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Half-sandwich dichloro, alkyl chloro, dialkyl, alkyl methyl and amido methyl imido cyclopentadienyl niobium and tantalum(V) complexes. Dynamic behaviour of amido imido tantalum derivatives

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Abstract

Reactions of NbCp′Cl$_4$ (Cp′ = η^5-C$_5$H$_4$SiMe$_3$) and TaCp*Cl$_2$Me$_2$ (Cp* = η^5-C$_5$Me$_5$) with two equivalents of NHR^{1}SiMe$_3$ and two equivalents of CNR^1 (M = Nb, R^1 = 2,6-Me$_2$C$_6$H$_3$; 2,6-^{i}Pr$_2$C$_6$H$_3$; SiMe$_3$; M = Ta, R^1 = 2,6-Me$_2$C$_6$H$_3$), respectively, gave the dichloro imido derivatives [**MCpCl$_2$(NR^1)**] (M = Nb, Cp = Cp′, R^1 = 2,6-Me$_2$C$_6$H$_3$, **1**; 2,6-^{i}Pr$_2$C$_6$H$_3$, **2**; SiMe$_3$, **3**; M = Ta, Cp = Cp*, **4**). Alkyl chloro imido complexes [**MCpClR(NR^1)**], (R^1 = 2,6-Me$_2$C$_6$H$_3$; M = Nb, Cp = Cp′, R = Me, **5**; Cp*, **6**; M = Ta, Cp = Cp*, R = Me, **7**; NMe$_2$, **8**; O^{t}Bu, **9**) were obtained by treatment of dichloro derivatives **1** and **4** with the appropriate amount of alkylating reagent (**5**, **7** one equivalent of ZnMe$_2$; **6** four equivalents of LiCp*; **8**, **9** one equivalent of LiR). When the same reaction was carried out with two equivalents of MgClMe (**10**) or LiR(R=CH$_2$SiMe$_3$, **11**; CH$_2$CMe$_3$, **12**; NMe$_2$, **13**) and one equivalent of Mg(CH$_2$C$_6$H$_5$)$_2$(THF)$_2$ (**14**) or Li$_2$[*o*-(NSiMe$_3$)$_2$C$_6$H$_4$] (**15**) the corresponding dialkyl imido derivatives [**MCpR$_2$(NR^1)**], (R^1 = 2,6-Me$_2$C$_6$H$_3$; M = Nb, Cp = Cp′, R = Me, **10**; CH$_2$SiMe$_3$, **11**; CH$_2$CMe$_3$, **12**; NMe$_2$, **13**; CH$_2$C$_6$H$_5$, **14**; M = Ta, Cp=Cp*, R = *o*-(NSiMe$_3$)$_2$C$_6$H$_4$, **15**) can be prepared. The methyl complexes **5**, **7** reacted with one equivalent of LiR to give mixed alkyl methyl and amido methyl imido derivatives [**MCpMeR(NR^1)**] (R^1 = 2,6-Me$_2$C$_6$H$_3$; M = Nb, Cp = Cp′, R = CH$_2$SiMe$_3$, **16**; NMe$_2$, **17**; M = Ta, Cp = Cp*, R = NMe$_2$, **18**; N^{i}Pr$_2$, **19**; NH^{t}Bu, **20**). All the new complexes were characterized by usual IR and NMR spectroscopic methods. The rotation of 2,6-Me$_2$C$_6$H$_3$ ring and NR$_2$(R = Me, ^{i}Pr) amido ligands around C$_{ipso}$(aryl)–N$_{\mathrm{imido}}$ and N$_{\mathrm{amido}}$–Ta bonds, respectively, were observed for complexes **8**, **18** and **19** and studied by ^{1}H-DNMR spectroscopy. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: Niobium; Tantalum; Alkyl amido imido cyclopentadienyl complexes

1. Introduction

Complexes containing metal–ligand multiple bonds constitute extremely interesting subjects of research in organometallic chemistry, since they are implicated as effective reagents or catalysts for oxidations, metathesis reactions and ammoxidations [1]. In particular, transition metal–imido complexes have been studied as molecular precursors to thin films [2], models of hydrodenitrogenation [3] and probes of electronic structure via their luminescent properties [4].

Although the imide ligand has been employed as an ancillary group to support high-oxidation state metal centres, an increasing number of complexes having reactive imide ligands have been shown to participate in C–H bond activation [5] and cycloaddition reactions [6]. It is noteworthy that early transition metal–imido complexes are widely represented and a great number of established imido functional groups of d^0 niobium and tantalum has been reported during the last few years [7].

We previously reported a first study of the behaviour of pentamethylcyclopentadienyl arylimido tantalum complexes [TaCp*XY{N(2,6-Me$_2$C$_6$H$_3$)}] (X = Y = Cl; X = Cl, Y = Me) towards alkylating reagents [8] and in

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this article we report our efforts to complete the study, and also the results obtained with similar half-sandwich arylimido niobium complexes.

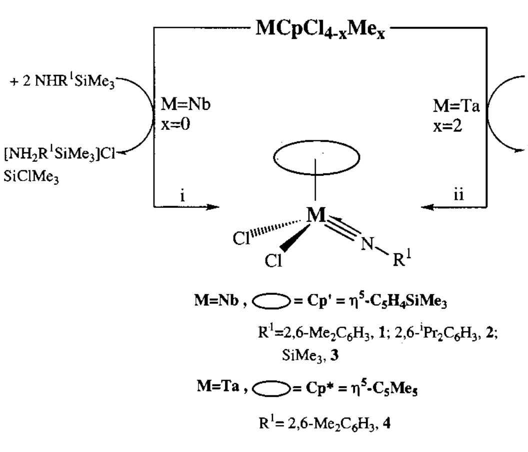
2. Results and discussion

The starting point for these studies are the pseudo-tetrahedral dichloro imido complexes [**NbCp′Cl$_2$(NR^1)**], (**R^1** = 2,6-Me$_2$C$_6$H$_3$, **1**; 2,6-^{i}Pr$_2$C$_6$H$_3$, **2**; SiMe$_3$, **3**) whose syntheses can be easily carried out when dichloromethane solutions of NbCp′Cl$_4$, (Cp′ = η^5-C$_5$H$_4$SiMe$_3$) are treated at room temperature (r.t.) with aryl trimethylsilyl amine NHR^{1}SiMe$_3$ (R^1 = 2,6-Me$_2$C$_6$H$_3$; 2,6-^{i}Pr$_2$C$_6$H$_3$; SiMe$_3$) in a 1:2 molar ratio, as shown in Scheme 1. Complex **4** was prepared as described previously [9].

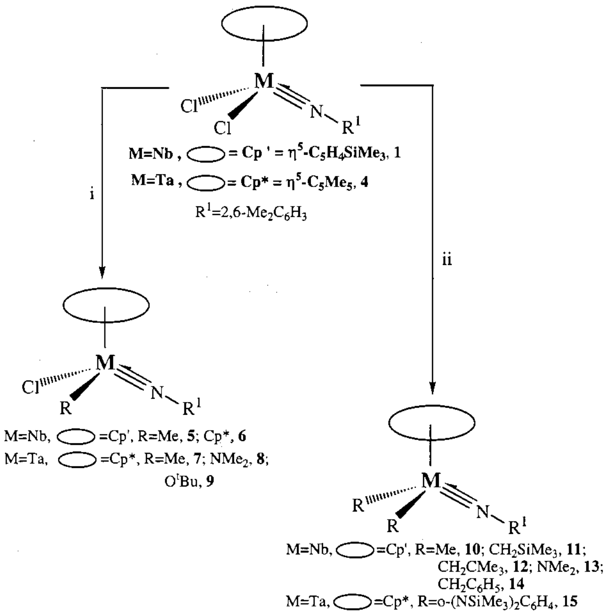
Reactions of **1** or **4** with the stoichiometric amounts of the alkylating reagent gave solutions from which the alkyl chloro imido [**MCpClR{N(2,6-Me$_2$C$_6$H$_3$)}**], (M = Nb, Cp = Cp′, R = Me, **5**; Cp*, **6**; M = Ta, Cp = Cp*, R = Me, **7**; NMe$_2$, **8**; O^{t}Bu, **9**) and dialkyl imido [**MCpR$_2$ {N(2,6-Me$_2$C$_6$H$_3$)}**] (M = Nb, Cp = Cp′, R = Me, **10**; CH$_2$SiMe$_3$, **11**; CH$_2$CMe$_3$, **12**; NMe$_2$, **13**; CH$_2$C$_6$H$_5$, **14**; M = Ta, Cp = Cp*, R = *o*-(NSiMe$_3$)$_2$C$_6$H$_4$, **15**) were isolated in good yields (see Scheme 2).

Furthermore, the reaction between chloro methyl imido complexes **5** or **7** and LiR at r.t in *n*-hexane gives the mixed alkyl methyl and amido methyl imido complexes [**MCpMeR{N(2,6-Me$_2$C$_6$H$_3$)}**] (M = Nb, Cp = Cp′, R = CH$_2$SiMe$_3$, **16**; NMe$_2$, **17**; M = Ta, Cp = Cp*, R = NMe$_2$, **18**; N^{i}Pr$_2$, **19**; NH^{t}Bu, **20**), as shown in Scheme 3.

Treatment of the starting dichloro imido niobium and tantalum complexes with one equivalent of ZnMe$_2$ gave the chloro methyl derivatives **5** and **7**, as the only products, but unidentified mixtures were obtained by using 0.5 equivalents of dimethyl zinc. Several attempts to prepare the pentamethylcyclopentadienyl niobium derivative **6** using a stoichiometric amount of LiCp* were unsuccessful, but the compound was obtained employed a large excess of lithium reagent. On the other hand [NbCp′(NMe$_2$)$_2${N(2,6-Me$_2$C$_6$H$_3$)}], **13**, can be easily prepared via the treatment of **1** with LiNMe$_2$ in a molar ratio 1:2, however, a related reaction of [TaCp*Cl$_2${N(2,6-Me$_2$C$_6$H$_3$)}], **4**, with this reagent afforded a mixture of the mono dimethylamido derivative **8** and an excess of the alkylating reagent.

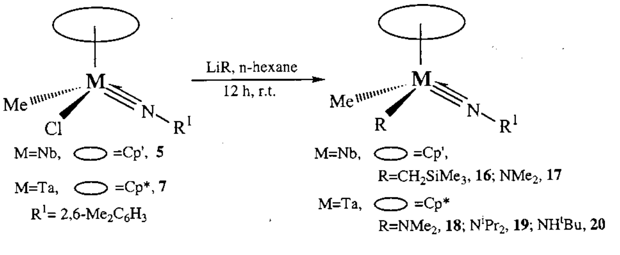


Scheme 1. Synthesis of dichloro imido complexes. Reagents and conditions: i–two equivalents of NHR^{1}SiMe$_3$, dichloromethane, 12 h, r.t. ii–Two equivalents of CNR^1, toluene, 24 h, r.t.



Scheme 2. Synthesis of alkyl chloro and dialkyl imido complexes. Reagents and conditions: i–**5**, **7** one equivalent of ZnMe$_2$, *n*-hexane, 12 h, r.t.; **6**, four equivalents of LiCp*: **8** and **9**, one equivalent of LiR, toluene, 12 h, r.t. ii–**10**, two equivalents of MgClMe; **11**–**13**, two equivalents of LiR; **14**, one equivalent of Mg(CH$_2$C$_6$H$_5$)$_2$(THF)$_2$; **15**, one equivalent of Li$_2$[*o*-(NSiMe$_3$)$_2$C$_6$H$_4$], toluene, 12 h, r.t.

All of the complexes **1**–**20** are soluble in most organic solvents including saturated hydrocarbons. They are extremely air- and moisture-sensitive, and rigorously dried solvents and handling under dry inert atmosphere were found to be imperative for successful preparations.



Scheme 3. Synthesis of alkyl methyl and amido methyl imido complexes.

Table 1
IR[a] data of the new complexes

	$\nu_{M=N}$	$\nu_{\delta s(Me_3Si)}$	$\nu_{C-C(Cp^*)}$	$\nu_{C-H(Cp')}$	ν_{M-C}	ν_{M-Cl}	Others
1	1300(vs)	1254(vs)		840(vs)		368(s)	1400(m), 1170(m), 1092(w), 1042(s), 902(m), 690(w), 632(m)
2	1329(m)	1252(vs)		841(vs)		379(s)	1170(m), 1048(s), 903(m), 690(w), 633(m)
3	1311(vs)	1249(vs)		840(vs)		387(m)	1170(m), 1103(w), 1049(s), 903(m), 697(w), 631(m)
5	1304(vs)	1252(vs)		836(vs)	634(m)	364(m)	1410(m), 1172(m), 1092(w), 1042(s), 902(m), 690(w), 480(m)
6	1299(vs)	1247(vs)	1020(m)	835(vs)	629(m)	342(m)	1405(m), 1096(w), 1040(s), 907(m)
8	1322(vs)		1027(m)			351(s)	1621(m), 1586(m), 1249(s), 1141(m), 1095(m), 962(vs), 798(vs), 763(m), 577(m), 395(m)
9	1331(vs)		1025(m)			342(s)	1589(w), 1234(m), 1177(s), 1096(m), 985(vs), 789(vs), 391(m)
10	1308(vs)	1252(vs)		834(vs)	632(m)		1420(m), 1174(m), 1096(w), 1040(s), 910(m), 690(w), 494(m),
11	1306(vs)	1248(vs)		839(vs)			1174(m), 1044(s), 700(m)
12	1301(vs)	1250(vs)		837(vs)	633(m)		1411(m), 1175(m), 1097(w), 1045(s), 906(w), 697(w)
13	1291(vs)	1245(vs)		837(vs)			1410(m), 1176(m), 1096(w), 1045(s), 906(m), 680(w), 632(m), 545(s)
14	1288(vs)	1245(vs)		833(vs)	632(m)		1177(m), 1094(w), 1032(s), 900(m), 692(w), 494(s)
15	1320(s)	1247(s)	1027(m)				1588(w), 1098(m), 941(s), 905(s), 839(vs), 790(m), 749(m), 723(m), 684(w), 500(w), 344(m), 288(w)
16	1306(vs)	1248(vs)		838(vs)	633(m)		1411(m), 1174(m), 1096(w), 1043(s), 903(m), 705(w), 485(m)
17	1307(vs)	1248(vs)		838(vs)			1413(m), 1173(m), 1096(w), 1043(s), 903(m), 705(w), 485(m)
18	1330(vs)		1026(m)				1634(w), 1589(m), 1159(m), 1141(m), 1095(m), 983(m), 964(m), 758(s), 489(m), 392(m), 349(s)
19	1323(vs)		1025(m)				1589(w), 1158(s), 1101(s), 982(m), 937(m), 818(m), 760(s), 723(m), 486(w), 344(m)
20	1331(vs)		1025(m)				3299(m), 1892(w), 1756(w), 1681(m), 1588(s), 1209(vs), 1094(s), 979(s), 942(m), 759(vs), 605(m), 575(m), 491 (m), 349(s), 272(m)

[a] Nujol mull, ν in cm^{-1}.

The IR spectra (see Table 1) of all complexes show the characteristic absorptions for the pentamethylcyclopentadienyl (ν_{C-C} ca. 1025 cm^{-1}) [10], trimethylsilylcyclopentadienyl (ν_{C-H} ca. 837 cm^{-1}) [11] rings and for the trimethylsilyl substituent ($\nu_{\delta s}CH_3$ ca. 1249 cm^{-1}) [11d, 12]. Absorptions due to the M=N, M–C and M–Cl stretching vibrations are observed at ca. 1304(Nb), 1326(Ta) [7i,m], 633(Nb), 517(Ta) [13] and 368(Nb), 346(Ta) [11d, 14] cm^{-1}, respectively.

At r.t. the chiral complexes **6** and **19** show the expected spectral ^{1}H-NMR (see Table 2) behaviour with both inequivalent *o*-methyl(phenyl) groups, however, for the analogous complexes **5**, **8**, **9**, **16**–**18** and **20**, such groups are equivalent. This difference is probably due to different rates of Berry pseudorotation processes [15] as we have observed for similar tantalum complexes [8]. The absence of local symmetry in the trimethylsilylcyclopentadienyl ring of the complexes **5**, **6**, **16** and **17** is consistent with the chiral character of the niobium atom.

The ^{1}H-NMR spectra of the complexes **11**, **12** and **14** show an AB and AA′BB′ spin system for the α-CH_2 groups and the trimethylsilylcyclopentadienyl ring, respectively, in accordance with the prochiral character of the metal center. Furthermore, complex **15** shows an AA′BB′ spin system for the phenyl ring protons. All the data are consistent with a C_s symmetry for complexes **10**–**15** and with a metal center in a characteristic three-legged piano-stool environment.

*2.1. Dynamic behaviour in solution of the amido imido complexes **8**, **18** and **19***

At r.t. the ^{1}H-NMR spectra of the complexes **8**, **13** and **18** show very broad signals for the resonances corresponding to the dimethylamido ligand. The ^{1}H-NMR spectrum of complex **19** also shows one broad resonance at δ 3.4 for two equivalent methyne protons and two broad signals at δ 1.2 and 1.1 for the methyl groups of the isopropylamido ligand, while in its $^{13}C\{^1H\}$ spectrum at the same temperature, the signals of this ligand are not observed. At 233 K the $^{13}C\{^1H\}$ spectrum of **19** shows very good resolved signals for Me–Ta at δ 24.08, for the Cp* ring at δ 114.4 and 11.03, for the methyl substituents of 2,6-$Me_2C_6H_3$ ring at δ 19.72 and 18.97, for the aromatic carbons of the $C_6H_3Me_2$ ring at δ 153.6(C_{ipso}), 136.2, 131.7(C_2, C_6), 127.05, 126.8(C_3, C_5) and 120.1(C_4), and also two signals at δ 52.1 and 48.6 for the inequivalent secondary carbon of the $CHMe_2$ group and four resonances at δ 30.0, 27.8, 26.8 and 20.9 for the inequivalent and diasterotopic methyl carbons of the $CHMe_2$ group in the bis-isopropylamido ligand. At 233 K the ^{1}H-NMR spectrum of this complex displays, besides other signals, two septuplets at δ 3.51 and 3.26 for the isopropylic proton and four doublets at δ 1.24, 1.21, 1.14 and 0.95, respectively, for the methyl groups of the bis-isopropylamido ligand. All these data are consistent with the absence of any symmetry into **19** at low temperatures

Table 2
^1H and $^{13}C\{^1H\}$-NMR data of the new complexes

	^1H	$^{13}C\{^1H\}$
1	[a]6.80 (t, 1H, $^3J_{H-H} = 7.2$ Hz), 6.65 (d, 2H, $^3J_{H-H} = 7.2$ Hz, $\boldsymbol{H}_3C_6Me_2N$), 6.24 (m, 2H), 5.90 (m, 2H, $\boldsymbol{H}_4C_5SiMe_3$), 2.40 (s, 6H, $\boldsymbol{Me}_2C_6H_3N$), 0.19 (s, 9H, $\boldsymbol{Me}_3SiC_5H_4$)	[a]153.54 (C_i, $\boldsymbol{C}_6H_3Me_2N$), 134.99 (C_o, $\boldsymbol{C}_6H_3Me_2N$), 126.7 (C_p, $\boldsymbol{C}_6H_3Me_2N$), 125.94 (C_m, $\boldsymbol{C}_6H_3Me_2N$), 125.77 (C_i, $\boldsymbol{C}_5H_4SiMe_3$), 122.95 ($C_{2,5}$, $\boldsymbol{C}_5H_4SiMe_3$), 113.07 ($C_{3,4}$, $\boldsymbol{C}_5H_4SiMe_3$), 19.22 ($\boldsymbol{Me}_2C_6H_3N$), −0.76 ($\boldsymbol{Me}_3SiC_5H_4$)
2	[a]7.01 (d, 2H, $^3J_{H-H} = 7.7$ Hz), 6.89 (t, 1H, $^3J_{H-H} = 7.7$ Hz, $\boldsymbol{H}_3C_6^iPr_2N$), 6.27 (m, 2H), 6.01 (m, 2H, $\boldsymbol{H}_4C_5SiMe_3$), 3.74 [m, 2H, $(\boldsymbol{H}CMe_2)_2C_6H_3N$]. 1.28 [d, 2H, $^2J_{H-H} = 6.6$ Hz, $(\boldsymbol{Me}_2CH)_2C_6H_3N$], 0.20 (s, 9H, $\boldsymbol{Me}_3SiC_5H_4$)	[a]144.75 (C_i, $\boldsymbol{C}_6H_3^iPr_2N$), 126 ($C_i$, $\boldsymbol{C}_5H_4SiMe_3$), 125.19 ($C_o$, $\boldsymbol{C}_6H_3^iPr_2N$), 122.7 ($C_m$, $\boldsymbol{C}_6H_3^iPr_2N$), 120.93 ($C_p$, $\boldsymbol{C}_6H_3^iPr_2N$), 114.3 ($C_{2,5}$, $\boldsymbol{C}_5H_4SiMe_3$), 108.7 ($C_{3,4}$, $\boldsymbol{C}_5H_4SiMe_3$), 28.5 [$(\boldsymbol{C}HMe_2)_2C_6H_3N$], 24.25, 24 [$(HC\boldsymbol{Me}_2)_2C_6H_3N$], −0.59 ($\boldsymbol{Me}_3SiC_5H_4$)
3	[a]6.34 (m, 2H), 6.10 (m, 2H, $\boldsymbol{H}_4C_5SiMe_3$), 0.21 (s, 9H, $\boldsymbol{Me}_3SiC_5H_4$), 0.06 (s, 9H, $\boldsymbol{Me}_3SiN$)	[a]125.6 (C_i, $\boldsymbol{C}_5H_4SiMe_3$), 122 ($C_{2,5}$, $\boldsymbol{C}_5H_4SiMe_3$), 113.5 ($C_{3,4}$, $C_5H_4SiMe_3$), 0.37 ($\boldsymbol{Me}_3SiN$), −0.5 ($\boldsymbol{Me}_3SiC_5H_4$)
5	[a]6.90 (d, 2H, $^3J_{H-H} = 7.8$ Hz), 6.76 (t, 1H, $^3J_{H-H} = 7\ 8$ Hz, $\boldsymbol{H}_3C_6Me_2N$), 6.14 (m, 1H), 5.87 (m, 1H), 5.70 (m, 1H), 5.59 (m, 1H, $\boldsymbol{H}_4C_5SiMe_3$), 2.42 (s, 6H, $\boldsymbol{Me}_2C_6H_3N$), 1.37 (s, 3H, $\boldsymbol{Me}$–Nb), 0.16 (s, 9H, $\boldsymbol{Me}_3SiC_5H_4$)	[a]140.3, 135.5, 134.4, 124.4, 121.8 (several phenyl, $\boldsymbol{C}_6H_3Me_2N$), 121.8, 120.2, 114.8, 114.6, 109.4 ($C_{i,2,3,4,5}$, $\boldsymbol{C}_5H_4SiMe_3$), 69.5 ($\boldsymbol{Me}$–Nb), 19.6 ($\boldsymbol{Me}_2C_6H_3N$), −0 62 ($\boldsymbol{Me}_3SiC_5H_4$)
6	[a]6.96 (d, 1H, $^3J_{H-H} = 7.5$ Hz), 6.88 (d, 1H, $^3J_{H-H} = 7.5$ Hz), 6.65 (t, 1H, $^3J_{H-H} = 7.5$ Hz, $\boldsymbol{H}_3C_6Me_2N$), 6.34 (m, 2H), 5.79 (m, 1H), 5.40 (m, 1H, $\boldsymbol{H}_4C_5SiMe_3$), 2.41 (s, 3H), 2.27 (s, 3H, $\boldsymbol{Me}_2C_6H_3N$), 1.67 (s, 15H, $C_5\boldsymbol{Me}_5$), 0.26 (s, 9H, $\boldsymbol{Me}_3SiC_5H_4$)	[a]156.1 (C_i, $\boldsymbol{C}_6H_3Me_2N$), 140.3 (C_i, $\boldsymbol{C}_5H_4SiMe_3$), 130.1, 127.2, 125.6, 124.9, 122.2 ($C_{2,3,4,5,6}$, $\boldsymbol{C}_6H_3Me_2N$), 121.4, 120.9, 110.6, 107.4 ($\boldsymbol{C}_5H_4SiMe_3$), 120.5 ($\boldsymbol{C}_5Me_5$), 20.5, 19.2 ($\boldsymbol{Me}_2C_6H_3N$), 12.1 ($\boldsymbol{C}_5Me_5$), 0.1 ($\boldsymbol{Me}_3SiC_5H_4$)
8	[b]6.93 (d, 2H, $^3J_{H-H} = 7.3$ Hz), 6.65 (t, 1H, $^3J_{H-H} = 7.3$ Hz, $\boldsymbol{H}_3C_6Me_2N$), 3.53 (br, 6H, $\boldsymbol{Me}_2N$), 2.32 (s, 6H, $\boldsymbol{Me}_2C_6H_3N$), 2.04 (s, 15H, $C_5\boldsymbol{Me}_5$)	[b]152.5, 130.3, 127, 121.6 (C_i, C_o, C_m, C_p, $\boldsymbol{C}_6H_3Me_2N$), 117.5 ($\boldsymbol{C}_5Me_5$), 51.8 (br, $\boldsymbol{Me}_2N$), 19 ($\boldsymbol{Me}_2C_6H_3N$), 11 ($C_5\boldsymbol{Me}_5$)
9	[a]7.05 (d, 2H, $^3J_{H-H} = 7.5$ Hz), 6.73 (t, 1H, $^3J_{H-H} = 7.5$ Hz, $\boldsymbol{H}_3C_6Me_2N$), 2.53 (s, 6H, $\boldsymbol{Me}_2C_6H_3N$), 1.9 (s, 15H, $C_5\boldsymbol{Me}_5$), 1.27 (s, 9H, $\boldsymbol{Me}_3C$)	[a]153, 128.3, 127.5, 122 (C_i, C_o, C_m, C_p, $\boldsymbol{C}_6H_3Me_2N$) 119.1 ($\boldsymbol{C}_5Me_5$), 81 ($\boldsymbol{C}Me_3$), 31.9 ($\boldsymbol{Me}_3C$), 19.8 ($\boldsymbol{Me}_2C_6H_3N$), 11.1 ($C_5\boldsymbol{Me}_5$)
10	[a]7.01 (d, 2H, $^3J_{H-H} = 7.3$ Hz), 6.8 (t, 1H, $^3J_{H-H} = 7.3$ Hz, $\boldsymbol{H}_3C_6Me_2N$), 5.93 (m, 2H), 5.80 (m, 2H, $\boldsymbol{H}_4C_5SiMe_3$), 2.51 (s, 6H, $\boldsymbol{Me}_2C_6H_3N$), 0.77 (s, 6H, $\boldsymbol{Me}_2$–Nb), 0.05 (s, 9H, $\boldsymbol{Me}_3SiC_5H_4$)	[a]149.5, 140, 134.6, 123.1 (C_i, C_o, C_p, C_m, $\boldsymbol{C}_6H_3Me_2N$), 117 (C_i, $\boldsymbol{C}_5H_4SiMe_3$), 114.4 ($C_{2,5}$, $\boldsymbol{C}_5H_4SiMe_3$), 111.9 ($C_{3,4}$, $\boldsymbol{C}_5H_4SiMe_3$), 72.1 ($\boldsymbol{Me}_2$–Nb), 19.9 ($\boldsymbol{Me}_2C_6H_3N$), 0.52 ($\boldsymbol{Me}_3SiC_5H_4$)
11	[a]7.02 (d, 2H, $^3J_{H-H} = 7.6$ Hz), 6.83 (t, 1H, $^3J_{H-H} = 7.6$ Hz, $\boldsymbol{H}_3C_6Me_2N$), 6.66 (m, 2H), 5.78 (m, 2H, $\boldsymbol{H}_4C_5SiMe_3$), 2.53 (s, 6H, $\boldsymbol{Me}_2C_6H_3N$), 1.54, 0.77 (AB, 2H, $^2J_{H-H} = 9.36$ Hz, $\boldsymbol{H}_2CSiMe_3$), 0.24 (s, 9H, $\boldsymbol{Me}_3SiC_5H_4$), 0.09 (s, 9H, $\boldsymbol{Me}_3SiCH_2$)	[a]140.5, 133.5, 128.3, 122.7 (C_i, C_o, C_p, C_m, $\boldsymbol{C}_6H_3Me_2N$), 123 (C_i. $\boldsymbol{C}_5H_4SiMe_3$), 118.7 ($C_{2,5}$, $\boldsymbol{C}_5H_4SiMe_3$), 105.6 ($C_{3,4}$, $\boldsymbol{C}_5H_4SiMe_3$), 56.5 (br, $\boldsymbol{C}H_2SiMe_3$), 20.5 ($\boldsymbol{Me}_2C_6H_3N$), 2.85 ($\boldsymbol{Me}_3SiCH_2$), −0.02 ($\boldsymbol{Me}_3SiC_5H_4$)
12	[a]6.99 (d, 2H, $^3J_{H-H} = 7.8$ Hz), 6.79 (t, 1H, $^3J_{H-H} = 7.8$ Hz, $\boldsymbol{H}_3C_6Me_2N$), 6.60 (m, 2H), 5.89 (m, 2H, $\boldsymbol{H}_4C_5SiMe_3$), 2.56 (s, 6H, $\boldsymbol{Me}_2C_6H_3N$), 2.17. 0.79 (AB, 2H, $^2J_{H-H} = 6.54$ Hz, $\boldsymbol{H}_2CCMe_3$), 1.11 (s, 18H, $\boldsymbol{Me}_3CCH_2$), 0.12 (s, 9H, $\boldsymbol{Me}_3SiC_5H_4$)	[a]155, 138, 134.5, 123.25 (C_i, C_o, C_p, C_m, $\boldsymbol{C}_6H_3Me_2N$), 117.9 (C_i, $\boldsymbol{C}_5H_4SiMe_3$), 116.7 ($C_{2,5}$, $C\ _5H_4SiMe_3$), 109.3 ($C_{3,4}$, $\boldsymbol{C}_5H_4SiMe_3$), 85.5 (br, $\boldsymbol{C}H_2CMe_3$), 37.4 ($\boldsymbol{Me}_3CCH_2$), 35.8 ($Me_3\boldsymbol{C}CH_2$), 20.8 ($\boldsymbol{Me}_2C_6H_3N$), 0.6 ($\boldsymbol{Me}_3SiC_5H_4$)
13	[a]7.00 (d, 2H, $^3J_{H-H} = 7.3$ Hz), 6.78 (t, 1H, $^3J_{H-H} = 7.3$ Hz, $\boldsymbol{H}_3C_6Me_2N$), 6.16 (m, 2H), 6.07 (m, 2H, $\boldsymbol{H}_4C_5SiMe_3$), 3.22 (s, 12H, $\boldsymbol{Me}_2N$), 2.52 (s, 6H, $\boldsymbol{Me}_2C_6H_3N$), 0.14 (s, 9H, $\boldsymbol{Me}_3SiC_5H_4$)	[a]152.4, 140.5, 132.2, 122.4 (C_i, C_o, C_p, C_m, $\boldsymbol{C}_6H_3Me_2N$), 117.6 (C_i, $\boldsymbol{C}_5H_4SiMe_3$), 115.6 ($C_{2,5}$, $\boldsymbol{C}_5H_4SiMe_3$), 112.8 ($C_{3,4}$, $\boldsymbol{C}_5H_4SiMe_3$), 52.9 ($\boldsymbol{Me}_2N$), 20.2 ($\boldsymbol{Me}_2C_6H_3N$), −0.02 ($\boldsymbol{Me}_3SiC_5H_4$)
14	[a]7.03–6.73 (several phenyl, $\boldsymbol{H}_3C_6Me_2N$, $\boldsymbol{H}_5C_6CH_2$), 6 85 (m, 2H), 5.67 (m, 2H, $\boldsymbol{H}_4C_5SiMe_3$), 2.35 (s, 6H, $\boldsymbol{Me}_2C_6H_3N$), 2.17, 1.86 (AB, 2H, $^2J_{H-H} = 8.7$ Hz, $\boldsymbol{H}_2CC_6H_5$), 0.07 (s, 9H, $\boldsymbol{Me}_3SiC_5H_4$)	[a]155.4, 140.6, 134.6, 130, 129.1, 128.2, 125.6, 123.1 (several phenyl, $\boldsymbol{C}_6H_3Me_2N$, $\boldsymbol{C}_6H_5CH_2$), 115.6 ($C_{2,5}$, $\boldsymbol{C}_5H_4SiMe_3$), 113.9 ($C_i$, $\boldsymbol{C}_5H_4SiMe_3$). 112.8 ($C_{3,4}$, $\boldsymbol{C}_5H_4SiMe_3$), 47 ($\boldsymbol{C}H_2C_6H_5$), 20.44 ($\boldsymbol{Me}_2C_6H_3N$), −0.16 ($\boldsymbol{Me}_3SiC_5H_4$)
15	[a]7.12 (d, 2H, $^3J_{H-H} = 7.5$ Hz), 6.76 (t, 1H, $^3J_{H-H} = 7\ 5$ Hz, $\boldsymbol{H}_3C_6Me_2N$), 7.00 [m, 4H, $\boldsymbol{H}_4C_6(NSiMe_3)_2$], 2.58 (s, 6H, $\boldsymbol{Me}_2C_6H_3N$) 1.66 (s, 15H, $C_5\boldsymbol{Me}_5$), 0.28 [s, 18H, $(\boldsymbol{Me}_3SiN)_2C_6H_4$]	[a]155.4, 131.9, 127.9, 121.2 (C_i, C_o, C_m, C_p, $\boldsymbol{C}_6H_3Me_2N$), 135.4, 128.3, 125.6, 122.9 [$\boldsymbol{C}_6H_4(NSiMe_3)_2$], 115.9 ($\boldsymbol{C}_5Me_5$), 20.9 ($\boldsymbol{Me}_2C_6H_3N$), 10.8 ($C_5\boldsymbol{Me}_5$), 3.37 [$(\boldsymbol{Me}_3SiN)_2C_6H_4$]
16	a, 7.01 (d, 2H, $^3J_{H-H} = 7.5$ Hz), 6.8 (t, 1H, $^3J_{H-H} = 7.5$ Hz, $\boldsymbol{H}_3C_6Me_2N$), 6.29 (m, 1H), 5.91 (m, 1H), 5.83 (m, 1H), 5.79 (m, 1H, $\boldsymbol{H}_4C_5SiMe_3$), 2.53 (s, 6H, $\boldsymbol{Me}_2C_6H_3N$), 1.47, 0.45 (AB, 2H, $^2J_{H-H} = 10.5$ Hz, $\boldsymbol{H}_2CSiMe_3$), 0.74 (s. 3H, $\boldsymbol{Me}$–Nb), 0.14 (s, 9H, $\boldsymbol{Me}_3SiC_5H_4$), 0.07 (s, 9H, $\boldsymbol{Me}_3SiCH_2$)	a, 154.8, 140.3, 134.2, 123 (C_i, C_o, C_p, C_m, $\boldsymbol{C}_6H_3Me_2N$), 118.4, 118.7, 112.3, 112.1, 110.4 ($C_{i,2,3,4,5}$, $\boldsymbol{C}_5H_4SiMe_3$), 60.4 (br, $\boldsymbol{C}H_2SiMe_3$), 36.3 (br, $\boldsymbol{Me}$–Nb), 20.3 ($\boldsymbol{Me}_2C_6H_3N$), 2.33 ($\boldsymbol{Me}_3SiCH_2$), −0.4 ($\boldsymbol{Me}_3SiC_5H_4$)
17	[a]7.01 (d, 2H, $^3J_{H-H} = 7.5$ Hz), 6.77 (t, 1H, $^3J_{H-H} = 7.5$ Hz, $\boldsymbol{H}_3C_6Me_2N$), 6.15 (m, 1H), 6 (m, 1H), 5.9 (m, 1H), 5.74 (m, 1H, $\boldsymbol{H}_4C_5SiMe_3$), 3.13 (s, br, 6H, $\boldsymbol{Me}_2N$), 2.52 (s, 6H, $\boldsymbol{Me}_2C_6H_3N$), 0.75 (s, 3H, $\boldsymbol{Me}$–Nb), 0.08 (s, 9H, $\boldsymbol{Me}_3SiC_5H_4$)	[a]155.3, 140.2,133.6, 122.5 (C_i, C_o, C_p, C_m, $\boldsymbol{C}_6H_3Me_2N$), 117.1, 117.7, 112.9, 111.8, 110.6 ($C_{i,2,3,4,5}$, $\boldsymbol{C}_5H_4SiMe_3$), 52.7 (s, $\boldsymbol{Me}_2N$), 38.5 ($\boldsymbol{Me}$–Nb), 19.9 ($\boldsymbol{Me}_2C_6H_3N$), −0.3 ($\boldsymbol{Me}_3SiC_5H_4$)
18	[a]7.11 (d, 2H, $^3J_{H-H} = 7.5$ Hz), 6.79 (t, 1H, $^3J_{H-H} = 7.5$ Hz, $\boldsymbol{H}_3C_6Me_2N$), 3.16 (br, 6H, $\boldsymbol{Me}_2N$), 2.48 (s, 6H, $\boldsymbol{Me}_2C_6H_3N$), 1.76 (s, 15H, $C_5\boldsymbol{Me}_5$), 0.50 (s, 3H, $\boldsymbol{Me}$–Ta)	[a]154.5, 128.3, 127.5, 121 (C_i, C_o, C_m, C_p, $\boldsymbol{C}_6H_3Me_2N$), 114.7 ($\boldsymbol{C}_5Me_5$), 50.9 (br, $\boldsymbol{Me}_2N$), 25.7 ($\boldsymbol{Me}$–Ta), 19.4 ($\boldsymbol{Me}_2C_6H_3N$), 10.7 ($C_5\boldsymbol{Me}_5$)
19	[b]6.97 (d, 1H, $^3J_{H-H} = 7.2$ Hz), 6.9 (d, 1H, $^3J_{H-H} = 7.2$ Hz), 6.61 (t, 1H, $^3J_{H-H} = 7.2$ Hz, $\boldsymbol{H}_3C_6Me_2N$), 3.41 (br, 2H, $\boldsymbol{H}CMe_2$), 2.5 (s, 3H), 2.12 (s, 3H, $\boldsymbol{Me}_2C_6H_3N$), 1.95 (s, 15H, $C_5\boldsymbol{Me}_5$), 1.18 (br, 12H, $\boldsymbol{Me}_2CH$), 0.14 (s, 3H, $\boldsymbol{Me}$–Ta)	[b]153.7, 136.1, 131.1, 126.9, 126.8, 120.2 (C_i, $C_{2,3,4,5,6}$, $\boldsymbol{C}_6H_3Me_2N$), 114.6 ($\boldsymbol{C}_5Me_5$), 50.3 (vbr, $\boldsymbol{C}HMe_2$), 28 ($\boldsymbol{Me}$–Ta), 24.3 (vbr, $\boldsymbol{Me}_2CH$), 20.6, 19.8 ($\boldsymbol{Me}_2C_6H_3N$), 11 ($C_5\boldsymbol{Me}_5$)
20	[a]7.13 (d, 2H, $^3J_{H-H} = 7.5$ Hz), 6.79 (t, 1H, $^3J_{H-H} = 7.5$ Hz, $\boldsymbol{H}_3C_6Me_2N$), 5.04 (br, 1H, $\boldsymbol{H}N^tBu$), 2.56 (s, 6H, $\boldsymbol{Me}_2C_6H_3N$), 1.74 (s, 15H, $C_5\boldsymbol{Me}_5$), 1.23 (s, 9H, $\boldsymbol{Me}_3CNH$), 0.46 (s, 3H, $\boldsymbol{Me}$–Ta)	[a]154.7, 128.3, 127.6, 120.9 (C_i, C_o, C_m, C_p, $\boldsymbol{C}_6H_3Me_2N$), 114.4 ($\boldsymbol{C}_5Me_5$), 56.34 ($\boldsymbol{C}Me_3NH$), 33.8 ($\boldsymbol{Me}_3CNH$), 24.7 ($\boldsymbol{Me}$–Ta), 19.9 (br, $\boldsymbol{Me}_2C_6H_3N$), 10.8 ($C_5\boldsymbol{Me}_5$)

[a] Chemical shifts in δ: benzene-d_6.

[b] Chemical shifts in δ: chloroform-d.

At 288 K the ^{1}H-NMR spectrum of **19** allows the detection of the coalescence of the *H* CMe$_2$ proton isopropylic resonances ($\Delta G^{\neq 288\ \mathrm{K}} = 13.9$ kcal mol^{-1}) corresponding to the slow rotation around the Ta–N^{i}Pr$_2$ bond and due to the multiple character of the mentioned bond.

This result moved us to study the fluxional behaviour of the dimethylamido derivatives **8** and **18**, by variable temperature ^{1}H-NMR spectroscopy. At 193 K the NMR spectra of both complexes showed sharp resonances for the methyl groups of the dimethylamido ligand at δ 3.92, 3.04 (**8**) and 3.72, 2.82 (**18**) and also for the *o*-methyl(phenyl) group of the imido ligand at δ 2.34, 2.08 (**8**) and 2.45, 2.05 (**18**). At higher temperatures typical dynamic behaviour involving the exchange of two equally populated signals occur [16] and it is possible to observe the collapse point of the 2,6-Me$_2$C$_6$H$_3$ methyl proton resonances for **8** ($\Delta G^{\neq 238\ \mathrm{K}} = 11.7$ kcal mol^{-1}) and **18** ($\Delta G^{\neq 233\ \mathrm{K}} = 12.0$ kcal mol^{-1}) and also of the NMe$_2$ methyl proton resonances for **8** (A$G^{\neq 278\ \mathrm{K}} =$ 14.2 kcal mol^{-1}) and **18** ($\Delta G^{\neq 251\ \mathrm{K}} = 12.6$ kcal mol^{-1}).

The kinetic parameters of this dynamic process (see Tables 3 and 4) which were calculated on the basis of ^{1}H-DNMR data by NMR line shape analysis and DNMR5 program [16] are in good agreement with an intramolecular process (log A ca. 12.97; 13.75) and takes place without any change of the entropy factor ($\Delta S^{\neq}$ ca. 0).

In the ground state, the complexes **8**, **18** and **19** do not present rotation around the Ta–N$_{\mathrm{imido}}$ and N$_{\mathrm{imido}}$–C$_{ipso}$(aryl) bonds, probably due to the positive charge delocalization into the N$_{\mathrm{imido}}$–Ta–N$_{\mathrm{amido}}$ moiety (Scheme 4), as has been reported for bis-dimethylamido titanium(IV) derivatives [17]. The $\Delta G^{\neq}$ values for the rotation of the 2,6-Me$_2$C$_6$H$_3$ ring around the N$_{\mathrm{imido}}$–C$_{ipso}$(aryl) bond are similar for **8** and **18** and therefore independent of the substituent X (X = Cl, **8**; Me, **18**). However, in the case of complex **19** with bulkier substituents (Z = ^{i}Pr) such effect is not observed at higher temperatures or at minor magnetic fields [18]. Therefore, the absence of rotation around the N$_{\mathrm{imido}}$–C$_{ipso}$(aryl) bond is not due to the positive charge delocalization by π-interaction in the ring but to the steric hindrance of the Z and Cp* groups.

The kinetic parameters for the rotation of the NMe$_2$ ligand around the N$_{\mathrm{amido}}$–Ta bond clearly depend of the electronic and steric properties of the substituent X = Cl, **8**; Me, **18** and it can be considered as a diamido–amido imido exchange process (Scheme 4), in agreement with the negligible $\Delta S^{\neq}$ values.

Further studies will be carried out to probe the similarities and differences in the reactivity of these alkyl imido cyclopentadienyl niobium and tantalum systems with carbon monoxide and isocyanides and the intramolecular rearrangements of the insertion products.

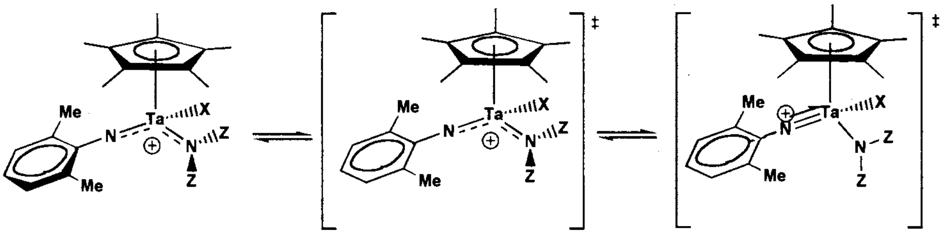
3. Experimental

3.1. General considerations

All reactions and manipulations were carried out under an argon atmosphere using standard Schlenk-tube and cannula techniques or in a conventional argon-filled glove-box. Solvents were refluxed over an appropriate drying agent and distilled and degassed prior to use: dichloromethane (P$_4$O$_{10}$), *n*-hexane (Na/K alloy) and toluene (Na). Literature methods were employed for the synthesis of starting materials NbCp′Cl$_4$ [19] and [TaCp*Cl$_2${N(2,6-Me$_2$C$_6$H$_3$)}] [9], alkyl lithium LiR (R = C$_5$Me$_5$ [20], CH$_2$SiMe$_3$ [21], CH$_2$CMe$_3$ [21], N^{i}Pr$_2$ [20], NH^{t}Bu [20], O^{t}Bu [20]), Li$_2$[*o*-(NSiMe$_3$)$_2$C$_6$H$_4$] [22] and dibenzyl magnesium Mg(CH$_2$C$_6$H$_5$)$_2$(THF)$_2$ [23]. The reagents NHR^{1}SiMe$_3$ (R^1 = 2,6-Me$_2$C$_6$H$_3$; 2,6-^{i}Pr$_2$C$_6$H$_3$) were prepared in the usual way by treatment of amines R^{1}NH$_2$ with Li^{n}Bu followed by SiClMe$_3$. All commercial products were purchased from Aldrich and were used without further purification as follows: LiNMe$_2$, MgClMe 3 M in diethyl ether, ZnMe$_2$ 2 M in toluene, R^{1}NH$_2$ (R^1 = 2,6-Me$_2$C$_6$H$_3$; 2,6-^{i}Pr$_2$C$_6$H$_3$) and NH(SiMe$_3$)$_2$.

Table 3
Kinetic parameters of rotation of 2,6-Me$_2$C$_6$H$_3$ ring around N$_{\mathrm{imido}}$–C$_{ipso}$(aryl) bond

	Log A	E_a (kcal mol^{-1})	$\Delta H^{\neq}$ (kcal mol^{-1})	$\Delta S^{\neq}$ (e.u.)	$\Delta G^{\neq 298\ \mathrm{K}}$ (kcal mol^{-1})
8	13.55 ± 0.17 $r = 0.998$	11.8 ± 0.2	11.3 ± 0.2 $r = 0.998$	1.9 ± 1.0	10.7
18	12.4 ± 0.1 $r = 0.999$	10.1 ± 0.1	9.6 ± 0.1 $r = 0.999$	−3.5 ± 10.4	10.6



X = Cl; Z = Me **8**
X = Me; Z = Me **18**
X = Me; Z = ^{i}Pr **19**

Scheme 4.

IR spectra were recorded on a Perkin-Elmer 583 spectrophotometer (4000–200 cm^{-1}) as Nujol mulls between CsI or polyethylene pellets. ^{1}H and ^{13}C{^{1}H}-NMR spectra were recorded on Varian Unity 300 and Varian Unity 500 Plus spectrometers and chemical shifts were measured relative to residual ^{1}H and ^{13}C resonances in the deuterated solvents C_6D_6 (δ 7.15), $CDCl_3$ (δ 7.24), C_6D_6 (δ 128) and $CDCl_3$ (δ 77), respectively. C, H and N analyses were carried out with a Perkin-Elmer 240C microanalyzer.

3.2. Synthesis of [NbCp′Cl$_2$(NR^1)], (R^1 = 2,6-Me$_2$C$_6$H$_3$, *1*; 2,6-^{i}Pr$_2$C$_6$H$_3$, *2*; SiMe$_3$, *3*)

A solution of NHR^{1}SiMe$_3$ (26.90 mmol; R^1 = 2,6-Me$_2$C$_6$H$_3$, 5.74 ml; 2,6-^{i}Pr$_2$C$_6$H$_3$, 7.14 ml; SiMe$_3$, 5.62 ml) in dichloromethane (10 ml) was added at r.t. to a red solution of NbCp′Cl$_4$ (5.00 g, 13.45 mmol) in dichloromethane (150 ml) and the mixture was stirred for 12 h. The supernatant solution was filtered from the [NH$_2$R^{1}SiMe$_3$]Cl residue. The solvent removed in vacuo and the oily red solid residue obtained was heated at 100°C and at reduced pressure during the 4 h to eliminate volatiles. Extraction of the residue into *n*-hexane (2 × 50 ml) afforded a red solution which was filtered, concentrated to ca. 25 ml and cooled to −40°C to give **1**–**3** as oily red solids.

1: Yield 5.02 g (89%). Anal. Found: C, 45.66; H, 5.52; N, 3.44. $C_{16}H_{22}Cl_2NSiNb$. Calc.: C, 45.73; H, 5.28; N, 3.33%.

2: Yield 5.69 g (89%). Anal. Found: C, 50.15; H, 6.33; N, 2.95. $C_{20}H_{30}Cl_2NSiNb$. Calc.: C, 50.24; H, 6.35; N, 2.94%.

3: Yield 4.64 g (89%). Repeated attempts to obtain satisfactory microanalysis on this material were unsuccessful.

3.3. Synthesis of [MCpClR{N(2,6-Me$_2$C$_6$H$_3$)}], (M = Nb, Cp = Cp′, R = Me, *5*; Cp*, *6*; M = Ta, Cp = Cp*, R = NMe$_2$, *8*; O^{t}Bu, *9*)

A 2 M solution of ZnMe$_2$ in toluene (0.60 ml, 1.19 mmol) was added at r.t. to a red solution of NbCp′Cl$_2$(NR^1) (0.50 g, 1.19 mmol) in *n*-hexane (50 ml) and the mixture was stirred for 12 h. The solution was filtered and the solvent reduced to dryness to give a brown residue which was extracted with *n*-hexane (2 × 20 ml). Subsequently, the solution was concentrated to ca. 5 ml and cooled to −40°C overnight to afford **5** as an extremely air-sensitive brown microcrystalline solid.

5: Yield 0.38 g (80%). Satisfactory elemental analysis could not be obtained for this compound due to its extreme air and moisture sensitivity.

3.3.1. Synthesis of *6*, *8* and *9*

LiR (R = Cp*, 8 mmol, 1.13 g; 2 mmol, R = NMe$_2$, 0.10 g; O^{t}Bu, 0.19 g) was added under rigorously anhydrous conditions to a solution of MCpCl$_2$(NR^1) (2

Table 4
Kinetic parameters of rotation of NZ$_2$ (Z = Me, **8**, **18**; ^{i}Pr, **19**) ligand around the N$_{amido}$–Ta bond

	Log A	E_a (kcal mol^{-1})	$\Delta H^{\neq}$ (kcal mol^{-1})	$\Delta S^{\neq}$ (e.u.)	$\Delta G^{\neq 298\text{ K}}$ (kcal mol^{-1})
8	14.1 ± 0.2 $r = 0.998$	13.8 ± 0.25	13.3 ± 0.25 $r = 0.998$	4.4 ± 1.0	12
18	13.4 ± 0.25 $r = 0.998$	11.7 ± 0.25	11.2 ± 0.25 $r = 0.998$	1.4 ± 1.0	10.8
19	–	–	–	–	13.9[a]

[a] Value determinated at 288 K in the collapse point of ***H***CMe$_2$ signals.

mmol; M = Nb, 0.84 g; Ta, 1.00 g) in toluene (50 ml) and the reaction mixture was stirred for 48 (**6**) or 12 (**8** and **9**) h. The resulting suspension was filtered, the solvent reduced to dryness and the residue extracted into *n*-hexane (2 × 10 ml). The solution was concentrated to half volume and cooling to −40°C afforded **6**, **8** and **9** as red–brown (**6**) and brown (**8** and **9**) microcrystalline solids.

6: Yield 0.41 g (40%). Anal. Found: C, 60.20; H, 7.32; N, 2.67. $C_{26}H_{37}ClNSiNb$. Calc.: C, 60.07; H, 7.12; N, 2.69%.

8: Yield 0.77 g (75%). Anal. Found: C, 46.74; H, 5.81; N, 5.63. $C_{20}H_{30}ClN_2Ta$. Calc.: C, 46.66; H, 5.87; N, 5.44%.

9: Yield 0.81 g (75%). Anal. Found: C, 48.52; H, 6.47; N, 2.40. $C_{22}H_{33}ClONTa$. Calc.: C, 48.58; H, 6.41; N, 2.57%.

*3.4. Synthesis of [MCpR$_2${N(2,6-Me$_2$C$_6$H$_3$)}] (M = Nb, Cp = Cp′, R = Me, **10**; CH$_2$SiMe$_3$, **11**; CH$_2$CMe$_3$, **12**; NMe$_2$, **13**; CH$_2$C$_6$H$_5$, **14**; M = Ta, Cp = Cp*, R = o-(NSiMe$_3$)$_2$C$_6$H$_4$, **15**)*

A 3 M solution of MgClMe in diethyl ether (0.8 ml, 2.38 mmol) or LiR (2.38 mmol; R = CH_2SiMe_3, 0.22 g; CH_2CMe_3, 0.19 g; NMe_2, 0.12 g) or $Mg(CH_2C_6H_5)_2(THF)_2$ (0.42 g, 1.19 mmol) or $Li_2[o\text{-}(NSiMe_3)_2C_6H_4]$ (0.31 g, 1.19 mmol) was added to a toluene (30 ml) solution of $[MCpCl_2\{N(2,6\text{-}Me_2C_6H_3)\}]$ (1.19 mmol; M = Nb, Cp = Cp′, 0.50 g; M = Ta, Cp = Cp*, 0.60 g) under rigorously anhydrous conditions and the reaction mixture stirred for 12 h. The resulting suspension was filtered, the solvent evaporated to dryness and the residue extracted into *n*-hexane (2 × 10 ml). The solution was concentrated to half volume and cooled to −40°C to yield **10**–**15** as brown (**10**–**14**) or yellow (**15**) microcrystalline solids.

10: Yield 0.36 g (80%). Anal. Found: C, 56.81; H, 7.40; N, 3.51. $C_{18}H_{28}NSiNb$. Calc.: C, 56.98; H, 7.44; N, 3.69%.

11: Yield 0.42 g (80%). Anal. Found: C, 54.76; H, 8.36; N, 2.52. $C_{24}H_{44}NSi3Nb$. Calc.: C, 55.03; H, 8.47; N, 2.67%.

12: Yield 0.46 g (80%). Anal. Found: C, 63.45; H, 8.97; N, 2.67. $C_{26}H_{44}NSiNb$. Calc.: C, 63.52; H, 9.02; N, 2.85%.

13: Yield 0.40 g (80%). Anal. Found: C, 54.85; H, 7.76; N, 9.50. $C_{20}H_{34}N_3SiNb$. Calc.: C, 54.91; H, 7.83; N, 9.60%.

14: Yield 0.50 g (80%). Anal. Found: C, 67.58; H, 6.87; N, 2.53. $C_{30}H_{36}NSiNb$. Calc.: C, 67.78; H, 6.82; N, 2.63%.

15: Yield 0.57 g (70%). Anal. Found: C, 52.97; H, 6.67; N, 5.90. $C_{30}H_{46}N_3Si_2Ta$. Calc.: C, 52.54; H, 6.76; N, 6.02%.

*3.5. Synthesis of [MCpMeR{N(2,6-Me$_2$C$_6$H$_3$)}] (M = Nb, Cp = Cp′, R = CH$_2$SiMe$_3$, **16**; NMe$_2$, **17**; M = Ta, Cp = Cp*, R = NMe$_2$, **18**; N^{i}Pr$_2$, **19**; NH^{t}Bu, **20**)*

At r.t., *n*-hexane (50 ml) was added to a mixture of the compound $[MCpClMe\{N(2,6\text{-}Me_2C_6H_3)\}]$ (1.25 mmol; M = Nb, Cp = Cp′, 0.50 g; M = Ta, Cp = Cp*, 0.61 g) and LiR (1.25 mmol; R = CH_2SiMe_3, 0.12 g; NMe_2, 0.06 g; N^iPr_2, 0.13 g; NH^tBu, 0.10 g). The mixture was stirred for 12 h, during which time a brown solution and a pale gelatinous precipitate of LiCl were formed. Filtration of the supernatant solution from the solid, followed by concentration to ca. 10 ml and cooling to −40°C, afforded **16**–**18** as brown, **19** yellow and **20** oily brown microcrystalline solids.

16: Yield 0.39 g (70%). Anal. Found: C, 55.72; H, 7.97:N, 3.15. $C_{21}H_{36}NSi_2Nb$. Calc.: C, 55.85; H, 8.03; N, 3.10%.

17: Yield 0.35 g (70%). Anal. Found: C, 55.80; H, 7.55; N, 6.68. $C_{19}H_{31}N_2SiNb$. Calc.: C, 55.87; H, 7.65; N, 6.86%.

18: Yield 0.43 g (70%). Anal. Found: C, 50.80; H, 6.43; N, 5.60. $C_{21}H_{33}N_2Ta$. Calc.: C, 51.00; H, 6.73; N, 5.66%.

19: Yield 0.44 g (65%). Anal. Found: C, 54.47; H, 7.20; N, 4.90. $C_{25}H_{41}N_2Ta$. Calc.: C, 54.54; H, 7.50; N, 5.09%.

20: Yield 0.42 g (65%). Anal. Found: C, 53.29; H, 7.24; N, 5.15. $C_{23}H_{37}N_2Ta$. Calc.: C, 52.87; H, 7.14; N, 5.36%.

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