Isocyanide insertion reactivity of dinuclear niobium and tantalum imido complexes: X-ray crystal structure of [{Nb(η^5-C$_5$H$_4$SiMe$_3$)(CH$_2$Ph)$_2$}$_2$(μ-1,4-NC$_6$H$_4$N)]

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Abstract

The reactivity of dinuclear niobium and tantalum imido complexes with the isocyanide compound 2,6-Me$_2$C$_6$H$_3$NC has been studied. The trialkyl complexes [{NbR$_3$(CH$_3$CN)}$_2$(μ-1,3-NC$_6$H$_4$N)], [{NbR$_3$(CH$_3$CN)}$_2$(μ-1,4-NC$_6$H$_4$N)] and [{TaR$_3$(CH$_3$CN)}$_2$-(μ-1,4-NC$_6$H$_4$N)] (R = CH$_2$SiMe$_3$) gave [{Nb(η^2-RC=NAr)$_2$R}$_2$(μ-1,3-NC$_6$H$_4$N)] (1), [{Nb(η^2-RC=NAr)$_2$R}$_2$(μ-1,4-NC$_6$H$_4$N)] (2) and [{Ta(η^2-RC=NAr)$_2$R}$_2$(μ-1,4-NC$_6$H$_4$N)] (3) (R = CH$_2$SiMe$_3$; Ar = 2,6-Me$_2$C$_6$H$_3$), from the isocyanide insertion in two of the metal alkyl carbon bonds. The reaction of the isocyanide reagent with the di-alkyl mono-cyclopentadienyl derivatives [{Nb(η^5-C$_5$H$_4$SiMe$_3$)R$_2$}$_2$(μ-1,3-NC$_6$H$_4$N)] (R = Me, CH$_2$Ph, CH$_2$SiMe$_3$), [{Nb(η^5-C$_5$H$_4$SiMe$_3$)R$_2$}$_2$(μ-1,4-NC$_6$H$_4$N)] (R = Me, CH$_2$Ph (4), CH$_2$SiMe$_3$) and [{Ta(η^5-C$_5$Me$_5$)(CH$_2$SiMe$_3$)$_2$}$_2$(μ-1,4-NC$_6$H$_4$N)] yielded [{Nb(η^5-C$_5$H$_4$SiMe$_3$)(η^2-RC=NAr)R}$_2$(μ-1,3-NC$_6$H$_4$N)] (R = Me (5), CH$_2$Ph (6), CH$_2$SiMe$_3$ (7)), [{Nb(η^5-C$_5$H$_4$SiMe$_3$)(η^2-RC=NAr)R}$_2$(μ-1,4-NC$_6$H$_4$N)] (R = Me (8), CH$_2$Ph (9), CH$_2$SiMe$_3$ (10)) and [{Ta(η^5-C$_5$Me$_5$)(η^2-Me$_3$SiCH$_2$C=NAr)CH$_2$SiMe$_3$}$_2$(μ-1,4-NC$_6$H$_4$N)] (11) (Ar = 2,6-Me$_2$C$_6$H$_3$), respectively, from a single insertion process. The reaction with the mono-alkyl complex [{Nb(η^5-C$_5$H$_4$SiMe$_3$)(Me)Cl}$_2$(μ-1,4-NC$_6$H$_4$N)] gave [{Nb(η^5-C$_5$H$_4$SiMe$_3$)(η^2-MeC=NAr)Cl}$_2$(μ-1,4-NC$_6$H$_4$N)] (12), produced from the isocyanide insertion in the metal-alkyl carbon bond. The alkyl-amido complex [{Nb(η^5-C$_5$H$_4$SiMe$_3$)(Me)NMe$_2$}$_2$(μ-1,4-NC$_6$H$_4$N)] gave, from the preferential isocyanide insertion in the metal-amide nitrogen bond, [{Nb(η^5-C$_5$H$_4$SiMe$_3$)(η^2-Me$_2$NC=NAr)Me}$_2$(μ-1,4-NC$_6$H$_4$N)] (13). The molecular structure of one of the alkyl precursors, [{Nb(η^5-C$_5$H$_4$SiMe$_3$)(CH$_2$Ph)$_2$}$_2$(μ-1,4-NC$_6$H$_4$N)] (4), has been determined.
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1. Introduction

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

The use of imido groups in the organometallic chemistry of group 5 elements is widespread [3]. A re-view of our contribution to this field has recently been published [4]. Part of our research work has been fo-cussed on the incorporation of di-imido ligands that bridge two metal centres and we have previously

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Table 1
¹H NMR data for **1–3** and **5–13**[a,b]

Compound	M–R	NC–R	$Me_2C_6H_3$	NC_6H_4N, $Me_2C_6H_3$ and Ph	Cp
[{Nb(η²-Me₃SiCH₂-C=NAr)₂CH₂SiMe₃}₂(μ-1,3-NC₆H₄N)] (**1**)	0.26 (s, 18H, CH₂SiMe₃), 0.69 (s, 4H, CH₂SiMe₃)	0.07 (s, 36H, CH₂SiMe₃), 2.77 (4H), 2.86 (4H) (d, CH₂SiMe₃) ²J(¹H–¹H) 10.1 Hz	1.91 (s, 12H), 2.42 (s, 12H)	6.59 (m, 3H, NC₆H₄N), 6.95–7.07 (m, 13H, NC₆H₄N and Me₂C₆H₃)	
[{Nb(η²-Me₃SiCH₂-C=NAr)₂CH₂SiMe₃}₂(μ-1,4-NC₆H₄N)] (**2**)	0.25 (s, 18H, CH₂SiMe₃), 0.57 (s, 4H, CH₂SiMe₃)	0.03 (s, 36H, CH₂SiMe₃), 2.71 (4H), 2.79 (4H) (d, CH₂SiMe₃) ²J(¹H–¹H) 10.4 Hz	1.86 (s, 12H), 2.32 (s, 12H)	6.92–6.97 (m, 16H, NC₆H₄N and Me₂C₆H₃)	
[{Ta(η²-Me₃SiCH₂-C=NAr)₂CH₂SiMe₃}₂(μ-1,4-NC₆H₄N)] (**3**)	0.24 (s, 18H, CH₂SiMe₃), 0.32 (s, 4H, CH₂SiMe₃)	0.02 (s, 36H, CH₂SiMe₃), 2.82 (4H), 3.84 (4H) (d, CH₂SiMe₃) ²J(¹H–¹H) 10.0 Hz	1.89 (s, 12H), 2.33 (s, 12H)	6.80–7.00 (m, 16H, NC₆H₄N and Me₂C₆H₃)	
[{Nb(η⁵-C₅H₄SiMe₃)(η²-MeC=NAr)Me}₂(μ-1,3-NC₆H₄N)] (**5**)	0.88 (s, 12H, Me)*	1.94 (6H), 1.97 (6H) (s, Me)	1.59 (s, 12H)*, 2.15 (s, 12H)*	6.54 (m, 6H, NC₆H₄N)*, 6.88–6.94 (m, 14H, NC₆H₄N and Me₂C₆H₃)	0.35 (18H), 0.36 (18H) (s, C₅H₄SiMe₃), 5.57 (4H), 5.88 (4H), 6.03 (4H), 6.27 (4H) (m, C₅H₄)*
[{Nb(η⁵-C₅H₄SiMe₃)(η²-PhCH₂C=NAr)CH₂Ph}₂(μ-1,3-NC₆H₄N)] (**6**)	3.07 (4H), 3.33 (4H) (d, CH₂Ph)* ²J(¹H–¹H) 10.1 Hz	3.65 (4H), 3.77 (4H) (d, CH₂Ph)* ²J(¹H–¹H) 15.7 Hz	1.65 (s, 6H), 1.66 (s, 6H), 1.78 (s, 6H), 1.81 (s, 6H)	6.47–7.26 (m, 60H, NC₆H₄N, Me₂C₆H₃, ArNCCH₂Ph and Nb–CH₂Ph)*	0.23 (18H), 0.26 (18H) (s, C₅H₄SiMe₃), 5.38 (4H)*, 5.56 (2H), 5.59 (2H), 6.06 (4H)*, 6.07 (4H)* (m, C₅H₄)
[{Nb(η⁵-C₅H₄SiMe₃)(η²-Me₃SiCH₂C=NAr)CH₂SiMe₃}₂(μ-1,3-NC₆H₄N)] (**7**)	0.26 (18H), 0.28 (18H) (s, CH₂SiMe₃), 0.63 (2H), 0.64 (2H), 0.86 (2H), 0.88 (2H) (d, CH₂SiMe₃) ²J(¹H–¹H) 12.4 Hz	0.00 (18H), 0.01 (18H) (s, CH₂SiMe₃), 2.43 (2H), 2.44 (2H), 2.55 (2H), 2.57 (2H) (d, CH₂SiMe₃) ²J(¹H–¹H) 10.8 Hz	1.71 (s, 6H), 1.72 (s, 6H), 2.49 (s, 6H), 2.51 (s, 6H)	6.55–6.98 (m, 20H, NC₆H₄N and Me₂C₆H₃)*	0.24 (18H), 0.25 (18H) (s, C₅H₄SiMe₃), 5.97 (4H), 6.17 (4H), 6.44 (4H), 6.52 (4H) (m, C₅H₄)*
[{Nb(η⁵-C₅H₄SiMe₃)(η²-MeC=NAr)Me}₂(μ-1,4-NC₆H₄N)] (**8**)	0.87 (s, 12H, Me)*	1.89 (6H), 1.90 (6H) (s, Me)	1.59 (s, 12H)*, 2.10 (s, 12H)*	6.82–6.91 (m, 12H, Me₂C₆H₃)*, 6.79 (4H), 6.80 (4H) (s, NC₆H₄N)	0.31 (18H), 0.32 (18H) (s, C₅H₄SiMe₃), 5.55 (4H), 5.85 (4H), 6.01 (4H), 6.23 (4H) (m, C₅H₄)*
[{Nb(η⁵-C₅H₄SiMe₃)(η²-PhCH₂C=NAr)CH₂Ph}₂(μ-1,4-NC₆H₄N)] (**9**)	3.02 (4H), 3.29 (4H) (d, CH₂Ph)* ²J(¹H–¹H) 10.1 Hz	3.58 (4H), 3.69 (4H) (d, CH₂Ph)* ²J(¹H–¹H) 15.7 Hz	1.65 (s, 6H), 1.66 (s, 6H), 1.69 (s, 6H), 1.70 (s, 6H)	6.69–7.26 (m, 52H, Me₂C₆H₃, ArNCCH₂Ph and Nb–CH₂Ph)*, 6.73 (4H), 6.74 (4H) (s, NC₆H₄N)	0.20 (18H), 0.21 (18H) (s, C₅H₄SiMe₃), 5.37 (4H), 5.62 (4H), 6.01 (4H), 6.02 (4H) (m, C₅H₄)*
[{Nb(η⁵-C₅H₄SiMe₃)(η²-Me₃SiCH₂C=NAr)CH₂SiMe₃}₂(μ-1,4-NC₆H₄N)] (**10**)	0.26 (18H), 0.27 (18H) (s, CH₂SiMe₃), 0.60 (2H), 0.61 (2H), 0.83 (2H), 0.84 (2H) (d, CH₂SiMe₃) ²J(¹H–¹H) 12.4 Hz	−0.05 (18H), −0.04 (18H) (s, CH₂SiMe₃), 2.40 (2H), 2.41 (2H), 2.50 (2H), 2.51 (2H) (d, ArNCCH₂SiMe₃) ²J(¹H–¹H) 10.8 Hz	1.70 (s, 6H), 1.71 (s, 6H), 2.31 (s, 6H), 2.33 (s, 6H)	6.86–6.92 (m, 12H, Me₂C₆H₃)*, 6.85 (s, 8H, NC₆H₄N)*	0.20 (18H), 0.21 (18H) (s, C₅H₄SiMe₃), 5.91 (4H), 5.95 (4H), 6.35 (4H), 6.48 (4H) (m, C₅H₄)*
[{Ta(η⁵-C₅Me₅)(η²-Me₃SiCH₂C=NAr)CH₂SiMe₃}₂(μ-1,4-NC₆H₄N)] (**11**)	0.37 (18H), 0.38 (18H) (s,CH₂SiMe₃), −0.30 (4H), 0.18 (4H) (d, Ta-CH₂SiMe₃)* ²J(¹H–¹H) 14.0 Hz	0.00 (18H), 0.01 (18H) (s, CH₂SiMe₃), 2.12 (4H), 2.63 (4H) (d, CH₂SiMe₃)* ²J(¹H–¹H) 10.8 Hz	1.70 (s, 12H)*, 2.34 (s, 12H)*	6.85–6.91 (m, 12H, Me₂C₆H₃)*, 6.95 (4H), 6.96 (4H) (s, NC₆H₄N)	1.96 (30H), 1.97 (30H) (s, C₅Me₅)

Table 1 (*continued*)

Compound	M–R	NC–R	Me₂C₆H₃	NC₆H₄N, Me₂C₆H₃ and Ph	Cp
[{Nb(η⁵-C₅H₄SiMe₃)(η²-MeC=NAr)Cl}₂(μ-1,4-NC₆H₄N)] (12)		1.73 (s, 12H, *Me*)*	2.01 (s, 6H), 2.02 (s, 6H), 2.03 (s, 6H), 2.04 (s, 6H)	6.81–6.90 (m, 12H, Me₂C₆*H₃*)*, 6.78 (4H), 6.79 (4H) (s, NC₆*H₄*N)	0.37 (18H), 0.39 (18H) (s, C₅H₄Si*Me₃*), 5.62 (4H), 6.05 (4H), 6.38 (4H), 6.41 (4H) (m, C₅*H₄*)*
[{Nb(η⁵-C₅H₄SiMe₃)(η²-Me₂NC=NAr)Me}₂(μ-1,4-NC₆H₄N)] (13)	0.73 (s, 12H, *Me*)*	1.94 (6H), 1.96 (6H), 2.80 (6H), 2.82 (6H) (s, N*Me₂*)	1.86 (s, 12H)*, 2.16 (s, 12H)*	6.86–6.94 (m, 12H, Me₂C₆*H₃*)*, 6.82 (4H), 6.83 (4H) (s, NC₆*H₄*N)	0.33 (18H), 0.35 (18H) (s, C₅H₄Si*Me₃*), 5.54 (4H), 5.99 (4H), 6.22 (4H), 6.41 (4H) (m, C₅*H₄*)*

[a] 300 MHz, C₆D₆, chemical shifts in δ.

[b] * indicates that the signals for the two diastereoisomers coincide.

reported the preparation of metallocene, monocyclopentadienyl, alkyl, hydride and benzamidinate derivatives [5]. Following from this we now report our studies into the reactivity of various di-imido group 5 complexes towards isocyanide insertion processes in order to synthesize new types of dinuclear niobium and tantalum imido complexes linked by conjugated π systems.

2. Results and discussion

The migratory insertion of alkyl groups towards isocyanide ligands allow the introduction of iminoacyl groups which are present in different coordination modes. For high valent oxophilic early transition metals, the iminoacyl group typically adopts an η²-coordination mode through both the nitrogen and carbon atoms [6]. Similarly an η²-coordination mode is proposed for the iminoacyl ligand in **1–3** and **5–13** on the basis of IR and ¹³C NMR spectroscopy which show the characteristic stretching vibration ν(C=N) at ca. 1600 cm⁻¹ and iminoacyl quaternary carbon atom signal at ca. δ 250, respectively [6,7].

The reaction of the trialkyl dinuclear bis imido complexes, [{Nb(CH₂SiMe₃)₃(CH₃CN)}₂(μ-1,3-NC₆H₄N)], [{Nb(CH₂SiMe₃)₃(CH₃CN)}₂(μ-1,4-NC₆H₄N)] and [{Ta(CH₂SiMe₃)₃(CH₃CN)}₂(μ-1,4-NC₆H₄N)] with the isocyanide reagent, 2,6-C₆H₃Me₂NC, gave the products, [{Nb(η²-Me₃SiCH₂C=NAr)₂CH₂SiMe₃}₂(μ-1,3-NC₆H₄N)] (**1**), [{Nb(η²-Me₃SiCH₂C=NAr)₂CH₂SiMe₃}₂(μ-1,4-NC₆H₄N)] (**2**) and [{Ta(η²-Me₃SiCH₂C=NAr)₂CH₂SiMe₃}₂(μ-1,4-NC₆H₄N)] (**3**) (Ar = 2,6-Me₂C₆H₃), respectively (Eq. (1)). The final products originate from the insertion of the isocyanide molecules into two of the niobium carbon σ-bonds. There was no evidence for the formation of the single insertion product even when the stoichiometry was adjusted to favour this, i.e. when the reaction was carried out in deficiency of the isocyanide reagent.

1–3 were characterized by IR and NMR spectroscopy. In addition to the band assigned to the imido group (Nb=N) at ca. 1330 cm⁻¹, a band was observed for the C=N of the η²-iminoacyl group at ca. 1570 cm⁻¹ in the IR spectra. The ¹H NMR spectra (Table 1) showed an AB spin system for the diastereoscopic methylene protons of the inserted alkyl at ca. δ 2.7 and a singlet for the methylene group of the uninserted alkyl groups at ca. δ 0.6. The ¹³C NMR spectra (Table 2) showed a downfield shift of the signals corresponding to the methylene carbons of the inserted alkyl groups (ca. δ 30) with respect to the methylene carbon of the uninserted alkyl moiety (ca. δ 22). In addition the iminoacyl quaternary carbon atom signal was observed at ca. δ 240 in agreement with the data previously reported for η²-iminoacyl systems [7].

R = CH₂SiMe₃
Ar = 2,6-Me₂C₆H₃

M = Nb; 1,3-NC₆H₄N (**1**)
M = Nb; 1,4-NC₆H₄N (**2**)
M = Ta; 1,4-NC₆H₄N (**3**)
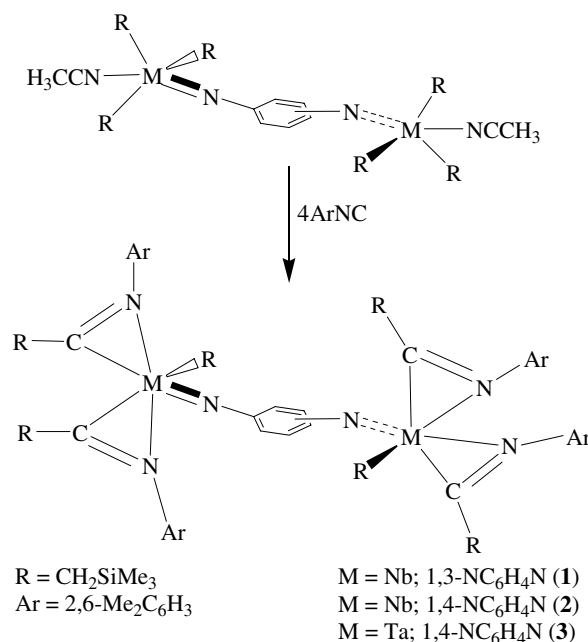
(1)

Table 2
$^{13}C\{^{1}H\}$NMR data for **1–3** and **5–13**[a,b]

Compound	M–R	NC–R	$Me_2C_6H_3$,	NC_6H_4N	$Me_2C_6H_3$ and Ph	Cp	CN
[{Nb(η^2-Me$_3$SiCH$_2$C=NAr)$_2$CH$_2$SiMe$_3$}$_2$(μ-1,3-NC$_6$H$_4$N)] (**1**)	3.9 (CH$_2$SiMe_3), 22.0 (CH$_2$SiMe$_3$)	0.0 (CH$_2$SiMe_3), 32.2 (CH$_2$SiMe$_3$)	19.1, 19.5	117.9, 119.0, 127.1, 158.1 (ipso-C)	126.2, 128.4, 128.9, 129.0, 131.1, 144.9 (Me$_2$C$_6$H$_3$)		239.4
[{Nb(η^2-Me$_3$SiCH$_2$C=NAr)$_2$CH$_2$SiMe$_3$}$_2$(μ-1,4-NC$_6$H$_4$N)] (**2**)	3.7 (CH$_2$SiMe_3), 21.9 (CH$_2$SiMe$_3$)	−0.2 (CH$_2$SiMe_3), 32.1 (CH$_2$SiMe$_3$)	19.0, 19.1	124.0, 153.1 (ipso-C)	126.1, 128.9, 129.0, 131.0, 144.9, 153.1 (Me$_2$C$_6$H$_3$)		239.6
[{Ta(η^2-Me$_3$SiCH$_2$C=NAr)$_2$CH$_2$SiMe$_3$}$_2$(μ-1,4-NC$_6$H$_4$N)] (**3**)	3.8 (CH$_2$SiMe_3), 27.0 (CH$_2$SiMe$_3$)	−0.2 (CH$_2$SiMe_3), 32.6 (CH$_2$SiMe$_3$)	18.9, 19.0	124.2, 154.3 (ipso-C)	126.3, 128.3, 128.9, 129.0, 131.2, 144.4 (Me$_2$C$_6$H$_3$)		252.1
[{Nb(η^5-C$_5$H$_4$SiMe$_3$)(η^2-MeC=NAr)Me}$_2$(μ-1,3-NC$_6$H$_4$N)] (**5**)	9.2 (*Me*)*	22.9 (*Me*)*	17.8*, 18.0*	118.2, 118.3, 119.1, 119.2, 128.0, 128.1, 157.6 (ipso-C), 157.7 (ipso-C)	126.1, 127.9, 128.6, 129.4, 130.8, 141.5 (Me$_2$C$_6$H$_3$)*	0.5 (C$_5$H$_4$SiMe_3)*, 111.6, 111.7, 114.3, 114.5, 118.3 (ipso-C) (C$_5$H$_5$)*	229.0*
[{Nb(η^5-C$_5$H$_4$SiMe$_3$)(η^2-PhCH$_2$C=NAr)CH$_2$Ph}$_2$(μ-1,3-NC$_6$H$_4$N)] (**6**)	39.3 (CH$_2$Ph)*	43.2 (CH$_2$Ph)*	18.2*, 18.4*	118.6, 118.7, 119.7, 119.8, 128.0, 128.1, 157.5 (ipso-C), 157.6 (ipso-C)	121.1(*), 126.3(*), 127.3(*), 127.8(*), 128.3(*), 128.9(*), 129.0(*), 129.7(*), 130.0(*), 131.1(*), 135.7, 135.8, 141.2, 141.3, 154.0(*) (Me$_2$C$_6$H$_3$ ArNCC$_2$Ph and Nb–C$_2$Ph)	0.5 (C$_5$H$_4$SiMe_3)* 108.0, 108.1, 110.2, 110.3, 114.1, 114.3, 115.0 (ipso-C), 115.1 (ipso-C), 115.4, 115.7 (C$_5$H$_5$)	230.8*
[{Nb(η^5-C$_5$H$_4$SiMe$_3$)(η^2-Me$_3$SiCH$_2$C=NAr)CH$_2$SiMe$_3$}$_2$(μ-1,3-NC$_6$H$_4$N)] (**7**)	3.8 (CH$_2$SiMe_3)*, 13.6 (CH$_2$SiMe$_3$)*	−0.2 (CH$_2$SiMe_3)*, 32.0 (CH$_2$SiMe$_3$)*	19.0*, 19.3*	117.7, 177.8, 118.6, 118.7, 128.0, 128.1, 157.8 (ipso-C), 157.9 (ipso-C)	125.8, 126.3, 129.2, 130.4, 132.6, 141.7 (Me$_2$C$_6$H$_3$)*	0.5 (C$_5$H$_4$SiMe_3)*, 108.2, 108.4, 108.7, 108.8, 111.6, 111.7, 113.3 (ipso-C), 113.4 (ipso-C), 114.4, 114.6 (C$_5$H$_5$)	228.2*
[{Nb(η^5-C$_5$H$_4$SiMe$_3$)(η^2-MeC=NAr)Me}$_2$(μ-1,4-NC$_6$H$_4$N)] (**8**)	9.1 (*Me*)*	22.8 (*Me*)*	17.8*, 17.9*	123.9*, 153.1* (ipso-C)	126.0, 127.8, 128.6, 129.3, 130.8, 141.5 (Me$_2$C$_6$H$_3$)*	0.5 (C$_5$H$_4$SiMe_3)*, 108.6, 109.1, 111.5 (ipso-C), 112.7, 113.7 (C$_5$H$_5$)*	228.9*.
[{Nb(η^5-C$_5$H$_4$SiMe$_3$)(η^2-PhCH$_2$C=NAr)CH$_2$Ph}$_2$(μ-1,4-NC$_6$H$_4$N)] (**9**)	39.3 (CH$_2$Ph)*	43.0 (CH$_2$Ph)*	18.0*, 18.4*	124.4*, 153.0* (ipso-C)	121.0(*), 126.3(*), 127.2(*), 127.7(*), 128.3(*), 128.8(*), 129.0(*), 129.6(*), 130.0(*), 131.0, 131.1, 135.7, 135.8, 141.2(*), 154.1, 154.2 (Me$_2$C$_6$H$_3$ ArNCC$_2$Ph and Nb–C$_2$Ph)	0.4 (C$_5$H$_4$SiMe_3)*, 107.8, 107.9, 110.0, 110.1, 114.5, 114.6, 114.7 (ipso-C), 114.8 (ipso-C), 115.0, 115.1 (C$_5$H$_5$)	230.6*
[{Nb(η^5-C$_5$H$_4$SiMe$_3$)(η^2-Me$_3$SiCH$_2$C=NAr)CH$_2$SiMe$_3$}$_2$(μ-1,4-NC$_6$H$_4$N)] (**10**)	3.6 (CH$_2$SiMe_3)*, 13.2 (CH$_2$SiMe$_3$)*	−0.5 (CH$_2$SiMe_3)*, 31.7 (CH$_2$SiMe$_3$)*	18.7*, 18.8*	123.6*, 153.2* (ipso-C)	125.8, 126.2, 129.0, 129.1, 132.4, 141.7 (Me$_2$C$_6$H$_3$)*	0.6 (C$_5$H$_4$SiMe_3)*, 108.4, 109.3, 111.1, 112.9 (ipso-C), 114.1 (C$_5$H$_5$)*	228.5*
[{Ta(η^5-C$_5$Me$_5$)(η^2-Me$_3$SiCH$_2$C=NAr)CH$_2$SiMe$_3$}$_2$(μ-1,4-NC$_6$H$_4$N)] (**11**)	4.9 (CH$_2$SiMe_3)*, 17.9 (CH$_2$SiMe$_3$)*	0.6 (CH$_2$SiMe_3)*, 30.0 (CH$_2$SiMe$_3$)*	19.1*, 19.9*	124.5*, 152.4* (ipso-C)	125.8, 126.1, 129.1, 129.4, 132.2, 141.8 (Me$_2$C$_6$H$_3$)*	12.0 (C$_5$$Me_5$)*, 113.2 (C$_5Me_5$)*	241.8*

Table 2 (continued)

Compound	M–R	NC–R	$Me_2C_6H_3$	NC_6H_4N	$Me_2C_6H_3$ and Ph	Cp	CN
[{Nb(η^5-C$_5$H$_4$SiMe$_3$)(η^2-MeC=NAr)Cl}$_2$(μ-1,4-NC$_6$H$_4$N)] (12)		22.4 (Me)*	18.2*, 18.3*	123.3*, 154.1* (ipso-C)	126.0, 126.6, 128.8, 129.7, 131.2, 140.0 (Me$_2$C$_6$H$_3$)*	0.4 (C$_5$H$_4$SiMe$_3$)*, 107.6, 107.7, 111.6, 111.7, 111.8, 112.1, 115.7 (ipso-C), 115.8 (ipso-C), 121.1, 121.4 (C$_5$H$_5$)	226.5*
[{Nb(η^5-C$_5$H$_4$SiMe$_3$)(η^2-Me$_2$NC=NAr)Me}$_2$(μ-1,4-NC$_6$H$_4$N)] (13)	9.5 (Me)*	36.1, 44.3 (NMe$_2$)*	18.5*, 18.8*	123.6*, 153.0* (ipso-C)	124.7, 126.3, 127.4, 132.0, 132.7, 143.2 (Me$_2$C$_6$H$_3$)*	0.4 (C$_5$H$_4$SiMe$_3$)*, 104.8, 104.9, 107.9, 108.0, 110.4, 110.5, 113.6 (ipso-C), 113.7 (ipso-C), 117.4, 117.6 (C$_5$H$_5$)	192.4*

[a] 75 MHz, C$_6$D$_6$, chemical shifts in δ.
[b] * indicates that the signals for the two diastereoisomers coincide.

1–3 can be considered as six coordinate complexes with an octahedral disposition or as a pseudo-tetrahedral structure where the η^2-iminoacyl groups occupy one coordination site each. The latter hypothesis has been observed in similar η^2-iminoacyl group 5 metal complexes which show, in their X-ray structures, that the η^2-iminoacyl group occupies one coordination site [8]. Rothwell and co-workers have prepared similar group 4 compounds, [M(OPh-2,6-Bu$^t_2$)$_2$(η^2-RNCR')$_2$] (M = Hf, R = Ph, R' = Me; M = Zr, R = Bu^t, R' = CH$_2$Ph), where pseudo tetrahedral geometries were also observed [7c]. Taking into account these previous reports, we propose that 1–3 also adopt a pseudo tetrahedral conformation. The final disposition of the two η^2-iminoacyl ligands will allow for the possibility of cis or trans arrangements. NMR spectroscopy, however, showed the presence of a solitary final product, although this may be explained by the rapid interchange, in solution, in the orientation of the carbon and nitrogen atoms of the η^2-iminoacyl groups. Indeed this type of behaviour is quiet typical in these systems with the transformation being carried out via rotation in the MCN plane of the η^2-iminoacyl ligand or via η^2–η^1–η^2 coordination [6].

We have also studied the insertion reactions of half sandwich bis-alkyl imido complexes to compare and contrast their behaviour with their electron deficient trialkyl analogues. Previous to this we carried out the X-ray single crystal structure determination of one of the dialkyl monocyclopentadienyl precursors, namely [{Nb(η^5-C$_5$H$_4$SiMe$_3$)(CH$_2$Ph)$_2$}$_2$(μ-1,4-NC$_6$H$_4$N)] (4). The molecular structure of 4 and atomic numbering scheme are shown in Fig. 1, selected bond lengths and angles are given in Table 3.

Fig. 1. Molecular structure and atom-labeling scheme for [{Nb(η^5-C$_5$H$_4$SiMe$_3$)(CH$_2$Ph)$_2$}$_2$(μ-1,4-NC$_6$H$_4$N)] (4), with thermal ellipsoids at 30% probability.

Table 3
Selected bond lengths (Å) and angles (°) for **4**

	4a	4b
Bond lengths (Å)		
Nb(1)–N	1.79(1)	1.75(1)
Nb(1)–Cp(1)	2.156	2.161
Nb(1)–C(4)	2.468(9)	2.53(2)
Nb(1)–C(5)	2.54(2)	2.51(2)
Nb(1)–C(6)	2.45(1)	2.44(2)
Nb(1)–C(7)	2.42(2)	2.43(2)
Nb(1)–C(8)	2.45(2)	2.43(2)
Nb(1)–C(9)	2.22(2)	2.25(1)
Nb(1)–C(1)0	2.29(1)	2.22(2)
N(1)–C(1)	1.38(2)	1.38(2)
Bond angles (°)		
N(1)–Nb(1)–C(9)	101.4(6)	97.2(6)
N(1)–Nb(1)–C(10)	96.9(5)	96.9(6)
C(9)–Nb(1)–C(10)	122.9(7)	123.1(7)
Nb(1)–N(1)–C(1)	159(1)	168(1)
Cp(1)–Nb(1)–C(9)	109.0	108.7
Cp(1)–Nb(1)–C(10)	108.4	109.5
Cp(1)–Nb(1)–N(1)	118.4	121.8

Cp(1) is the centroid of C(4)–C(8).

Suitable X-ray quality crystals of **4** were obtained by the slow evaporation of a toluene solution. The compound crystallizes in $P1$ space group, triclinic and with two distinct molecules in the asymmetric unit. The structure of **4** consists of a dinuclear complex where the metal atoms are bound to the cyclopentadienyl ring in an η^5 mode. In addition, the niobium atoms are linked to two methylene groups from CH_2Ph and to the nitrogen of the imido group. **4** adopts a three-legged piano-stool conformation about the metal centres. The cyclopentadienyl rings are in a *trans* disposition with respect to each other and in a typical eclipsed disposition with respect to the imido group [9]. The metal atom is

out of the plane defined by N(1), C(1), C(2) and C(3), by 0.45(2) and 0.22(2) Å.

The niobium–nitrogen distances of 1.79(1) and 1.75(1) Å lie within the range expected for a triple bond [9,10]. The Nb(1)–N(1)–C(1) angles of 159(1)° and 168(1)° deviate slightly from linear. Such deviations from linear are normally in the range of 12–15° (see Table 4). In the case of [Nb(=NPh)(η^5-$C_5H_4SiMe_3$)$_2$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 [11]. Therefore we propose that in **4** the nitrogen atom is sp hybridized.

The distances of 2.58(1) and 2.52(1) Å between the *ipso* carbon atom C(11) of the benzyl ligand and the niobium atom indicates a weak interaction between these two atoms. This interaction only occurs with one of the benzyl groups with the other being situated at a greater distance to the niobium atom (Nb(1)–C(21) 3.22(1) and 3.17(1) Å). This type of η^2 coordinative behaviour of the benzyl ligand in d^0 early transition metal complexes is not uncommon and several examples have previously been reported [12].
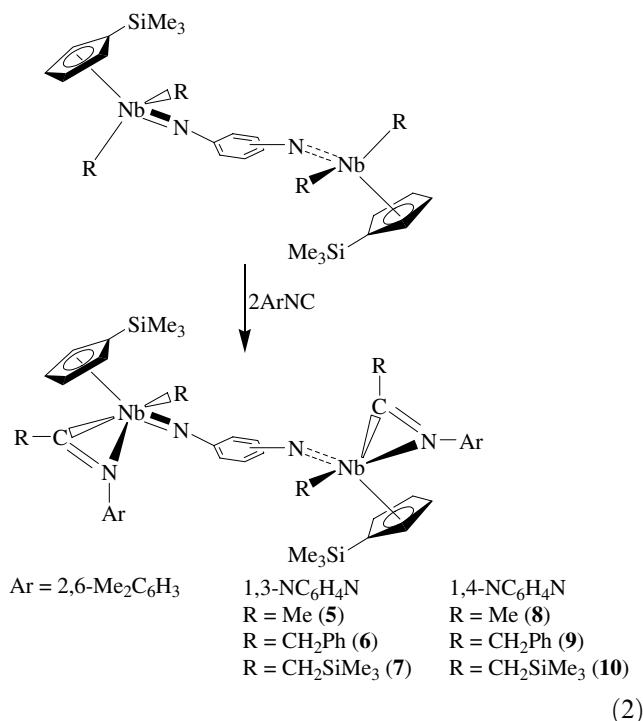
In a similar manner to the synthesis of **1–3**, the half sandwich complexes, [{Nb(η^5-$C_5H_4SiMe_3$)(η^2-RC=NAr)R}$_2$(μ-1,3-NC_6H_4N)] (R = Me (**5**), CH_2Ph (**6**), CH_2SiMe_3 (**7**)), [{Nb(η^5-$C_5H_4SiMe_3$)(η^2-RC=NAr)R}$_2$(μ-1,4-NC_6H_4N)] (R = Me (**8**), CH_2Ph (**9**), CH_2SiMe_3 (**10**)) and [{Ta(η^5-C_5Me_5)(η^2-$Me_3SiCH_2C=NAr$)CH_2SiMe_3}$_2$(μ-1,4-NC_6H_4N)] (**11**) (Ar = 2,6-$Me_2C_6H_3$), were prepared via isocyanide reaction with the corresponding bis-alkyl precursors (Eq. (2)). Attempts to insert a second isocyanide molecule were unsuccessful.

Table 4
Selected structural data of some group 5 metal imido complexes

	M–N (Å)	M–N–C (°)	Reference
[{Nb(η^5-$C_5H_4SiMe_3$)(CH_2Ph)$_2$}$_2$(μ-1,4-NC_6H_4N)] (**4**)	1.79(1)	159(1)	This work
	1.75(1)	168(1)	
[{Nb(η^5-$C_5H_4SiMe_3$)Cl$_2$}$_2$(μ-1,4-NC_6H_4N)]	1.776(8)	160.9(7)	[5d]
[{Ta(η^5-C_5Me_5)Cl$_2$}$_2$(μ-1,4-NC_6H_4N)]	1.783(5)	166.4(5)	[5d]
[{Ta(η^5-C_5Me_5)(CH_2SiMe_3)$_2$}$_2$(μ-1,4-NC_6H_4N)]	1.794(5)	167.4(5)	[5d]
[Nb(=NAr)(η^5-C_5H_5)(NHBu^t)Cl][a]	1.793	168.5	[10b]
[Nb(=NAr)(η^5-C_5H_5)Cl$_2$][a]	1.761	165.6	[9]
[Nb(=NAr)(η^5-C_5H_5)Cl$_2$][b]	1.763	166.6	[10c]
[Nb(=NAr)(η^5-C_5H_5)(η^2-NHBu^t)(CH_2Bu^t)H][a]	1.787	174.6	[10d]
[Ta(=NAr)(η^5-C_5Me_5)Cl$_2$][a]	1.780	171.3	[3]
[Ta(=NAr)(η^5-C_5Me_5)Cl$_2$][b]	1.774	169.9	[10a]
[Ta(=NAr)(η^5-C_5Me_5)(CO){Si(SiMe$_3$)$_3$}H][a]	1.812	171.4	[10e]
[Ta(=NAr)(η^5-C_5H_5)(PMe$_3$)(SiMe$_2$Cl)H][a]	1.821	171.8	[10f]

[a] Ar = 2,6-Pr$_2^i$C$_6$H$_3$.
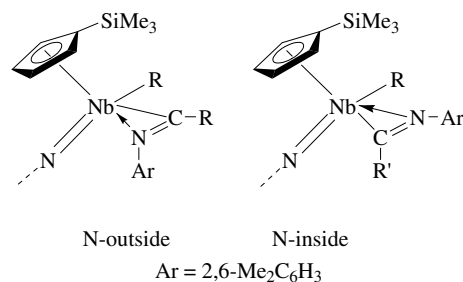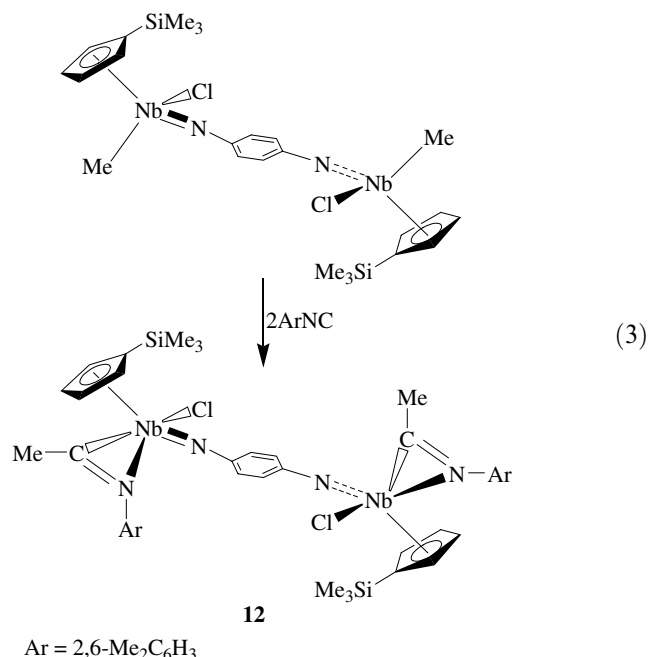[b] Ar = 2,6-Me$_2$C$_6$H$_3$.

(2)

Fig. 2. Two possible conformations for the iminoacyl metal complexes **5–10**.

stereoisomers that arise from the two niobium chiral centres (Fig. 3). The chemical shifts for the isomers are very similar and in many cases the signals from the two isomers overlap (see Tables 1 and 2).

$[\{Nb(\eta^5\text{-}C_5H_4SiMe_3)(\eta^2\text{-}MeC=NAr)Cl\}_2(\mu\text{-}1,4\text{-}NC_6H_4N)]$ (**12**) was prepared in a similar manner to **5–11** (Eq. (3)). The characterization of **12** by spectroscopic methods revealed that it was similar to complexes **8–10** in all aspects (see Tables 1 and 2).

The IR spectra of **5–11** showed bands at ca. 1315 and 1630 cm^{-1} assigned to the imido group and the C=N of the η^2-iminoacyl group, respectively. The chiral nature of the niobium atoms in **5–10** means that for the cyclopentadienyl protons, four multiplets, corresponding to an ABCD system, are observed in the ^{1}H NMR spectra. The presence of the η^2-iminoacyl was confirmed by the existence of a signal at ca. 230 ppm characteristic for this group [7]. For **6**, **7**, **8**, **10** and **11** the ^{1}H NMR spectra showed an AB spin system for the methylene protons of the inserted alkyl displaced downfield with respect to that observed for the AB system of the diastereopic protons of the remaining alkyl group (see Table 1). The restricted rotation of the isocyanide phenyl ring leads to the inequivalency of its two methyl substituents and thus two signals were observed in the ^{1}H NMR spectra.

If we assume that the η^2-iminoacyl group occupies one coordination site then we can consider that the complexes **5–11** will adopt a pseudo tetrahedral geometry. The iminoacyl group can position itself in two distinct conformations with respect to the uninserted alkyl group, the "proximal" or "N-outside" and the "distal" or "N-inside" configurations (see Fig. 2), which would lead to the possibility of various isomers in the final product. However, it is more likely that either rapid exchange occurs between the two iminoacyl conformations as proposed in **1–3** or that the final product obtained is that from thermodynamic control with the iminoacyl group adopting only the N-inside configuration as seen in similar metallocene complexes [13]. NMR spectroscopy showed only the presence of the two dia-

(3)

Ar = 2,6-Me$_2$C$_6$H$_3$

The reaction of the alkyl amido complex, $[\{Nb(\eta^5\text{-}C_5H_4SiMe_3)(Me)(NMe_2)\}_2(\mu\text{-}1,4\text{-}NC_6H_4N)]$, with the isocyanide reagent only occurred at elevated temperatures. The insertion reaction took place preferentially at the Nb–NMe$_2$ bond to give the η^2-iminocarbamoyl derivative $[\{Nb(\eta^5\text{-}C_5H_4SiMe_3)(\eta^2\text{-}Me_2NC=NAr)Me\}_2(\mu\text{-}1,4\text{-}NC_6H_4N)]$ (**13**) (Eq. (4)). This selective migration of the amide rather than the methyl group is in agreement with that previously reported for similar niobium and tantalum complexes [14]. However this behaviour is unusual, as shown in the reactivity of alkyl amide complexes of titanium [15], zirconium [16],
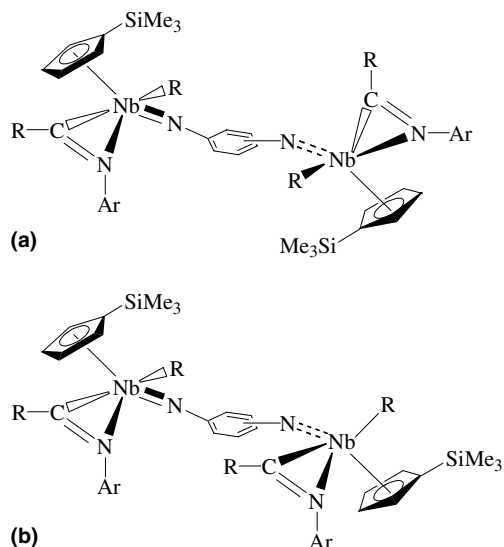
Fig. 3. (a) Proposed structure for *meso*-[{Nb(η^5-C$_5$H$_4$SiMe$_3$)(η^2-RC=NAr)R}$_2$(μ-NC$_6$H$_4$N)]. (b) Proposed structure for *rac*-[{Nb(η^5-C$_5$H$_4$SiMe$_3$)(η^2-RC=NAr)R}$_2$(μ-NC$_6$H$_4$N)].

tungsten [17], uranium [18], tantalum [19] and niobium [20], where the isocyanide insertion takes place at the M–C(alkyl) bond. The presence of the η^2-iminocarbamoyl in **13** was confirmed by ^{13}C NMR spectroscopy. The signal corresponding to the carbon of the η^2-iminocarbamoyl group was observed at δ 200 shifted upfield with relation to that observed in η^2-iminoacyl complexes (ca. δ 230).

$$2ArNC \qquad (4)$$

13

Ar = 2,6-Me$_2$C$_6$H$_3$
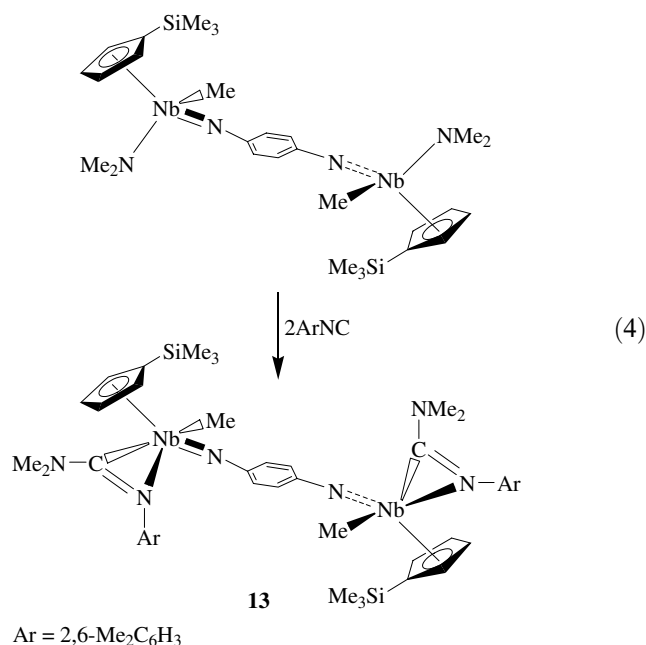
Our numerous attempts to determine the molecular structure of the isocyanide insertion products, **1–3** and **5–13**, were always unsuccessful. Our efforts were

thwarted by the great difficulty encountered in obtaining crystals of sufficient quality for X-ray diffraction analysis.

3. Conclusions

In this paper we report the synthesis of new iminoacyl derivatives of dinuclear niobium and tantalum imido complexes via isocyanide insertion reactions of their alkyl precursors. The molecular structure of one of these alkyl precursors has been determined by single crystal X-ray diffraction studies and shows that one of the benzyl ligands adopts an η^2 coordination mode with respect to the metal atom.

4. Experimental

4.1. Materials and procedures

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. 2,6-Me$_2$C$_6$H$_3$NC was purchased from Aldrich and used directly. The compounds [{NbR$_3$}$_2$(μ-1,3-NC$_6$H$_4$N)], [{NbR$_3$}$_2$(μ-1,4-NC$_6$H$_4$N)], [{TaR$_3$}$_2$(μ-1,4-NC$_6$H$_4$N)] (R = CH$_2$SiMe$_3$), [{Nb(η^5-C$_5$H$_4$SiMe$_3$)R$_2$}$_2$(μ-1,3-NC$_6$H$_4$N)] (R = Me, CH$_2$Ph, CH$_2$SiMe$_3$), [{Nb(η^5-C$_5$H$_4$SiMe$_3$)R$_2$}$_2$(μ-1,4-NC$_6$H$_4$N)] (R = Me, CH$_2$Ph (**4**), CH$_2$SiMe$_3$), [{Ta(η^5-C$_5$Me$_5$)(CH$_2$SiMe$_3$)$_2$}$_2$(μ-1,4-NC$_6$H$_4$N)], [{Nb(η^5-C$_5$H$_4$SiMe$_3$)(Me)Cl}$_2$(μ-1,4-NC$_6$H$_4$N)] and [{Nb(η^5-C$_5$H$_4$SiMe$_3$)(Me)NMe$_2$}$_2$(μ-1,4-NC$_6$H$_4$N)] were prepared as described earlier [5d]. IR spectra were recorded on a Perkin–Elmer PE 883 IR spectrophotometer. ^{1}H and ^{13}C spectra (Tables 1 and 2) were recorded on a Varian FT-300 spectrometer and referenced to the residual deuterated solvent. Microanalyses were carried out with a Perkin–Elmer 2400 microanalyzer.

4.2. Synthesis of [{Nb(η^2-Me$_3$SiCH$_2$C=NC$_6$H$_3$Me$_2$-2,6)$_2$(CH$_2$SiMe$_3$)}$_2$(μ-1,3-NC$_6$H$_4$N)] (1)

A hexane solution (20 ml) of 2,6-Me$_2$C$_6$H$_3$NC (0.21 g, 1.60 mmol) was added dropwise to [{Nb(CH$_3$CN)(CH$_2$SiMe$_3$)$_3$}$_2$(μ-1,3-NC$_6$H$_4$N)] (0.37 g, 0.41 mmol) in hexane (100 ml) at room temperature and stirred for 20 min. The resulting suspension was filtered and solvent removed, from the filtrate, in vacuo to give a yellow solid corresponding to the title complex (0.40 g, 73%). IR (Nujol/CsI): $\nu_{Nb=N}$ 1344, $\nu_{C=N}$ 1562 cm^{-1}. Anal. Calc. for C$_{66}$H$_{106}$N$_6$Nb$_2$Si$_6$: C, 59.25; H, 7.99; N, 6.28. Found C, 59.43; H, 8.11; N, 6.66%.

4.3. Synthesis of [{Nb(η²-Me₃SiCH₂C=NC₆H₃Me₂-2,6)₂(CH₂SiMe₃)}₂(μ-1,4-NC₆H₄N)] (2)

The preparation of **2** was carried out in an identical manner to **1**. 2,6-$Me_2C_6H_3NC$ (0.200 g, 1.52 mmol) and [{Nb(CH₃CN)(CH₂SiMe₃)₃}₂(μ-1,4-NC₆H₄N)] (0.350 g, 0.39 mmol). Yield: 0.38 g, 72%. IR (Nujol/CsI): $v_{Nb=N}$ 1316, $v_{C=N}$ 1571 cm⁻¹. Anal. Calc. for C₆₆H₁₀₆-N₆Nb₂Si₆: C, 59.25; H, 7.99; N, 6.28. Found C, 59.21; H, 7.98; N, 6.36%.

4.4. Synthesis of [{Ta(η²-Me₃SiCH₂C=NC₆H₃Me₂-2,6)₂(CH₂SiMe₃)}₂(μ-1,4-NC₆H₄N)] (3)

The preparation of **3** was carried out in an identical manner to **1**. 2,6-$Me_2C_6H_3NC$ (0.10 g, 0.75 mmol) and [{Ta(CH₃CN)(CH₂SiMe₃)₃}₂(μ-1,4-NC₆H₄N)] (0.20 g, 0.19 mmol). Yield: 0.22 g, 78%. IR (Nujol/CsI): $v_{Ta=N}$ 1331, $v_{C=N}$ 1565 cm⁻¹. Anal. Calc. for C₆₆H₁₀₆-N₆Ta₂Si₆: C, 52.36; H, 7.06; N, 5.55. Found C, 52.21; H, 7.02; N, 5.60%.

4.5. Synthesis of [{Nb(η⁵-C₅H₄SiMe₃)(η²-MeC=NC₆H₃Me₂-2,6)Me}₂(μ-1,3-NC₆H₄N)] (5)

The preparation of **5** was carried out in an identical manner to **1**. 2,6-$Me_2C_6H_3NC$ (0.42 g, 3.20 mmol) and [{Nb(η⁵-C₅H₄SiMe₃)Me₂}₂(μ-1,3-NC₆H₄N)] (1.00 g, 1.60 mmol). Yield: 1.33 g, 94%. IR (Nujol/CsI): $v_{Nb=N}$ 1316, $v_{C=N}$ 1620 cm⁻¹. Anal. Calc. for C₄₄H₆₀N₄Nb₂Si₂: C, 59.58; H, 6.82; N, 6.32. Found C, 59.41; H, 6.77; N, 6.34%.

4.6. Synthesis of [{Nb(η⁵-C₅H₄SiMe₃)(η²-PhCH₂C=NC₆H₃Me₂-2,6)CH₂Ph}₂(μ-1,3-NC₆H₄N)] (6)

The preparation of **6** was carried out in an identical manner to **1**. 2,6-$Me_2C_6H_3NC$ (0.24 g, 1.82 mmol) and [{Nb(η⁵-C₅H₄SiMe₃)(CH₂Ph)₂}₂(μ-1,3-NC₆H₄N)] (0.85 g, 0.91 mmol). Yield: 0.99 g, 91%. IR (Nujol/CsI): $v_{Nb=N}$ 1314, $v_{C=N}$ 1633 cm⁻¹. Anal. Calc. for C₆₈H₇₆N₄Nb₂Si₂: C, 68.56; H, 6.43; N, 4.70. Found C, 68.37; H, 6.45; N, 4.76%.

4.7. Synthesis of [{Nb(η⁵-C₅H₄SiMe₃)(η²-Me₃SiCH₂C=NC₆H₃Me₂-2,6)CH₂SiMe₃}₂(μ-1,3-NC₆H₄N)] (7)

The preparation of **7** was carried out in an identical manner to **1**. 2,6-$Me_2C_6H_3NC$ (0.29 g, 2.18 mmol) and [{Nb(η⁵-C₅H₄SiMe₃)(CH₂SiMe₃)₂}₂(μ-1,3-NC₆H₄N)] (1.00 g, 1.09 mmol). Yield: 1.21 g, 94%. IR (Nujol/CsI): $v_{Nb=N}$ 1316, $v_{C=N}$ 1625 cm⁻¹. Anal. Calc. for C₅₆H₉₂N₄Nb₂Si₆: C, 57.21; H, 7.89; N, 4.77. Found C, 57.04; H, 7.88; N, 4.81%.

4.8. Synthesis of [{Nb(η⁵-C₅H₄SiMe₃)(η²-MeC=NC₆H₃Me₂-2,6)Me}₂(μ-1,4-NC₆H₄N)] (8)

The preparation of **8** was carried out in an identical manner to **1**. 2,6-$Me_2C_6H_3NC$ (0.17 g, 1.28 mmol) and [{Nb(η⁵-C₅H₄SiMe₃)Me₂}₂(μ-1,4-NC₆H₄N)] (0.40 g, 0.64 mmol). Yield: 0.52 g, 93%. IR (Nujol/CsI): $v_{Nb=N}$ 1317, $v_{C=N}$ 1642 cm⁻¹. Anal. Calc. for C₄₄H₆₀N₄Nb₂Si₂: C, 59.58; H, 6.82; N, 6.32. Found C, 59.39; H, 6.75; N, 6.36%.

4.9. Synthesis of [{Nb(η⁵-C₅H₄SiMe₃)(η²-PhCH₂C=NC₆H₃Me₂-2,6)CH₂Ph}₂(μ-1,4-NC₆H₄N)] (9)

The preparation of **9** was carried out in an identical manner to **1**. 2,6-$Me_2C_6H_3NC$ (0.15 g, 1.12 mmol) and [{Nb(η⁵-C₅H₄SiMe₃)(CH₂Ph)₂}₂(μ-1,4-NC₆H₄N)] (0.53 g, 0.56 mmol). Yield: 0.61 g, 91%. IR (Nujol/CsI): $v_{Nb=N}$ 1315, $v_{C=N}$ 1627 cm⁻¹. Anal. Calc. for C₆₈H₇₆N₄Nb₂Si₂: C, 68.56; H, 6.43; N, 4.70. Found C, 68.30; H, 6.47; N, 4.67%.

4.10. Synthesis of [{Nb(η⁵-C₅H₄SiMe₃)(η²-Me₃SiCH₂C=NC₆H₃Me₂-2,6)CH₂SiMe₃}₂(μ-1,4-NC₆H₄N)] (10)

The preparation of **10** was carried out in an identical manner to **1**. 2,6-$Me_2C_6H_3NC$ (0.31 g, 2.36 mmol) and [{Nb(η⁵-C₅H₄SiMe₃)(CH₂SiMe₃)₂}₂(μ-1,4-NC₆H₄N)] (1.08 g, 1.18 mmol). Yield: 1.30 g, 93%. IR (Nujol/CsI): $v_{Nb=N}$ 1320, $v_{C=N}$ 1617 cm⁻¹. Anal. Calc. for C₅₆H₉₂-N₄Nb₂Si₆: C, 57.21; H, 7.89; N, 4.77. Found C, 57.11; H, 7.96; N, 4.66%.

4.11. Synthesis of [{Ta(η⁵-C₅Me₅)(η²-Me₃SiCH₂C=NC₆H₃Me₂-2,6)CH₂SiMe₃}₂(μ-1,4-NC₆H₄N)] (11)

The preparation of **11** was carried out in an identical manner to **1**. 2,6-$Me_2C_6H_3NC$ (0.10 g, 0.76 mmol) and [{Ta(η⁵-C₅Me₅)(CH₂SiMe₃)₂}₂(μ-1,4-NC₆H₄N)] (0.41 g, 0.38 mmol). Yield: 0.41 g, 80%. IR (Nujol/CsI): $v_{Ta=N}$ 1325, $v_{C=N}$ 1620 cm⁻¹. Anal. Calc. for C₆₀H₉₆N₄Si₄Ta₂: C, 53.47; H, 7.18; N, 4.16. Found C, 53.30; H, 7.13; N, 4.21%.

4.12. Synthesis of [{Nb(η⁵-C₅H₄SiMe₃)(η²-MeC=NC₆H₃Me₂-2,6)Cl}₂(μ-1,4-NC₆H₄N)] (12)

The preparation of **12** was carried out in an identical manner to **1**. 2,6-$Me_2C_6H_3NC$ (0.26 g, 1.96 mmol) and [{Nb(η⁵-C₅H₄SiMe₃)(Me)Cl}₂(μ-1,4-NC₆H₄N)] (0.65 g, 0.98 mmol). Yield: 0.45 g, 49%. IR (Nujol/CsI): $v_{Nb=N}$ 1316, $v_{C=N}$ 1663 cm⁻¹. Anal. Calc. for C₄₂H₆₀-N₄Cl₂Nb₂Si₂: C, 54.37; H, 5.87; N, 6.04. Found C, 54.50; H, 5.90; N, 5.99%.

4.13. Synthesis of [{Nb(η⁵-C₅H₄SiMe₃)(η²-Me₂NC=NC₆H₃Me₂-2,6)Me}₂(μ-1,4-NC₆H₄N)] (13)

The preparation of **13** was carried out in an identical manner to **1**. 2,6-Me₂C₆H₃NC (0.37 g, 2.78 mmol) and [{Nb(η⁵-C₅H₄SiMe₃)(Me)NMe₂}₂(μ-1,4-NC₆H₄N)] (0.95 g, 1.39 mmol). Yield: 1.15 g, 88%. IR (Nujol/CsI): $\nu_{Nb=N}$ 1315, $\nu_{C=N}$ 1639 cm^{-1}. Anal. Calc. for C₄₆H₆₆N₆Nb₂Si₂: C, 58.46; H, 7.04; N, 8.89. Found C, 58.81; H, 7.07; N, 8.92%.

4.14. X-ray structure determination of [{Nb(η⁵-C₅H₄SiMe₃)(CH₂Ph₂)₂(μ-1,4-NC₆H₄N)] (4)

Intensity data were collected on a NONIUS-MACH3 diffractometer equipped with a graphite monochromator (Mo Kα radiation, $\lambda = 0.71073$ Å) using an $\omega/2\theta$ scan technique. The specimens diffracted only weakly. The final unit cell parameters were determined from 25 well-centered reflections and refined by the least-squares method. The space group was determined from the systematic absences and this was vindicated by the success of the subsequent solutions and refinements. Two standard reflections, measured every 98 reflections, showed an intensity decay of 28% at the end of the process. The structure was solved by direct methods using the SHELXS computer program [21] and refined in F^2 by full-matrix least-squares (SHELXL-97) [22]. 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 optimized in the final cycles. The crystal data and details of data collection and structure analyses are summarized in Table 5.

5. Supplementary material

Crystallographic data for the structural analysis of **4** have been deposited with the Cambridge Crystallographic Data Centre, CCDC-205741. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033; E-mail: deposit@ccdc.cam.ac.uk or http//www.ccdc.cam.ac.uk).

Table 5
Crystal data and structure refinement for **4**

Empirical formula	C₅₀H₅₈N₂Nb₂Si₂
Formula weight	928.98
Temperature (K)	293(2)
Crystal system	Triclinic
Space group	$P\bar{1}$
a (Å)	10.925(4)
b (Å)	13.134(4)
c (Å)	20.153(5)
α (°)	71.60(3)
β (°)	76.29(3)
γ (°)	71.39(4)
V (Å³)	2570.4(3)
Z	2
D_c (g cm^{-3})	1.200
μ (mm^{-1})	0.524
F (000)	964
Crystal dimension (mm)	$0.2 \times 0.4 \times 0.3$
θ range (°)	2.11–27.99
$h\,k\,l$ ranges	$-14 \leqslant h \leqslant 14,\ -16 \leqslant k \leqslant 17,$ $0 \leqslant l \leqslant 26$
Data/parameters	12730/505
Goodness-of-fit on F^2	0.901
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.1148$; $wR_2 = 0.2516$
Largest diffraction peak (e Å^{-3})	1.452/−0.372

$R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|$; $wR_2 = \left[\sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2] \right]^{0.5}$.

References

[1] (a) C. Creutz, Prog. Inorg. Chem. 30 (1983) 1;
(b) C. Creutz, H. Taube, J. Am. Chem. Soc. 91 (1969) 3988;
(c) A. Haim, Prog. Inorg. Chem. 30 (1983) 273;
(d) T.J. Meyer, Prog. Inorg. Chem. 30 (1983) 389;
(e) T.J. Meyer, in: D.B. Brown (Ed.), Mixed-Valence Compounds, Reidel, Dordrecht, 1980, p. 75;
(f) J.E. Miller, Adv. Chem. Ser. 150 (1976) 18.
[2] (a) E.A. Maatta, D.D. Devore, Angew. Chem., Int. Ed. Engl. 27 (1988) 569;
(b) E.A. Maatta, C. Kim, Inorg. Chem. 28 (1989) 624;
(c) R.K. Rosen, R.A. Anderson, N.M. Edelstein, J. Am. Chem. Soc. 112 (1990) 4588;
(d) W. Clegg, R.J. Errington, D.C.R. Hockless, J.M. Kirck, C. Redshaw, Polyhedron 11 (1992) 381;
(e) C. Redshaw, G. Wilkinson, B. Hussain-Bates, M.B. Hursthouse, J. Chem. Soc., Dalton Trans. (1992) 555;
(f) G. Hogart, R.L. Mallors, T.J. Norman, J. Chem. Soc., Chem. Commun. (1993) 1721.
[3] D.E. Wigley, Prog. Inorg. Chem. 42 (1994) 239.
[4] A. Antiñolo, M. Fajardo, A. Otero, S. Prashar, Eur. J. Inorg. Chem. (2003) 17.
[5] (a) A. Antiñolo, F. Carrillo-Hermosilla, A. Otero, M. Fajardo, A. Garcés, P. Gómez-Sal, C. López-Mardomingo, A. Martín, C. Miranda, J. Chem. Soc., Dalton Trans. (1998) 59;
(b) I. Dorado, A. Garcés, C. López-Mardomingo, M. Fajardo, A. Rodríguez, A. Antiñolo, A. Otero, J. Chem. Soc., Dalton Trans. (2000) 2375;
(c) A. Antiñolo, I. Dorado, M. Fajardo, A. Garcés, M.M. Kubicki, C. López-Mardomingo, A. Otero, Dalton Trans. (2003) 910;

(d) A. Antiñolo, I. Dorado, M. Fajardo, A. Garcés, I. López-Solera, C. López-Mardomingo, M.M. Kubicki, A. Otero, S. Prashar, Eur. J. Inorg. Chem., in press.

[6] L.D. Durfee, I.P. Rothwell, Chem. Rev. 88 (1988) 1059.

[7] (a) E.W. Abel, F.G.A. Stone, G. Wilkinson (Eds.), Comprehensive Organometallic Chemistry, second ed, vol. 5, Pergamon, Oxford, 1995;
(b) K.G. Moloy, P.J. Fagan, J.M. Manríquez, T.J. Marks, J. Am. Chem. Soc. 108 (1986) 56;
(c) L.R. Chamberlain, L.D. Durfee, P.E. Fanwick, L. Kobriger, S.L. Latesky, A.K. McMullen, I.P. Rothwell, K. Folting, J.C. Huffman, W.E. Streib, R. Wang, J. Am. Chem. Soc. 109 (1987) 390.

[8] L.R. Chamberlain, I.P. Rothwell, J.C. Huffman, J. Chem. Soc., Chem. Commun. (1986) 1203.

[9] 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.

[10] (a) M.V. Galakhov, M. Gómez, G. Jiménez, M.A. Pellinghelli, P. Royo, A. Tiripicchio, Organometallics 13 (1994) 1564;
(b) 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;
(c) M.J. Humphries, M.L.H. Green, R.E. Douthwaite, L.H. Rees, J. Chem. Soc., Dalton Trans. (2000) 4555;
(d) A.D. Poole, D.N. Williams, A.M. Kenwright, V.C. Gibson, W. Clegg, D.C.R. Hockless, P.A. O'Neil, Organometallics 12 (1993) 2549;
(e) U. Burckhardt, T.D. Tilley, J. Am. Chem. Soc. 121 (1999) 6328;
(f) 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.

[11] A. Antiñolo, P. Espinosa, M. Fajardo, P. Gómez-Sal, C. López-Mardomingo, A. Martin-Alonso, A. Otero, J. Chem. Soc., Dalton Trans. (1995) 1007.

[12] See for example: C. Pellecchia, A. Immirzi, D. Pappalardo, A. Peluso, Organometallics 13 (1994) 3773.

[13] (a) G. Erker, Acc. Chem. Res. 17 (1984) 103;
(b) A. Antiñolo, R. Fernández-Galán, B. Gallego, A. Otero, S. Prashar, A.M. Rodríguez, Eur. J. Inorg. Chem. (2003) 2626;
(c) A. Antiñolo, R. Fernández-Galán, I. Orive, A. Otero, S. Prashar, Eur. J. Inorg. Chem. (2002) 2470.

[14] A. Castro, M.V. Galakhov, M. Gómez, P. Gómez-Sal, A. Martín, F. Sánchez, J. Organomet. Chem. 595 (2000) 36.

[15] (a) L. Kloppenburg, J.L. Petersen, Organometallics 16 (1997) 3548;
(b) M.A. Putzer, B. Neumüller, K. Dehnicke, Z. Anorg. Allg. Chem. 624 (1998) 57.

[16] R.P. Planalp, R.A. Andersen, Organometallics 2 (1983) 1675.

[17] R.L. Huff, S.-Y. Wang, K. Abboud, J.M. Boncella, Organometallics 16 (1997) 1779.

[18] (a) A. Dormond, A. Aaliti, A. Moise, J. Chem. Soc., Chem. Commun. (1985) 1231;
(b) P. Zanella, N. Brianese, U. Castellato, F. Ossala, M. Porchin, G. Rosetto, R. Graziani, J. Chem. Soc., Dalton Trans. (1987) 2039.

[19] T.C. Gountchev, T.D. Tilley, J. Am. Chem. Soc. 19 (1997) 12831.

[20] M.I. Alcalde, P. Gómez-Sal, P. Royo, Organometallics 18 (1999) 546.

[21] G.M. Sheldrick, Acta Crystallogr. Sect. A 46 (1990) 467.

[22] G.M. Sheldrick, Program for the Refinement of Crystal Structures from Diffraction Data, University of Göttingen, Göttingen, Germany, 1997.