligand.

## 4. Experimental

### 4.1. General procedures

All reactions were carried out using Schlenk techniques. Oxygen and water were excluded by the use of vacuum lines supplied with purified N<sub>2</sub>. Toluene was distilled from sodium. Pentane was distilled from sodium/potassium alloy. Diethyl ether and thf were distilled from sodium benzophenone. All solvents were deoxygenated prior to use. Complexes [Cp'<sub>2</sub>Nb(H)<sub>3</sub>] (**1**), [Cp'<sub>2</sub>Nb(H)(CNXylyl)] (**9**) and [Cp'<sub>2</sub>Nb(H)(P(OMe)<sub>3</sub>)] (**13**) were prepared as described in the literature [24,2a]. Deuterated solvents were dried over 4 Å molecular sieves and degassed prior to use. The different heterocycles, namely benzothiazole, benzoxazole and triazine were used as purchased from Aldrich. NMR spectra were recorded on a Varian Unity 300 (300 MHz for <sup>1</sup>H, 75 MHz for <sup>13</sup>C) spectrometer. Chemical shifts were measured relative to partially deuterated solvent peaks and are reported relative to TMS. IR spectra were recorded on a Perkin–Elmer 883 spectrophotometer in Nujol mulls over CsI windows.



### 4.2. Synthesis of [Cp'<sub>2</sub>Nb(κ<sup>2</sup>-X,S-Xbzta)], X = NH (**2**), O (**3**), S (**4**)

The complex [Cp'<sub>2</sub>Nb(H)<sub>3</sub>] (**1**) (0.75 g; 2.25 mmol) was dissolved in 30 mL of dry thf and to this solution was added NH<sub>2</sub>-bzta in a 1:1 stoichiometry (0.34 g; 70 μmol). The mixture was stirred at 343 K for 5 h. The resulting dark-red solution was filtered and evaporated to dryness.



Complex **2** was obtained as a dark red oil from a saturated hexane solution at  $-30\text{ }^{\circ}\text{C}$  (0.30 g; 90%). Complexes **3** and **4** were prepared in a similar manner to **2** (86% and 88% yield, respectively).

Complex **2**: IR (Nujol/PET  $\text{cm}^{-1}$ )  $\nu$  (N–H); 3230, (C=N) 1615.  $^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ ):  $\delta$  0.02 (s, 18H,  $\text{SiMe}_3$ ), 3.18 (s, 1H, N–H), 4.15, 4.20, 5.19, 5.59 (2H each a complex signal,  $\text{C}_5\text{H}_4\text{SiMe}_3$ ), 6.69, 6.63 (1H each t,  $^3J_{\text{HH}} = 7\text{ Hz}$ ,  $\text{H}^5$ ,  $\text{H}^6$  aromatic system of bzta), 7.35, 7.68 (1H each d,  $^3J_{\text{HH}} = 7\text{ Hz}$ ,  $\text{H}^4$ ,  $\text{H}^7$  aromatic system of bzta).  $^{13}\text{C}$  { $^1\text{H}$ } NMR ( $\text{C}_6\text{D}_6$ ):  $\delta$  0.8 ( $\text{SiMe}_3$ ), 94.3 ( $\text{C}^1$ ,  $\text{C}_5\text{H}_4\text{SiMe}_3$ ), 102.0, 103.4, 104.1, 112.0 ( $\text{C}^{2-5}$ , exact assignment not possible,  $\text{C}_5\text{H}_4\text{SiMe}_3$ ), 122.1 ( $\text{C}^{5-6}$  aromatic system of bzta), 123.2, 123.6 ( $\text{C}^{4-7}$  aromatic system of bzta), 146.3 ( $\text{C}^3$  aromatic system of bzta), 172.3 ( $\text{C}^7$  aromatic system of bzta), 182.1 ( $\text{C}^2$  aromatic system of bzta).

Complex **3**: IR (Nujol/PET  $\text{cm}^{-1}$ )  $\nu$  (C=N) 1583.  $^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ ):  $\delta$  0.04 (s, 18H,  $\text{SiMe}_3$ ), 4.30, 4.37, 5.25, 5.95 (2H each a complex signal,  $\text{C}_5\text{H}_4\text{SiMe}_3$ ), 6.80, 6.91 (1H each t,  $^3J_{\text{HH}} = 7.3\text{ Hz}$ ,  $\text{H}^5$ ,  $\text{H}^6$  aromatic system of bzta), 7.43, 7.70 (1H each d,  $^3J_{\text{HH}} = 7\text{ Hz}$ ,  $\text{H}^4$ ,  $\text{H}^7$  aromatic system of bzta).  $^{13}\text{C}$  { $^1\text{H}$ } NMR ( $\text{C}_6\text{D}_6$ ):  $\delta$  0.8 ( $\text{SiMe}_3$ ), 89.3 ( $\text{C}^1$ ,  $\text{C}_5\text{H}_4\text{SiMe}_3$ ), 97.8, 99.9, 103.8, 104.7 ( $\text{C}^{2-5}$ , exact assignment not possible,  $\text{C}_5\text{H}_4\text{SiMe}_3$ ), 125.1, 126.3 ( $\text{C}^{5-6}$  aromatic system of bzta), 128.5, 129.3 ( $\text{C}^{4-7}$  aromatic system of bzta), 132.5 ( $\text{C}^3$  aromatic system of bzta), 157.5 ( $\text{C}^7$  aromatic system of bzta), 176.3 ( $\text{C}^2$  aromatic system of bzta).

Complex **4**: IR (Nujol/PET  $\text{cm}^{-1}$ )  $\nu$  (C=N) 1629.  $^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ ):  $\delta$  0.05 (s, 18H,  $\text{SiMe}_3$ ), 4.15, 4.71, 5.19, 5.40 (2H each a complex signal,  $\text{C}_5\text{H}_4\text{SiMe}_3$ ), 6.72, 6.92 (1H each t,  $^3J_{\text{HH}} = 7.2\text{ Hz}$ ,  $\text{H}^5$ ,  $\text{H}^6$  aromatic system of bzta), 7.39, 8.10 (1H each d,  $^3J_{\text{HH}} = 8\text{ Hz}$ ,  $\text{H}^4$ ,  $\text{H}^7$  aromatic system of bzta).  $^{13}\text{C}$  { $^1\text{H}$ } NMR ( $\text{C}_6\text{D}_6$ ):  $\delta$  1.1 ( $\text{SiMe}_3$ ), 89.8 ( $\text{C}^1$ ,  $\text{C}_5\text{H}_4\text{SiMe}_3$ ), 98.1, 100.2, 103.9, 105.9 ( $\text{C}^{2-5}$ , exact assignment not possible,  $\text{C}_5\text{H}_4\text{SiMe}_3$ ), 120.3, 120.4 ( $\text{C}^{5-6}$  aromatic system of bzta), 122.2, 126.6 ( $\text{C}^{4-7}$  aromatic system of bzta), 128.2 ( $\text{C}^3$  aromatic system of bzta), 142.2 ( $\text{C}^7$  aromatic system of bzta), 173.7 ( $\text{C}^2$  aromatic system of bzta).

#### 4.3. Synthesis of [ $\text{Cp}'_2\text{Nb}(\kappa^2\text{-S,N-Sbzoa})$ ] (**5**)

The complex [ $\text{Cp}'_2\text{Nb}(\text{H})_3$ ] (**1**) (0.75 g; 2.25 mmol) was dissolved in 30 mL of dry thf and to this solution was added bzoa-OH in a 1:1 stoichiometry (0.34 g; 70 mmol). The mixture was stirred at 343 K for 3 h. The resulting dark-red solution was filtered and evaporated to dryness. Complex **2** was obtained as a dark red oil from a saturated hexane solution at  $-30\text{ }^{\circ}\text{C}$  (0.30 g; 85%).

Complex **5**: IR (Nujol/PET  $\text{cm}^{-1}$ )  $\nu$  (C=N) 1580.  $^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ ):  $\delta$  0.04 (s, 18H,  $\text{SiMe}_3$ ), 4.06, 4.36, 5.40, 5.45 (2H each a complex signal,  $\text{C}_5\text{H}_4\text{SiMe}_3$ ), 6.70, 6.80 (1H each t,  $^3J_{\text{HH}} = 7.5\text{ Hz}$ ,  $\text{H}^5$ ,  $\text{H}^6$  aromatic system of bzoa), 7.62, 7.80 (1H each d,  $^3J_{\text{HH}} = 7.3\text{ Hz}$ ,  $\text{H}^4$ ,  $\text{H}^7$  aromatic system of bzoa).  $^{13}\text{C}$  { $^1\text{H}$ } NMR ( $\text{C}_6\text{D}_6$ ):  $\delta$  0.6 ( $\text{SiMe}_3$ ), 96.8, 99.4, 103.5, 104.6 ( $\text{C}^{2-5}$ , exact assignment

not possible,  $\text{C}_5\text{H}_4\text{SiMe}_3$ ), 109.6 ( $\text{C}^1$ ,  $\text{C}_5\text{H}_4\text{SiMe}_3$ ), 113.6, 122.6 ( $\text{C}^{4-7}$  aromatic system of bzoa), 124.1 ( $\text{C}^{5-6}$  aromatic system of bzoa), 140.9 ( $\text{C}^3$  aromatic system of bzoa), 149.9 ( $\text{C}^7$  aromatic system of bzoa), 181.1 ( $\text{C}^2$  aromatic system of bzoa).

#### 4.4. Synthesis of [ $(\text{Cp}'_2\text{Nb})_3(\kappa^2\text{-X,N-X}_3(\text{C}_3\text{N}_3))$ ], $\text{X} = \text{NH}$ (**6**), $\text{O}$ (**7**), $\text{S}$ (**8**)

A mixture of [ $\text{Cp}'_2\text{Nb}(\text{H})_3$ ] (**1**) (0.75 g; 2.25 mmol) and the corresponding triazine  $\text{C}_3\text{N}_3(\text{XH})_3$  (where  $\text{X} = \text{NH}$ ,  $\text{O}$ ,  $\text{S}$ ) in a 3:1 stoichiometry (0.75 mmol; 0.09, 0.09, 0.13 g, respectively) was stirred with 30 mL of dry thf at 343 K for 4 h. After that time the solution was dark green in colour; the solvent was evaporated under vacuum to dryness. The dark green oily residue was extracted with 10 mL of cold hexane. The resulting solution was filtered and evaporated to dryness. A dark green solid was isolated, yielding 90% of **6**. Complexes **7** and **8** were prepared in a similar way.

Complex **6**: IR (Nujol/PET  $\text{cm}^{-1}$ )  $\nu$  (N–H) 3200.  $^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ ):  $\delta$  0.12 (s, 54H,  $\text{SiMe}_3$ ), 2.3 (s, 3H, N–H), 4.11, 4.14, 5.35, 5.48 (6H each a complex signal,  $\text{C}_5\text{H}_4\text{SiMe}_3$ ).  $^{13}\text{C}$  { $^1\text{H}$ } NMR ( $\text{C}_6\text{D}_6$ ):  $\delta$  0.7 ( $\text{SiMe}_3$ ), 87.8 ( $\text{C}^1$ ,  $\text{C}_5\text{H}_4$ ), 97.6, 98.8, 103.4, 104.6 ( $\text{C}^{2-5}$ , exact assignment not possible,  $\text{C}_5\text{H}_4\text{SiMe}_3$ ), 172.7 [ $\text{C}^{\text{ipso}}$ , ( $\text{NH})_3\text{C}_3\text{N}_3$ ]. Anal. Calc. for  $\text{C}_{51}\text{H}_{84}\text{N}_6\text{Nb}_3\text{Si}_6$ : C, 49.86; H, 6.89; N, 6.84. Found: C, 49.75; H, 6.85; N, 6.79%.

Complex **7**:  $^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ ):  $\delta$   $-0.01$  (s, 54H,  $\text{SiMe}_3$ ), 3.84, 4.10, 5.43, 5.73 (6H each a complex signal,  $\text{C}_5\text{H}_4\text{SiMe}_3$ ).  $^{13}\text{C}$  { $^1\text{H}$ } NMR ( $\text{C}_6\text{D}_6$ ):  $\delta$  0.7 ( $\text{SiMe}_3$ ), 91.2 ( $\text{C}^1$ ,  $\text{C}_5\text{H}_4$ ), 102.2, 103.7, 105.3, 106.5 ( $\text{C}^{2-5}$ , exact assignment not possible,  $\text{C}_5\text{H}_4\text{SiMe}_3$ ), 178.2 [ $\text{C}^{\text{ipso}}$ , ( $\text{O})_3\text{C}_3\text{N}_3$ ]. Anal. Calc. for  $\text{C}_{51}\text{H}_{81}\text{N}_3\text{Nb}_3\text{O}_3\text{Si}_6$ : C, 49.74; H, 6.63; N, 3.41. Found: C, 49.70; H, 6.59; N, 6.33%.

Complex **8**:  $^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ ):  $\delta$  0.10 (s, 54H,  $\text{SiMe}_3$ ), 4.27, 4.79, 4.92, 5.60 (6H each a complex signal,  $\text{C}_5\text{H}_4\text{SiMe}_3$ ).  $^{13}\text{C}$  { $^1\text{H}$ } NMR ( $\text{C}_6\text{D}_6$ ):  $\delta$  0.6 ( $\text{SiMe}_3$ ), 93.7 ( $\text{C}^1$ ,  $\text{C}_5\text{H}_4$ ), 94.1, 99.9, 101.7, 107.0 ( $\text{C}^{2-5}$ , exact assignment not possible,  $\text{C}_5\text{H}_4\text{SiMe}_3$ ), 196.6 [ $\text{C}^{\text{ipso}}$ , ( $\text{S})_3\text{C}_3\text{N}_3$ ]. Anal. Calc. for  $\text{C}_{51}\text{H}_{81}\text{N}_3\text{Nb}_3\text{S}_3\text{Si}_6$ : C, 47.87; H, 6.39; N, 3.28. Found: C, 47.79; H, 6.35; N, 3.25%.

#### 4.5. Synthesis of [ $\text{Cp}'_2\text{Nb}(\kappa^1\text{-S-Sbzta})(\text{L})$ ], $\text{L} = \text{CNXyllyl}$ (**10**)

A mixture of complex **9** (0.75 g; 2.25 mmol) and bzta-SH (0.38 g; 2.25 mmol) was stirred with 30 mL of dry thf at room temperature for 3 h. After that time, the solution was green in colour. The solvent was evaporated under vacuum to dryness and the green oily residue was extracted with 10 mL of hexane. The resulting solution was filtered and evaporated to dryness. A green oil was isolated, yielding 85% of **10**.

Complex **10**: IR (Nujol/PET  $\text{cm}^{-1}$ )  $\nu$  (C=N) 2060, (C=N) 1585.  $^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ ):  $\delta$  0.08 (s, 18H,  $\text{SiMe}_3$ ), 2.22 (s, 6H,  $\text{C}_6\text{H}_3\text{-2,6-Me}_2$ ), 5.06 (m, 4H, a complex signal,

$C_5H_4SiMe_3$ ), 5.45, 5.70 (2H each a complex signal,  $C_5H_4SiMe_3$ ), 6.57, 6.88 (1H each t,  $^3J_{HH} = 7.2$  Hz,  $H^5$ ,  $H^6$  aromatic system of bzta), 7.26, 7.67 (1H each d,  $^3J_{HH} = 7$  Hz,  $H^4$ ,  $H^7$  aromatic system of bzta), 6.75 (s, 3H,  $C_6H_3$ -2,6- $Me_2$ ).  $^{13}C$  { $^1H$ } NMR ( $C_6D_6$ ):  $\delta$  0.8 ( $SiMe_3$ ), 20.0 ( $C_6H_3$ -2,6- $Me_2$ ), 96.2 ( $C^1$ ,  $C_5H_4$ ), 96.9, 101.8, 105.2, 107.3 ( $C^{2-5}$ , exact assignment not possible,  $C_5H_4SiMe_3$ ), 120.6, 120.7, 124.0, 133.8 ( $C^{1-6}$ , exact assignment not possible,  $C_6H_3$ -2,6- $Me_2$ ), ( $C_{ortho}$  of Xylyl), ( $C_1$  of Xylyl), 123.9, 126.0 ( $C^{5-6}$  aromatic system of bzta), 127.8, 129.2 ( $C^{4-7}$  aromatic system of bzta), 139.1 ( $C^{3'}$  aromatic system of bzta), 156.3 ( $C^{7'}$  aromatic system of bzta), 185.4 ( $C^2$  aromatic system of bzta), 215.2 ( $C\equiv N$ ).

#### 4.6. Synthesis of [ $Cp'_2Nb(\kappa^1-S-Sbzoa)(CNXylyl)$ ] (**11**)

A mixture of [ $Cp'_2Nb(H)(XylylNC)$ ] (**9**) (1.12 g; 2.25 mmol) and bzoa-SH (0.34 g; 2.25 mmol) was stirred with 30 mL of dry thf at 60 °C for 4 h. After this time, the solution was green in colour. The solvent was evaporated under vacuum to dryness and the green oily residue was extracted with 10 mL of hexane. The resulting solution was filtered and evaporated to dryness. A red oil was isolated, yielding 90% of **11**.

Complex **11**: IR (Nujol/PET  $cm^{-1}$ )  $\nu$  ( $C\equiv N$ ) 2050, ( $C=N$ ) 1565.  $^1H$  NMR ( $C_6D_6$ ):  $\delta$  0.00 (s, 18H,  $SiMe_3$ ), 2.14 (s, 6H,  $C_6H_3$ -2,6- $Me_2$ ), 4.95, 5.00, 5.42, 5.60 (2H each a complex signal,  $C_5H_4SiMe_3$ ), 6.59, 6.90 (1H each t,  $^3J_{HH} = 7$  Hz,  $H^5$ ,  $H^6$  aromatic system of bzoa), 7.00, 7.54 (1H each d,  $^3J_{HH} = 7.5$  Hz,  $H^4$ ,  $H^7$  aromatic system of bzoa), 6.53 (s, 3H,  $H_{arom}$  of Xylyl).  $^{13}C$  { $^1H$ } NMR ( $C_6D_6$ ):  $\delta$  0.2 ( $SiMe_3$ ), 19.1 ( $C_6H_3$ -2,6- $Me_2$ ), 95.3 ( $C^1$ ,  $C_5H_4$ ), 94.4, 100.2, 105.1, 105.6 ( $C^{2-5}$ , exact assignment not possible,  $C_5H_4SiMe_3$ ), 108.6, 109.4, 111.5, 116.7 ( $C^{1-6}$ , exact assignment not possible,  $C_6H_3$ -2,6- $Me_2$ ), 122.1, 122.8 ( $C^{5-6}$  aromatic system of bzoa), 123.3, 124.1 ( $C^{4-7}$  aromatic system of bzoa), 132.4 ( $C^{3'}$  aromatic system of bzoa), 155.9 ( $C^{7'}$  aromatic system of bzoa), 190.3 ( $C^2$  aromatic system of bzoa), 206.2 ( $C\equiv N$ ).

#### 4.7. Synthesis of [ $\{Cp'_2Nb(CNXylyl)\}_3(\kappa^1-S-S_3C_3N_3)$ ] (**12**)

A mixture of [ $Cp'_2Nb(H)(XylylNC)$ ] (**9**) (1.12 g; 2.25 mmol) and the triazine  $C_3N_3(SH)_3$  with a 3:1 stoichiometry, (0.13 g; 0.75 mmol), was stirred with 30 mL of dry thf at 60 °C for 4 h. After that time, the solution was green in colour. The solvent was evaporated under vacuum to dryness and the green oily residue was extracted with 10 mL of hexane. The resulting solution was filtered and evaporated to dryness. A green oil was isolated, yielding 90% of **12**.

Complex **12**: IR (Nujol/PET  $cm^{-1}$ )  $\nu$  ( $C\equiv N$ ) 2050.  $^1H$  NMR ( $C_6D_6$ ):  $\delta$  0.10 (s, 54H,  $SiMe_3$ ), 1.99 (s, 18H,  $C_6H_3$ -2,6- $Me_2$ ), 4.82, 4.91, 5.37, 5.48 (6H each a complex signal,  $C_5H_4SiMe_3$ ) 6.72 (m, 9H,  $H_{arom}$  of Xylyl).  $^{13}C$  { $^1H$ } NMR ( $C_6D_6$ ):  $\delta$  -0.2 ( $SiMe_3$ ), 18.9 ( $C_6H_3$ -2,6- $Me_2$ ),

101.0 ( $C^1$ ,  $C_5H_4$ ), 95.8, 101.9, 103.5, 104.9 ( $C^{2-5}$ , exact assignment not possible,  $C_5H_4SiMe_3$ ), 127.5, 128.3, 133.5 ( $C^{1-6}$ , exact assignment not possible,  $C_6H_3$ -2,6- $Me_2$ ), 174.7 [ $C^{ipso}$ , ( $S$ ) $_3C_3N_3$ ], 209.8 ( $C\equiv N$ ). Anal. Calc. for  $C_{100}H_{108}N_6Nb_3S_3Si_6$ : C, 61.99; H, 5.62; N, 4.34. C, 61.92; H, 5.58; N, 4.30.

#### 4.8. Synthesis of [ $Cp'_2Nb(CNXylyl)_2$ ][ $I_3$ ] (**15**)

To a solution of **11** (0.25 g; 2.25 mmol) in 30 mL of toluene was added MeI (25 mmol). The mixture was stirred for 4 h at 60 °C and, after this time, the solution was red in colour. The solvent was evaporated under vacuum to dryness. A red solid was formed by addition of 10 mL of diethyl ether. The red solid was isolated by filtration and evaporated to dryness. A red solid was isolated, yielding 38% of **15**.

Complex **15**: IR (Nujol/PET  $cm^{-1}$ )  $\nu$  ( $C\equiv N$ ) 2124.  $^1H$  NMR (Acetone- $d_6$ ):  $\delta$  0.25 (s, 18H,  $SiMe_3$ ), 2.46 (s, 6H,  $C_6H_3$ -2,6- $Me_2$ ), 5.74, 5.99 (4H each a complex signal,  $C_5H_4SiMe_3$ ), 7.24 (m, 3H,  $C_6H_3$ -2,6- $Me_2$ ).  $^{13}C$  { $^1H$ }

Table 5  
Crystal data and structure refinement for **15** and **14**

	<b>15</b>	<b>14</b>
Empirical formula	$C_{34}H_{44}I_3N_2NbSi_2$	$C_{19}H_{36}NbO_3PSi_2 \times C_8H_8N_2S$
Formula weight	1010.5	656.76
Temperature (K)	250(2)	230(2)
Wavelength (Å)	0.71073	0.71073
Crystal system	Triclinic	Triclinic
Space group	$P\bar{1}$	$P\bar{1}$
$a$ (Å)	9.452(1)	10.167(3)
$b$ (Å)	19.570(1)	12.191(2)
$c$ (Å)	23.024(1)	13.886(1)
$\alpha$ (°)	71.54(1)	71.713(3)
$\beta$ (°)	87.25(1)	86.155(5)
$\gamma$ (°)	78.95(1)	81.095(2)
Volume (Å <sup>3</sup> )	3964.5(5)	1614.2(6)
$Z$	4	2
$D_{calc}$ (g/cm <sup>3</sup> )	1.693	1.351
Absorption coefficient (mm <sup>-1</sup> )	2.724	0.591
$F(000)$	1960	688
Crystal size (mm)	0.3 × 0.3 × 0.1	0.3 × 0.2 × 0.1
$\theta$ Range for data collection (°)	1.12–25.01	2.03–28.02
Index ranges	$-11 \leq h \leq 11$ $-22 \leq k \leq 23$ $0 \leq l \leq 27$	$-13 \leq h \leq 13$ $-15 \leq k \leq 16$ $0 \leq l \leq 18$
Reflections collected	14317	8096
Independent reflections	13932 [ $R_{int} = 0.1130$ ]	7780 [ $R_{int} = 0.0767$ ]
Data/restraints/parameters	13932/0/762	7780/0/356
Goodness-of-fit on $F^2$	0.928	1.054
Final $R$ indices [ $I > 2\sigma(I)$ ]	$R_1 = 0.0875$ , $wR_2 = 0.1665$	$R_1 = 0.0683$ , $wR_2 = 0.1430$
$R$ indices (all data)	$R_1 = 0.3602$ , $wR_2 = 0.2466$	$R_1 = 0.1596$ , $wR_2 = 0.1726$
Largest difference in peak and hole (e Å <sup>-3</sup> )	0.918/−1.186	0.818/−0.983

NMR ( $C_6D_6$ ):  $\delta$  -0.0 ( $SiMe_3$ ), 19.1 ( $C_6H_3$ -2,6- $Me_2$ ), 98.1 ( $C^1$ ,  $C_5H_4$ ), 97.2, 102.2 ( $C^{2-5}$ , exact assignment not possible,  $C_5H_4SiMe_3$ ), 127.5, 128.3, 133.5 ( $C^{1-6}$ , exact assignment not possible,  $C_6H_3$ -2,6- $Me_2$ ), 226.1 ( $C\equiv N$ ). Anal. Calc. for  $C_{34}H_{35}I_3N_2NbSi_2$ : C, 40.78; H, 3.52; N, 2.80. Found: C, 40.70; H, 3.48; N, 2.75%.

#### 4.9. X-ray structure determinations for complexes

$[Cp'_2Nb(CNXylyl)_2][I_3]$  and  $[Cp'_2Nb(H)(P(OMe)_3)] \cdot (bzta)'-NH_2$ .  $[(bzta)'-NH_2 = 2\text{-amino-6-methylbenzothiazole}]$  (**15**) and (**14**)

Single crystals were mounted in inert oil in the cold gas stream of the diffractometer. The X-ray diffraction data were collected with a Nonius-Mach3 diffractometer with a  $\omega$ - $2\theta$  scan technique using graphite monochromated  $Mo K\alpha$  adiation ( $\lambda = 0.71073 \text{ \AA}$ ). Data were corrected for Lorentz and polarization effects and absorption correction was made for **14** ( $\psi$  scans) [25] but was not necessary for **15**. The structures were solved by direct methods using the SHELXS computer program [26] completed by subsequent difference Fourier synthesis and refined by full-matrix least-squares procedures (SHELXL-97) [27] on  $F^2$ . All the non-hydrogen atoms were refined with anisotropic thermal parameters. The hydrogen atoms were included in calculated positions and refined “riding” on their parent carbon atoms except H1, H2 and H3 for **14**, which were found in the Fourier map and refined freely. Relevant crystal and data parameters are presented in Table 5. Crystals of **15** contained two independent molecules per asymmetric unit cell.

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#### Appendix A. Supplementary material

CCDC 644685 and 644686 contain the supplementary crystallographic data for **14** and **15**. These data can be obtained free of charge via <http://www.ccdc.cam.ac.uk/conts/retrieving.html>, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: [deposit@ccdc.cam.ac.uk](mailto:deposit@ccdc.cam.ac.uk). Supplementary data associated with this article can be found, in the online version, at [doi:10.1016/j.jorganchem.2007.03.038](https://doi.org/10.1016/j.jorganchem.2007.03.038).

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