

Synthesis, Structural Characterisation and Reactivity of New Dinuclear Monocyclopentadienyl Imidoniobium and -tantalum Complexes – X-ray Crystal Structures of $[\{\text{Nb}(\eta^5\text{-C}_5\text{H}_4\text{SiMe}_3)\text{Cl}_2\}_2(\mu\text{-1,4-NC}_6\text{H}_4\text{N})]$, $[\{\text{Ta}(\eta^5\text{-C}_5\text{Me}_5)\text{Cl}_2\}_2(\mu\text{-1,4-NC}_6\text{H}_4\text{N})]$ and $[\{\text{Ta}(\eta^5\text{-C}_5\text{Me}_5)(\text{CH}_2\text{SiMe}_3)_2\}_2(\mu\text{-1,4-NC}_6\text{H}_4\text{N})]$

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The preparation of a family of dinuclear monocyclopentadienyl imidoniobium and -tantalum complexes was achieved by two different synthetic routes. The diimido complexes $[\{\text{M}(\text{Cp}')\text{Cl}_2\}_2(\mu\text{-1,4-NC}_6\text{H}_4\text{N})]$ [$\text{Cp}' = \eta^5\text{-C}_5\text{H}_4\text{SiMe}_3$, $\text{M} = \text{Nb}$, $i = 4$ (**1**); $\text{Cp}' = \eta^5\text{-C}_5\text{H}_4\text{SiMe}_3$, $\text{M} = \text{Nb}$, $i = 3$ (**2**); $\text{Cp}' = \eta^5\text{-C}_5\text{H}_4\text{SiMe}_3$, $\text{M} = \text{Nb}$, $i = 2$ (**3**); $\text{Cp}' = \eta^5\text{-C}_5\text{Me}_5$, $\text{M} = \text{Nb}$, $i = 4$ (**4**); $\text{Cp}' = \eta^5\text{-C}_5\text{Me}_5$, $\text{M} = \text{Nb}$, $i = 3$ (**5**); $\text{Cp}' = \eta^5\text{-C}_5\text{H}_4\text{SiMe}_3$, $\text{M} = \text{Ta}$, $i = 4$ (**6**); $\text{Cp}' = \eta^5\text{-C}_5\text{H}_4\text{SiMe}_3$, $\text{M} = \text{Ta}$, $i = 3$ (**7**)] were prepared by the reaction of one equivalent of the trichloro precursor $[\text{MCl}_3]_2(\mu\text{-1,4-NC}_6\text{H}_4\text{N})]$ ($\text{M} = \text{Nb}$, Ta , $i = 4$, 3 or 2) with two equivalents of either $\text{C}_5\text{H}_4(\text{SiMe}_3)_2$ or $\text{C}_5\text{Me}_5(\text{SiMe}_3)$. Complexes **1–7** can also be prepared by the reaction of two equivalents of $[\text{MCp}'\text{Cl}_4]$ ($\text{Cp}' = \eta^5\text{-C}_5\text{H}_4\text{SiMe}_3$, $\text{M} = \text{Nb}$, Ta ; $\text{Cp}' = \eta^5\text{-C}_5\text{Me}_5$, $\text{M} = \text{Nb}$, Ta) with one equivalent of the corresponding aniline compound, N,N,N',N' -tetrakis(trimethylsilyl)-1,4-, -1,3-, or -1,2-phenylenediamine, respectively. The synthesis of $[\{\text{Ta}(\text{Cp}')\text{Cl}_2\}_2(\mu\text{-1,4-NC}_6\text{H}_4\text{N})]$ [$\text{Cp}' = \eta^5\text{-C}_5\text{Me}_5$, $i = 4$ (**8**); $\text{Cp}' = \eta^5\text{-C}_5\text{Me}_5$, $i = 3$ (**9**)] was only successful with the second preparative method. The reaction of

1, **2** and **8** with alkylating reagents gave the corresponding tetraalkyl derivatives, $[\{\text{M}(\text{Cp}')\text{R}_2\}_2(\mu\text{-1,4-NC}_6\text{H}_4\text{N})]$ [$\text{Cp}' = \eta^5\text{-C}_5\text{H}_4\text{SiMe}_3$, $\text{M} = \text{Nb}$, $\text{R} = \text{Me}$, $i = 4$ (**10**); $\text{Cp}' = \eta^5\text{-C}_5\text{H}_4\text{SiMe}_3$, $\text{M} = \text{Nb}$, $\text{R} = \text{CH}_2\text{SiMe}_3$, $i = 4$ (**11**); $\text{Cp}' = \eta^5\text{-C}_5\text{H}_4\text{SiMe}_3$, $\text{M} = \text{Nb}$, $\text{R} = \text{CH}_2\text{Ph}$, $i = 4$ (**12**); $\text{Cp}' = \eta^5\text{-C}_5\text{H}_4\text{SiMe}_3$, $\text{M} = \text{Nb}$, $\text{R} = \text{Me}$, $i = 3$ (**13**); $\text{Cp}' = \eta^5\text{-C}_5\text{H}_4\text{SiMe}_3$, $\text{M} = \text{Nb}$, $\text{R} = \text{CH}_2\text{SiMe}_3$, $i = 3$ (**14**); $\text{Cp}' = \eta^5\text{-C}_5\text{H}_4\text{SiMe}_3$, $\text{M} = \text{Nb}$, $\text{R} = \text{CH}_2\text{Ph}$, $i = 3$ (**15**); $\text{Cp}' = \eta^5\text{-C}_5\text{Me}_5$, $\text{M} = \text{Ta}$, $\text{R} = \text{Me}$, $i = 4$ (**16**); $\text{Cp}' = \eta^5\text{-C}_5\text{Me}_5$, $\text{M} = \text{Ta}$, $\text{R} = \text{CH}_2\text{SiMe}_3$, $i = 4$ (**17**); $\text{Cp}' = \eta^5\text{-C}_5\text{Me}_5$, $\text{M} = \text{Ta}$, $\text{R} = \text{CH}_2\text{Ph}$, $i = 4$ (**18**)]. The alkylated complexes with other stoichiometries, $[\{\text{M}(\text{Cp}')(\text{Me})(\text{X})\}_2(\mu\text{-1,4-NC}_6\text{H}_4\text{N})]$ [$\text{Cp}' = \eta^5\text{-C}_5\text{H}_4\text{SiMe}_3$, $\text{M} = \text{Nb}$, $\text{X} = \text{Cl}$ (**19**); $\text{Cp}' = \eta^5\text{-C}_5\text{H}_4\text{SiMe}_3$, $\text{M} = \text{Nb}$, $\text{X} = \text{NMe}_2$ (**20**); $\text{Cp}' = \eta^5\text{-C}_5\text{Me}_5$, $\text{M} = \text{Ta}$, $\text{X} = \text{Cl}$ (**21**)], were also prepared. The molecular structures of complexes **1**, **8** and **17** were determined by single-crystal X-ray diffraction studies.

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Introduction

Imido derivatives of early transition metals have been widely studied and, in particular, a large number of well-

established imido compounds of the d^0 metals niobium and tantalum are known.^[1] For example, half-sandwich imido compounds of Nb and Ta of general formula $\text{M}(\eta^5\text{-C}_5\text{R}_5')(\text{NR})\text{X}_2$ are well documented^[2] and these are of considerable interest since an “isolobal” relationship between $[\text{M}(\eta^5\text{-C}_5\text{R}_5')(\text{NR})]$ ($\text{M} = \text{group 5 metal}$) and $[\text{M}(\eta^5\text{-C}_5\text{R}_5')_2]$ ($\text{M} = \text{Group 4 metal}$) fragments has been established.^[3] In fact, it has been claimed that monocyclopentadienyl imido group 5 metal complexes could behave in a similar manner to metallocenes of group 4 metals in olefin polymerisation catalytic processes.^[2g] However, to date several species of this type have been used as catalysts without much success.^[4] Two main preparative pathways have been employed in the synthesis of half-sandwich imido group 5 metal complexes. Firstly, reaction of the appropriate cyclopentadienide reagent with imido-containing $[\text{M}(\text{NR})\text{Cl}_3\text{L}_2]$ ($\text{M} = \text{Nb}$, Ta) precursors^[5] has been employed and, sec-

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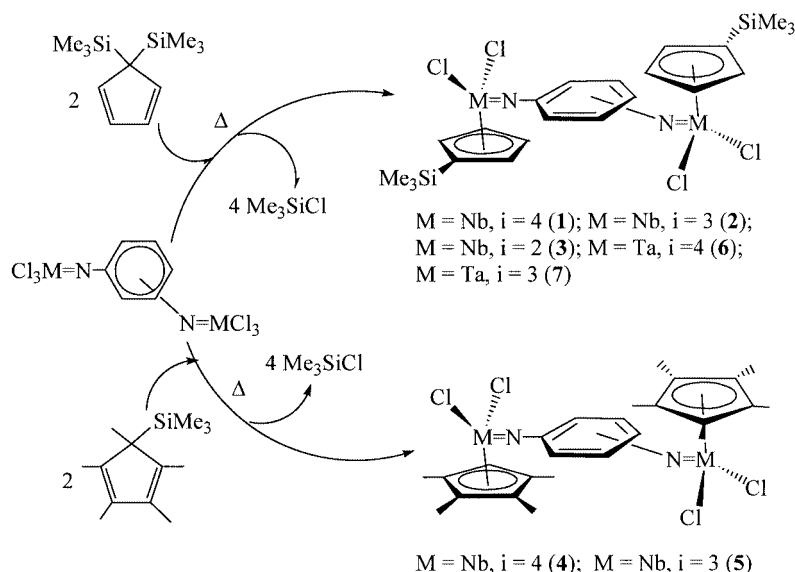
only, the most general method involves the introduction of the imido group into precursors containing the cyclopentadienyl ligand.^[6] On considering the different possible pathways to achieve this transformation, the one that is particularly noteworthy is that in which the imido group is incorporated by breaking the Si–N bond of a silylamine or -amide derivative.^[7] The use of this last method, developed by our research group, gives rise to an interesting series of organo-diimido complexes $[\{Nb(L)_2Cl_3\}_2(\mu-1,i-NC_6H_4N)]$ ($L = CH_3CN$ or $tBupy$) by reaction of $NbCl_5$ with the appropriate aniline N,N,N',N' -tetrakis(trimethylsilyl)-1,4-, -1,3-, or -1,2-phenylenediamine in the presence of CH_3CN or $tBupy$.^[8] As a continuation of our research in this field^[9] we are currently interested in the preparation of half-sandwich diimidoniobium and -tantalum complexes in order to synthesise new types of dinuclear complexes in which the two metal centres are linked by conjugated π -systems. This class of diimido complex is rare, particularly with an aryl ligand.^[10] The work described in this paper focuses on the synthesis and structural characterisation of half-sandwich imidoniobium and -tantalum complexes, and some aspects of their reactivity.

Results and Discussion

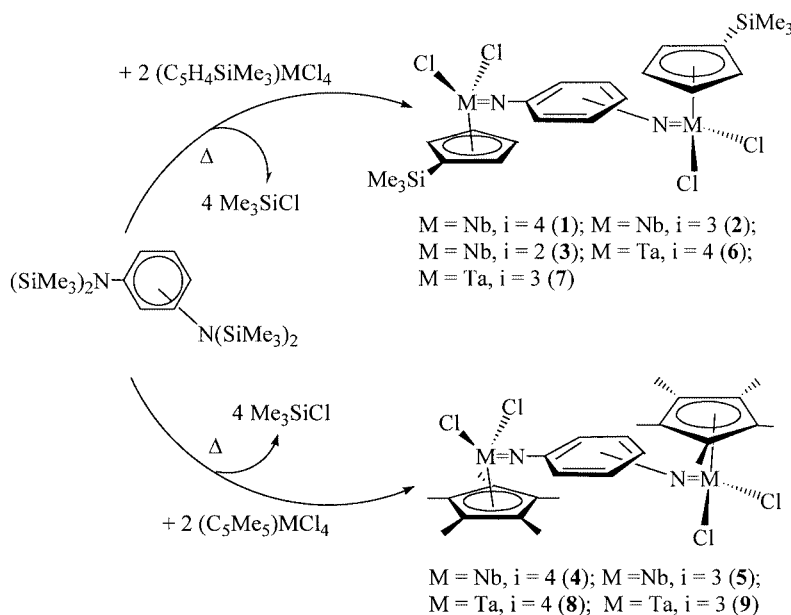
The preparation of derivatives $[\{M(Cp')Cl_2\}_2(\mu-1,i-NC_6H_4N)]$ ($Cp' = \eta^5-C_5H_4SiMe_3$, $\eta^5-C_5Me_5$; $M = Nb$, Ta ; $i = 3, 4$) was initially undertaken by reaction of the appropriate complex $[\{M(L)_2Cl_3\}_2(\mu-1,i-NC_6H_4N)]$ ($L = CH_3CN$; $M = Nb$, Ta ; $i = 3, 4$)^[8] with different cyclopentadienyl reagents, namely $M(C_5H_4SiMe_3)$ ($M = Li$, Na , K) or $K(C_5Me_5)$, in several solvents and under different experimental conditions. However, in all cases an intractable mixture of products was obtained. As an alternative method to prepare the aforementioned complexes, we decided to use milder cyclopentadienyl transfer reagents, such

as the silylated compounds $C_5H_4(SiMe_3)_2$ and $C_5Me_5(SiMe_3)$. This method has previously been used by Green et al.^[11] to prepare cyclopentadienyl-imido complexes with constrained geometry and by Maatta et al.^[12] for the preparation of imido-containing monocyclopentadienyl vanadium derivatives. However, the trichloro complexes $[\{M(L)_2Cl_3\}_2(\mu-1,i-NC_6H_4N)]$ ($L = CH_3CN$; $M = Nb$, Ta ; $i = 3, 4$), do not react with the silylated cyclopentadienyl reagents. This lack of reactivity is probably due to the presence of two additional ligands (L) in the coordination sphere which diminishes the acidity of the metal centre making the elimination of the expected $SiMe_3Cl$ by-product unfavourable. In order to increase the reactivity of the diimidoniobium and -tantalum precursors towards the cyclopentadienyl reagents, alternative compounds without donor ligands were employed, namely $[\{MCl_3\}_2(\mu-1,i-NC_6H_4N)]$ ($M = Nb$, Ta), which were prepared from the reaction of MCl_5 with the appropriate N,N,N',N' -tetrakis(trimethylsilyl)phenylenediamine in CH_2Cl_2 .^[8] When these diimido complexes were reacted with the appropriate silylated cyclopentadienyl reagents in a 1:2 molar ratio in CH_2Cl_2 at 90 °C (see Exp. Sect.), the cyclopentadienyl-containing dinuclear species $[\{M(Cp')Cl_2\}_2(\mu-1,i-NC_6H_4N)]$ [$Cp' = \eta^5-C_5H_4SiMe_3$, $M = Nb$, $i = 4$ (**1**); $Cp' = \eta^5-C_5H_4SiMe_3$, $M = Nb$, $i = 3$ (**2**); $Cp' = \eta^5-C_5H_4SiMe_3$, $M = Nb$, $i = 2$ (**3**); $Cp' = \eta^5-C_5Me_5$, $M = Nb$, $i = 4$ (**4**); $Cp' = \eta^5-C_5Me_5$, $M = Nb$, $i = 3$ (**5**); $Cp' = \eta^5-C_5H_4SiMe_3$, $M = Ta$, $i = 4$ (**6**); $Cp' = \eta^5-C_5H_4SiMe_3$, $M = Ta$, $i = 3$ (**7**)] were isolated (Scheme 1).

A number of reactions did not, however, give the desired products. These involved tantalum derivatives formed from $C_5Me_5(SiMe_3)$ and the derivatives $[\{MCl_3\}_2(\mu-1,2-NC_6H_4N)]$ ($M = Nb$, Ta) formed from the reagents $C_5Me_5(SiMe_3)$ and $C_5H_4(SiMe_3)_2$. This procedure has provided a useful synthetic route to dinuclear monocyclopentadienyl imido species of these metals, particularly with the reagent $C_5H_4(SiMe_3)_2$, in high yields (about 80% for the tantalum



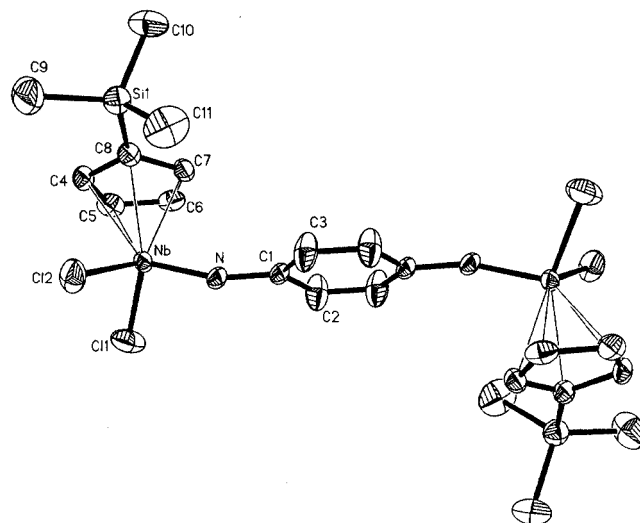
Scheme 1



Scheme 2

complexes and quantitative yields for the niobium complexes). The overall reactions for the tantalum species require long reaction times of about one week. In order to improve this, an alternative method was considered to prepare the complexes. This method consisted of the reaction of the appropriate $\text{MCp}'\text{Cl}_4$ precursor ($\text{Cp}' = \eta^5\text{-C}_5\text{H}_4\text{SiMe}_3$, $\eta^5\text{-C}_5\text{Me}_5$; $\text{M} = \text{Nb}, \text{Ta}$) with the corresponding N,N,N',N' -tetrakis(trimethylsilyl)phenylenediamine derivative (Scheme 2).

This synthetic route, which is an adaptation of that previously described by Gibson et al.^[3a] for the preparation of imido-containing niobium complexes, is an easy way to prepare cleanly (by elimination of SiMe_3Cl) the corresponding diimidoniobium and -tantalum complexes **1–7** as well as the new tantalum complexes [$\{\text{Ta}(\eta^5\text{-C}_5\text{Me}_5)\text{Cl}_2\}_2(\mu\text{-}1,i\text{-NC}_6\text{H}_4\text{N})$] [$i = 4$ (**8**), $i = 3$ (**9**)] in quantitative yields (see Exp. Sect.). On using this method the reaction times for the preparation of tantalum complexes are considerably shortened (to about 30 h). In wet solvents the materials evolve to the appropriate oxo-containing complexes with elimination of the corresponding diamine.^[13] For example, solutions of **8** or **9** in wet CH_2Cl_2 give rise to the oxo complex [$\{\text{Ta}(\eta^5\text{-C}_5\text{Me}_5)\text{Cl}_3\}_2(\mu\text{-O})$].^[14] Complexes **1–9**, as well as other complexes described in this work, were characterised by ^1H , ^{13}C NMR and IR spectroscopy (see Exp. Sect.). The ^1H and ^{13}C NMR spectra of **1–9** exhibit the characteristic signals for both the cyclopentadienyl and phenylene groups. This observation agrees with a structural situation where a diimidophenylene group bridges two metal atoms, which are, in turn, located in the plane formed by this ligand, in a three-legged piano-stool geometry around each metal centre (see Scheme 1). Free rotation around the N–C bond would be expected in solution and, for this reason, although a *trans*-disposition of both cyclopentadienyl ligands was considered in Scheme 1, alternative dispositions corresponding to other rotamers should also be considered.



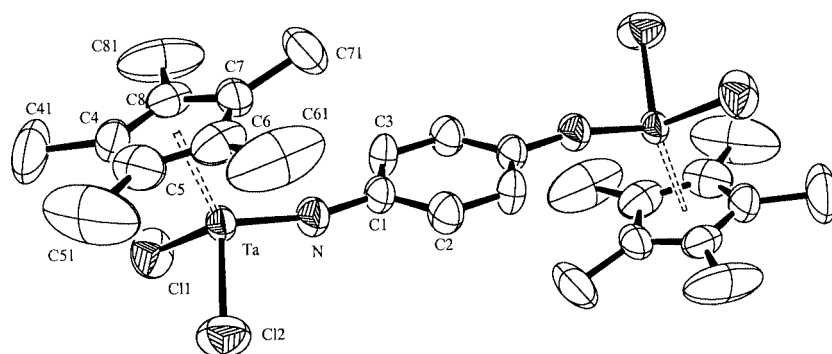


Figure 2. Molecular structure and atom-labelling scheme for $[\text{Ta}(\eta^5\text{-C}_5\text{Me}_5)\text{Cl}_2]_2(\mu\text{-1,4-NC}_6\text{H}_4\text{N})$ (**8**), with thermal ellipsoids at 30% probability

Table 1. Selected bond lengths (Å) and angles (°) for **1** and **8**

	1	8
M–N	1.776(8)	1.783(5)
M–Cl1	2.343(3)	2.325(2)
M–Cl2	2.344(3)	2.339(2)
M–C4	2.468(9)	2.468(7)
M–C5	2.47(1)	2.478(7)
M–C6	2.39(1)	2.382(7)
M–C7	2.36(1)	2.365(6)
M–C8	2.42(1)	2.382(6)
N–C1	1.39(1)	1.377(7)
N–M–Cl1	101.7(3)	102.3(2)
N–M–Cl2	103.5(3)	104.3(2)
Cl1–M–Cl2	106.0(1)	105.4(1)
M–N–C1	161.0(7)	166.4(5)

The structures of **1** and **8** consist of dinuclear complexes of niobium and tantalum, respectively. The metal atoms are bound to the cyclopentadienyl ring in an η^5 mode, to two chlorine atoms and to the nitrogen from the imido group in a three-legged piano-stool conformation. The cyclopentadienyl rings are in a *trans* disposition with respect to each other. The metal atom is out of the plane defined by N, C1, C2 and C3 by 0.54(2) and 0.39(1) Å for complexes **1** and **8**, respectively.

The metal-nitrogen distances lie within the range expected for a triple bond^[3a,16,17] [1.776(8) and 1.783(5) Å for **1** and **8**, respectively]. The M–N–C1 angles of 161.0(7)° for **1** and 166.4(5)° for **8** deviate slightly from linear. Such deviations are normally in the range 12–15° (see Table 2). In the case of $[\text{Nb}(=\text{NPh})(\eta^5\text{-C}_5\text{H}_4\text{SiMe}_3)_2\text{Cl}]$ extended-Hückel molecular-orbital calculations established that the imido bond angles for “linear imide” in this class of complex can vary up to 140° with little effect on the Nb–N bonding.^[18] Therefore we propose that in **1** and **8** the nitrogen atom is sp hybridized.

The cyclopentadienyl group is in a typical^[3a] eclipsed fashion with respect to the imido group for both complexes (see Figure 3a). The slight lengthening of the M–C4 [2.468(9) and 2.468(7) Å for **1** and **8**, respectively] and M–C5 [2.47(1) and 2.478(7) Å for **1** and **8**, respectively] distances with respect to other M–C ring distances may be due to the *trans* influence of the imido group.

The second part of this work involves the study of alkylation reactions of complexes **1**, **2** and **8**. The reaction of alkylating reagents, MeLi, $\text{Me}_3\text{SiCH}_2\text{MgCl}$ or $\text{Mg}(\text{CH}_2\text{C}_6\text{H}_5)_2(\text{THF})_2$, in a 1:4 molar ratio with **1**, **2** or **8** afforded the per-alkylated complexes, $[\{\text{M}(\text{Cp}')\text{R}_2\}_2(\mu\text{-1,4-NC}_6\text{H}_4)]$ [$\text{Cp}' = \eta^5\text{-C}_5\text{H}_4\text{SiMe}_3$, M = Nb, R = Me, *i* = 4 (**10**); $\text{Cp}' = \eta^5\text{-C}_5\text{H}_4\text{SiMe}_3$, M = Nb, R = CH_2SiMe_3 , *i* = 4 (**11**); $\text{Cp}' = \eta^5\text{-C}_5\text{H}_4\text{SiMe}_3$, M = Nb, R = CH_2Ph , *i* = 4

Table 2. Selected structural data for imido complexes

	M–N (Å)	M–N–C (°)	Ref.
$[\{\text{Nb}(\eta^5\text{-C}_5\text{H}_4\text{SiMe}_3)\text{Cl}_2\}_2(\mu\text{-1,4-NC}_6\text{H}_4\text{N})]$ (1)	1.776(8)	160.9(7)	This work
$[\{\text{Ta}(\eta^5\text{-C}_5\text{Me}_5)\text{Cl}_2\}_2(\mu\text{-1,4-NC}_6\text{H}_4\text{N})]$ (8)	1.783(5)	166.4(5)	This work
$[\{\text{Ta}(\eta^5\text{-C}_5\text{Me}_5)(\text{CH}_2\text{SiMe}_3)_2\}_2(\mu\text{-1,4-NC}_6\text{H}_4\text{N})]$ (17)	1.794(5)	167.4(5)	This work
$[\text{Nb}(=\text{NAr})(\eta^5\text{-C}_5\text{H}_5)(\text{NH}t\text{Bu})\text{Cl}]^{[a]}$	1.793	168.5	[17a]
$[\text{Nb}(=\text{NAr})(\eta^5\text{-C}_5\text{H}_5)\text{Cl}_2]^{[a]}$	1.761	165.6	[3a]
$[\text{Nb}(=\text{NAr})(\eta^5\text{-C}_5\text{H}_5)\text{Cl}_2]^{[b]}$	1.763	166.6	[17b]
$[\text{Nb}(=\text{NAr})(\eta^5\text{-C}_5\text{H}_5)(\eta^2\text{-NH}t\text{Bu})(\text{CH}_2t\text{Bu})\text{H}]^{[a]}$	1.787	174.6	[17c]
$[\text{Ta}(=\text{NAr})(\eta^5\text{-C}_5\text{Me}_5)\text{Cl}_2]^{[a]}$	1.780	171.3	[3a]
$[\text{Ta}(=\text{NAr})(\eta^5\text{-C}_5\text{Me}_5)\text{Cl}_2]^{[b]}$	1.774	169.9	[16]
$[\text{Ta}(=\text{NAr})(\eta^5\text{-C}_5\text{Me}_5)(\text{CO})\{\text{Si}(\text{SiMe}_3)_3\}\text{H}]^{[a]}$	1.812	171.4	[17d]
$[\text{Ta}(=\text{NAr})(\eta^5\text{-C}_5\text{H}_5)(\text{PMe}_3)(\text{SiMe}_2\text{Cl})\text{H}]^{[a]}$	1.821	171.8	[17e]

[a] Ar = $\text{C}_6\text{H}_3\text{iPr}_2\text{-2,6}$. [b] Ar = $\text{C}_6\text{H}_3\text{Me}_2\text{-2,6}$.

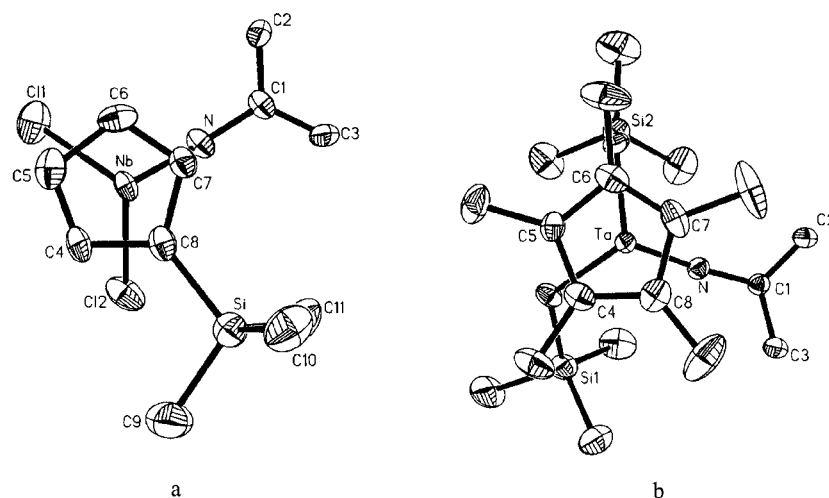
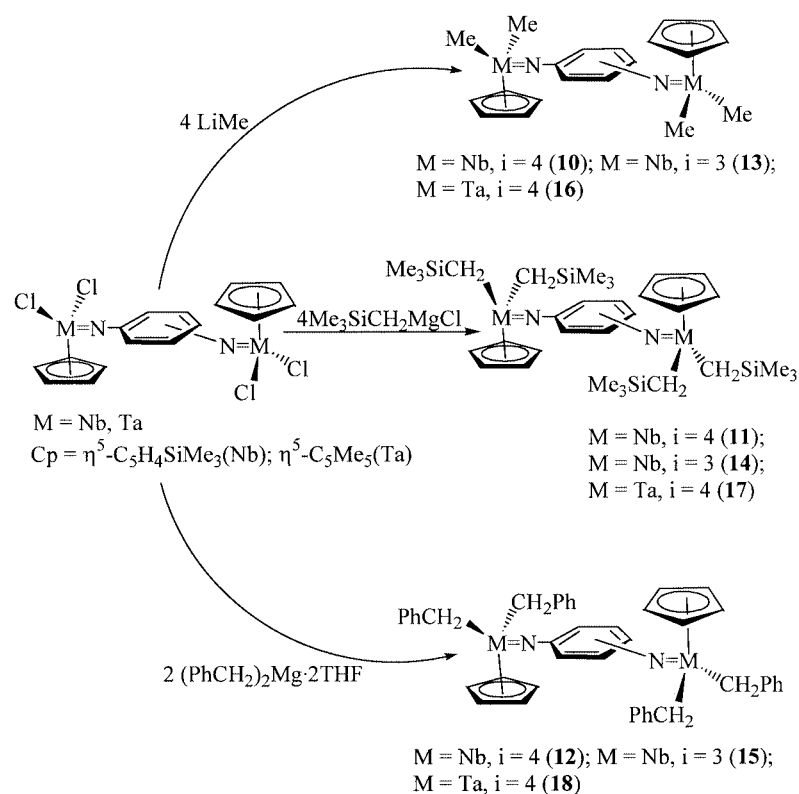


Figure 3. View along the ring centroid-metal vector (a) for compound **1**, and (b) for compound **17**

(**12**); $\text{Cp}' = \eta^5\text{-C}_5\text{H}_4\text{SiMe}_3$, $\text{M} = \text{Nb}$, $\text{R} = \text{Me}$, $i = 3$ (**13**); $\text{Cp}' = \eta^5\text{-C}_5\text{H}_4\text{SiMe}_3$, $\text{M} = \text{Nb}$, $\text{R} = \text{CH}_2\text{SiMe}_3$, $i = 3$ (**14**); $\text{Cp}' = \eta^5\text{-C}_5\text{H}_4\text{SiMe}_3$, $\text{M} = \text{Nb}$, $\text{R} = \text{CH}_2\text{Ph}$, $i = 3$ (**15**); $\text{Cp}' = \eta^5\text{-C}_5\text{Me}_5$, $\text{M} = \text{Ta}$, $\text{R} = \text{Me}$, $i = 4$ (**16**); $\text{Cp}' = \eta^5\text{-C}_5\text{Me}_5$, $\text{M} = \text{Ta}$, $\text{R} = \text{CH}_2\text{SiMe}_3$, $i = 4$ (**17**); $\text{Cp}' = \eta^5\text{-C}_5\text{Me}_5$, $\text{M} = \text{Ta}$, $\text{R} = \text{CH}_2\text{Ph}$, $i = 4$ (**18**) (Scheme 3).

Finally, the reactions of **1** and **8** with the milder alkylating agent ZnMe_2 , in a 1:2 molar ratio yielded the chloromethyl complexes $[\{\text{M}(\text{Cp}')(\text{Me})(\text{Cl})\}_2(\mu\text{-1,4-NC}_6\text{H}_4\text{N})]$ [$\text{Cp}' = \eta^5\text{-C}_5\text{H}_4\text{SiMe}_3$, $\text{M} = \text{Nb}$ (**19**); $\text{Cp}' = \eta^5\text{-C}_5\text{Me}_5$, $\text{M} = \text{Ta}$ (**21**)], while the reaction of **19** with LiNMe_2 in a 1:2 molar ratio (see Exp. Sect.) afforded the amido-containing



Scheme 3

complex $[\{\text{Nb}(\eta^5\text{-C}_5\text{H}_4\text{SiMe}_3)(\text{Me})(\text{NMe}_2)\}_2(\mu\text{-1,4-NC}_6\text{H}_4\text{N})]$ (**20**).

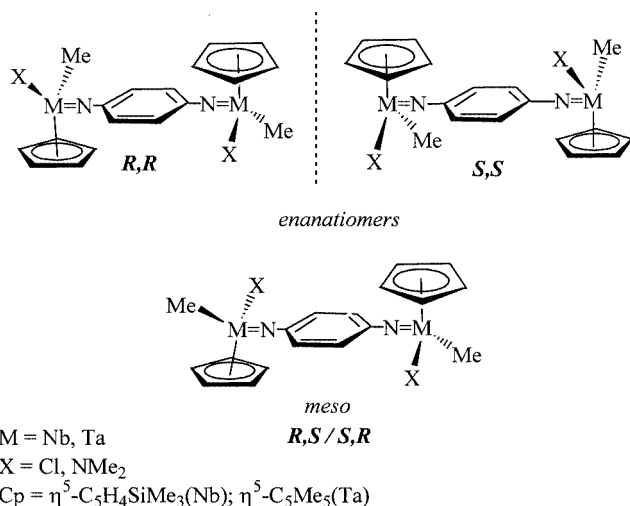
The ^1H and ^{13}C NMR spectra for complexes **10–18** are similar to those found for the parent complexes with regards to both the cyclopentadienyl and phenylene groups (see Exp. Sect.). In addition, the spectra also contain the resonances due to the alkyl groups attached to the metal centre. In these complexes the four alkyl groups are both chemically and magnetically equivalent and only one set of signals for these groups is present. For example, one singlet corresponding to methyl groups for complexes **10**, **13** and **16** was observed in the ^1H NMR spectra. Furthermore, in all the complexes the metal atom is a pro-chiral centre and so the protons of the methylene groups (for CH_2SiMe_3 or CH_2Ph) for complexes **11**, **12**, **14**, **15**, **17** and **18** are diastereotopic and, therefore, give rise to two doublets of an AB spin-system in their ^1H NMR spectra (see Exp. Sect.). For **19–21** the two metal atoms of the binuclear moiety are chiral centres and the stereoisomer the *meso*-(*R,S*) and the enantiomers *rac*-(*R,R*) and -(*S,S*) are formed (see

Scheme 4). The ^1H and ^{13}C NMR spectra of these complexes exhibit two sets of signals in a 1:1 ratio, corresponding to the presence of both diastereomers (*R,R/S,S*) and (*R,S*) (see Exp. Sect.).

The IR spectra of complexes **10–21** show a band at ca. $1300\text{--}1350\text{ cm}^{-1}$, which is characteristic of the terminal imido ligand.^[3a] In accordance with the different spectroscopic data described for alkyl-containing complexes, a structural disposition similar to that found for the chloro complexes can be expected (see Scheme 3). The X-ray crystal-structure determination for **17** confirmed this situation. The molecular structure and atomic numbering scheme are shown in Figure 4. Selected bond lengths and angles for **17** are given in Table 3.

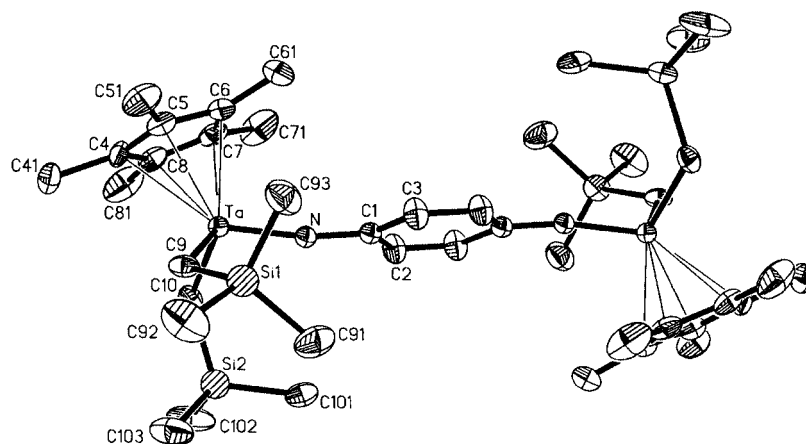
Table 3. Selected bond lengths (Å) and angles (°) for **17**

M–N	1.794(5)
M–C4	2.473(7)
M–C5	2.533(6)
M–C6	2.492(7)
M–C7	2.397(7)
M–C8	2.428(7)
M–C9	2.149(6)
M–C10	2.193(7)
N–C1	1.377(8)
N–M–C9	104.7(3)
N–M–C10	100.9(3)
C9–M–C10	104.0(3)
M–N–C1	167.4(5)



Scheme 4

The structure of **17** consists of a dinuclear complex where the metal atoms are bound to the cyclopentadienyl rings in an η^5 mode. In addition, the tantalum atoms are linked to two methylene groups from CH_2SiMe_3 and to the nitrogen atom from the imido group. Complex **17** adopts a three-legged piano-stool conformation about the metal centres. The cyclopentadienyl rings are in a *trans* disposition with respect to each other. The metal atom is out of the plane defined by N, C1, C2 and C3, by $0.36(1)\text{ Å}$. The metal-



nitrogen distance of 1.794(5) Å and the M–N–C1 angle of 167.4(5)° lie within the range expected for a triple bond (see Table 2).^[3a,16,17]

The cyclopentadienyl group in **17** is in a staggered disposition with respect to the imido group (Figure 3b), in contrast to the eclipsed disposition observed in **1** and **8** (Figure 3a). The slight lengthening of the M–C4 [2.473(7) Å] and M–C5 [2.533(6) Å] distances is probably due to the *trans* influence of the imido group.

Conclusions

In this paper we report the synthesis of new dinuclear monocyclopentadienyl imidoniobium and -tantalum complexes and their reactivity towards different alkylating agents. The molecular structures of several of these complexes have been determined by single-crystal X-ray diffraction studies.

Experimental Section

General Remarks: All reactions were performed using standard Schlenk-tube techniques under an atmosphere of dry nitrogen. Solvents were distilled from appropriate drying agents and degassed before use. Literature methods were employed for the synthesis of the following compounds: *N,N,N',N'*-tetrakis(trimethylsilyl)phenylenediamine,^[19] [Nb(η⁵-C₅H₄SiMe₃)Cl₄],^[20] [{NbCl₃}₂(μ-1,*i*-NC₆H₄N)] (*i* = 4, 3 or 2),^[8a] C₅H₄(SiMe₃)₂,^[21] [Ta(η⁵-C₅H₄SiMe₃)Cl₄],^[22] [TaCl₃]₂(μ-1,*i*-NC₆H₄N)] (*i* = 4 or 3),^[8b] [Ta(η⁵-C₅Me₅)Cl₄],^[23] C₅Me₅(SiMe₃)₂,^[24] [Nb(η⁵-C₅Me₅)Cl₄],^[25] and [Mg(CH₂Ph)₂(THF)₂].^[25] All commercial products were purchased from Aldrich and were used without further purification: LiMe, Mg(CH₂SiMe₃)Cl, ZnMe₂ and LiNMe₂. IR spectra were recorded on a Perkin–Elmer 883 and Perkin–Elmer IR-FT Spectrophotometer 2000. ¹H and ¹³C NMR spectra were recorded on a Gemini-200 and/or UNITY-300 (Varian) spectrometer. Chemical shifts were measured relative to residual ¹H and ¹³C resonances for [D₁]chloroform and [D₆]benzene 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 microanalyzer.

Preparation of [{Nb(η⁵-C₅H₄SiMe₃)Cl₂}₂(μ-1,4-NC₆H₄N)] (1**), [{Nb(η⁵-C₅H₄SiMe₃)Cl₂}₂(μ-1,3-NC₆H₄N)] (**2**) and [{Nb(η⁵-C₅H₄SiMe₃)Cl₂}₂(μ-1,2-NC₆H₄N)] (**3**). Method A:** CH₂Cl₂ (70 mL) was added to a mixture of [Nb(η⁵-C₅H₄SiMe₃)Cl₄] and the corresponding *N,N,N',N'*-tetrakis(trimethylsilyl)phenylenediamine in a Teflon valve ampoule. The ampoule was placed in an oil bath and heated at 65 °C for 24 h. The solvent was removed under vacuum and the solids obtained were identified as **1**, **2** and **3**, respectively.

Complex 1: From [Nb(η⁵-C₅H₄SiMe₃)Cl₄] (1.15 g, 3.09 mmol) and 1,4-[(Me₃Si)₂N]₂C₆H₄ (0.61 g, 1.54 mmol). 1.08 g of a red solid was obtained (Yield: 100%).

Complex 2: From [Nb(η⁵-C₅H₄SiMe₃)Cl₄] (1.05 g, 2.83 mmol) and 1,3-[(Me₃Si)₂N]₂C₆H₄ (0.56 g, 1.41 mmol). 1.0 g of a red solid was obtained (Yield: 100%).

Complex 3: From [Nb(η⁵-C₅H₄SiMe₃)Cl₄] (1.01 g, 2.72 mmol) and 1,2-[(Me₃Si)₂N]₂C₆H₄ (0.54 g, 1.36 mmol). 0.96 g of a dark brown solid was obtained (Yield: 100%).

Method B: CH₂Cl₂ (60 mL) was added to the corresponding complex [{NbCl₃}₂(μ-1,*i*-NC₆H₄N)] (*i* = 4, 3 or 2) in a Teflon valve ampoule. C₅H₄(SiMe₃)₂ was added to this green suspension and the ampoule was placed in an oil bath and heated at 90 °C for 24 h. The initial green suspension changed to a red solution. The solvent was removed under vacuum and the solids obtained were identified as **1**, **2** and **3**, respectively.

Complex 1: From [{NbCl₃}₂(μ-1,4-NC₆H₄N)] (0.80 g, 1.59 mmol) and C₅H₄(SiMe₃)₂ (0.74 mL, 3.18 mmol). 1.12 g of a red solid was obtained (Yield: 100%). ¹H NMR (300 MHz, CDCl₃, 25 °C): δ = 0.26 (s, 18 H, 2 × C₅H₄SiMe₃), 6.60 and 6.75 (2m, each 4 H, 2 × C₅H₄), 6.89 (s, 4 H, C₆H₄) ppm. ¹³C{¹H} NMR (75 MHz, CDCl₃, 25 °C): δ = −0.5 (C₅H₄SiMe₃), 114.7, 122.0 and 125.9 (*C*^{*ipso*}; C₅H₄SiMe₃) 124.3 and 153.9 (*C*^{*ipso*}; C₆H₄) ppm. IR (CsI/Nujol): ν̃ = 3090m, 1483s, 1395m, 1370s, 1311vs, 1253vs, 1172s, 1099m, 1074w, 1045s, 1004w, 990m, 903s, 840vs, 764m, 703w, 635w, 530w, 423m, 380s and 330m cm^{−1}. C₂₂H₃₀Cl₄N₂Nb₂Si₂ (706.3): calcd. C 37.41, H 4.28, N 3.97; found C 37.05, H 4.48, N 4.08.

Complex 2: From [{NbCl₃}₂(μ-1,3-NC₆H₄N)] (0.71 g, 1.41 mmol) and C₅H₄(SiMe₃)₂ (0.66 mL, 2.82 mmol). 1.0 g of a red solid was obtained (Yield: 100%). ¹H NMR (300 MHz, CDCl₃, 25 °C): δ = 0.29 (s, 18 H, 2 × C₅H₄SiMe₃), 6.62 and 6.76 (2m, each 4 H, 2 × C₅H₄), 6.62 (1 H), 6.72 (2 H) and 7.13 (1 H) (3m, C₆H₄) ppm. ¹³C{¹H} NMR (50 MHz, CDCl₃, 25 °C): δ = −0.5 (C₅H₄SiMe₃), 114.4, 122.2 and 126.3 (*C*^{*ipso*}; C₅H₄SiMe₃), 118.9, 122.1, 128.3 and 155.6 (*C*^{*ipso*}; C₆H₄) ppm. IR (KBr): ν̃ = 3093m, 2953m, 2598m, 1567s, 1462s, 1410m, 1370m, 1332m, 1306m, 1283m, 1250s, 1170s, 1047s, 1036s, 971w, 903s, 839vs, 780s, 757s, 694s, 680m, 630s, 419w and 374s cm^{−1}. C₂₂H₃₀Cl₄N₂Nb₂Si₂ (706.3): calcd. C 37.41, H 4.28, N 3.97; found C 37.40, H 4.55, N 3.68.

Complex 3: From [{NbCl₃}₂(μ-1,2-NC₆H₄N)] (0.77 g, 1.53 mmol) and C₅H₄(SiMe₃)₂ (0.72 mL, 3.06 mmol). 1.08 g of a red solid was obtained (Yield: 100%). ¹H NMR (300 MHz, CDCl₃, 25 °C): δ = 0.28 (s, 18 H, 2 × C₅H₄SiMe₃), 6.68 and 6.76 (2m, each 4 H, 2 × C₅H₄), 6.93 (m, 4 H, C₆H₄) ppm. ¹³C{¹H} NMR (75 MHz, CDCl₃, 25 °C): δ = −0.6 (C₅H₄SiMe₃), 114.1, 124.2 and 125.9 (*C*^{*ipso*}; C₅H₄SiMe₃), 125.5, 126.1, and 150.1 (*C*^{*ipso*}; C₆H₄) ppm. IR (CsI/Nujol): ν̃ = 3101w, 1577w, 1436m, 1395w, 1371m, 1328m, 1315m, 1253s, 1170m, 1115w, 1048m, 1039w, 987w, 966(m), 933w, 903s, 842vs, 754s, 748s, 632w, 398m, 379s and 336m cm^{−1}. C₂₂H₃₀Cl₄N₂Nb₂Si₂ (706.3): calcd. C 37.41, H 4.28, N 3.97; found C 36.62, H 4.06, N 4.06.

Preparation of [{Nb(η⁵-C₅Me₅)Cl₂}₂(μ-1,4-NC₆H₄N)] (4**). Method A:** Dichloromethane (60 mL) was added to a mixture of [{NbCl₃}₂(μ-1,4-NC₆H₄N)] (0.62 g, 1.23 mmol) and C₅Me₅(SiMe₃) (0.60 mL, 2.47 mmol) in a Teflon valve ampoule. The ampoule was placed in an oil bath and heated to 90 °C for 24 h. The resulting solution was allowed to cool down to room temperature, filtered and the solvent removed under vacuum to give 0.83 g of **4** as a purple, analytically pure, crystalline solid. (Yield: 100%).

Method B: A Teflon valve NMR tube was charged with a solution of [Nb(η⁵-C₅Me₅)Cl₄] (15 mg, 0.04 mmol) and [1,4-[(SiMe₃)₂N]₂C₆H₄] (8 mg, 0.02 mmol) in CDCl₃. The mixture was placed in an oil bath, heated to 65 °C and monitored by ¹H NMR spectroscopy. After 24 h the reaction was complete and gave **4** as the only product. ¹H NMR (300 MHz, CDCl₃, 25 °C): δ = 2.07 (s, 30 H, 2 × C₅Me₅), 6.79 (s, 4 H, C₆H₄) ppm. ¹³C{¹H} NMR (75 MHz, CDCl₃, 25 °C): δ = 11.8 (C₅Me₅), 123.9 (C₅Me₅) 125.1 and 151.1 (*C*^{*ipso*}; C₆H₄) ppm. IR (CsI/Nujol): ν̃ = 1476s, 1311s, 1262w, 1094w, 1022m, 1003w, 990w, 840m, 799w, 488w, 393m and

366 cm⁻¹. C₂₆H₃₄Cl₄N₂Nb₂ (702.2): calcd. C 44.47, H 4.88, N 3.99; found C 44.04, H 4.92, N 4.22.

Preparation of [Nb(η⁵-C₅Me₅)Cl₂]₂(μ-1,3-NC₆H₄N)] (5): The synthesis of **5** was carried out in an identical manner to **4**.

Method A: [NbCl₃]₂(μ-1,3-NC₆H₄N)] (1.42 g, 2.82 mmol) and C₅Me₅(SiMe₃) (1.38 mL, 5.63 mmol). 1.98 g of **5** was obtained as a pink solid (Yield: 100%).

Method B: [Nb(η⁵-C₅Me₅)Cl₄] (17 mg, 0.046 mmol) and [1,3-{(SiMe₃)₂N}₂C₆H₄] (9 mg, 0.023 mmol). (Yield: 100%). ¹H NMR (300 MHz, CDCl₃, 25 °C): δ = 2.09 (s, 30 H, 2 × C₅Me₅), 6.43 (1 H), 6.60 (2 H) and 7.08 (1 H) (3m, C₆H₄) ppm. ¹³C{¹H} NMR (75 MHz, CDCl₃, 25 °C): δ = 11.9 (C₅Me₅), 124.0 (C₅Me₅) 120.2, 122.2, 128.2 and 153.6 (C^{ipso}; C₆H₄) ppm. IR (CsI/Nujol): ν̄ = 1566s, 1415m, 1338m, 1284s, 1236s, 1149w, 1079w, 1026m, 971w, 897w, 865m, 847w, 791m, 687w, 485w, 469w, 402m and 362s cm⁻¹. C₂₆H₃₄Cl₄N₂Nb₂ (702.2): calcd. C 44.47, H 4.88, N 3.99; found C 44.21, H 5.06, N 4.07.

Preparation of [Ta(η⁵-C₅H₄SiMe₃)Cl₂]₂(μ-1,4-NC₆H₄N)] (6) and [Ta(η⁵-C₅H₄SiMe₃)Cl₂]₂(μ-1,3-NC₆H₄N)] (7): **Method A:** CH₂Cl₂ (40 mL) was added to a mixture of [Ta(η⁵-C₅H₄SiMe₃)Cl₄] and the corresponding *N,N,N',N'*-tetrakis(trimethylsilyl)phenylenediamine in a Teflon valve ampoule. The ampoule was placed in an oil bath and heated at 70 °C for 16 h. The resulting deep-red solution was allowed to cool down to room temperature. The solution was filtered and the solvent removed under reduced pressure. The final products obtained were identified as **6** and **7**, respectively.

Complex 6: From [Ta(η⁵-C₅H₄SiMe₃)Cl₄] (0.81 g, 1.76 mmol) and 1,4-{(Me₃Si)₂N}₂C₆H₄ (0.35 g, 0.88 mmol). 0.78 g of a red solid was obtained (Yield: 100%).

Complex 7: From [Ta(η⁵-C₅H₄SiMe₃)Cl₄] (0.81 g, 1.76 mmol) and 1,3-{(Me₃Si)₂N}₂C₆H₄ (0.35 g, 0.88 mmol). 0.78 g of a yellow oil was obtained (Yield: 100%).

Method B: CH₂Cl₂ (40 mL) was added to the corresponding [TaCl₃]₂(μ-1,*i*-NC₆H₄N)] (*i* = 4 or 3) in a Teflon valve ampoule. C₅H₄(SiMe₃)₂ was added to this red suspension and the ampoule was placed in an oil bath and heated at 90 °C for 72 h. The resulting red solution was filtered and the solvent was removed under vacuum. The final products were washed several times with hexane at -40 °C and identified as **6** and **7**, respectively.

Complex 6: From [(TaCl₃)₂(μ-1,4-NC₆H₄N)] (1.71 g, 2.52 mmol) and C₅H₄(SiMe₃)₂ (1.30 mL, 5.02 mmol). 1.72 g of a red solid was obtained (Yield: 78%). ¹H NMR (300 MHz, CDCl₃, 25 °C): δ = 0.25 (s, 18 H, 2 × C₅H₄SiMe₃), 6.59 and 6.71 (2m, each 4 H, 2 × C₅H₄), 6.75 (s, 4 H, C₆H₄) ppm. ¹³C{¹H} NMR (75 MHz, CDCl₃, 25 °C): δ = -0.4 (C₅H₄SiMe₃), 114.3, 120.6 and 123.1 (C^{ipso}; C₅H₄SiMe₃) 125.0 and 153.0 (C^{ipso}; C₆H₄) ppm. IR (CsI/Nujol): ν̄ = 3090w, 1491s, 1333vs, 1254s, 1172m, 1043m, 905s, 841vs and 413m cm⁻¹. C₂₂H₃₀Cl₄N₂Si₂Ta₂ (882.4): calcd. C 29.95, H 3.43, N 3.17; found C 29.62, H 3.61, N 3.15.

Complex 7: From [(TaCl₃)₂(μ-1,3-NC₆H₄N)] (1.71 g, 2.52 mmol) and C₅H₄(SiMe₃)₂ (1.30 mL, 5.02 mmol). 1.57 g of a yellow oil was obtained (Yield: 71%). ¹H NMR (300 MHz, CDCl₃, 25 °C): δ = 0.28 (s, 18 H, 2 × C₅H₄SiMe₃), 6.60 and 6.72 (2m, each 4 H, 2 × C₅H₄), 6.26 (1 H), 6.39 (2 H) and 7.17 (1 H) (3m, C₆H₄) ppm. ¹³C{¹H} NMR (75 MHz, CDCl₃, 25 °C): δ = -0.4 (C₅H₄SiMe₃), 113.9, 120.8 and 123.6 (C^{ipso}; C₅H₄SiMe₃), 121.9, 122.7, 127.1 and 154.9 (C^{ipso}; C₆H₄) ppm. IR (CsI/Nujol): ν̄ = 3098w, 1573vs, 1470vs, 1320vs, 1252vs, 1171s, 905s, 840vs and 417m cm⁻¹.

C₂₂H₃₀Cl₄N₂Si₂Ta₂ (882.4): calcd. C 29.95, H 3.43, N 3.17; found C 29.76, H 3.65, N 3.31.

Preparation of [Ta(η⁵-C₅Me₅)Cl₂]₂(μ-1,4-NC₆H₄N)] (8): Dichloromethane (40 mL) was added to a mixture of [Ta(η⁵-C₅Me₅)Cl₄] (1.72 g, 3.76 mmol) and [1,4-{(SiMe₃)₂N}₂C₆H₄] (0.75 g, 1.88 mmol) in a Teflon valve ampoule. The ampoule was placed in an oil bath and heated to 90 °C for 48 h. The resulting solution was allowed to cool down to room temperature, filtered and the solvent removed under vacuum to give 2.00 g of **8** as a red, analytically pure, crystalline solid. (Yield: 100%). An X-ray-quality sample was obtained from a saturated dichloromethane solution at -40 °C. ¹H NMR (300 MHz, CDCl₃, 25 °C): δ = 2.16 (s, 30 H, 2 × C₅Me₅), 6.65 (s, 4 H, C₆H₄) ppm. ¹³C{¹H} NMR (75 MHz, CDCl₃, 25 °C): δ = 11.4 (C₅Me₅), 121.6 (C₅Me₅) 125.4 and 150.7 (C^{ipso}; C₆H₄) ppm. IR (CsI/Nujol): ν̄ = 1485vs, 1338vs, 1091m, 1028s, 995m and 844s cm⁻¹. C₂₆H₃₄Cl₄N₂Ta₂ (878.3): calcd. C 35.56, H 3.90, N 3.19; found C 35.50, H 4.07, N 3.47.

Preparation of [Ta(η⁵-C₅Me₅)Cl₂]₂(μ-1,3-NC₆H₄N)] (9): The synthesis of **9** was carried out in an identical manner to **8**, from [Ta(η⁵-C₅Me₅)Cl₄] (0.81 g, 1.75 mmol) and [1,3-{(SiMe₃)₂N}₂C₆H₄] (0.35 g, 0.88 mmol). 0.96 g of **9** was obtained as an orange solid (Yield: 100%). ¹H NMR (300 MHz, CDCl₃, 25 °C): δ = 2.18 (s, 30 H, 2 × C₅Me₅), 6.11 (1 H), 6.28 (2 H) and 7.10 (1 H) (3m, C₆H₄) ppm. ¹³C{¹H} NMR (75 MHz, CDCl₃, 25 °C): δ = 11.5 (C₅Me₅), 121.8 (C₅Me₅) 122.4, 122.5, 127.0 and 153.7 (C^{ipso}; C₆H₄) ppm. IR (CsI/Nujol): ν̄ = 1568vs, 1315vs, 1026s, 864m and 351s cm⁻¹. C₂₆H₃₄Cl₄N₂Ta₂ (878.3): calcd. C 35.56, H 3.90, N 3.19; found C 35.23, H 4.00, N 3.19.

Preparation of [Nb(η⁵-C₅H₄SiMe₃)Me₂]₂(μ-1,4-NC₆H₄N)] (10) and [Nb(η⁵-C₅H₄SiMe₃)Me₂]₂(μ-1,3-NC₆H₄N)] (13): MeLi was added at -78 °C to a suspension of complex **1** or **2** in hexane (50 mL). The mixture was allowed to warm up to room temperature and was stirred for 5 h. The solution was filtered and the residue extracted with hexane (2 × 20 mL). The extracts and the solution were combined and the solvent was removed in vacuo to give a solid, which was identified as **10** or **13**, respectively.

Complex 10: From [Nb(η⁵-C₅H₄SiMe₃)Cl₂]₂(μ-1,4-NC₆H₄N)] (0.85 g, 1.20 mmol) and MeLi (3.44 mL, 4.81 mmol). 0.70 g of a brown solid was obtained (Yield: 93%). ¹H NMR (300 MHz, C₆D₆, 25 °C): δ = 0.09 (s, 18 H, 2 × C₅H₄SiMe₃), 0.77 (s, 12 H, 4 × Nb-Me), 5.91 (m, 8 H, 2 × C₅H₄), 7.19 (s, 4 H, C₆H₄) ppm. ¹³C{¹H} NMR (75 MHz, C₆D₆, 25 °C): δ = -0.1 (C₅H₄SiMe₃), 37.8 (Nb-Me), 113.0, 113.1 and 116.7 (C^{ipso}; C₅H₄SiMe₃) 125.4 and 153.7 (C^{ipso}; C₆H₄) ppm. IR (CsI/Nujol): ν̄ = 1477m, 1407m, 1317m, 1251s, 1174m, 1091w, 1046m, 982w, 904m, 879w, 838vs, 807m, 756m, 695w, 631w, 493w and 422w cm⁻¹. C₂₆H₄₂N₂Nb₂Si₂ (624.6): calcd. C 50.00, H 6.78, N 4.48; found C 50.15, H 6.70, N 4.26.

Complex 13: From [Nb(η⁵-C₅H₄SiMe₃)Cl₂]₂(μ-1,3-NC₆H₄N)] (1.66 g, 2.35 mmol) and MeLi (6.71 mL, 9.40 mmol). 1.35 g of a brown solid was obtained (Yield: 92%). ¹H NMR (300 MHz, C₆D₆, 25 °C): δ = 0.10 (s, 18 H, 2 × C₅H₄SiMe₃), 0.75 (s, 12 H, 4 × Nb-Me), 5.89 and 5.93 (2m, each 4 H, 2 × C₅H₄), 7.02 (3 H) and 7.30 (1 H) (2m, C₆H₄) ppm. ¹³C{¹H} NMR (50 MHz, C₆D₆, 25 °C): δ = -0.2 (C₅H₄SiMe₃), 38.1 (Nb-Me), 112.6, 113.2 and 117.4 (C^{ipso}; C₅H₄SiMe₃), 121.1, 121.3, 128.0 and 157.4 (C^{ipso}; C₆H₄) ppm. IR (CsI/Nujol): ν̄ = 1567s, 1409m, 1338m, 1303m, 1250s, 1174m, 1150m, 1045m, 956w, 904m, 838vs, 780m, 757m, 693w, 632w and 495w cm⁻¹. C₂₆H₄₂N₂Nb₂Si₂ (624.6): calcd. C 50.00, H 6.78, N 4.48; found C 50.04, H 7.10, N 4.09.

Preparation of [Nb(η⁵-C₅H₄SiMe₃)(CH₂SiMe₃)₂]₂(μ-1,4-NC₆H₄N)] (11): A slight excess of [Mg(CH₂SiMe₃)Cl] (4.3 mL,

4.3 mmol) was added, at -78°C , to a suspension of complex **1** (0.68 g, 0.97 mmol) in hexane (50 mL). The mixture was allowed to warm up to room temperature and was stirred overnight. The solution was filtered and the residue extracted with hexane (2×20 mL). The extracts and the solution were combined. The resulting orange solution was concentrated to 25 mL. Cooling of this solution to -40°C gave compound **11** (0.70 g, 0.77 mmol) as an orange crystalline solid. (Yield: 79%). ^1H NMR (300 MHz, C_6D_6 , 25°C): $\delta = 0.18$ (s, 18 H, $2 \times \text{C}_5\text{H}_4\text{SiMe}_3$), 0.24 (s, 36 H, $4 \times \text{CH}_2\text{SiMe}_3$), 0.16 and 1.53 (2d, $^2J_{\text{H,H}} = 10.2$ Hz, each 4 H, $4 \times \text{CH}_2\text{SiMe}_3$), 5.78 and 6.21 (2m, each 4 H, $2 \times \text{C}_5\text{H}_4$), 7.21 (s, 4 H, C_6H_4) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (75 MHz, C_6D_6 , 25°C): $\delta = 0.0$ ($\text{C}_5\text{H}_4\text{SiMe}_3$), 2.8 (CH_2SiMe_3), 55.0 (CH_2SiMe_3), 108.0, 115.8 and 119.6 (C^{ipso} ; $\text{C}_5\text{H}_4\text{SiMe}_3$) 125.1 and 153.6 (C^{ipso} ; C_6H_4) ppm. IR (CsI/Nujol): $\tilde{\nu} = 1478\text{s}$, 1408w, 1314s, 1241s, 1174m, 1092w, 1048m, 1040m, 1003w, 988m, 938s, 901s, 831vs, 814s, 755m, 735m, 701m, 682m, 632w, 549w, 534w, 468m, 416w and 373w cm^{-1} . $\text{C}_{38}\text{H}_{74}\text{N}_2\text{Nb}_2\text{Si}_6$ (913.3): calcd. C 49.97, H 8.17, N 3.07; found C 50.05, H 8.26, N 3.30.

Preparation of $[\{\text{Nb}(\eta^5\text{-C}_5\text{H}_4\text{SiMe}_3)(\text{CH}_2\text{SiMe}_3)_2\}_2(\mu\text{-1,3-NC}_6\text{H}_4\text{N})]$ (14**):** A slight excess of $[\text{Mg}(\text{CH}_2\text{SiMe}_3)\text{Cl}]$ (5.2 mL, 5.2 mmol) was added, at -78°C , to a suspension of complex **2** (0.83 g, 1.17 mmol) in hexane (50 mL). The mixture was allowed to warm up to room temperature and was stirred overnight. The solution was filtered and the residue extracted with hexane (2×20 mL). The extracts and the solution were combined. The solvent was removed and the resulting yellow oil was identified as **14** (0.95 g, 1.04 mmol) (Yield: 89%). ^1H NMR (300 MHz, C_6D_6 , 25°C): $\delta = 0.20$ (s, 18 H, $2 \times \text{C}_5\text{H}_4\text{SiMe}_3$), 0.27 (s, 36 H, $4 \times \text{CH}_2\text{SiMe}_3$), 0.21 and 1.57 (2d, $^2J_{\text{H,H}} = 10.5$ Hz, each 4 H, $4 \times \text{CH}_2\text{SiMe}_3$), 5.89 and 6.28 (2m, each 4 H, $2 \times \text{C}_5\text{H}_4$), 6.92 (2 H), 7.08 (1 H) and 7.16 (1 H) (3m, C_6H_4) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (50 MHz, C_6D_6 , 25°C): $\delta = 0.0$ ($\text{C}_5\text{H}_4\text{SiMe}_3$), 2.9 (CH_2SiMe_3), 55.2 (CH_2SiMe_3), 107.8, 115.9 and 120.2 (C^{ipso} ; $\text{C}_5\text{H}_4\text{SiMe}_3$) 120.4, 120.6, 128.3 and 157.4 (C^{ipso} ; C_6H_4) ppm. IR (CsI/Nujol): $\tilde{\nu} = 1566\text{s}$, 1409m, 1336m, 1302s, 1280s, 1246s, 1175m, 1152w, 1045m, 931s, 905s, 838vs, 754s, 697s, 633w, 572w, 472w and 416w cm^{-1} . $\text{C}_{38}\text{H}_{74}\text{N}_2\text{Nb}_2\text{Si}_6$ (913.3): calcd. C 49.97, H 8.17, N 3.07; found C 49.41, H 8.18, N 3.24.

Preparation of $[\{\text{Nb}(\eta^5\text{-C}_5\text{H}_4\text{SiMe}_3)(\text{CH}_2\text{Ph})_2\}_2(\mu\text{-1,4-NC}_6\text{H}_4\text{N})]$ (12**) and $[\{\text{Nb}(\eta^5\text{-C}_5\text{H}_4\text{SiMe}_3)(\text{CH}_2\text{Ph})_2\}_2(\mu\text{-1,3-NC}_6\text{H}_4\text{N})]$ (**15**):** Diethyl ether (60 mL) was added at -78°C to a mixture of complex **1** or **2** and $[\text{Mg}(\text{CH}_2\text{Ph})_2(\text{THF})_2]$. The mixture was allowed to warm up to room temperature and was stirred overnight. The solution was filtered and the residue was extracted with diethyl ether (2×20 mL). The extracts and the solution were combined. The solvent was removed to give a yellow and a pale yellow solid, respectively, and these were identified as the corresponding compounds **12** and **15**.

Complex 12: From **1** (0.75 g, 1.06 mmol) and $[\text{Mg}(\text{CH}_2\text{Ph})_2(\text{THF})_2]$ (0.74 g, 2.12 mmol). 0.88 g was obtained (Yield: 90%). ^1H NMR (300 MHz, C_6D_6 , 25°C): $\delta = 0.11$ (s, 18 H, $2 \times \text{C}_5\text{H}_4\text{SiMe}_3$), 1.55 and 2.13 (2d, $^2J_{\text{H,H}} = 8.1$ Hz, each 4 H, $4 \times \text{CH}_2\text{Ph}$), 5.63 and 5.72 (2m, each 4 H, $2 \times \text{C}_5\text{H}_4$), 6.79 (s, 4 H, C_6H_4), 6.81–7.07 (m, 20 H, $4 \times \text{CH}_2\text{Ph}$) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (75 MHz, C_6D_6 , 25°C): $\delta = 0.1$ ($\text{C}_5\text{H}_4\text{SiMe}_3$), 43.4 (CH_2Ph), 111.6, 112.5 and 112.2 (C^{ipso} ; $\text{C}_5\text{H}_4\text{SiMe}_3$) 124.9 and 153.5 (C^{ipso} ; C_6H_4), 125.4, 129.0, 130.5 and 138.9 (C^{ipso} ; CH_2Ph) ppm. IR (CsI/Nujol): $\tilde{\nu} = 1594\text{m}$, 1477s, 1408m, 1314s, 1250s, 1205m, 1176s, 1093m, 1035s, 1004w, 995w, 985m, 920w, 902m, 885w, 835vs, 817vs, 760s, 750s, 696vs, 632w, 537w, 515w, 446w and 428w cm^{-1} . $\text{C}_{50}\text{H}_{58}\text{N}_2\text{Nb}_2\text{Si}_2$ (929.0): calcd. C 64.64, H 6.29, N 3.02; found C 65.33, H 6.94, N 2.74.

Complex 15: From **2** (0.75 g, 1.06 mmol) and $[\text{Mg}(\text{CH}_2\text{Ph})_2(\text{THF})_2]$ (0.74 g, 2.12 mmol). 0.85 g was obtained (Yield: 86%). ^1H NMR (300 MHz, C_6D_6 , 25°C): $\delta = 0.15$ (s, 18 H, $2 \times \text{C}_5\text{H}_4\text{SiMe}_3$), 1.70 and 2.11 (2d, $^2J_{\text{H,H}} = 8.1$ Hz, each 4 H, $4 \times \text{CH}_2\text{Ph}$), 5.64 and 5.79 (2m, each 4 H, $2 \times \text{C}_5\text{H}_4$), 6.612 (2 H), 6.73 (1 H) and 7.16 (1 H) (3m, C_6H_4), 6.85–7.08 (m, 20 H, $4 \times \text{CH}_2\text{Ph}$) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (75 MHz, C_6D_6 , 25°C): $\delta = 0.2$ ($\text{C}_5\text{H}_4\text{SiMe}_3$), 43.6 (CH_2Ph), 111.9, 112.3 and 112.9 (C^{ipso} ; $\text{C}_5\text{H}_4\text{SiMe}_3$) 119.8, 120.7, 128.0 and 157.3 (C^{ipso} ; C_6H_4), 125.5, 129.1, 130.6 and 138.8 (C^{ipso} ; CH_2Ph) ppm. IR (CsI/Nujol): $\tilde{\nu} = 1592\text{s}$, 1565s, 1549m, 1513w, 1484s, 1409m, 1367m, 1343m, 1304s, 1290s, 1251s, 1234s, 1207m, 1177m, 1159w, 1123w, 1084w, 1043m, 1025m, 995w, 901m, 837vs, 820s, 805s, 784w, 758s, 695m, 686m, 633w, 541w, 516w, 499w, 443w and 430w cm^{-1} . $\text{C}_{50}\text{H}_{58}\text{N}_2\text{Nb}_2\text{Si}_2$ (929.0): calcd. C 64.64, H 6.29, N 3.02; found C 64.69, H 6.85, N 2.88.

Preparation of $[\{\text{Ta}(\eta^5\text{-C}_5\text{Me}_5)\text{Me}_2\}_2(\mu\text{-1,4-NC}_6\text{H}_4\text{N})]$ (16**):** A solution of MeLi (2.28 mmol) diluted in Et₂O (10 mL) was added dropwise, at -78°C , to a suspension of complex **8** (0.5 g, 0.57 mmol) in hexane (50 mL). The mixture was stirred overnight at room temperature. The resulting yellow solution was filtered and the residue extracted with hexane (2×25 mL). The solvent was removed in vacuo to give 0.36 g of a yellow solid, which was identified as complex **16** (Yield: 80%). ^1H NMR (300 MHz, CDCl_3 , 25°C): $\delta = 0.01$ (s, 12 H, $4 \times \text{Ta-Me}$), 1.96 (s, 30 H, $2 \times \text{C}_5\text{Me}_5$), 6.68 (s, 4 H, C_6H_4) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (75 MHz, CDCl_3 , 25°C): $\delta = 10.7$ (C_5Me_5), 46.5 (Ta-Me), 115.9 (C_5Me_5) 125.0 and 151.9 (C^{ipso} ; C_6H_4) ppm. IR (CsI/Nujol): $\tilde{\nu} = 1493\text{s}$, 1332vs, 1086m, 1026m, 1007m, 835s, 804m and 500m cm^{-1} . $\text{C}_{30}\text{H}_{46}\text{N}_2\text{Ta}_2$ (796.6): calcd. C 45.23, H 5.82, N 3.52; found C 44.82, H 5.79, N 3.36.

Preparation of $[\{\text{Ta}(\eta^5\text{-C}_5\text{Me}_5)(\text{CH}_2\text{SiMe}_3)_2\}_2(\mu\text{-1,4-NC}_6\text{H}_4\text{N})]$ (17**):** A solution of $\text{Mg}(\text{CH}_2\text{SiMe}_3)\text{Cl}$ (2.28 mmol) diluted in Et₂O (10 mL) was added dropwise, at -78°C , to a suspension of complex **8** (0.5 g, 0.57 mmol) in hexane (50 mL). The mixture was stirred overnight at room temperature. The resulting yellow solution was filtered and the residue was extracted with hexane (2×25 mL). The solvent was removed in vacuo to give 0.53 g of a yellow solid, which was identified as complex **17** (Yield: 86%). ^1H NMR (300 MHz, CDCl_3 , 25°C): $\delta = 0.04$ (s, 36 H, $4 \times \text{CH}_2\text{SiMe}_3$), -1.14 and 0.21 (2d, $^2J_{\text{H,H}} = 11.9$ Hz, each 4 H, $4 \times \text{CH}_2\text{SiMe}_3$), 1.97 (s, 30 H, $2 \times \text{C}_5\text{Me}_5$), 6.63 (s, 4 H, C_6H_4) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (75 MHz, CDCl_3 , 25°C): $\delta = 2.8$ (CH_2SiMe_3), 11.1 (C_5Me_5), 58.5 (CH_2SiMe_3), 115.6 (C_5Me_5) 125.1 and 151.7 (C^{ipso} ; C_6H_4) ppm. IR (CsI/Nujol): $\tilde{\nu} = 1489\text{s}$, 1332vs, 1241s, 1089m, 1024m, 962m, 850vs and 465m cm^{-1} . $\text{C}_{42}\text{H}_{78}\text{N}_2\text{Si}_4\text{Ta}_2$ (1085.3): calcd. C 46.48, H 7.24, N 2.58; found C 46.46, H 7.28, N 2.96.

Preparation of $[\{\text{Ta}(\eta^5\text{-C}_5\text{Me}_5)(\text{CH}_2\text{Ph})_2\}_2(\mu\text{-1,4-NC}_6\text{H}_4\text{N})]$ (18**):** A solution of $\text{Mg}(\text{CH}_2\text{Ph})_2(\text{THF})_2$ (0.4 g, 1.14 mmol) diluted in Et₂O (20 mL) was added dropwise, at -78°C , to a solution of complex **8** (0.5 g, 0.57 mmol) in Et₂O (30 mL). The mixture was stirred overnight at room temperature. The solvent was removed in vacuo and the resulting yellow residue was extracted with CH_2Cl_2 (2×15 mL). The filtrate was placed in a freezer at -40°C to afford 0.44 g of **18**, after 16 h, as a yellow crystalline solid. The product contained ca. 0.25 equivalents of residual CH_2Cl_2 (by ^1H NMR spectroscopy and elemental analysis). Yield: 68%. ^1H NMR (300 MHz, CDCl_3 , 25°C): $\delta = 1.35$ and 2.06 (2d, $^2J_{\text{H,H}} = 11.3$ Hz, each 4 H, $4 \times \text{CH}_2\text{Ph}$), 1.94 (s, 30 H, $2 \times \text{C}_5\text{Me}_5$), 6.40 (s, 4 H, C_6H_4), 6.90–7.10 (m, 20 H, $4 \times \text{CH}_2\text{Ph}$) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (75 MHz, CDCl_3 , 25°C): $\delta = 11.0$ (C_5Me_5), 67.5 (CH_2Ph), 115.3 (C_5Me_5) 124.7 and 151.2 (C^{ipso} ; C_6H_4), 123.2, 127.9, 129.7 and 144.6 (C^{ipso} ; CH_2Ph) ppm. IR (CsI/Nujol): $\tilde{\nu} = 1593\text{s}$, 1483vs, 1332vs, 1200m, 1024m, 835s, 742s and 452m cm^{-1} .

$C_{54}H_{62}N_2Ta_2 \cdot 0.25CH_2Cl_2$ (1122.2): calcd. C 58.06, H 5.61, N 2.50; found C 57.84, H 5.73, N 2.88.

Preparation of $[Nb(\eta^5-C_5H_4SiMe_3)CIME]_2(\mu-1,4-NC_6H_4N)$ (19**):** $ZnMe_2$ (1.13 mL, 2.26 mmol) was added at room temperature to a suspension of complex **1** (1.60 g, 2.26 mmol) in toluene (50 mL). The mixture was stirred for 12 h. The red solution was filtered and the residue extracted with toluene (3×20 mL). The extracts and the solution were combined. The solvent was removed to give a brown solid, which was identified as **19** (1.3 g; yield: 86%). 1H NMR (300 MHz, C_6D_6 , 25 °C, two isomers): δ = 0.16 (s, 36 H, $4 \times C_5H_4SiMe_3$), 1.34 and 1.35 (2s, each 6 H, $4 \times Nb-Me$), 5.69, 5.84, 5.85 and 6.17 (4m, each 4 H, $4 \times C_5H_4$), 6.93 (s, 8 H, $2 \times C_6H_4$) ppm. $^{13}C\{^1H\}$ NMR (75 MHz, C_6D_6 , 25 °C, two isomers): δ = -0.4 ($C_5H_4SiMe_3$), 38.8 (Nb-Me), 110.5, 110.6, 113.5, 113.6, 115.6, 115.7, 116.7 (C^{ipso}) and 116.8 (C^{ipso} ; $C_5H_4SiMe_3$), 124.7 and 154.1 (C^{ipso} ; C_6H_4) ppm. IR (CsI/Nujol): $\tilde{\nu}$ = 1595w, 1512w, 1310s, 1250s, 1171m, 1093m, 1045m, 1004w, 986m, 903m, 837vs, 757s, 631m, 523w, 477w, 419m and 377w cm^{-1} . $C_{24}H_{36}Cl_2N_2Nb_2Si_2$ (665.5): calcd. C 43.32, H 5.45, N 4.21; found C 43.00, H 5.26, N 3.93.

Preparation of $[Nb(\eta^5-C_5H_4SiMe_3)(NMe_2)Me]_2(\mu-1,4-NC_6H_4N)$ (20**):** Diethyl ether (50 mL) was added at -78 °C to a mixture of complex **19** (1.15 g, 1.73 mmol) and an excess of $LiNMe_2$ (0.19 g, 3.80 mmol). The mixture was allowed to warm up to room temperature and was stirred for 12 h. The solution was filtered and the residue was extracted with diethyl ether (2×20 mL). The extracts and the solution were combined. The solvent was removed and the residue was extracted with pentane (2×30 mL). The resulting solution was concentrated to dryness to give a dark brown oil, which was identified as **7** (1.05 g, Yield: 89%). 1H NMR (300 MHz, C_6D_6 , 25 °C, two isomers): δ = 0.16 (s, 36 H, $4 \times C_5H_4SiMe_3$), 0.72 (s, 12 H, $4 \times Nb-Me$), 3.28 (br., 24 H, $4 \times NMe_2$), 5.86, 5.92,

5.97 and 6.07 (4m, each 4 H, $4 \times C_5H_4$), 6.97 (s, 8 H, $2 \times C_6H_4$) ppm. $^{13}C\{^1H\}$ NMR (50 MHz, C_6D_6 , 25 °C, two isomers): δ = 0.2 ($C_5H_4SiMe_3$), 13.7 (Nb-Me), 53.3 (NMe_2), 113.2, 113.3, 113.4, 113.5 and 113.6 (C^{ipso} ; $C_5H_4SiMe_3$), 124.6 and 153.2 (C^{ipso} ; C_6H_4) ppm. IR (CsI/Nujol): $\tilde{\nu}$ = 1485s, 1419w, 1315s, 1249m, 1178w, 1090w, 1040m, 987w, 962m, 904w, 837vs, 802m, 756w, 632w, 543w, 489w, and 383w cm^{-1} . $C_{28}H_{48}N_4Nb_2Si_2$ (682.7): calcd. C 49.26, H 7.09, N 8.21; found C 48.68, H 6.71, N 7.32.

Preparation of $[Ta(\eta^5-C_5Me_5)CIME]_2(\mu-1,4-NC_6H_4N)$ (21**):** A solution of $ZnMe_2$ (1.26 mmol, 2 M in toluene) was added, at room temperature, to a suspension of complex **8** (0.55 g, 0.63 mmol) in toluene (50 mL). The mixture was stirred overnight at room temperature. The resulting yellow solution was filtered and the solvent was removed in vacuo to give 0.39 g of a yellow solid, which was identified as complex **21** (Yield: 75%). 1H NMR (300 MHz, C_6D_6 , 25 °C, two isomers): δ = 0.82 and 0.83 (2s, each 6 H, $4 \times Ta-Me$), 1.80 (s, 60 H, $4 \times C_5Me_5$), 6.91 (s, 8 H, $2 \times C_6H_4$) ppm. $^{13}C\{^1H\}$ NMR (75 MHz, C_6D_6 , 25 °C, two isomers): δ = 10.8 (C_5Me_5), 41.2 and 41.3 (Ta-Me), 118.1 (C_5Me_5) 125.6 and 152.1 (C^{ipso} ; C_6H_4) ppm. IR (CsI/Nujol): $\tilde{\nu}$ = 1491s, 1335vs, 1088m, 1026m, 994m, 837s and 491m cm^{-1} . $C_{28}H_{40}Cl_2N_2Ta_2$ (837.4): calcd. C 40.16, H 4.81, N 3.35; found C 40.05, H 4.68, N 3.16.

X-ray Structure Determinations for $[M(Cp)Cl_2]_2(\mu-1,4-NC_6H_4N)$ [$M = Nb$, $Cp = \eta^5-C_5H_4SiMe_3$ (1**); $M = Ta$, $Cp = \eta^5-C_5Me_5$ (**8**)] and $[M(Cp)(CH_2R)]_2(\mu-1,4-NC_6H_4N)$ [$M = Ta$, $Cp = \eta^5-C_5Me_5$, $R = SiMe_3$ (**17**)]:** Intensity data for compounds **1** and **17** were collected on a Nonius-Mach3 diffractometer equipped with a graphite monochromator (Mo- K_α radiation, λ = 0.71073 Å) using an $\omega/2\theta$ scan technique. In the case of **1** the specimen diffracted only weakly. The final unit-cell parameters were determined from 25 well-centred reflections and refined by the least-squares method. The space group was determined from the systematic absences and

Table 4. Crystal data and structure refinement for **1**, **8** and **17**

	1	8	17
Formula	$C_{22}H_{30}Cl_4N_2Nb_2Si_2$	$C_{26}H_{34}Cl_4N_2Ta_2$	$C_{42}H_{78}N_2Si_4Ta_2$
Mol. mass	706.28	878.25	1085.32
<i>T</i> (K)	293(2)	110(1)	250(2)
Cryst. syst.	orthorhombic	monoclinic	triclinic
Space group	<i>Pbca</i>	<i>P2₁/a</i>	<i>P</i> $\bar{1}$
<i>a</i> (Å)	13.331(1)	13.269(1)	9.617(1)
<i>b</i> (Å)	12.547(1)	8.5840(1)	10.547(1)
<i>c</i> (Å)	17.796(1)	13.802(1)	14.943(1)
β (deg)		100.33(1)	72.84(1)
<i>V</i> (Å ³)	2976.6(4)	1546.6(2)	1301.0(2)
<i>Z</i>	4	2	1
<i>D_c</i> (g cm ⁻³)	1.576	1.886	1.385
μ (mm ⁻¹)	1.223	7.432	4.321
<i>F</i> (000)	1416	836	546
Crystal dimensions (mm)	0.3 × 0.2 × 0.2	0.40 × 0.18 × 0.15	0.3 × 0.3 × 0.4
θ range (deg)	2.29 to 27.95	3.08 to 27.53	2.15 to 28.00
<i>hkl</i> ranges	-17 ≤ <i>h</i> ≤ 0 0 ≤ <i>k</i> ≤ 16 0 ≤ <i>l</i> ≤ 23	-13 ≤ <i>h</i> ≤ 17 -10 ≤ <i>k</i> ≤ 11 -17 ≤ <i>l</i> ≤ 17	-12 ≤ <i>h</i> ≤ 12 -13 ≤ <i>k</i> ≤ 13 0 ≤ <i>l</i> ≤ 19
Data/parameters	3577/142	3454/154	6505/226
Goodness-of-fit on <i>F</i> ²	1.135	1.233	1.129
Final <i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)] ^[a]	<i>R</i> ₁ = 0.0746 <i>wR</i> ₂ = 0.1800	<i>R</i> ₁ = 0.0345 <i>wR</i> ₂ = 0.0792	<i>R</i> ₁ = 0.0461 <i>wR</i> ₂ = 0.1508
Largest diff. peak (e ⁻ Å ⁻³)	0.827/-0.650	0.850/-0.881	2.494/-2.221

^[a] $R_1 = \Sigma(F_o - F_c)/\Sigma(F_o)$; $wR_2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{0.5}$

this was vindicated by the success of the subsequent solutions and refinements. Empirical absorption correction was performed for compound **17**. Intensities for **8** were measured on a Nonius-Kap-paCCD diffractometer at low temperature and treated with Scal-pack and DENZO routines.^[27] The crystal data and details of data collection and structure analyses are summarised in Table 4.

All structures were solved by direct methods using the SHELXS computer program^[28] and refined in F^2 by a full-matrix least-squares procedure (SHELXL-97).^[29] All non-hydrogen atoms were refined with anisotropic thermal parameters for all compounds. The hydrogen atoms were included in calculated positions and were refined with an overall isotropic temperature factor using a riding model. Weights were optimised in the final cycles.

CCDC-205739 (for **1**), -205740 (for **8**) and -205742 (for **17**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: (internat.) + 44-1223/336-0333; E-mail: deposit@ccdc.cam.ac.uk].

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- [1] D. E. Wigley, *Prog. Inorg. Chem.* **1994**, *42*, 239–482.
- [2] See for example: [2a] V. C. Gibson, D. N. Williams, W. Clegg, D. C. R. Hockless, *Polyhedron* **1989**, *8*, 1819–1820. [2b] U. Siemeling, V. C. Gibson, *J. Organomet. Chem.* **1992**, *426*, C25–C27. [2c] V. C. Gibson, A. D. Poole, U. Siemeling, D. N. Williams, W. Clegg, D. C. R. Hockless, *J. Organomet. Chem.* **1993**, *462*, C12–C14. [2d] T. C. Baldwin, S. R. Huber, M. A. Bruck, D. E. Wigley, *Inorg. Chem.* **1993**, *32*, 5682–5686. [2e] A. D. Poole, V. C. Gibson, W. Clegg, *J. Chem. Soc., Chem. Commun.* **1992**, 237–239. [2f] J. K. Cockcroft, V. C. Gibson, J. A. K. Howard, A. D. Poole, U. Siemeling, C. Wilson, *J. Chem. Soc., Chem. Commun.* **1992**, 1668–1670. [2g] M. C. W. Chan, J. M. Cole, V. C. Gibson, J. A. K. Howard, C. Lehmann, A. D. Poole, U. Siemeling, *J. Chem. Soc., Dalton Trans.* **1998**, 103–112. [2h] M. L. H. Green, J. T. James, J. F. Saunders, J. Souter, *J. Chem. Soc., Dalton Trans.* **1997**, 1281–1288.
- [3] See for example: [3a] D. N. Williams, J. P. Mitchell, A. D. Poole, U. Siemeling, W. Clegg, D. C. R. Hockless, P. A. O’Neil, V. C. Gibson, *J. Chem. Soc., Dalton Trans.* **1992**, 739–751. [3b] V. C. Gibson, *Angew. Chem.* **1994**, *106*, 1640–1648; *Angew. Chem. Int. Ed. Engl.* **1994**, *33*, 1565–1573. [3c] V. C. Gibson, *J. Chem. Soc., Dalton Trans.* **1994**, 1607–1618. [3d] V. C. Gibson, A. D. Poole, *J. Chem. Soc., Chem. Commun.* **1995**, 2261–2262.
- [4] [4a] M. P. Coles, V. C. Gibson, *Polym. Bull.* **1994**, *33*, 529–533. [4b] S. Scheuer, J. Fischer, J. Kress, *Organometallics* **1995**, *14*, 2627–2629. [4c] D. M. Antonelli, A. Leins, J. M. Stryker, *Organometallics* **1997**, *16*, 2500–2502. [4d] M. C. W. Chan, K. C. Chew, C. I. Dalby, V. C. Gibson, A. Kohlmann, I. R. Little, W. Reed, *Chem. Commun.* **1998**, 1673–1674.
- [5] See for example: [5a] S. Schmidt, J. Sundermeyer, *J. Organomet. Chem.* **1994**, *472*, 127–138. [5b] Y.-W. Chao, P. A. Wexler, D. E. Wigley, *Inorg. Chem.* **1990**, *29*, 4592–4594. [5c] A. Antiñolo, M. Fajardo, C. Huertas, A. Otero, S. Prashar, A. M. Rodríguez, *J. Organomet. Chem.* **1999**, *585*, 154–161.
- [6] See for example: [6a] M. L. H. Green, J. T. James, J. F. Saunders, *Chem. Commun.* **1996**, 1343–1344. [6b] M. I. Alcalde, P. Gómez-Sal, A. Martín, P. Royo, *Organometallics* **1999**, *18*, 1144–1150.
- [7] See for example: [7a] A. Castro, M. V. Galakhov, M. Gómez, F. Sánchez, *J. Organomet. Chem.* **1999**, *580*, 161–168. [7b] T. I. Gountchev, T. D. Tilley, *J. Am. Chem. Soc.* **1997**, *119*, 12831–12841.
- [8] [8a] I. Dorado, A. Garcés, C. López-Mardomingo, M. Fajardo, A. Rodríguez, A. Antiñolo, A. Otero, *J. Chem. Soc., Dalton Trans.* **2000**, 2375–2382. [8b] I. Dorado, A. Garcés, C. López-Mardomingo, M. Fajardo, M. Kubicki, A. Antiñolo, A. Otero, *Dalton Trans.* **2003**, 910–917.
- [9] A. Antiñolo, M. Fajardo, A. Otero, S. Prashar, *Eur. J. Inorg. Chem.* **2003**, 17–28.
- [10] See for example: [10a] E. A. Maatta, D. D. Devore, *Angew. Chem.* **1988**, *100*, 583–585; *Angew. Chem. Int. Ed. Engl.* **1988**, *27*, 569–571. [10b] E. A. Maatta, C. Kim, *Inorg. Chem.* **1989**, *28*, 623–624. [10c] R. K. Rosen, R. A. Andresen, N. M. Edelstein, *J. Am. Chem. Soc.* **1990**, *112*, 4588–4590. [10d] G. Hogarth, R. L. Mallors, T. Norman, *J. Chem. Soc., Chem. Commun.* **1993**, 1721–1723. [10e] W. Clegg, R. J. Errington, D. C. R. Hockless, J. M. Kirk, C. Redshaw, *Polyhedron* **1992**, *11*, 381–384. [10f] D. E. Wheeler, J.-F. Wu, E. A. Maatta, *Polyhedron* **1998**, *17*, 969–976. [10g] M. Liangand, E. A. Maatta, *Inorg. Chem.* **1992**, *31*, 953–956. [10h] G. Hogarth, D. E. Humphry, N. Kaltsoyanis, W.-F. Kim, M. Lee, T. Norman, S. P. Redmond, *J. Chem. Soc., Dalton Trans.* **1999**, 2705–2723.
- [11] [11a] D. M. Antonelli, M. L. H. Green, P. Mountford, *J. Organomet. Chem.* **1992**, *438*, C4–C8. [11b] P. T. Gomes, M. L. H. Green, A. M. Martín, P. Mountford, *J. Organomet. Chem.* **1997**, *541*, 121–125.
- [12] [12a] D. D. Devore, J. D. Lichtenhan, F. Takusayawa, E. A. Maatta, *J. Am. Chem. Soc.* **1987**, *109*, 7408–7416. [12b] E. A. Maatta, *Inorg. Chem.* **1984**, *23*, 2560–2561.
- [13] A. Antiñolo, I. López-Solera, A. Otero, S. Prashar, *J. Organomet. Chem.* **2001**, *631*, 151–164.
- [14] P. Jernakoff, C. M. Bellef, G. L. Geoffroy, A. L. Rheingold, S. J. Geib, *Organometallics* **1987**, *6*, 1362–1364.
- [15] [15a] A. V. Korolov, A. L. Rheingold, D. S. William, *Inorg. Chem.* **1997**, *36*, 2647–2655. [15b] K. S. Heinselman, V. M. Mis-kowski, S. J. Geib, L. C. Wang, M. D. Hopkins, *Inorg. Chem.* **1997**, *36*, 5530–5538.
- [16] M. V. Galakhov, M. Gómez, G. Jiménez, M. A. Pellinghelli, P. Royo, A. Tiripicchio, *Organometallics* **1994**, *13*, 1564–1566.
- [17] [17a] M. J. Humphries, M. L. H. Green, M. A. Leech, V. C. Gibson, M. Jolly, D. N. Williams, M. R. J. Elsegood, W. Clegg, *J. Chem. Soc., Dalton Trans.* **2000**, 4044–4051. [17b] M. J. Humphries, M. L. H. Green, R. E. Douthwaite, L. H. Rees, *J. Chem. Soc., Dalton Trans.* **2000**, 4555–4562. [17c] A. D. Poole, D. N. Williams, A. M. Kenwright, V. C. Gibson, W. Clegg, D. C. R. Hockless, P. A. O’Neil, *Organometallics* **1993**, *12*, 2549–2555. [17d] U. Burckhardt, T. D. Tilley, *J. Am. Chem. Soc.* **1999**, *121*, 6328–6329. [17e] G. I. Nikonov, P. Mountford, J. C. Green, P. A. Cooke, M. A. Leech, A. J. Blake, J. A. K. Howard, D. A. Lemenovskii, *Eur. J. Inorg. Chem.* **2000**, 1917–1921.
- [18] A. Antiñolo, P. Espinosa, M. Fajardo, P. Gómez-Sal, C. López-Mardomingo, A. Martín-Alonso, A. Otero, *J. Chem. Soc., Dalton Trans.* **1995**, 1007–1013.
- [19] H. Bock, J. Meuret, C. Näther, U. Krynitz, *Chem. Ber.* **1994**, *127*, 55–65.
- [20] A. M. Andreu, F. A. Jalón, A. Otero, P. Royo, A. M. M. Lan-franchi, A. Tiripicchio, *J. Chem. Soc., Dalton Trans.* **1987**, 953–956.
- [21] E. W. Abel, M. O. Dunster, *J. Organomet. Chem.* **1971**, *33*, 161–167.
- [22] M. J. Bunker, A. DeCian, M. L. H. Green, J. J. E. Moreau, N. Sigantoria, *J. Chem. Soc., Dalton Trans.* **1980**, 2155–2161.
- [23] R. D. Sanner, S. T. Carter, W. J. Bruton, *J. Organomet. Chem.* **1982**, *240*, 157–162.
- [24] G. Hidalgo, M. Mena, F. Palacios, P. Royo, R. Serrano, *J. Organomet. Chem.* **1988**, *340*, 37–40.

- [25] [25a] H. Yasuda, T. Okamoto, A. Nakamura, in *Organometallic Syntheses* (Eds.: R. B. King, J. J. Eisch), Elsevier, Amsterdam, **1988**, vol. 4, p. 40. [25b] J. de la Mata, R. Fandos, M. Gómez, P. Gómez-Sal, S. Martínez-Carrera, P. Royo, *Organometallics* **1990**, 9, 2846–2850.
- [26] R. R. Schrock, *J. Organomet. Chem.* **1976**, 122, 209–225.
- [27] Z. Otwinowski, W. Minor, *Methods Enzymol.* **1997**, 276, 307–326.
- [28] G. M. Sheldrick, *Acta Crystallogr., Sect. A* **1990**, 46, 467–473.
- [29] G. M. Sheldrick, *Program for the Refinement of Crystal Structures from Diffraction Data*, University of Göttingen, Göttingen, Germany, **1997**.

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