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Synthesis and structural characterisation of new organo-diimido tantalum and niobium complexes

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The organo-diimido tantalum complexes [{Ta(L_2)Cl_3}$_2$(μ-1,*n*-NC_6H_4N)], L = MeCN (**1**) and 4-^{t}Bupy (**2**), have been prepared by two alternative experimental methods: (1) the initial formation of the corresponding $TaCl_5$·L adduct, L = 4-^{t}Bupy or CH_3CN, followed by addition of the appropriate phenylenediamine, or (2) the initial formation of the corresponding organo-diimido species and subsequent addition of the ligand L. These complexes, as well as some related niobium complexes, were alkylated using the appropriate Grignard reagent to afford the alkyl-containing complexes [{M(L)R_3}$_2$(μ-1,*n*-NC_6H_4N)] (**4**, **5**, **6**, **7**, **8**, **9**) (M = Nb, Ta; *n* = 3, 4; L = MeCN, R = CH_2SiMe_3, CH_2CMe_3, CH_2CMe_2Ph). These complexes can be prepared by treating the corresponding chloro-complexes with dialkylmagnesium reagents $MgR_2(THF)_2$. Niobium complexes containing THF ligands, *i.e.* [{Nb(THF)R_3}$_2$(μ-1,3-NC_6H_4N)] (**10**, **11**) (R = CH_2SiMe_3, CH_2CMe_3), were isolated by using THF as the solvent and also from the acetonitrile-containing complexes **8b** and **9b** by simply adding THF. The complex [{Nb(CH_2CMe_2Ph)$_3$}$_2$(μ-1,4-NC_6H_4N)] (**12a**) was prepared by addition of the corresponding Grignard reagent to a suspension of [{Nb(MeCN)$_2Cl_3$}$_2$(μ-1,4-NC_6H_4N)] in THF. The reaction of complexes [{M(MeCN)$_2Cl_3$}$_2$(μ-1,*n*-NC_6H_4N)] (M = Ta, Nb; *n* = 3, 4) with Li[$C_5H_4SiMe_3$] was carried out and afforded the tetrakis-cyclopentadienyl-diimido complexes [{M(η^5-$C_5H_4SiMe_3$)$_2$Cl}$_2$(μ-1,*n*-NC_6H_4N)] [M = Ta, *n* = 4 (**13a**); M = Ta, *n* = 3 (**13b**); M = Nb, *n* = 4 (**14a**); M = Nb, *n* = 3 (**14b**)]. The structure of **13a** has been solved by X-ray diffraction. Finally, we have performed the reactions between the diimido-containing compounds [{M(MeCN)$_2Cl_3$}$_2$(μ-1,*n*-NC_6H_4N)] (M = Ta, Nb; *n* = 3, 4) and the lithium benzamidinate Li[PhC(NSiMe_3)$_2$] to afford the benzamidinate-containing complexes [{M[PhC(NSiMe_3)$_2$]$_2$Cl}$_2$(μ-1,*n*-NC_6H_4N)] [M = Ta, *n* = 4 (**15a**); M = Ta, *n* = 3 (**15b**); M = Nb, *n* = 4 (**16a**)]. The structures of the different families of compounds were determined by spectroscopic methods.

Introduction

Transition metal complexes in which the metal centres are linked by a bridging ligand that has a delocalized π-system are well known and have been the subject of intense research due to their potential applications in the design of low-dimensional, polymeric materials with novel electrical and/or magnetic properties.[1] Several such complexes that incorporate aryldiimido bridges have been described previously.[2]

We reported the preparation of niobocene organo-diimido complexes, namely [{Nb(η^5-$C_5H_4SiMe_3$)$_2$Cl}$_2$(μ-$N_2C_6H_4$)], by the reaction of [{Nb(η^5-$C_5H_4SiMe_3$)$_2$Cl}$_2$] with the appropriate amount of the corresponding aniline, 1,4- or 1,3-phenylenediamine.[3] More recently, we described the preparation of organo-diimido niobium and titanium complexes [{Nb(L_2)Cl_3}$_2$(μ-1,*n*-NC_6H_4N)] (where L = CH_3CN or 4-^{t}Bupy and *n* = 2, 3, 4) and [{Ti(L_2)Cl_2}$_2$(μ-1,*n*-NC_6H_4N)] (where L = 4-^{t}Bupy or L_2 = TMEDA and *n* = 3, 4) by treating $NbCl_5$ or $TiCl_4$ in the presence of L with the appropriate amount of the corresponding aniline, 1,4-, 1,3- or 1,2-phenylenediamine. In addition, we reported the synthesis of organo-imido titanium complexes [{Ti(L_2)Cl_2}(1,*n*-NC_6H_4N(SiMe_3)$_2$)] (where L = 4-^{t}Bupy or L_2 = TMEDA and *n* = 3, 4) by treatment of $TiCl_4$ in the presence of L with the appropriate amount of the corresponding aniline, 1,4- or 1,3-phenylenediamine.[4] Another aspect of our studies concerned the reaction of [{Nb(CH_3CN)$_2Cl_3$}$_2$(μ-1,4-NC_6H_4N)] with appropriate alkylating agents to give the corresponding alkyl complexes, namely [{NbLR_3}$_2$(μ-1,4-NC_6H_4N)] (L = THF, CH_3CN and R = CH_2SiMe_3, CH_2CMe_3). As a continuation of our research in this field we report here the reactivity of $TaCl_5$ towards different 1,*n*-phenylenediamines and the reactivity of both tantalum complexes and the previously prepared niobium complexes toward alkylating agents. The aim of this work was to synthesize new types of binuclear organo-diimido niobium and tantalum complexes in which both metallic centres are linked by conjugated π-systems.

Results and discussion

The preparation of organo-diimido tantalum complexes will be considered first. In fact, $TaCl_5$ reacts with the appropriate N,N,N′,N′-tetrakis(trimethylsilyl)-1,4-, -1,3- or -1,2-phenylenediamine in CH_2Cl_2 in the presence of acetonitrile or 4-^{t}Bupy to afford the corresponding organo-diimido tantalum complexes [{Ta(L_2)Cl_3}$_2$(μ-1,*n*-NC_6H_4N)] (**1** and **2**), eqn. (1). In these reactions, which were carried out under mild conditions, a selective elimination of $SiMe_3Cl$ takes place as a consequence of the complete substitution of the four trimethylsilyl groups to give the appropriate organo-diimido species in high yields.

The reactions were carried out by two alternative experimental methods. The first involved the initial formation of the corresponding $TaCl_5$·L adduct, L = 4-^{t}Bupy or CH_3CN, followed by addition of the appropriate phenylenediamine. The

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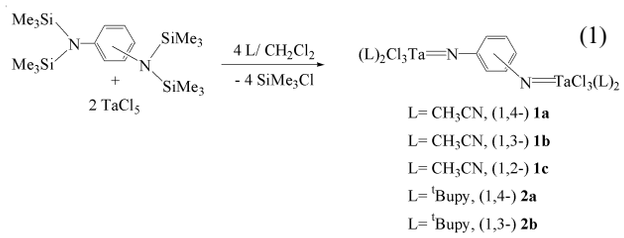


adduct $TaCl_5$·4-^{t}Bupy (**3**) was isolated and fully characterized. The second method consisted of the initial formation of the corresponding organo-diimido species and subsequent addition of the ligand L. These two methods can be used in all cases although the second one affords the final products more rapidly than the first, probably due to the lower solubility of the starting material $TaCl_5$ in CH_2Cl_2. Alternatively, complexes containing 4-^{t}Bupy (*i.e.* **2**) can be prepared from the corresponding acetonitrile complexes **1** by simple addition of 4-^{t}Bupy on the basis that this ligand displaces the more labile acetonitrile.

The method described above constitutes a very easy and selective route for the preparation of imido complexes because the formation of the volatile by-product $SiMe_3Cl$ facilitates the isolation of the corresponding diimido complex. These organo-diimido complexes, as well as the other complexes described in this work, were characterized by ^{1}H, ^{13}C NMR spectroscopy, elemental analysis and IR spectroscopy (see Experimental).

The ^{1}H NMR spectra of complexes **2** exhibit two resonances for the two non-equivalent ^{t}Bupy units around each tantalum atom, while the analogous spectra for acetonitrile-containing complexes **1** in CD_3CN each show a single signal corresponding to free CH_3CN, which is removed from the metal by the deuterated solvent. In order to confirm the presence of two coordinated acetonitrile ligands for each metal centre in this type of complex, the spectra were acquired in CD_3NO_2. In this case two signals were observed at lower field than the corresponding signals in acetonitrile and these are due to the two ligands in *cis* positions. The ^{13}C NMR spectra contain the signals of the phenyl groups of the phenylene ligand at δ 152.4 (C_{ipso}), 128.7 and 153.7 (C_{ipso}) and 128.1, 125.1 and 122.4 for 1,4- and 1,3-phenylene complexes, respectively (see Experimental). On the basis of both the spectroscopic and analytical data, it can be concluded that two acetonitrile or 4-^{t}Bupy ligands are present in the proposed octahedral environment with a *mer* disposition for the Cl ligands and *cis* dispositions for the ligands L (Fig. 1).

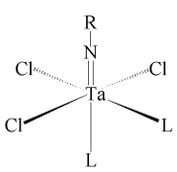


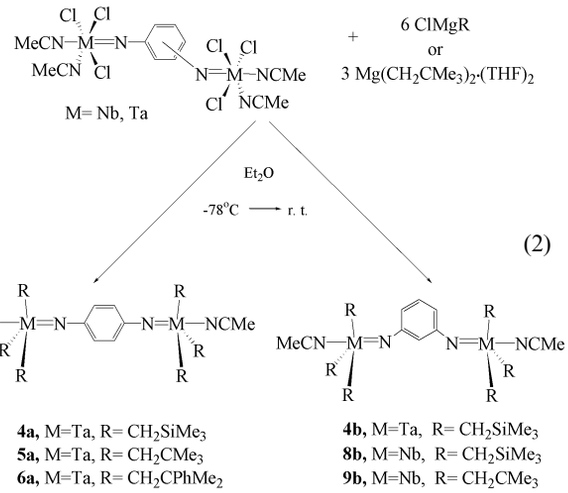
Fig. 1 Structural disposition proposed around each tantalum atom for complexes **1** and **2**.

A similar structure was found in analogous organo-diimido niobium complexes.[3] In the structure of **1** and **2** a diimido-phenylene group bridges two tantalum atoms, which are probably located in the plane formed by this ligand.

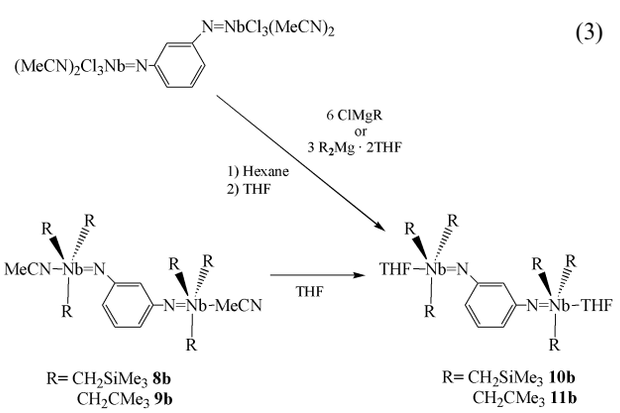
In addition, we propose that both nitrogen atoms are *sp* hybridized with the following two limiting descriptions, $Ta^-\equiv N^+$–R and Ta=N–R, which are an accurate representation of the bonding situation.[5]

Complex **1** and some related niobium complexes[3] were alkylated using the appropriate Grignard reagents in a 1 : 6 molar ratio. The reactions afforded the corresponding alkyl-containing complexes [{M(L)R_3}$_2$(μ-1,*n*-NC_6H_4N)] (**4**, **5**, **6**, **7**, **8**, **9**) (M = Nb, Ta; *n* = 3, 4; L = MeCN, R = CH_2SiMe_3, CH_2CMe_3, CH_2CMe_2Ph) in good yields (80–90%), eqn. (2).

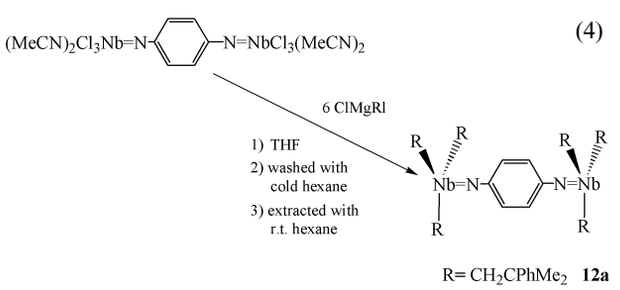
Alternatively, these complexes can be prepared in similar yields by treating the corresponding chloro-complexes with di-



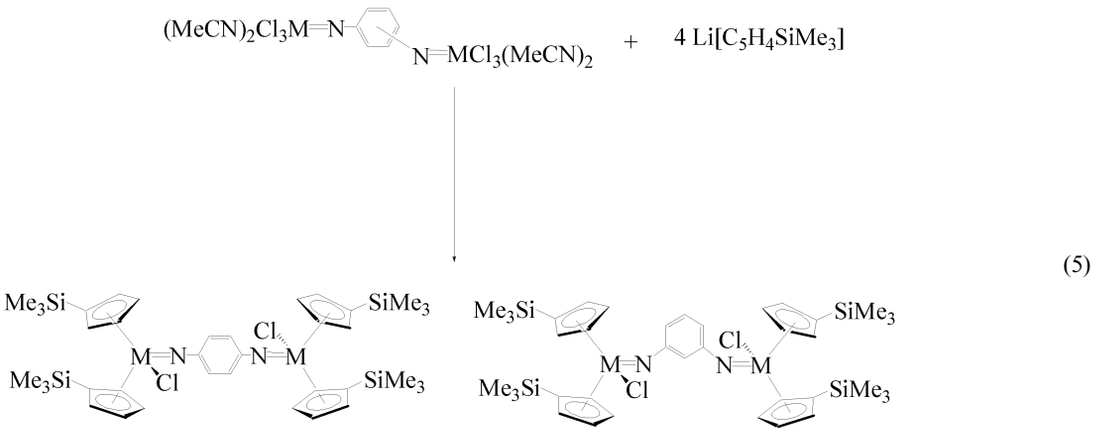
alkylmagnesium reagents $MgR_2(THF)_2$ (see, as illustrative examples, the preparation of **5a** and **9b** in the Experimental section). Niobium complexes containing THF ligands, [{Nb(THF)R_3}$_2$(μ-1,3-NC_6H_4N)] (**10**, **11**) (R = CH_2SiMe_3, CH_2CMe_3, respectively), were isolated when THF was employed as the solvent because the acetonitrile was replaced by THF. Moreover, these same complexes can be prepared from the acetonitrile-containing complexes **8b** and **9b** by simply adding THF, eqn. (3).



Finally, the complex [{Nb(CH_2CMe_2Ph)$_3$}$_2$(μ-1,4-NC_6H_4N)] (**12a**) was prepared by addition of the corresponding Grignard reagent to a suspension of [{Nb(MeCN)$_2$Cl$_3$}$_2$(μ-1,4-NC_6H_4N)] in THF and after removal of the solvent, the residue was washed with cold hexane and extracted with hexane at room temperature. The coordination of THF does not take place, probably due to the more space required for the alkyl group around the metal, eqn. (4).



The different alkyl complexes were isolated as air-sensitive yellow crystalline solids after the appropriate work-up and all are sparingly soluble in alkanes but soluble in Et_2O and THF. The structural characterization of the alkyl compounds was carried out by spectroscopic studies. The ^{1}H and ^{13}C NMR spectra for complexes **4**–**12** show the characteristic resonances



(5)

M=Ta, **13a**
M=Nb, **14a**

M=Ta, **13b**
M=Nb, **14b**

of alkyl groups bound to a metal atom (see Experimental). When the coordinated acetonitrile was replaced by THF, *i.e.* complexes **10** and **11**, the ^{1}H and ^{13}C resonances were shifted slightly with respect to the signals of the free ligand. The ^{13}C NMR spectra of these complexes exhibit a broad signal between δ 61 and 93 for the methylene group resulting from the niobium quadrupole, indicating its coordination with the niobium atom.

On the basis of these spectroscopic data and of those of the molecular structure previously described for an analogous niobium complex, namely [{Nb(MeCN)(CH_2SiMe_3)$_3$}$_2$(μ-1,4-NC_6H_4N)],[4] a trigonal bipyramidal geometry for each metal centre can be proposed for the different metal-alkyl complexes studied. The ligand L occupies therein a *trans* position with respect to the imido ligand. This type of structure, where a labile ligand like acetonitrile or pyridine is located in a coordination site *trans* to the imido ligand, has already been observed in several imido-containing early transition metal complexes.[6]

A further alkylation reaction was also performed. We carried out the reaction of complexes [{M(MeCN)$_2$Cl$_3$}$_2$(μ-1,*n*-NC_6H_4N)] (M = Ta, Nb; *n* = 3, 4) with Li[$C_5H_4SiMe_3$] in a 1 : 4 molar ratio. The reactions take place by substitution of the chloride ligand and elimination of the labile acetonitrile molecules to afford the tetrakis-cyclopentadienyl-diimido complexes [{M(η^5-$C_5H_4SiMe_3$)$_2$Cl}$_2$(μ-1,*n*-NC_6H_4N)] [M = Ta, *n* = 4 (**13a**); M = Ta, *n* = 3 (**13b**); M = Nb, *n* = 4 (**14a**); M = Nb, *n* = 3 (**14b**)], eqn. (5).

Some of these complexes have been already prepared in our group by the treatment of [{Nb(η^5-$C_5H_4SiMe_3$)$_2$Cl}$_2$] with the appropriate amount of the corresponding aniline, 1,4- or 1,3-phenylenediamine or, alternatively, by heating the corresponding diisocyanate derivatives.[3] These compounds were cleanly isolated in good yields and were characterized by elemental analysis and ^{1}H and ^{13}C NMR spectroscopy (see Experimental). The ^{1}H NMR spectra provide evidence for the presence of an ABCD system for the cyclopentadienyl rings and a singlet or an A_2BC system for the phenylene ring in 1,4- or 1,3-phenylene complexes, respectively. In order to confirm unequivocally the proposed structure of these complexes, we were able to obtain crystals suitable for a molecular structure determination by X-ray diffraction in the case of compound **13a**. An ORTEP drawing of this complex is depicted in Fig. 2 and selected bond lengths and angles are given in Table 1.

13a crystallizes in the $P2_1/n$ space group with two molecules per unit cell and, consequently, the dinuclear molecule lies over a symmetry centre. The Ta(1) and Ta(1′) deviate by less than 0.3 Å from the plane formed by the bridging diimidophenylene ligand. The cyclopentadienyl rings adopt an *anti* conformation. The Ta–N bond length of 1.792(7) Å falls into the intermediate range expected for a double and a triple Ta–N bond. The

Table 1 Selected bond lengths (Å) and angles (°) for complex **13a**

Ta–N	1.792(7)	Ta–C(6)	2.497(10)
Ta–Cl(1)	2.430(3)	Ta–C(7)	2.508(10)
Ta–C(1)	2.471(10)	Ta–C(8)	2.546(10)
Ta–C(2)	2.431(10)	Ta–C(9)	2.468(11)
Ta–C(3)	2.463(10)	Ta–C(10)	2.429(10)
Ta–C(4)	2.579(10)	Ta–CT(1)	2.186
Ta–C(5)	2.520(10)	Ta–CT(2)	2.184
N–C(17)	1.381(11)	CT(1)–Ta–CT(2)	124.8
Cl–Ta–N	90.1(3)	Ta–N–C(17)	168.6(7)

CT(1) is a geometrical centre of C(1)–C(5) atoms, CT(2) is that of C(6)–C(10) atoms.

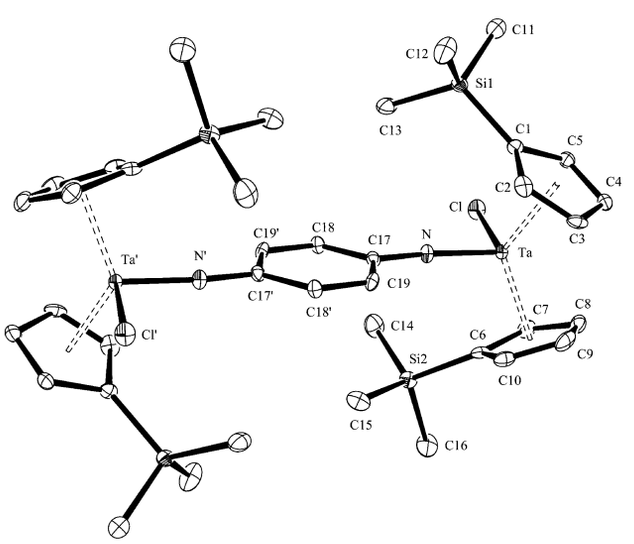
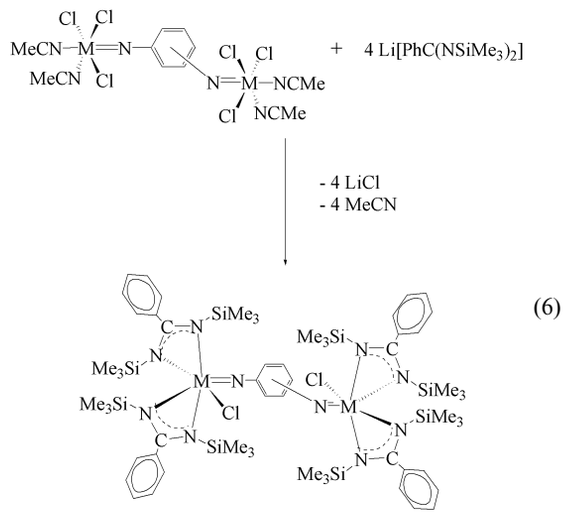


Fig. 2 ORTEP drawing (30% probability level) for **13a**.

Ta–N–C17 (*ipso*) angle [168.6(7)°] agrees with the values previously reported by us for other similar complexes.[3] Consequently, we propose that the nitrogen atom is sp hybridized with the two limiting structures, Ta^{-}≡N^{+}–R and Ta=N–R, in which the nitrogen lone pair is involved in the delocalized conjugated Ta–bridging ligand bonding. Finally, the chlorine atoms were found to be in a *trans* disposition with respect to the Ta–Ta vector.

On the other hand, imidinate compounds have been proposed as alternative ligands to the cyclopentadienyl rings.[7,8] In order to extend the study of the reactivity of our trichlorodiimido complexes, an additional alkylation reaction was undertaken. We carried out the reaction of the diimido-containing compounds [{M(MeCN)$_2$Cl$_3$}$_2$(μ-1,*n*-NC_6H_4N)] (M = Ta, Nb; *n* = 3, 4) with the lithium benzamidinate Li[PhC($NSiMe_3$)$_2$] in a

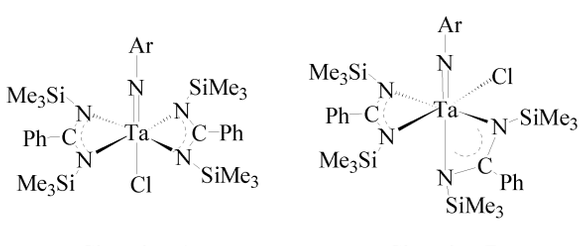
1 : 4 molar ratio. The process afforded the benzamidinate-containing complexes $[\{M[PhC(NSiMe_3)_2]_2Cl\}_2(\mu\text{-}1,n\text{-}NC_6H_4N)]$ [M = Ta, n = 4 (**15a**); M = Ta, n = 3 (**15b**); M = Nb, n = 4 (**16a**)], eqn. (6).



(6)

(1,4-), M=Ta, **15a**
(1,3-), M=Ta, **15b**
(1,4-), M=Nb, **16a**

The complexes were isolated as air-sensitive red solids and are soluble in common organic solvents. These materials were characterized by elemental analysis and ^{1}H and ^{13}C NMR and IR spectroscopy (see Experimental). In each case the IR spectrum shows the ν_{N-C-N} band at *ca.* 1522 cm^{-1}. The ^{1}H NMR spectra of these complexes include a single signal for the eight $SiMe_3$ groups at *ca.* −0.07 ppm, even when the spectra were acquired at −80 °C, and this fact could indicate a local symmetry around the metal centre with a *trans* disposition of the imido and chloro-ligands in an octahedral environment (see Fig. 3, situation **A**) or, alternatively, a *cis* disposition of these ligands around the metal centre with a fluxional behaviour (see Fig. 3, situation **B**) in an octahedral environment. In the case where static behaviour is observed in situation B, one would expect four signals in the ^{1}H NMR spectrum for the $SiMe_3$ groups.



Situation A **Situation B**

Fig. 3

For the complexes $[V(=N\text{-}4\text{-}C_6H_4Me)\{PhC(NSiMe_3)_2\}_2Cl]$[9] and $[Nb(O)\{4\text{-}C_6H_4Me)C(NSiMe_3)_2\}_2Cl]$,[10] situation **B** was proposed on the basis of crystallographic and NMR data. VTNMR experiments carried out for these species indicate a fluxional behaviour even at low temperatures. The ^{1}H NMR spectrum of the complex $[Ta(=N\text{-}2,6\text{-}C_6H_3{}^iPr_2)\{PhC(NSiMe_3)_2\}_2Cl]$[11] shows only one signal for the $SiMe_3$ groups and two signals for the ^{i}Pr groups – a result of restricted rotation around the N–C bond in the imido ligand. Likewise, it is common in benzamidinate complexes to observe the type of fluxional behaviour proposed in our complexes.[9,10,12]

On the basis of the data outlined above we propose geometry **B** as the more probable for our complexes with a fluxional behaviour even at −80 °C, although geometry **A** cannot be ruled out.

Experimental

General methods and instrumentation

All manipulations were carried out under an argon atmosphere using either standard Schlenk techniques or an MBraun glovebox. Solvents were dried and distilled under argon: tetrahydrofuran and diethyl ether from sodium benzophenone ketyl, hexane and pentane from sodium and potassium alloy, CH_2Cl_2 from P_2O_5, acetonitrile and $CDCl_3$ from finely ground calcium hydride.

4-*tert*-Butylpyridine was dried under argon over activated 4A molecular sieves and stored under argon. Other reagents were obtained from commercial sources and used as received or prepared as reported elsewhere: N,N,N′,N′-Tetrakis(trimethylsilyl)phenylendiamine,[13] $[\{Nb(CH_3CN)_2Cl_3\}_2(\mu\text{-}1,4\text{-}NC_6H_4N)]$,[4] $[\{Nb(CH_3CN)_2Cl_3\}_2(\mu\text{-}1,3\text{-}NC_6H_4N)]$,[4] $Mg(Me_3CCH_2)_2\cdot 2THF$,[14] $Li[PhC(NSiMe_3)_2]$,[7a] $Li[C_5H_4SiMe_3]$.[15]

IR spectra were recorded in Nujol mulls between CsI pellets over the range 4000–370 cm^{-1} on a Perkin-Elmer model 883 spectrophotometer and/or a Perkin-Elmer IR-FT Spectrophotometer 2000. ^{1}H and ^{13}C NMR spectra were recorded on a Gemini-200 and/or UNITY-300 (Varian) spectrometer. Chemical shifts (δ ppm) were measured relative to residual ^{1}H and ^{13}C resonances for acetonitrile-d_3, nitromethane-d_3, chloroform-d_1 and benzene-d_6 as solvents. C, H and N analyses were carried out with a Perkin-Elmer 240–13, Perkin-Elmer 240 C and/or Heraeus-CHN-O-Rapid microanalyser.

Preparations

$[\{Ta(CH_2CN)_3Cl_3\}_2(\mu\text{-}1,4\text{-}NC_6H_4N)]$ (1a) and $[\{Ta(CH_3CN)_2Cl_3\}_2(\mu\text{-}1,3\text{-}NC_6H_4N)]$ (1b). To a solution of $TaCl_5$ in acetonitrile was added dropwise at room temperature over 45 min a solution in CH_2Cl_2 of the corresponding N,N,N′,N′-tetrakis(trimethylsilyl)phenylendiamine in a 2 : 1 molar ratio. Vigorous stirring was required during the addition. The initial yellow solution changed to deep red for **1a** and to orange for complex **1b**. The mixture was vigorously stirred overnight at room temperature. The solvent was removed *in vacuo*, the solids were washed several times with hexane and identified as **1a** or **1b**, respectively.

Complex **1a**: from $TaCl_5$ (3.60 g, 10.00 mmol), 1,4-$\{(Me_3Si)_2N\}_2C_6H_4$ (2.00 g, 5.02 mmol) and CH_3CN (100 ml), (yield: quantitative). NMR (CD_3CN): ^{1}H (300 MHz), δ 1.95 (s, 12H, CH_3CN), 6.92 (s, 4H, phenylene ring); (CD_3NO_2): ^{1}H (300 MHz), δ 2.37 and 2.58 (s, br, 12H, CH_3CN), 6.99 (s, 4H, phenylene ring); ^{13}C-{^{1}H} (75 MHz), δ 1.7 (CH_3CN), 127.0 (phenylene ring), 128.7 (CH_3CN), 152.4 (C_{ipso} of phenylene ring); (CD_3NO_2): ^{1}H (300 MHz), δ 2.37 and 2.58 (s, br, 12H, CH_3CN), 6.99 (s, 4H, phenylene ring). IR: 2318s, 2290s, 1489s, 1346s, 1095m, 847s, 522m and 318s cm^{-1}. [Found (Calc. for $Ta_2Cl_6N_6C_{14}H_{16}$): C, 19.55 (19.95); H, 1.93 (1.91); N, 9.60 (9.97)%].

Complex **1b**: from $TaCl_5$ (0.90 g, 2.52 mmol), 1,3-$\{(Me_3Si)_2N\}_2C_6H_4$ (0.50 g, 1.26 mmol) and CH_3CN (30 ml), (yield: quantitative). NMR (CD_3CN): ^{1}H (300 MHz), δ 1.99 (s, 12H, CH_3CN), 6.44 (part A_2 of an A_2BC spin system, 2H, phenylene ring), 6.47 (part B of an A_2BC spin system, 1H, phenylene ring), 7.31 (part C of an A_2BC, 1H, phenylene ring); ^{13}C-{^{1}H} (75 MHz), δ 1.7 (CH_3CN), 122.4, 125.1, 128.1 (phenylene ring), 128.3 (CH_3CN), 153.7 (C_{ipso} of phenylene ring). IR: 2316s, 2288s, 1571vs, 1331s, 1031m, 874m and 789m cm^{-1}. [Found (Calc. for $Ta_2Cl_6N_6C_{14}H_{16}$): C, 20.32 (19.95); H, 2.02 (1.91); N, 9.74 (9.97)%].

$[\{Ta(CH_3CN)_2Cl_3\}_2(\mu\text{-}1,2\text{-}NC_6H_4N)]$ (1c). To a vigorously stirred suspension of $TaCl_5$ (1.80 g, 5.02 mmol) in CH_2Cl_2 (50 ml) was added dropwise a solution of 1,2-$\{(Me_3Si)_2N\}_2C_6H_4$

(1.00 g, 2.51 mmol) in CH_2Cl_2 (25 ml). The initial yellow suspension changed to a brown suspension. The mixture was stirred during 6 d and during this time the suspension changed to a deeper red solution. The solvent was removed *in vacuo* and CH_3CN (15 ml) was added. The mixture was stirred for 15 min and the solvent was evaporated to dryness to give 1.74 g of complex **1c** as a brown solid, which was washed with hexane (3 × 15 ml) and dried *in vacuo* (yield: 82%). NMR (CD_3CN): ^{1}H (300 MHz), δ 1.95 (s, 12H, CH_3CN), 6.90 (part AA′ of an AA′BB′ spin system, 2H, phenylene ring), 7.18 (part BB′ of an AA′BB′ spin system, 2H, phenylene ring); ^{13}C-{^{1}H} (75 MHz), δ 1.7 (*C*H_3CN), 125.9, 130.4 (phenylene ring), 129.1 (CH_3*C*N), 149.7 (C_{ipso} of phenylene ring). IR: 2315s, 2287s, 1441s, 1354s, 1027m, 847s and 759m cm^{-1}. [Found (Calc. for $Ta_2Cl_6N_6C_{14}H_{16}$): C, 20.15 (19.95); H, 1.94 (1.91); N, 10.08 (9.97)%].

[{Ta(^{t}Bupy)$_2$Cl$_3$}$_2$(μ-1,4-NC$_6$H$_4$N)] (2a) and [{Ta(^{t}Bupy)$_2$Cl$_3$}$_2$-(μ-1,3-NC$_6$H$_4$N)] (2b). To a vigorously stirred suspension of $TaCl_5$ in CH_2Cl_2 (25 ml) was added ^{t}Bupy in a 1 : 2 molar ratio. The initial suspension changed to a colourless solution. To this solution was added dropwise over 45 min a solution of the corresponding N,N,N′,N′-tetrakis(trimethylsilyl)phenylendiamine in CH_2Cl_2 (25 ml) at room temperature. The mixture was vigorously stirred during 18 h at room temperature. The solvent was removed *in vacuo* and the solids obtained were washed with hexane (3 × 15 ml) and identified as **2a** or **2b**.

Complex **2a**: from $TaCl_5$ (0.45 g, 1.26 mmol), 1,4-{$(Me_3Si)_2$N}$_2$C$_6$H$_4$ (0.25 g, 0.63 mmol) and 4-*tert*-butylpyridine (0.4 ml, 2.70 mmol). This compound was recrystallized from CH_2Cl_2–hexane (1 : 1) and 0.65 g of an orange microcrystalline solid was obtained (yield: 84%). NMR ($CDCl_3$): ^{1}H (300 MHz), δ 1.31 (s, 18H, *trans*-C*Me*$_3$), 1.35 (s, 18H, *cis*-C*Me*$_3$), 7.07 (s, 4H, phenylene ring), 7.35 (AA′ part of an AA′BB′ spin system, 4H, *trans m*-NC$_5$H$_4$Bu^t), 7.42 (AA′ part of an AA′BB′ spin system, 4H, *cis m*-NC$_5$H$_4$Bu^t), 8.65 (BB′ part of an AA′BB′ spin system, 4H, *trans o*-NC$_5$H$_4$Bu^t), 9.01 (BB′ part of an AA′BB′ spin system, 4H, *cis o*-NC$_5$H$_4$Bu^t); ^{13}C-{^{1}H} (50 MHz), δ 30.1 (*trans*-C*Me*$_3$), 30.3 (*cis*-C*Me*$_3$), 35.2 (*trans*-*C*Me$_3$), 35.6 (*cis*-*C*Me$_3$), 121.5 (*trans m*-NC$_5$H$_4$Bu^t), 122.0 (*cis m*-NC$_5$H$_4$Bu^t), 126.6 (phenylene ring), 151.4 (*trans o*-NC$_5$H$_4$Bu^t), 151.5 (*cis o*-NC$_5$H$_4$Bu^t), 151.9 (C_{ipso} of phenylene ring), 163.6 (*trans p*-NC$_5$H$_4$Bu^t), 165.3 (*cis p*-NC$_5$H$_4$Bu^t). IR: 1618vs, 1421m, 1343s, 1275m, 1067s, 831vs and 572s cm^{-1}. [Found (Calc. for $Ta_2Cl_6C_{42}H_{56}N_6$): C, 41.18 (41.36); H, 4.93 (4.63); N, 7.44 (6.89)%].

Complex **2b**: from $TaCl_5$ (0.90 g, 2.52 mmol), 1,3-{$(Me_3Si)_2$N}$_2$C$_6$H$_4$ (0.50 g, 1.26 mmol) and 4-*tert*-butylpyridine (0.8 ml, 5.40 mmol). This compound was recrystallized from toluene–hexane (1 : 1) to give 1.20 g of a yellow microcrystalline solid (yield: 78%). NMR ($CDCl_3$): ^{1}H (300 MHz), δ 1.30 (s, 18H, *trans*-C*Me*$_3$), 1.34 (s, 18H, *cis*-C*Me*$_3$), 6.68, 6.70 and 7.31 (m, 4H, phenylene ring), 7.41 (AA′ part of an AA′BB′ spin system, 4H, *trans m*-NC$_5$H$_4$Bu^t), 7.44 (AA′ part of an AA′BB′ spin system, 4H, *cis m*-NC$_5$H$_4$Bu^t), 8.70 (BB′ part of an AA′BB′ spin system, 4H, *trans o*-NC$_5$H$_4$Bu^t), 9.02 (BB′ part of an AA′BB′ spin system, 4H, *cis o*-NC$_5$H$_4$Bu^t); ^{13}C-{^{1}H} (75 MHz), δ 30.1 (*trans*-C*Me*$_3$), 30.2 (*cis*-C*Me*$_3$), 35.2 (*trans*-*C*Me$_3$), 35.5 (*cis*-*C*Me$_3$), 121.5 (*trans m*-NC$_5$H$_4$Bu^t), 122.0 (*cis m*-NC$_5$H$_4$Bu^t), 124.7, 125.5 and 126.7 (phenylene ring), 151.5 (*trans o*-NC$_5$H$_4$Bu^t), 151.7 (*cis o*-NC$_5$H$_4$Bu^t), 152.8 (C_{ipso} of phenylene ring), 163.5 (*trans p*-NC$_5$H$_4$Bu^t), 165.3 (*cis p*-NC$_5$H$_4$Bu^t). IR: 1617vs, 1570s, 1343s, 1233s, 1067s, 831vs and 571s cm^{-1}. [Found (Calc. for $Ta_2Cl_6C_{42}H_{56}N_6$): C, 41.87 (41.36); H, 4.81 (4.63); N, 6.72 (6.89)%].

[Ta(^{t}Bupy)Cl$_5$] (3). To a suspension of $TaCl_5$ (0.47 g 1.31 mmol) in CH_2Cl_2 (25 ml) was added 4-*tert*-butylpyridine (0.2 ml, 1.35 mmol). The solution formed was stirred for 30 min and filtered. The solvent was evaporated to dryness and the white solid obtained was washed with hexane (3 × 15 ml), dried *in vacuo* and identified as **3**. (yield: 92%). NMR ($CDCl_3$): ^{1}H (300 MHz), δ 1.37 (s, 9H, C*Me*$_3$) 7.55 (AA′ part of an AA′BB′ spin system, 2H, *m*-H of NC$_5$H$_4$Bu^t), 9.30 (BB′ part of an AA′BB′ spin system, 2H, *o*-H of NC$_5$H$_4$Bu^t); ^{13}C-{^{1}H} (75 MHz), δ 30.1 [NC$_5$H$_4$C(*C*H$_3$)$_3$], 35.8 [NC$_5$H$_4$*C*(CH$_3$)$_3$], 122.3 (*m*-NC$_5$H$_4$Bu^t), 152.6 (*o*-NC$_5$H$_4$Bu^t), 166.9 (C_{ipso} of NC$_5$H$_4$Bu^t). IR: 1620s, 1273m, 1237m, 1064m, 1024s, 831s, 730m and 392s cm^{-1}. [Found (Calc. for $TaCl_5C_9H_{13}N$): C, 22.46 (21.91); H, 2.85 (2.66); N, 2.81 (2.84)%].

[{Ta(CH$_3$CN)(CH$_2$SiMe$_3$)$_3$}$_2$(μ-1,4-NC$_6$H$_4$N)] (4a), [{Ta(CH$_3$-CN)(CH$_2$CMe$_3$)$_3$}$_2$(μ-1,4-NC$_6$H$_4$N)] (5a) and [{Ta(CH$_3$CN)-(CH$_2$CPhMe$_2$)$_3$}$_2$(μ-1,4-NC$_6$H$_4$N)] (6a). To a suspension of complex **1a** in Et_2O (25 ml) was added dropwise, at −78 °C, a solution of the corresponding Grignard reagent diluted in Et_2O (25 ml). The mixture was stirred overnight at room temperature. During this time the initial red suspension became a yellow solution. The solution was filtered and the residue was extracted with Et_2O (3 × 15 ml). The solvent was removed *in vacuo* and a yellow solid (oil for complex **6a**) was obtained and identified as complex **4a**, **5a** or **6a**.

Complex **4a**: from **1a** (0.50 g, 0.59 mmol) and Me_3SiCH_2-MgCl (3.50 mmol). 0.48 g of a yellow solid was obtained (yield: 76%). NMR (C_6D_6): ^{1}H (300 MHz), δ 0.26 [s, 54H, Si(C*H*$_3$)$_3$], 0.58 (br, s, 6H, CH_3CN), 0.64 (s, 12H, C*H*$_2$), 7.59 (s, 4H, phenylene ring); ^{13}C-{^{1}H} (75 MHz), δ 1.4 (*C*H$_3$CN), 3.2 [Si(*C*H$_3$)$_3$], 74.4 (Ta–*C*H$_2$), 121.4 (CH$_3$*C*N), 125.7 (phenylene ring) and 154.5 (C_{ipso} of phenylene ring). IR: 2309m, 2282m, 1494vs, 1341vs, 1244vs, 908vs, 847vs, 743s, 702s and 485w cm^{-1}. [Found (Calc. for $Ta_2N_4C_{34}H_{76}Si_6$): C, 38.00 (38.12); H, 7.27 (7.15); N, 4.94 (5.23)%].

Complex **5a**: from **1a** (0.36 g, 0.43 mmol) and $(Me_3CCH_2)_2$-Mg·2THF (0.4 g, 1.29 mmol). 0.34 g of a pale-yellow solid was obtained (yield: 81%). NMR (C_6D_6): ^{1}H (300 MHz), δ 0.48 (br, s, 6H, CH_3CN), 0.94 (s, 12H, C*H*$_2$), 1.24 [s, 54H, C(C*H*$_3$)$_3$], 7.71 (s, 4H, phenylene ring); ^{13}C-{^{1}H} (50 MHz), δ 1.4 (*C*H$_3$CN), 35.1 [C(*C*H$_3$)$_3$], 36.2 (*C*Me$_3$), 107.5 (Ta–*C*H$_2$), 118.6 (CH$_3$*C*N), 126.3 (phenylene ring) and 154.6 (C_{ipso} of phenylene ring). IR: 2302m, 2275m, 1484vs, 1332vs, 1230s, 1025s and 571w cm^{-1}. [Found (Calc. for $Ta_2N_4C_{40}H_{76}$): C, 49.54 (49.28); H, 7.90 (7.86); N, 5.36 (5.75)%].

Complex **6a**: from **1a** (0.50 g, 0.59 mmol) and Me_2PhCCH_2-MgCl (3.50 mmol). 0.61 g of yellow oil was obtained (yield: 77%). NMR (C_6D_6): ^{1}H (300 MHz), δ 0.43 (br, s, 6H, CH_3CN), 0.97 (s, 12H, C*H*$_2$), 1.52 [s, 36H, C(C*H*$_3$)$_2$], 7.08, 7.23 and 7.40 (m, 30H, C–C$_6$*H*$_5$), 7.35 (s, 4H, phenylene ring); ^{13}C-{^{1}H} (75 MHz), δ 0.2 (*C*H$_3$CN), 34.0 [C(*C*H$_3$)$_2$], 42.2 (*C*Me$_2$Ph), 106.9 (Ta–*C*H$_2$), 118.6 (CH$_3$*C*N), 125.7, 125.8 and 128.6 (*C*$_6$H$_5$), 126.0 (phenylene ring) 154.1 (C_{ipso} of *C*$_6$H$_5$) and 154.3 (C_{ipso} of phenylene ring). IR: 2311m, 2276m, 1494vs, 1339vs, 764f, 698f and 553w cm^{-1}.

[{Nb(CH$_3$CN)(CH$_2$PhMe$_2$)$_3$}$_2$(μ-1,4-NC$_6$H$_4$N)] (7a). To a suspension of complex [{Nb(CH$_3$CN)$_2$Cl$_3$}$_2$(μ-1,4-NC$_6$H$_4$N)] (0.66 g, 0.98 mmol) in Et_2O (40 ml) was added dropwise, at −78 °C, a solution of Me_2PhCCH_2MgCl (11.80 ml, 5.90 mmol) diluted in Et_2O (40 ml) and the mixture was stirred overnight at room temperature. The initial green suspension became a yellow solution. The solution was filtered and the residue was extracted with Et_2O (4 × 20 ml). The solvent was removed *in vacuo* to give 0.9 g of a yellow oil, which was identified as complex **7a** (yield: 79%). NMR (C_6D_6): ^{1}H (300 MHz), δ 0.46 (br, s, 6H, C*H*$_3$CN), 1.30 (s, 12H, C*H*$_2$), 1.48 [s, 36H, C(C*H*$_3$)$_2$], 7.06–7.41 (m, 34H, C–C$_6$*H*$_5$ and phenylene ring); ^{13}C-{^{1}H} (75 MHz), δ 0.2 (*C*H$_3$CN), 33.5 [C(*C*H$_3$)$_2$], 41.9 (*C*Me$_2$Ph), 90.7 (br, Nb–*C*H$_2$), 119.8 (CH$_3$*C*N), 125.5 (phenylene ring), 125.9, 128.6 and another signal hidden by the solvent (*C*$_6$H$_5$), 153.9 (C_{ipso} of *C*$_6$H$_5$) and 154.1 (C_{ipso} of phenylene ring). IR: 2316w, 2288w, 1599w 1487m, 1318m, 1262w, 1179w, 1082w, 1030w, 834w, 802w, 763m, 699s, 583w and 549w cm^{-1}.

[{Ta(CH$_3$CN)(CH$_2$SiMe$_3$)$_3$}$_2$(μ-1,3-NC$_6$H$_4$N)] (4b). To a suspension of complex **1b** (0.5 g, 0.59 mmol) in Et$_2$O (25 ml) was added dropwise, at −78 °C, a solution of Me$_3$SiCH$_2$MgCl (3.50 mmol) diluted in Et$_2$O (25 ml). The mixture was stirred overnight at room temperature. The initial red suspension became a yellow solution. The solution was filtered and the residue was extracted with Et$_2$O (3 × 15 ml). The solvent was removed *in vacuo* to give 0.46 g of a yellow solid and this was identified as complex **4b** (Yield: 73%). NMR (C$_6$D$_6$): ^{1}H (300 MHz), δ 0.29 [s, 54H, Si(CH_3)$_3$], 0.58 (br, s, 6H, CH$_3$CN), 0.64 (s, 12H, CH_2), 7.13, 7.34 and 7.42 (m, 4H, phenylene ring); ^{13}C-{^{1}H} (75 MHz), δ 1.4 (*C*H$_3$CN), 3.1 [Si(*C*H$_3$)$_3$], 77.0 (Ta–*C*H$_2$), 121.5 (CH$_3$*C*N), 120.6, 122.8 and 128.5 (phenylene ring) and 158.9 (C$_{ipso}$ of phenylene ring). IR: 2301m, 2275m, 1566vs, 1324vs, 1242vs, 908vs, 847vs, 743s, 696s and 490m cm^{-1}. [Found (Calc. for Ta$_2$N$_4$C$_{34}$H$_{76}$Si$_6$): C, 37.89 (38.12); H, 7.27 (7.15); N, 5.56 (5.23)%].

[{Nb(CH$_3$CN)(CH$_2$SiMe$_3$)$_3$}$_2$(μ-1,3-NC$_6$H$_4$N)] (8b) and [{Nb(CH$_3$CN)(CH$_2$CMe$_3$)$_3$}$_2$(μ-1,3-NC$_6$H$_4$N)] (9b). To a suspension of [{Nb(CH$_3$CN)$_2$Cl$_3$}$_2$(μ-1,3-NC$_6$H$_4$N)] in hexane (20 ml) was added Et$_2$O (30 ml). A solution of the corresponding Grignard reagent diluted in Et$_2$O (40 ml) was then added dropwise at −78 °C and the mixture was stirred overnight at room temperature. The initial pink suspension became a yellow solution. The solution was filtered and the residue was extracted with Et$_2$O (4 × 20 ml). The solvent was removed *in vacuo* to give a yellow solid, which was identified as complex **8b** or **9b**.

Complex **8b**: from [{Nb(CH$_3$CN)$_2$Cl$_3$}$_2$(μ-1,3-NC$_6$H$_4$N)] (0.76 g, 1.13 mmol) and Me$_3$SiCH$_2$MgCl (6.80 ml, 6.80 mmol). 0.8 g of a yellow solid was obtained (yield: 79%). NMR (C$_6$D$_6$): ^{1}H (300 MHz), δ 0.34 [s, 54H, Si(CH_3)$_3$], 0.63 (s, 6H, CH_3CN), 1.27 (s, 12H, CH_2), 7.32 (B part of an A$_2$BC spin system, $^3J_{AB}$ = 7.8 Hz, 1H, phenylene ring), 7.46 (A$_2$ part of an A$_2$BC spin system, 2H, phenylene ring), 7.95 (C part of an A$_2$BC spin system, $^4J_{AC}$ = 1.8 Hz, 1H, phenylene ring); ^{13}C-{^{1}H} (75 MHz), δ 0.3 (*C*H$_3$CN), 3.1 [Si(*C*H$_3$)$_3$], 62.1 (br, Nb–*C*H$_2$), 121.7 (CH$_3$*C*N), 120.7, 121.7 and 128.4 (phenylene ring) and 158.0 (C$_{ipso}$ of phenylene ring). IR: 2302w, 2275w, 1564m, 1548m, 1413m, 1348m, 1308m, 1282m, 1241s, 1152w, 1020w, 899s, 870m, 846vs, 780w, 743m, 695m, 609w, 574w and 497w cm^{-1}. [Found (Calc. for Nb$_2$N$_4$C$_{34}$H$_{76}$Si$_6$): C, 44.91 (45.61); H, 8.51 (8.56); N, 5.80 (6.26)%]

Complex **9b**: from [{Nb(CH$_3$CN)$_2$Cl$_3$}$_2$(μ-1,3-NC$_6$H$_4$N)] (0.59 g, 0.88 mmol) and (Me$_3$CCH$_2$)$_2$Mg·2THF (0.82 g, 2.65 mmol). 0.55 g of a pale yellow solid was obtained (yield: 78%). NMR (C$_6$D$_6$): ^{1}H (300 MHz), δ 0.50 (s, 6H, CH_3CN), 1.35 [s, 54H, C(CH_3)$_3$], 1.41 (s, 12H, CH_2), 7.29 (B part of an A$_2$BC spin system, $^3J_{AB}$ = 7.8 Hz, 1H, phenylene ring), 7.58 (A$_2$ part of an A$_2$BC spin system, 2H, phenylene ring) and 8.14 (C part of an A$_2$BC spin system, $^4J_{AC}$ = 1.8 Hz, 1H, phenylene ring); ^{13}C-{^{1}H} (75 MHz), δ 1.3 (*C*H$_3$CN), 34.7 [C(*C*H$_3$)$_3$], 35.9 (*C*Me$_3$), 91.0 (br, Nb–*C*H$_2$), 119.4 (CH$_3$*C*N), 121.4, 124.0, 128.5 (phenylene ring) and 158.5 (C$_{ipso}$ of phenylene ring). IR: 2303w, 2277w, 1567m, 1408m, 1355s, 1342s, 1303s, 1286s, 1261m, 1232s, 1154w, 1095w, 1027m, 933w, 875w, 802w, 779w, 690w, 590w, 556w and 494w cm^{-1}. [Found (Calc. for Nb$_2$N$_4$C$_{40}$H$_{76}$): C, 60.38 (60.14); H, 9.22 (9.59); N, 7.42 (7.01)%].

[{Nb(THF)(CH$_2$SiMe$_3$)$_3$}$_2$(μ-1,3-NC$_6$H$_4$N)] (10b) and [{Nb(THF)(CH$_2$CMe$_3$)$_3$}$_2$(μ-1,3-NC$_6$H$_4$N)] (11b). *Method A.* To a suspension of [{Nb(CH$_3$CN)$_2$Cl$_3$}$_2$(μ-1,3-NC$_6$H$_4$N)] in hexane (20 ml) was added THF (30 ml). A solution of the corresponding Grignard reagent diluted in THF (40 ml) was then added dropwise at −78 °C and the mixture was stirred overnight at room temperature. The initial pink suspension became a yellow solution. The solution was filtered and the solvent was removed *in vacuo*. The residue was extracted with Et$_2$O (4 × 20 ml). The solvent was removed and a yellow solid was obtained and identified as complex **10b** or **11b**.

Complex **10b**: from [{Nb(CH$_3$CN)$_2$Cl$_3$}$_2$(μ-1,3-NC$_6$H$_4$N)] (0.84 g, 1.27 mmol) and Me$_3$SiCH$_2$MgCl (7.60 ml, 7.60 mmol). 0.95 g of a yellow solid was obtained (yield: 78%). Complex **11b**: from [{Nb(CH$_3$CN)$_2$Cl$_3$}$_2$(μ-1,3-NC$_6$H$_4$N)] (0.57 g, 0.85 mmol) and (Me$_3$CCH$_2$)$_2$Mg·2THF (0.79 g, 2.55 mmol). 0.64 g of a pale yellow solid was obtained (yield: 83%).

Method B. To the complex **8b** or **9b** was added THF (20 ml) and the mixture was stirred for 1 h. The solvent was removed *in vacuo* and hexane (15 ml) was added. The solvent was removed *in vacuo* in order to remove excess THF. A yellow solid was obtained and identified as **10b** or **11b**.

Complex **10b**: from complex **8b** (0.38 g, 0.43 mmol). 0.41 g of a yellow solid was obtained (yield: 100%). NMR (C$_6$D$_6$): ^{1}H (300 MHz), δ 0.27 [s, 54H, Si(CH_3)$_3$], 0.98 (s, 12H, CH_2), 1.39 (m, 8H, C$_4H_8$O), 3.70 (m, 8H, C$_4H_8$O), 7.27 (B part of an A$_2$BC spin system, J_{AB} = 7.8 Hz, 1H, phenylene ring), 7.36 (A$_2$ part of an A$_2$BC spin system, J_{AB} = 7.8 Hz, J_{AC} = 1.8 Hz, 2H, phenylene ring) and 7.77 (C part of an A$_2$BC spin system, J_{AC} = 1.8 Hz, 1H, phenylene ring); ^{13}C-{^{1}H} (75 MHz), δ 3.1 [Si(*C*H$_3$)$_3$], 25.6 (*C*$_4$H$_8$O), 61.9 (br, Nb–*C*H$_2$), 70.0 (*C*$_4$H$_8$O), 120.9, 121.6 and 128.4 (phenylene ring) and 158.1 (C$_{ipso}$ of phenylene ring). IR: 1567m, 1549w, 1414w, 1347m, 1306m, 1287m, 1256m, 1244s, 1150w, 1075w, 1026m, 918w, 892s, 846vs, 828s, 777w, 745m, 697m, 611w, 564w and 479w cm^{-1}. [Found (Calc. for Nb$_2$N$_2$C$_{38}$H$_{86}$Si$_6$O$_2$): C, 48.32 (47.67); H, 8.96 (9.05); N, 3.26 (2.93)%].

Complex **11b**: from complex **9b** (0.37 g, 0.46 mmol). 0.42 g of a yellow solid was obtained (yield: 100%). NMR (C$_6$D$_6$): ^{1}H (300 MHz), δ 1.22 (s, 12H, CH_2), 1.30 [s, 54H, C(CH_3)$_3$], 1.37 (m, 8H, C$_4H_8$O), 3.80 (m, 8H, C$_4H_8$O), 7.26 (B part of an A$_2$BC spin system, $^3J_{AB}$ = 7.8 Hz, 1H, phenylene ring), 7.53 (A$_2$ part of an A$_2$BC spin system, 2H, phenylene ring) and 8.07 (C part of an A$_2$BC spin system, $^4J_{AC}$ = 1.8 Hz, 1H, phenylene ring); ^{13}C-{^{1}H} (75 MHz), δ 25.6 (*C*$_4$H$_8$O), 34.6 [C(*C*H$_3$)$_3$], 35.9 (*C*Me$_3$), 69.8 (*C*$_4$H$_8$O), 91.7 (br, Nb–*C*H$_2$), 121.5, 124.1, 128.5 (phenylene ring) and 158.5 (C$_{ipso}$ of phenylene ring). IR: 1568s, 1549m, 1407m, 1357s, 1341s, 1304s, 1286s, 1261m, 1232s, 1154w, 1097m, 1028s, 930w, 867m, 803w, 781m, 750w, 686w, 595w, 554w and 488w cm^{-1}. [Found (Calc. for Nb$_2$N$_2$C$_{44}$H$_{86}$O$_2$): C, 60.12 (61.38); H, 9.95 (10.07); N, 3.22 (3.25)%].

[{Nb(CH$_2$PhMe$_2$)$_3$}$_2$(μ-1,4-NC$_6$H$_4$N)] (12a). To a suspension of [{Nb(CH$_3$CN)$_2$Cl$_3$}$_2$(μ-1,4-NC$_6$H$_4$N)] (0.54 g, 0.81 mmol) in THF (40 ml) was added dropwise, at −78 °C, a solution of Me$_2$PhCCH$_2$MgCl (9.70 ml, 4.86 mmol) diluted in THF (40 ml). The mixture was stirred overnight at room temperature. The initial green suspension became a yellow solution. The solution was filtered and the solvent was removed *in vacuo*. The residue was washed with cold hexane (4 × 20 ml) and extracted with hexane at room temperature (5 × 30 ml). The solvent was removed *in vacuo* to give 0.5 g of a yellow oil, which was identified as complex **12a** (yield: 61%). NMR (C$_6$D$_6$): ^{1}H (300 MHz), δ 1.14 (s, 12H, CH_2), 1.39 [s, 36H, C(CH_3)$_2$], 7.06–7.37 (m, 34H, C–C$_6H_5$ and phenylene ring); ^{13}C-{^{1}H} (75 MHz), δ 33.3 [C(*C*H$_3$)$_2$], 41.3 (*C*Me$_2$Ph), 92.5 (br, Nb–*C*H$_2$), 125.1 (phenylene ring), 125.7, 126.0 and 129.1 (*C*$_6$H$_5$), 152.9 (C$_{ipso}$ of *C*$_6$H$_5$) and 155.0 (C$_{ipso}$ of phenylene ring). IR: 1599w 1495m, 1319m, 1261m, 1082m, 1030m, 836w, 802m, 763m, 699s and 668w cm^{-1}.

[{Ta(η^5-C$_5$H$_4$SiMe$_3$)$_2$Cl}$_2$(μ-1,4-NC$_6$H$_4$N)] (13a). Toluene (40 ml) was added to a mixture of complex **1a** (0.43 g, 0.51 mmol) and Li[C$_5$H$_4$SiMe$_3$] (0.30 g, 2.08 mmol) in a Teflon-valve ampoule. The ampoule was placed in an oil bath and heated to 100 °C for 16 h. The resulting solution was allowed to cool to room temperature and was filtered. The solvent removed under reduced pressure to give 0.43 g of **13a** as a red solid (yield: 78%). Samples prepared in this way are sufficiently pure (^{1}H NMR spectroscopy) to use in further studies. An analytically pure, X-ray-quality sample was obtained from a saturated

hexane–toluene (50%) solution at −40 °C. NMR (C_6D_6): ^{1}H (300 MHz), δ 0.29 [s, 36H, Si(CH_3)$_3$], 5.57, 5.93, 6.29 and 6.37 (m, 4 × 4H, C_5H_4), 6.47 (s, 4H, phenylene ring); ^{13}C-{^{1}H} (75 MHz), δ 0.39 [Si(*C*H$_3$)$_3$], 109.8, 111.0, 118.4 and 126.1 (C_5H_4), 116.2 (C_5H_4 C_{ipso}), 119.7 (phenylene ring), 154.6 (C_{ipso} of phenylene ring). IR: 1331s, 1246vs, 1176s, 1034s, 978s, 836vs, 630s and 409s cm^{-1}. [Found (Calc. for $Ta_2N_2C_{38}H_{56}Cl_2Si_4$): C, 42.07 (42.03); H, 5.14 (5.20); N, 2.90 (2.58)%].

[{Ta(η^5-$C_5H_4SiMe_3$)$_2$Cl}$_2$(μ-1,3-NC_6H_4N)] (13b). The synthesis of **13b** was carried out in an identical manner to **13a** using **1b** (0.38 g, 0.45 mmol) and Li[$C_5H_4SiMe_3$] (0.26 g, 1.80 mmol). 0.40 g of **13b** was obtained as a red solid (yield: 83%). NMR (C_6D_6): ^{1}H (300 MHz), δ 0.34 [s, 36H, Si(CH_3)$_3$], 5.49, 5.94, 6.29 and 6.46 (m, 4 × 4H, C_5H_4), 5.52 (t, $^4J_{AC}$ = 1.8 Hz, 1H, C part of an A_2BC spin system, phenylene ring), 5.85 (dd, 2H, A_2 part of an A_2BC spin system, phenylene ring), 6.36 (t, $^3J_{AB}$ = 7.5 Hz, 1H, B part of an A_2BC spin system, phenylene ring); ^{13}C-{^{1}H} (75 MHz), δ 0.43 [Si(*C*H$_3$)$_3$], 109.3, 109.9 118.4 and 126.6 (C_5H_4), 117.4 (C_5H_4 C_{ipso}), 109.7, 112.9 and 127.2 (phenylene ring), 159.6 (C_{ipso} of phenylene ring). IR: 1560s, 1322s, 1247s, 1174m, 1035m, 905s, 838vs, 632s and 411s cm^{-1}. [Found (Calc. for $Ta_2N_2C_{38}H_{56}Cl_2Si_4$): C, 42.03 (42.03); H, 5.18 (5.20); N, 2.95 (2.58)%].

[{Nb(η^5-$C_5H_4SiMe_3$)$_2$Cl}$_2$(μ-1,4-NC_6H_4N)] (14a). Toluene (60 ml) was added to a mixture of [{Nb(CH_3CN)$_2$Cl$_3$}$_2$(μ-1,4-NC_6H_4N)] (0.85 g, 1.27 mmol) and Li[$C_5H_4SiMe_3$] (0.77 g, 5.35 mmol) in a Teflon-valve ampoule. The ampoule was placed in an oil bath and heated at 100 °C for 24 h. The resulting solution was allowed to cool to room temperature and the resulting red solution was filtered. The solvent was removed under reduced pressure to give 0.95 g (yield: 82%) of a red solid, which was identified as **14a** by comparison of its ^{1}H NMR data with the literature values.[3]

[{Nb(η^5-$C_5H_4SiMe_3$)$_2$Cl}$_2$(μ-1,3-NC_6H_4N)] (14b). The synthesis of **14b** was carried out in an identical manner to **14a** from [{Nb(CH_3CN)$_2$Cl$_3$}$_2$(μ-1,3-NC_6H_4N)] (1.03 g, 1.54 mmol) and Li($C_5H_4SiMe_3$) (0.94 g, 6.49 mmol). 1.15 g of a red solid (yield: 82%) was obtained and identified as **14b** by comparison of its ^{1}H NMR data with the literature values.[3]

[{Ta[PhC(NSiMe$_3$)$_2$]$_2$Cl}$_2$(μ-1,4-NC_6H_4N)] (15a). Complex **1a** (0.40 g, 0.47 mmol) and Li[PhC(NSiMe$_3$)$_2$] (0.52 g, 1.92 mmol) were placed in a Teflon-valve ampoule along with toluene (35 ml). The ampoule was placed in an oil bath and heated at 100 °C for 14 h. The resulting solution was allowed to cool to room temperature and filtered. The solvent was removed under reduced pressure to give 0.57 g of **15a** as a red solid (yield: 76%). NMR ($CDCl_3$): ^{1}H (300 MHz), δ −0.08 [s, 72H, Si(CH_3)$_3$], 6.91 (s, 4H, phenylene ring), 7.28, 7.36 and 7.38 (m, 20H, C_6H_5); ^{13}C-{^{1}H} (75 MHz), δ 2.0 [Si(*C*H$_3$)$_3$], 126.6 (phenylene ring), 126.2, 128.1 and 129.0 (C_6H_5), 140.7 (C_{ipso} of C_6H_5), 151.7 (C_{ipso} of phenylene ring) 178.0 [Ph*C*(NSiMe$_3$)$_2$]. IR: 1522s, 1496vs, 1482vs, 1338vs, 1248vs, 1003s, 988vs, 920s, 840vs, 786s, 761s, 704vs and 504m cm^{-1}. [Found (Calc. for $Ta_2N_{10}C_{58}H_{96}Cl_2Si_8$): C, 44.29 (43.79); H, 6.17 (6.08); N, 8.91 (8.80)%].

[{Ta[PhC(NSiMe$_3$)$_2$]$_2$Cl}$_2$(μ-1,3-NC_6H_4N)] (15b). The synthesis of **15b** was carried out in an identical manner to **15a** from **1b** (0.8 g, 0.95 mmol) and Li[PhC(NSiMe$_3$)$_2$] (1.04 g, 3.84 mmol). 1.1 g of **15b** was obtained as an orange solid (yield: 73%). NMR ($CDCl_3$): ^{1}H (300 MHz), δ −0.06 [s, 72H, Si(CH_3)$_3$], 6.50 (dd, 2H, A_2 part of an A_2BX spin system, phenylene ring), 6.77 (t, $^4J_{AC}$ = 1.8 Hz, 1H, C part of an A_2BC spin system, phenylene ring), 7.14 (t, $^3J_{AB}$ = 7.8 Hz, 1H, B part of an A_2BC spin system, phenylene ring), 7.26–7.39 (m, 20H, C_6H_5); ^{13}C-{^{1}H} (75 MHz), δ 2.1 [Si(*C*H$_3$)$_3$], 122.6, 128.6 and 128.9 (phenylene ring), 126.3, 128.1 and 129.0 (C_6H_5), 140.7 (C_{ipso} of C_6H_5), 155.5 (C_{ipso} of phenylene ring), 178.1 [Ph*C*(NSiMe$_3$)$_2$]. IR: 1571vs, 1527s, 1323vs, 1248vs, 1005s, 988vs, 840vs, 762s, 705s and 503m cm^{-1}. [Found (Calc. for $Ta_2N_{10}C_{58}H_{96}Cl_2Si_8$): C, 43.02 (43.79); H, 5.90 (6.08); N, 8.90 (8.80)%].

[{Nb[PhC(NSiMe$_3$)$_2$]$_2$Cl}$_2$(μ-1,4-NC_6H_4N)] (16a). Et_2O (60 ml) was added to a mixture of [{Nb(CH_3CN)$_2$Cl$_3$}$_2$(μ-1,4-NC_6H_4N)] (0.65 g, 0.97 mmol) and Li[PhC(NSiMe$_3$)$_2$] (1.05 g, 3.89 mmol). The suspension was stirred for 12 h. The initial green suspension became a red solution. The solution was filtered and the residue was extracted with Et_2O (2 × 20 ml). The solvent was removed *in vacuo* to give 1.22 g of a brown solid, which was identified as **16a** (yield: 89%). NMR (C_6D_6): ^{1}H (300 MHz), δ 0.16 [s, 72H, Si(CH_3)$_3$], 6.97 (m, 12H, C_6H_5), 7.28 (m, 8H, C_6H_5) and 7.62 (s, 4H, phenylene ring); ^{13}C-{^{1}H} ($CDCl_3$, 75 MHz), δ 2.1 [Si(*C*H$_3$)$_3$], 125.8 (phenylene ring), 126.3, 128.1 and 129.0 (C_6H_5), 140.3 (C_{ipso} of C_6H_5), 151.9 (C_{ipso} of phenylene ring) and 178.7 [Ph*C*(NSiMe$_3$)$_2$]. IR: 1588w, 1570w, 1522m, 1325m, 1248m, 1169w, 1092w, 1002w, 979m, 841s, 762m, 743m, 703m, 506w, 378w and 321w cm^{-1}. [Found (Calc. for $Nb_2N_{10}C_{58}H_{96}Cl_2Si_8$): C, 50.17 (49.24); H, 7.00 (6.84); N, 9.67 (9.90)%].

X-Ray structure analysis of 13a

An irregularly shaped red crystal for X-ray measurements has been cut off from a larger twinned sample of crystallization and mounted on a Nonius KappaCCD diffractometer. *Crystallographic data*: $C_{38}H_{56}Cl_2N_2Si_4Ta_2$, M = 1086.01, monoclinic, $P2_1/n$, a = 6.9570(4), b = 26.464(2), c = 11.6880(7) Å, β = 97.408(3)°, V = 2133.9(3) Å^3, Z = 2, d_{calc} = 1.690 g cm^{-3}, μ = 5.39 mm^{-1}, F(000) = 1068, T = 110(2) K. Collected intensities have been further treated with DENZO/Scalpack routines.[16] The model structure has been found by direct methods implemented in SHELXS97 and refined with SHELXL97.[17] All non hydrogen atoms were refined with anisotropic thermal parameters, whereas the hydrogen atoms were included in calculated positions and refined in a riding isotropic model. The final R and R_w (on F^2) discrepancy factors calculated with 4378 observed reflections with $I>2\sigma(I)$ for 217 parameters are equal to 0.069 and 0.1762, respectively. Because of the rather low quality of the crystal some high residual electron density (ρ_{max} = 4.06 e Å^{-3}) has been found around the Ta atom (<1 Å). No presence of solvent molecules has been detected.

CCDC reference number 197351.

See http://www.rsc.org/suppdata/dt/b2/b211126h/ for crystallographic data in CIF or other electronic format.

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