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Alkyl Chlorido Hydridotris(3,5-dimethylpyrazolyl)borate Imido Niobium and Tantalum(V) Complexes: Synthesis, Conformational States of Alkyl Groups in Solid and Solution, X-Ray Diffraction and Multinuclear Magnetic Resonance Spectroscopy Studies.

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The alkylation of the starting pseudooctahedral dichlorido imido hydridotris(3,5-dimethylpyrazolyl)borate niobium and tantalum(V) compounds [MTp*Cl_2(N*t*Bu)] (M=Nb,Ta; Tp*=BH(3,5-$Me_2C_3HN_2)_3$) with MgClR in different conditions led to new alkyl chlorido imido derivatives [MTp*ClR(N*t*Bu)] (M=Nb/Ta, R=CH_2CH_3 **1a**/**1b**, CH_2Ph **2a/2b**, CH_2*t*Bu **3a/3b**, CH_2SiMe_3 **4a/4b**, CH_2CMe_2Ph **5a/5b**), whereas the dimethyl derivatives [MTp*Me_2(N*t*Bu)] (M=Nb **6a**, Ta **6b**) could be isolated as unitary species when the reaction was carried out using 2 equivalents of the magnesium reagent MgClMe. However, the chlorido methyl [MTp*ClMe(N*t*Bu)] (M=Nb **7a**, Ta **7b**) complexes were obtained by the heating at 50ºC of dichlorido and dimethyl imido complexes mixtures in 1:1 ratio. All complexes were studied by multinuclear magnetic resonance spectroscopy and the molecular structures of **1b**, **2a**/**b**, **3a**/**b**, **4a** and **5a**/**b** were determined by X-ray diffraction methods. In solid state the complexes **1b**, **4a** and **5a** exhibit only a ***gauche-anti*** and the complexes **2a/b**, **3a/b** and **5b** only a ***gauche-syn*** conformations of alkyl substituents, whereas both conformational states, which do not show mutual exchange in NMR time scale, were observed for **3a**/**b** in a benzene-d_6 solution. The ^{15}N chemical shifts of the complexes **1**-**7** are discussed.

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Introduction

Scorpionate- or hydridotris(pyrazolyl)borate groups are anionic tridentate chelate ligands useful in coordination chemistry[1] as a stabilizing group due to their strong electron donor ability capable to form stable complexes with metals in high oxidation state.[1-3] However, in this context, the development of a rich chemistry based in early transition metal was hampered by the absence of versatile synthetic methods to yield suitable starting materials. The preliminary reports in this field pointed to facile in situ decomposition of the compounds via hydrolysis and redox reactions, B-N bond cleavage or unexpected synthesis of ionic derivatives.[1]

The synthesis of group 5 metal complexes of the type [$MTpCl_4$] (M=V, Nb, Ta; Tp=generic hydridotris(pyrazolyl)borate) bearing Tp ligands in moderate to high yields were highly dependent on experimental details (solvent, temperature) and the byproducts formation precluded their use as accessible starting materials.[4] However, several classes of monoanionic hydrido(trispyrazolyl)borate niobium and tantalum complexes containing alkoxide, alkyl, alkyne, amido, chlorido, imido and oxo ancillary ligands have been prepared and their reactivity toward cationic species investigated.[4-8] Additionally, an extensive variety of high-activity vanadium,[9-11] niobium[12] and tantalum[11e,13]-based catalysts in olefin polymerization incorporating different ligand sets have been reported.

In this article, we report the synthesis of new alkyl chlorido and dimethyl imido hydridotris(3,5-dimethylpyrazolyl)borate niobium and tantalum(V) complexes [MTp*XR(N*t*Bu)] {M=Nb, Ta; Tp*=$HB(3,5\text{-}Me_2C_3HN_2)_3$; X=Cl, R=Me, CH_2CH_3, CH_2Ph,

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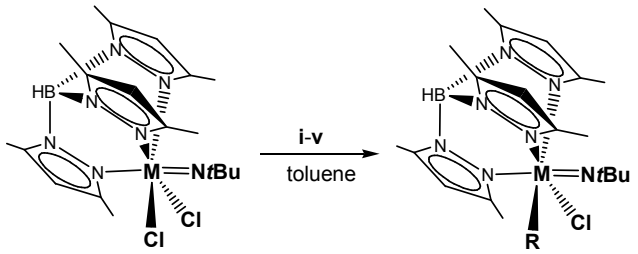
CH_2tBu, CH_2SiMe_3, CH_2CMe_2Ph; X=R=Me) and their structural study in solution and solid state.

Results and Discussion

A series of alkyl chlorido derivatives [MTp*ClR(N*t*Bu)] (M=Nb/Ta, R=CH_2CH_3 **1a**/**1b**, CH_2Ph **2a**/**2b**, CH_2tBu **3a**/**3b**, CH_2SiMe_3 **4a**/**4b**, CH_2CMe_2Ph **5a**/**5b**) were obtained in good yields by treatment of the dichlorido complexes [MTp*Cl_2(N*t*Bu)][5c,14] with 1 equivalent of the appropriate magnesium reagent in different conditions (see Scheme 1). However, several attempts in order to get dialkylated, mixed alkyl and alkyl aryl complexes in different experimental conditions proved unsuccessful.

Scheme 1



M=Nb,Ta	M	CH_2CH_3	CH_2Ph	CH_2tBu	CH_2SiMe_3	CH_2CMe_2Ph
	Nb / Ta	**1a / 1b**	**2a / 2b**	**3a / 3b**	**4a / 4b**	**5a / 5b**

Reagents and conditions
i- R=CH_2CH_3, 1 equiv MgClR, 12 h, r.t.
ii- R=CH_2Ph, 1 equiv MgClR, 12 h, r.t.
iii- R=CH_2tBu, excess MgClR; 12 h, r.t.(M=Nb), 5 days, 90°C (M=Ta)
iv- R=CH_2SiMe_3, slight excess MgClR; 8 days, 70°C (M=Nb), 11 days, 90°C (M=Ta)
v- R=CH_2CMe_2Ph, excess MgClR, 12 h, r.t. (M=Nb),11 days, 90°C (M=Ta)

In contrast, the dimethyl derivatives [MTp*Me_2(N*t*Bu)] (M=Nb **6a**, Ta **6b**) were prepared by treatment of the starting dichlorido compounds with 2 equivalents of the Grignard reagent (Scheme 2).

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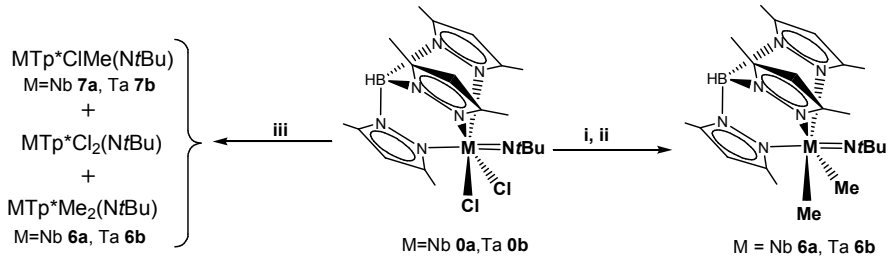
Scheme 2



Reagents and conditions

i- 2 equiv MgClMe, toluene, 2 h, r.t. **6a; ii**- 2 equiv MgClMe, toluene, 11 days, 90ºC **6b**

iii- 1 equiv MgClMe, benzene-d_6 or toluene;

The methylation of dichlorido imido niobium compound [NbTp*Cl_2(N*t*Bu)] by using a slight defect of MgClMe, in NMR tube at room temperature (see Scheme 2), led to a mixture of the chlorido methyl [NbTp*ClMe(N*t*Bu)] **7a** (60%), dimethyl [NbTp*Me_2(N*t*Bu)] **6a** (15%) and dichlorido starting (25%) complexes, that do not change after heating at 60ºC during 24 h. However, in the case of the dichlorido imido tantalum compound [TaTp*Cl_2(N*t*Bu)], the first ^{1}H NMR spectrum did not show reaction and after 24 hours at 60ºC a mixture of 60% of dichlorido, 20% of MgClMe, 5% of chlorido methyl [TaTp*ClMe(N*t*Bu)] **7b** and 15% of dimethyl **6b** complexes was observed. After one week at 60ºC (M=Nb) and 100ºC (M=Ta), respectively, were obtained the complexes **7a** (88%) and **7b** (20%). Finally, the mixed chlorido methyl imido tantalum complex **7b** was synthesized as major specie (70%), by the ligand exchange reaction[15] heating the equimolar mixtures of dichlorido and dimethyl imido **6b** compounds at 100ºC during 28 days. These data are according with a slower methylation of dichlorido imido tantalum complex with respect to the niobium analogue.

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All the complexes **1**-**7** are extremely moisture sensitive and soluble in most organic solvents, including saturated hydrocarbons.

The IR spectra of all complexes show the characteristic absorptions for Tp* ring [$\bar{\nu} \approx 2546$ (ν_{B-H}), 1545 ($\nu_{C=N}$) and 1547(Nb)/1448(Ta) (ν_{B-N}) cm^{-1}][6c,d,16] and for the trimethylsily1[17] substituent $\delta_s(CH_3)$ $\bar{\nu} \approx 1240$(Nb **6a**)/1260(Ta **6b**). Absorptions due to the M=N and M-C stretching vibrations[16d,e,18] are observed at $\bar{\nu} \approx 1367$ and 466 cm^{-1}, respectively.

The molecular structures of the complexes **1b**, **2a**/**b**, **3a**/**b**, **4a** and **5a**/**b** were studied by X-Ray diffraction methods. As an example of this, an ORTEP view of such structure and atom-labeling scheme for the complexes **5a**/**b**, for which the hydrogen atoms positions of α-CH_2R' (R'=CMe_2Ph) groups were experimentally determinate, is shown in the Figure 1. Selected bond distances and angles are summarized in Table 1. All the complexes are chiral, crystallize in a centrosymmetric space group and exhibit a core with a metal center bonded to three nitrogen atoms in a facial coordination of a Tp* ligand, a chlorine atom, an alkyl ligand and the axial-located imido moiety in a distorted octahedral geometry.

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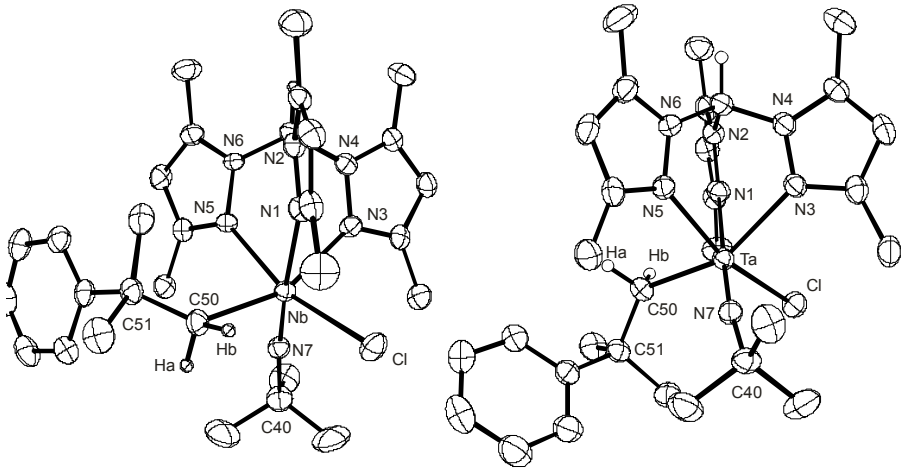

Figure 1. ORTEP drawing of [MTp*Cl(CH_2CMe_2Ph)(N*t*Bu)] (M=Nb **5a**, Ta **5b**). with the atom numbering scheme. Thermal ellipsoids are drawn at the 30% probability level.

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Table 1. More important bond lengths (Å) and angles (°) for complexes **1**-**5**

R	CH_2CH_3	CH_2Ph		CH_2CMe_3		CH_2SiMe_3	CH_2CMe_2Ph	
M	Ta **1b**	Nb **2a**	Ta **2b**	Nb **3a**	Ta **3b**	Nb **4a**	Nb **5a**	Ta **5b**
M-N7	1.725(12)	1.838(76)	1.773(6)	1.783(7)	1.823(7)	1.760(5)	1.761(5)	1.767(3)
M-N5	2.257(12)	2.360(5)	2.248(5)	2.259(6)	2.235(5)	2.264(5)	2.233(5)	2.232(3)
M-N3	2.248(13)	2.270(5)	2.269(5)	2.308(7)	2.306(5)	2.288(6)	2.264(5)	2.289(3)
M-N1	2.367(11)	2.402(5)	2.421(6)	2.461(7)	2.447(6)	2.433(5)	2.444(5)	2.454(3)
M-C50	2.206(16)	2.270(5)	2.258(7)	2.196(10)	2.127(8)	2.198(6)	2.232(7)	2.222(4)
M-H_a	2.65	2.72	2.71	2.60	2.52	2.59	2.71(9)	2.69(4)
M-H_b	2.65	2.72	2.71	2.60	2.52	2.59	2.32(6)	2.47(5)
C40-N7-M	171.9(11)	160.2(5)	170.0(4)	169.8(6)	171.0(5)	172.9(5)	168.2(5)	172.6(3)
C51-C50-M[1]	122.1(11)	118.6(4)	119.5(5)	132.7(8)	138.0(7)	135.0(3)	138.0(5)	131.7(3)
N7-M-C50	94.1(6)	98.3(2)	98.3(3)	101.9(4)	101.8(3)	96.9(2)	94.8(2)	102.1 (2)
H-C50-M	107.2	107.6	107.4	104.1	102.6	103.5	H_a 108.1(8), H_b 81.8(9)	H_a 107.4(3) H_b 97.2(4)
θ |N7-M-C50-C51|	144.7(6)	36.7(7)	30.5(6)	51.8(3)	49.1(9)	133.2(6)	129.4(7)	39.4(4)
θ (N7-M-C50-H_a)	21.3	85.7	92.1	73.1	76.5	8.0	18.5(5)	93.5 (3)
θ (N7-M-C50-H_b)	92.5	159.2	153.4	176.7	174.8	101.6	111.4(4)	160.1(4)

[1]In the complex **4a** C51=Si

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The average M-N7 distance (1.779 Å) and M-N7-C40 angle (169.51°) for the imido ligand are in the range of the reported for imido niobium and tantalum complexes; [15d,17,19] however, the only exception is the complex **2a** (M=Nb, R=CH_2Ph) with a larger Nb-N_{imido} distance (1.838(6) Å) and a minor Nb-N_{imido}-C40 (160.2(5)°) angle. Furthermore, the Ta-N7 bond length corresponding to the complex **1b** is 1.725(12) Å, which is the shortest reported value for a tantalum *tert*-butylimido bond.[6d,19b,g,20] The M-N1 bond length for the axial pyrazolyl group trans to imido (average 2.427 Å) is greater than the corresponding to M-N bonds for the pyrazolyl groups trans to the chlorido ligand (average M-N5 2.259 Å) and the alkyl group (average M-N3 2.279 Å). The average M-N distances (2.331 Å) and N-M-N angles (79.69°) formed by the tridentate Tp* ligand are similar to the reported for hydridotrispyrazolylborate niobium and tantalum derivatives.[6b,7a,8e] With respect to the alkyl group, the average M-C50 distance (Nb 2.223 Å, Ta 2.203 Å) and the M-C50-C51 angle (Nb 131.0°, Ta 127.85°) are within the range of the reported for some alkyl niobium and tantalum derivatives.[6a,7g,19,21]

In the solid state the complexes **1b**, **4a**, **5a** are characterized by *gauche-anti* whereas **2a**/**b**, **3a**/**b**, **5b** by *gauche-syn* (see Table 1 and Figure 2) conformational states of the alkyl group being the average ΘN7-M-C50-C51 torsion angle equal to 136° and 41°, respectively.

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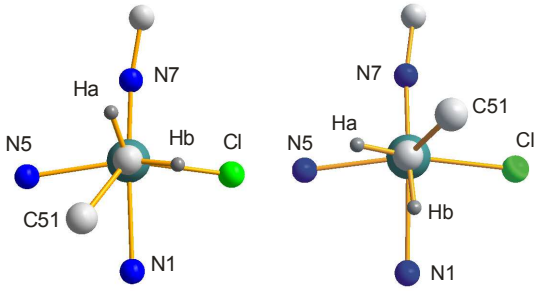

R=CH_2CH_3 **1b** R=CH_2Ph **2a/b**
CH_2SiMe_3 **4a** CH_2tBu **3a/b**
CH_2CMe_2Ph **5a** CH_2CMe_2Ph **5b**

Figure 2. Projection respect to M-C50 bond (C51=Si in **4a**) in the complexes **1b, 2a/b, 3a/b, 4a** and **5a/b**.

Moreover, in the complexes **5a**/**b** the α-methylene hydrogen atoms H_a and H_b of the C*H*$_2$CMe$_2$Ph group were located and isotropically refined. The short bond length M-H_b and the M-C50-H_a/H_b bond angles (see Figure 3) are according with the agostic interaction,[19h,21] as have been reported for analogous alkyl niobium[6a] and tantalum[19g] complexes, which also agrees with the ^{1}H NMR data (see below).

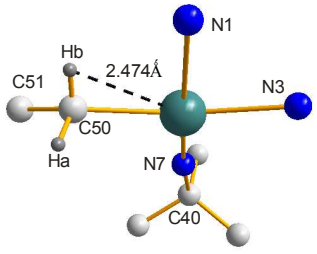

Figure 3. Structure of central core in the complexes **5a**/**b** M-H_b [R_{Nb-Hb}=2.32(6) Å, R_{Ta-Hb}=2.47(5) Å; ∠H_b-C50-Nb=81.8º, ∠H_b-C50-Ta=97.3º].

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The ^{1}H, ^{13}C and ^{15}N NMR data justify the C_s symmetry of the dimethyl complexes **6a**/**b** and the C_1 symmetry of the alkyl chlorido compounds **1**-**5** and **7** and are in agreement with the pseudooctahedral geometry of all of them.

In the ^{1}H NMR spectra of alkyl chlorido complexes **1-5** (see Table 2) we have observed an important difference between the chemical shifts of diastereotopic protons for α-***CH***$_2$R' (R'=Me **1**, Ph **2**, *t*Bu **3**, $SiMe_3$ **4**, CMe_2Ph **5**) moiety, mainly due to the high field chemical shift of H_b involved in a possible agostic interaction[5e,g,6a,8b,d,22] with the metal atom.

Table 2.

^{1}H and ^{13}C chemical shifts of -C***H***$_2$R' for the complexes **1-5** in C_6D_6 at 25ºC.

R'	M	MC**H**$_2$R'			
		δ ^{1}H			δ ^{13}C
		$\Delta\delta(H_a-H_b)$	δ_{av}	$\Delta\delta=\delta_{av}$Nb-δ_{av}Ta	
CH_3	Nb **1a**	4.42	2.51	0.45	74.7
	Ta **1b**	2.80	2.06		63.3
Ph	Nb **2a**	0.77	3.22	0.47	78.6
	Ta **2b**	1.05	2.75		76.0
*t*Bu	Nb **3a**	3.67	2.37	0.69	109
	Ta **3b**	2.04	1.68		92.3
$SiMe_3$	Nb **4a**	3.76	2.20	0.86	67.0
	Ta **4b**	2.28	1.34		59.6
CMe_2Ph	Nb **5a**	3.69	2.82	0.74	105.7
	Ta **5b**	2.03	2.09		90.9

The δ_{av} ^{1}H for methylene moiety are clearly great for the niobium complexes, as we have early observed for trialkyl imido complexes.[18b] Moreover, the differences of $\Delta\delta^{1}H$ between both metals (Table 2) depend on the volume of alkyl group and decreases in the

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following order: CH_2SiMe_3 > CH_2CMe_2Ph > CH_2tBu > CH_2Ph > CH_2CH_3. Besides, in the chlorido methyl **7a**/**b** and in the dimethyl **6a**/**b** imido complexes, the $\delta^{13}CH_3$ are slightly greater for the tantalum derivatives ($\Delta\delta$, 5.6 **6a/b**, 1.5 **7a/b**).

The ^{1}H NMR spectra of the [MTp*Cl(CH_2tBu)(N*t*Bu)] complexes show two sets of the signals in an 1:3 (M=Nb **3a**) and 1:6 (M=Ta **3b**) ratio (Figure 4), which are characterized by the same number of resonances in equal proportion and comparable chemical shifts. Additionally, both species have the same diffusion coefficient [D = (8.5± 0.3)·10^{-10} m^2/s], obtained by using Dbppste cc pulse sequence (see ESI-1), that justify the same hydrodynamic radius of such compounds. Furthermore, the very similar parameters of the AB spin system observed for α-C***H***$_2$R' moiety [δ_{av} 2.37, ^{2}J=12.2 Hz, $\Delta\delta(H_a–H_b)$ = 3.67 M-major **3a**; δ_{av} 2.43, ^{2}J=11.1 Hz, $\Delta\delta(H_a–H_b)$=5.06 m-minor **3b**] are probably due to an agostic interaction in both structures.

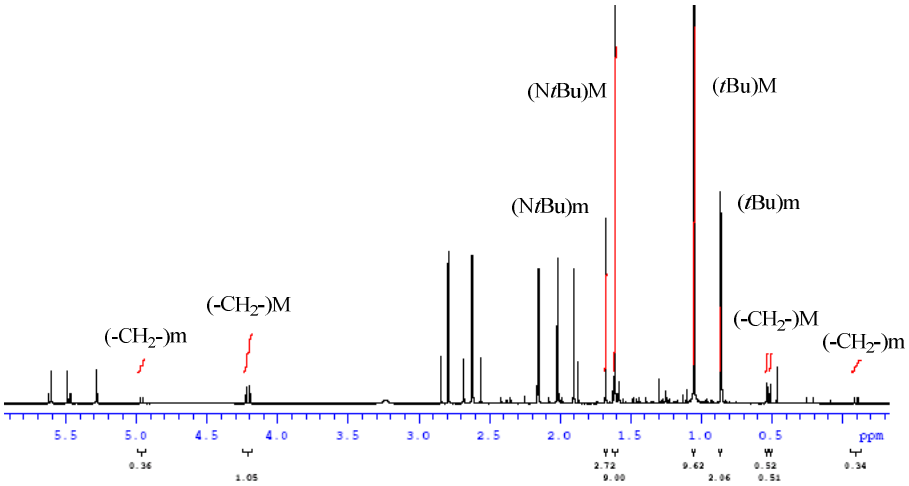

Figure 4. ^{1}H NMR spectrum of [NbTp*Cl(CH_2tBu)(N*t*Bu)] **3a** in C_6D_6 at 25ºC (M- major compound, m– minor compound)

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This behaviour suggests the existence of two isomers of the complex **3a**. In order to resolve 3D-structure of everyone, we have applied a standard procedure based on Nuclear Overhauser Enhancement. The 2D-ROESYAD and the Roesy1d spectra (see ESI-2) show all necessary cross-peaks were observed to determine the spatial mutual location of the most important group in both isomers (Figure 5), assuming that the H_b protons are characterized by high field resonances.

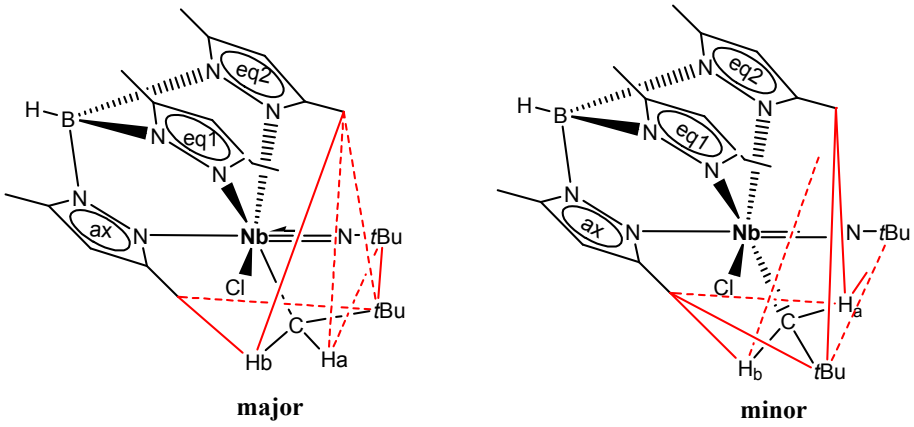

Figure 5. More important NOE interactions in the complex **3a**.

The observed structural situation is according with the existence in solution of two conformational states of alkyl group in the complex **3a**, as shown in the Figure 6. Moreover, according to the NOE data, the complex **3b** (Ta) exhibits the same conformational state that **3a** (Nb).

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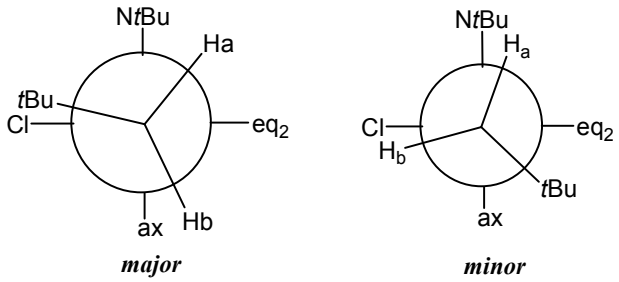

Figure 6. Conformational states of CH_2tBu groups in the complexes **3a**/**b.**
(Newman projection respect to the α-carbon-metal bond)

The chemical shifts of $^{15}N_1$ (see Figure 7) bonding directly to the boron atom have the same value δ -156±1, not only in the complexes **1-7,** but also in the starting dichlorido[18a] and in amido imido complexes.[14]

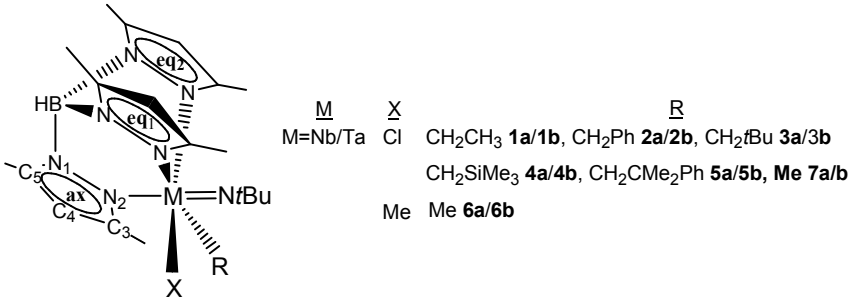

Figure 7. Numeration of the pyrazolyl rings and atom positions in the complexes **1**-**7**

The resonances corresponding to the $^{15}N_{imido}$ (Table 3) in the niobium complexes are considerably more deshielding than in the tantalum analogues (Δδ Nb-Ta=28 **2**-**5**, 25 **1**, 24 **7** and 20 **6**), due to the variation of the diamagnetic component of the magnetic shielding constant[23] and similar to that observed by us earlier.[14,18]

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Table 3. The ^{15}N chemical shifts for the complexes **1-7**.

R	M	$\delta\ ^{15}N_2$ Tp*			$\delta\ ^{15}NCMe_3$	$\Delta\delta^{15}N$
		N_{ec1}	N_{ec2}	N_{ax}		
CH_3	Nb **7a**	-121	-119	-112	27	24
	Ta **7b**	-121	-118	-115	3	
CH_2CH_3	Nb **1a**	-122	-117	-112	23	25
	Ta **1b**	-122	-117	-112	-2	
CH_2Ph	Nb **2a**	-122	-117	-113	35	28
	Ta **2b**	-122	-116	-115	7	
CH_2CMe_3	Nb **3a**	-122	-118	-111	31	28
	Ta **3b**	-123	-116	-112	3	
CH_2SiMe_3	Nb **4a**	-121	-119	-113	30	28
	Ta **4b**	-122	-117	-114	2	
CH_2CMe_2Ph	Nb **5a**	-122	-118	-112	32	28
	Ta **5b**	-123	-116	-113	4	
Me_2	Nb **6a**	-115		-107	5	20
	Ta **6b**	-117		-112	-15	

Finally, the $^{15}N_2$ chemical shifts of the N_{ax} bonding to the metal atom in axial position (δ -113.3±1.3), *trans*- respect to the strong donor imido group, is greater than both $\delta^{15}N_2$ bonding to the metal in equatorial positions (see Table 3). Moreover, the resonances of $^{15}N_{2eq2}$ (δ -117.3±1.1) situated in trans- position respect to electron acceptor chlorido ligand are more deshielding than the corresponding to N_{2eq1} (δ -121.7±0.8), trans- respect to

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the electron donor alkyl group. In other words, using only the inductive effect criteria of the ligands bonded to the metal atom we can explain the differences of δ ^{15}N for nitrogen atoms located in equatorial plane but not in axial position.

However, the larger bond length M-N_{ax} (2.42Å) with respect to M-N_{eq} (≈2.28Å), becomes smaller the diamagnetic contribution in the shielding constant[23] and therefore increases the chemical shift. Moreover, in a previous work[14] we have observed a discoordination-coordination process of the pyrazolyl axial ring allows us to propose that the deshielding of $^{15}N_{ax}$ resonance is probably due to a very fast exchange between free and coordinated states,[24] assuming that coordination, for example, of free pyridine to metal atom provokes the considerable shielding of its ^{15}N resonance.[18a,25]

A detailed study will be carried out to probe the reactivity of these alkyl chlorido imido Tp* niobium and tantalum derivatives with organic isocyanides.

Conclusions

Alkyl chlorido [MTp*ClR(N*t*Bu)] (M=Nb/Ta; R=CH_2CH_3 **1a**/**1b**, CH_2Ph **2a**/**2b**, CH_2*t*Bu **3a**/**3b**, CH_2SiMe_3 **4a**/**4b**, CH_2CMe_2Ph **5a**/**5b,** CH_3 **7a**/**7b**,) and dimethyl [MTp*Me_2(N*t*Bu)] (**6a**/**6b**) imido hydridotris(3,5-dimethylpyrazolyl)borate niobium and tantalum compounds were prepared by alkylation of the initial dichlorido [MTp*Cl_2(N*t*Bu)] (M=Nb, Ta; Tp*=BH(3,5-$Me_2C_3HN_2)_3$) complexes in different experimental conditions. In solid state, two *gauche*-conformational states of alkyl substituent respect to the imido group were found, being the torsion angle average θ(N7-M-C50-C51) ≈130º±10º for **1b**, **4a**, **5a**

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and ≈40º±10º for **2a/b**, **3a**/**b** and **5b** complexes, respectively. Both conformers but in different ratio were detected in solution for the complexes **3a**/**3b**. The ^{15}N imido chemical shifts are more shielding in tantalum than in niobium complexes ($\sigma_{dia.}$) and depend on the inductive effect of the substituents in equatorial position ($\sigma_{para.}$).

Experimental Section

All operations were carried out under a dry 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: C_6D_6 and hexane (Na/K alloy) and toluene (Na). Starting materials [MTp*Cl_2(N*t*Bu)][5c,14] (M=Nb, Ta) were prepared as described previously. Reagent grade MgClR (R=Me, 3M in THF; R=CH_2CH_3, 2M in diethyl ether; R=CH_2Ph, CH_2*t*Bu, CH_2SiMe_3, 1M in diethyl ether; R=CH_2CMe_2Ph, 0.5M in diethyl ether; Aldrich) and were purchased from commercial sources and were used without further purification.

Samples for IR spectroscopy were prepared as KBr pellets and recorded on a Perkin-Elmer Spectrum 2000 spectrophotometer (4000-400 cm^{-1}). NMR spectra were recorded on a Mercury-300, Unity^{Plus}-300 and VNMRS-500 spectrometers. The all 2D-spectra were processed by using 4K x 4K matrices. The ^{1}H and ^{13}C chemical shifts were referenced to the solvent signals and ^{15}N to external CH_3NO_2. Microanalyses (C, H, N) were performed in a LECO CHNS 932 microanalyzer.

Synthesis of [MTp*Cl(CH_2CH_3)(N*t*Bu)] (M=Nb **1a**, Ta **1b**).

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At room temperature, a 2 M solution of $MgCl(CH_2CH_3)$ in diethyl ether (M=Nb, 0.25 mL, 0.50 mmol; Ta, 0.24 mL, 0.48 mmol) was added to a toluene (30 mL) solution of [MTp*Cl_2(N*t*Bu)] (M=Nb, 0.31 g, 0.50 mmol; Ta, 0.30 g, 0.48 mmol) and the mixture was stirred for 12 h. The $MgCl_2$ was filtered off and the resulting solution was concentrated to dryness. The residue was extracted with hexane (3 x 15 mL), the solution was concentrated to ca. 5 mL and cooled to –40°C to give **1a** and **1b** as rose (M=Nb) and pale yellow (M=Ta) microcrystalline solids, respectively.

1a. Yield 0.14 g (71%). IR (KBr, $\bar{\nu}$ cm^{-1}): 3439 (w), 2963 (vs), 2925 (vs), 2541 (w), 1544 (vs), 1448 (vs), 1415 (s), 1366 (m), 1238 (vs), 1206 (vs), 1069 (vs), 1042 (s), 812 (m), 794 (m), 648 (m), 463 (w). ^{1}H NMR (δ ppm, C_6D_6): 5.66(m, 1H, Tp*$_{ax}$), 5.51(m, 1H, Tp*$_{eq2}$), 5.33(m, 1H, Tp*$_{eq1}$, 3,5-Me_2C_3**H**N_2), 4.70(ABX_3, 1H, J_{AB}=12.3 Hz, J_{AX3}=J_{BX3}=7.9 Hz, Nb-C**H**$_2$-CH_3), 4.68(q, 1H, J_{B-H}=119.6 Hz, B**H**), 2.69(s, 3H, Tp*$_{ax}$), 2.66(s, 3H, Tp*$_{eq1}$), 2.56(s, 3H, Tp*$_{eq2}$, 3,**5-Me**$_2C_3HN_2$), 2.18(s, 3H, Tp*$_{ax}$), 2.01(s, 3H, Tp*$_{eq2}$), 1.95(s, 3H, Tp*$_{eq1}$, **3**,5-**Me**$_2C_3HN_2$), 1.67(s, 9H, C**Me**$_3$), 1.12(ABX_3, 1H, J_{AB}=15.9 Hz, Nb-CH_2-C**H**$_3$), 0.30(ABX_3, 1H, J_{AB}=12.3 Hz, Nb-C**H**$_2$-CH_3). ^{13}C{^{1}H} NMR (δ ppm, C_6D_6): 152.5(Tp*$_{ax}$), 152(Tp*$_{eq1}$), 150.6(Tp*$_{eq2}$, C_3, 3,5-Me_2**C**$_3HN_2$), 145.5(Tp*$_{eq1}$), 144.3(Tp*$_{eq2}$), 143.1(Tp*$_{ax}$, C_5, 3,5-Me_2**C**$_3HN_2$), 107.7(Tp*$_{ax}$), 106.7(Tp*$_{eq2}$), 106.6(Tp*$_{eq1}$, C_4, 3,5-Me_2**C**$_3HN_2$), 74.7(Nb**C**H_2CH_3), not observed($NbCH_2$**C**H_3), 68.4(N**C**Me_3), 30.5(NC**Me**$_3$), 16.7(Tp*$_{eq1}$), 15.9(Tp*$_{eq2}$), 14.9(Tp*$_{ax}$, 3,**5-Me**$_2C_3HN_2$), 12.8(Tp*$_{eq2}$), 12.7(Tp*$_{ax}$), 12.4(Tp*$_{eq1}$, **3**,5-**Me**$_2C_3HN_2$). ^{15}N NMR (δ ppm, C_6D_6): 23.3(**N**CMe_3), -112.9(Tp*$_{ax}$), -117.7(Tp*$_{eq2}$), -121.9(Tp*$_{eq1}$, **N**2-Nb), -155.9(Tp*$_{ax}$), -156.3(Tp*$_{eq2}$), -157.3(Tp*$_{eq1}$, **N**1-B). Anal. Calcd. for $C_{21}H_{36}N_7BClNb$ (525.738): C, 47.98; H, 6.90; N, 18.65. Found: C, 48.00; H, 6.57; N, 18.73%.

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1b. Yield 0.22 g (75%). IR (KBr, $\bar{\nu}$ cm^{-1}): 3461 (m), 2961 (vs), 2923 (vs), 2543 (w), 1545 (vs), 1449 (vs), 1415 (s), 1366 (m), 1264 (vs), 1208 (vs), 1069 (vs), 1042 (s), 813 (m), 796 (m), 648 (m), 465 (w). ^{1}H NMR (δ ppm, C_6D_6): 5.64(m, 1H, Tp*$_{ax}$), 5.47(m, 1H, Tp*$_{eq2}$), 5.32(m, 1H, Tp*$_{eq1}$, 3,5-Me_2C_3**H**N_2), 4.58(q, 1H, J_{B-H}=121.9 Hz, B**H**), 3.46, 0.60(ABX_3, 2H, J_{A-B}=14.3Hz, J_{AX3}=J_{BX3}=7.6 Hz, Ta-C**H**$_2$-CH_3), 2.71(s, 3H, Tp*$_{ax}$), 2.68(s, 3H, Tp*$_{eq1}$), 2.63(m, 3H, Tp*$_{eq2}$, 3,**5**-**Me**$_2C_3HN_2$), 2.13(s, 3H, Tp*$_{ax}$), 1.97(s, 3H, Tp*$_{eq2}$), 1.91(m, 3H, Tp*$_{eq1}$, **3**,5-**Me**$_2C_3HN_2$), 1.68(s, 9H, NC**Me**$_3$), 1.48(ABX_3, 3H, J_{AB} =15.9 Hz, Ta-CH_2-C**H**$_3$). ^{13}C{^{1}H} NMR (δ ppm, C_6D_6): 153.1(Tp*$_{eq1}$), 152.6(Tp*$_{ax}$), 151.6(Tp*$_{eq2}$, C_3, 3,5-Me_2**C**$_3HN_2$), 145.3(Tp*$_{eq1}$), 144.5(Tp*$_{eq2}$), 142.7(Tp*$_{ax}$, C_5, 3,5-Me_2**C**$_3HN_2$), 107.9(Tp*$_{ax}$), 106.9(Tp*$_{eq2}$), 106.8(Tp*$_{eq1}$, C_4, 3,5-Me_2**C**$_3HN_2$), 65.5(N**C**Me_3), 63.3(Ta-**C**H_2-CH_3), not observed(Ta-CH_2-**C**H_3), 32.2(NC**Me**$_3$), 16.2(Tp*$_{eq2}$), 16.1(Tp*$_{eq1}$), 14.8(Tp*$_{ax}$, 3,**5**-**Me**$_2C_3HN_2$), 12.5(Tp*$_{eq2}$), 12.3(Tp*$_{ax}$), 12.0(Tp*$_{eq1}$, **3**,5-**Me**$_2C_3HN_2$). ^{15}N NMR (δ ppm, C_6D_6): -2(**N**CMe_3), -114.9(Tp*$_{ax}$), -117.7(Tp*$_{eq2}$), -121.4(Tp*$_{eq1}$, **N**2-Ta), -155.5(Tp*$_{eq2}$), -156.6(Tp*$_{eq1}$), -157.5(Tp*$_{ax}$, **N**1-B). Anal. Calcd. for $C_{21}H_{36}N_7BClTa$ (613.78): C, 41.09; H, 5.91; N, 15.97. Found: C, 41.30; H, 5.92; N, 15.89%.

Synthesis of [MTp*Cl(CH_2Ph)(N*t*Bu)] (M=Nb **2a**, Ta **2b**).

At room temperature, a 1 M solution of MgCl(CH_2Ph) in diethyl ether (0.50 mmol, 0.50 mL) was added to a toluene (30 mL) solution of [MTp*Cl_2(N*t*Bu)](0.50 mmol; M=Nb, 0.27 g; Ta, 0.31 g) and the mixture was stirred for 12 h. The $MgCl_2$ was filtered off and the resulting solution was concentrated to dryness. The residue was extracted with hexane (3 x 10 mL), the solution was concentrated to ca. 10 mL and cooled to –40°C to give **2a** and **2b** as garnet (M=Nb) and orange (M=Ta) microcrystalline solids, respectively.

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2a. Yield 0.13 g (60%). IR (KBr, $\bar{\nu}$ cm^{-1}): 3437 (m), 2959 (s), 2922 (s), 2548 (m), 1549 (m), 1542 (s), 1447 (s), 1363 (s), 1206 (s), 1034 (s), 800 (m), 694 (m), 464 (w), 411 (w). ^{1}H NMR (δ ppm, C_6D_6): 7.90(m, 2H, $\mathbf{H}_m$), 7.13(m, 2H, $\mathbf{H}_o$), 6.90(m, 1H, $\mathbf{H}_p$, $NbCH_2C_6\mathbf{H}_5$), 5.60(m, 1H, Tp^*_{ax}), 5.47(m, 1H, Tp^*_{eq2}), 5.29(m, 1H, Tp^*_{eq1}, 3,5-$Me_2C_3\mathbf{H}N_2$), 4.67(q, 1H, J_{B-H}=116.5 Hz, B**H**), 3.61, 2.84(AB, 2H, $^2J_{H-H}$=11.88 Hz, Nb-C$\mathbf{H}_2$Ph), 2.75(s, 3H, Tp^*_{ax}), 2.57(s, 3H, Tp^*_{eq1}), 2.49(s, 3H, Tp^*_{eq2}, 3,**5-Me**$_2C_3HN_2$), 2.19(s, 3H, Tp^*_{ax}), 2.05(s, 3H, Tp^*_{eq1}), 1.93(s, 3H, Tp^*_{eq2}, **3**,5-**Me**$_2C_3HN_2$), 1.42(s, 9H, NC**Me**$_3$). ^{13}C{^{1}H} NMR (δ ppm, C_6D_6): 152.5(Tp^*_{ax}), 152.1(Tp^*_{eq2}), 151.9(Tp^*_{eq1}, C_3, 3,5-$Me_2\mathbf{C}_3HN_2$), 145.6(Tp^*_{eq1}), 145.1(Tp^*_{eq2}), 143.1(Tp^*_{ax}, C_5, 3,5-$Me_2\mathbf{C}_3HN_2$), 142.5, 128.6, 126.4, 122.2(several phenyl, $NbCH_2\mathbf{C}_6H_5$), 108.1(Tp^*_{ax}), 107.1(Tp^*_{eq2}), 106.8(Tp^*_{eq1}, C_4, 3,5-$Me_2\mathbf{C}_3HN_2$), 78.6(Nb**C**$H_2C_6H_5$), 69.5(N**C**Me_3), 30.6(NC**Me**$_3$), 16.8(Tp^*_{eq2}), 16.2(Tp^*_{eq1}), 15.5(Tp^*_{ax}, 3,**5-Me**$_2C_3HN_2$), 12.8(Tp^*_{eq1}), 12.6(Tp^*_{ax}), 12.1(Tp^*_{eq2}, **3**,5-**Me**$_2C_3HN_2$). ^{15}N NMR (δ ppm, C_6D_6): 35.2(**N**CMe_3), -112.6(Tp^*_{ax}), -116.7(Tp^*_{eq2}), -122.7(Tp^*_{eq1}, **N**2-Nb), -156.4(Tp^*_{eq2}), -156.6(Tp^*_{ax}), -156.9(Tp^*_{eq1}, **N**1-B). Anal. Calcd. for $C_{26}H_{38}N_7BClNb$ (587.809): C, 53.13; H, 6.52; N, 16.68. Found: C, 52.95; H, 6.72; N, 16.58%.

2b. Yield 0.10 g (33%). IR (KBr, $\bar{\nu}$ cm^{-1}): 3437 (w), 2968 (s), 2922 (s), 2549 (m), 1596 (m), 1543 (s), 1447 (s), 1380 (w), 1261 (s), 1069 (s), 800 (m), 696 (m), 464 (w), 417 (w). ^{1}H NMR (δ ppm, C_6D_6): 7.29(m, 2H, $\mathbf{H}_m$), 7.25(m, 2H, $\mathbf{H}_o$), 6.92(m, 1H, $\mathbf{H}_p$, $TaCH_2C_6\mathbf{H}_5$), 5.56(m, 1H, Tp^*_{ax}), 5.46(m, 1H, Tp^*_{eq2}), 5.30(m, 1H, Tp^*_{eq1}, 3,5-$Me_2C_3\mathbf{H}N_2$), 4.61(q, 1H, J_{B-H}=115.9 Hz, B**H**), 3.28, 2.24(AB, 2H, $^2J_{H-H}$=13.81 Hz, Ta-C$\mathbf{H}_2$Ph), 2.72(m, 3H, Tp^*_{ax}), 2.62(m, 3H, Tp^*_{eq1}), 2.58(s, 3H, Tp^*_{eq2}, 3,**5-Me**$_2C_3HN_2$), 2.12(m, 3H, Tp^*_{ax}), 1.98(m, 3H, Tp^*_{eq1}), 1.89(s, 3H, Tp^*_{eq2}, **3**,5-**Me**$_2C_3HN_2$), 1.39(s, 9H, NC**Me**$_3$). ^{13}C{^{1}H} NMR (δ ppm, C_6D_6): 153.4(Tp^*_{ax}), 153.2(Tp^*_{eq2}), 152.7(Tp^*_{eq1}, C_3, 3,5-$Me_2\mathbf{C}_3HN_2$), 145.5(Tp^*_{eq1}),

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144.9(Tp*$_{eq2}$), 142.9(Tp*$_{ax}$, C_5, 3,5-Me$_2$**C**$_3$HN$_2$), 153.4, 145.6, 145.5, 143(several phenyl, TaCH$_2$**C**$_6$H$_5$), 108.5(Tp*$_{ax}$), 107.5(Tp*$_{eq2}$), 107.1(Tp*$_{eq1}$, C_4, 3,5-Me$_2$**C**$_3$HN$_2$), 76(Ta**C**H$_2$C$_6$H$_5$), 67.6(N**C**Me$_3$), 32.5(NC**Me**$_3$), 17.3(Tp*$_{eq2}$), 16.6(Tp*$_{eq1}$), 15.7(Tp*$_{ax}$, 3,**5**-**Me**$_2$C$_3$HN$_2$), 12.7(Tp*$_{eq1}$), 12.5(Tp*$_{ax}$), 12.4(Tp*$_{eq2}$, **3**,5-**Me**$_2$C$_3$HN$_2$). ^{15}N NMR (δ ppm, C_6D_6): 7.6(**N**CMe$_3$), -114.6(Tp*$_{ax}$), -115.8(Tp*$_{eq2}$), -122.1(Tp*$_{eq1}$, **N**2-Ta), -157.3(Tp*$_{eq2}$), -157.2(Tp*$_{ax}$), -155.9(Tp*$_{eq1}$, **N**1-B). Anal. Calcd. for $C_{26}H_{38}N_7BClTa$ (675.851): C, 46.21; H, 5.67; N, 14.51. Found: C, 46.06; H, 5.72; N, 14.58%.

Synthesis of [MTp*Cl(CH$_2$*t*Bu)(N*t*Bu)] (M=Nb **3a**, Ta **3b**).

Under rigorously anhydrous conditions (glove box), a toluene (30 mL) solution of [MTp*Cl$_2$(N*t*Bu)] (M=Nb, 0.42 g, 0.80 mmol; Ta, 0.31 g, 0.50 mmol) was treated with a 1M in diethyl ether solution of MgCl(CH$_2$CMe$_3$) (M=Nb, 1.00 mL, 1.00 mmol; Ta, 0.60 mL, 0.60 mmol). The mixture was stirred at room temperature for 12 h (M=Nb) and at 90ºC for 5 days (M=Ta). The resulting suspension was evaporated to dryness and the residue extracted with hexane (2 x 15 mL). The solution was filtered, concentrated to ca. 10 mL and cooled at –78°C during several minutes giving **3a** and **3b** as red (M=Nb) and orange (M=Ta) microcrystalline solids.

3a. Yield 0.30 g (66%). IR (KBr, $\bar{\nu}$ cm^{-1}): 3431 (w), 2931 (s), 2933 (s), 2552 (m), 1544 (vs), 1449 (s), 1415 (s), 1358 (m), 1208 (vs), 1073 (m), 1041 (m), 795 (m), 647 (w), 554 (w), 530 (w), 466 (w). ^{1}H NMR (δ ppm, in C_6D_6): 5.64(m, 1H, Tp*$_{ax}$), 5.52(m, 1H, Tp*$_{eq2}$), 5.32(m, 1H, Tp*$_{eq1}$, 3,5-Me$_2$C$_3$**H**N$_2$), 4.65(q, 1H, J_{B-H}=125.84 Hz, B**H**), 4.21, 0.52(AB, 2H, $^2J_{H-H}$=12.35 Hz, Nb-C**H**$_2$*t*Bu), 2.82(m, 3H, Tp*$_{ax}$), 2.65(m, 3H, Tp*$_{eq2}$), 2.64(m, 3H, Tp*$_{eq1}$, 3,**5**-**Me**$_2$C$_3$HN$_2$), 2.19(m, 3H, Tp*$_{ax}$), 2.05(m, 3H, Tp*$_{eq1}$), 1.93(m, 3H, Tp*$_{eq2}$, **3**,5-

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Me$_2$C$_3$HN$_2$), 1.42(s, 9H, NC**Me**$_3$), 1.08(s, 9H, Nb-CH$_2$C**Me**$_3$). ^{13}C{^{1}H} NMR (δ ppm, C$_6$D$_6$): 152.7(Tp*$_{ax}$), 151.8(Tp*$_{eq1}$), 151.4(Tp*$_{eq2}$, C$_3$, 3,5-Me$_2$**C**$_3$HN$_2$), 144.9(Tp*$_{eq1}$), 145.3(Tp*$_{eq2}$), 143.3(Tp*$_{ax}$, C$_5$, 3,5-Me$_2$**C**$_3$HN$_2$), 108.2(Tp*$_{ax}$), 106.9(Tp*$_{eq1}$), 106.7(Tp*$_{eq2}$, C$_4$, 3,5-Me$_2$**C**$_3$HN$_2$), 100.9(Nb-CH$_2$**C**Me$_3$), 99.3(Nb-**C**H$_2$*t*Bu), 68.5(N**C**Me$_3$), 37.6(Nb-CH$_2$C**Me**$_3$), 30.8(NC**Me**$_3$), 17.6(Tp*$_{eq2}$), 16.5(Tp*$_{eq1}$), 16.1(Tp*$_{ax}$, 3,**5**-**Me**$_2$C$_3$HN$_2$), 12.4(Tp*$_{eq1}$), 12.3(Tp*$_{ax}$), 12.1(Tp*$_{eq1}$, **3**,5-**Me**$_2$C$_3$HN$_2$). ^{15}N NMR (δ ppm, C$_6$D$_6$): 30.6(**N**CMe$_3$), -111.3(Tp*$_{ax}$), -118.3(Tp*$_{eq2}$), -121.5(Tp*$_{eq1}$, **N**2-Nb), -156.9(Tp*$_{eq1}$), -156.6(Tp*$_{eq2}$), -156.4(Tp*$_{ax}$, **N**1-B). Anal. Calcd. for C$_{24}$H$_{42}$N$_7$BClNb (567.819): C, 50.76; H, 7.46; N, 12.27. Found: C, 50.63; H, 7.42; N, 12.18%.

3b. Yield 0.13 g (40%). IR (KBr, $\bar{\nu}$ cm^{-1}): 3439 (w), 2946 (s), 2933 (s), 2552 (m), 1545 (s), 1449 (s), 1413 (m), 1357 (m), 1250 (s), 1209 (s), 1074 (m), 1035 (m), 795 (m), 647 (m), 554 (w), 530 (w), 462 (w). ^{1}H NMR (δ ppm, C$_6$D$_6$): 5.60(m, 1H, Tp*$_{ax}$), 5.50(m, 1H, Tp*$_{eq2}$), 5.35(m, 1H, Tp*$_{eq1}$, 3,5-Me$_2$C$_3$**H**N$_2$), 4.53(q, 1H, J_{B-H}=126.4 Hz, B**H**), 2.84(m, 3H, Tp*$_{ax}$), 2.75(m, 3H, Tp*$_{eq2}$), 2.67(m, 3H, Tp*$_{eq1}$, 3,**5**-**Me**$_2$C$_3$HN$_2$), 2.70, 0.66(AB, 2H, $^2J_{H-H}$=14.95 Hz, Ta-C**H**$_2$*t*Bu), 2.11(m, 3H, Tp*$_{ax}$), 1.95(m, 3H, Tp*$_{eq2}$), 1.91(m, 3H, Tp*$_{eq1}$, **3**,5-**Me**$_2$C$_3$HN$_2$), 1.63(s, 9H, NC**Me**$_3$), 1.44(s, 9H, Ta-CH$_2$C**Me**$_3$). ^{13}C{^{1}H} NMR (δ ppm, C$_6$D$_6$): 152.8(Tp*$_{ax}$), 152.3(Tp*$_{eq2}$), 152.5(Tp*$_{eq1}$, C$_3$, 3,5-Me$_2$**C**$_3$HN$_2$), 145.7(Tp*$_{eq2}$), 145.1(Tp*$_{eq1}$), 142.5(Tp*$_{ax}$, C$_5$, 3,5-Me$_2$**C**$_3$HN$_2$), 107.9(Tp*$_{ax}$), 106.9(Tp*$_{eq2}$), 106.8(Tp*$_{eq1}$, C$_4$, 3,5-Me$_2$**C**$_3$HN$_2$), 92(Ta-**C**H$_2$*t*Bu), 66.3(N**C**Me$_3$), 35.8(Ta-CH$_2$C**Me**$_3$), 33.2(NC**Me**$_3$), 33.7(Ta-CH$_2$**C**Me$_3$), 17.5(Tp*$_{eq2}$), 16.5(Tp*$_{eq1}$), 15.7(Tp*$_{ax}$, 3,**5**-**Me**$_2$C$_3$HN$_2$), 12.3(Tp*$_{eq2}$), 12.0(Tp*$_{ax}$), 11.8(Tp*$_{eq1}$, **3**,5-**Me**$_2$C$_3$HN$_2$). ^{15}N NMR (δ ppm, C$_6$D$_6$): 3.3(**N**CMe$_3$), -112.5(Tp*$_{ax}$), -116.3(Tp*$_{eq2}$), -122.7(Tp*$_{eq1}$, **N**2-Ta), -155.7(Tp*$_{eq2}$), -157.3(Tp*$_{ax}$),

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-157.5(Tp*$_{eq1}$, **N**1-B). Anal. Calcd. for $C_{24}H_{42}N_7BClTa$ (655.861): C, 43.95; H, 6.46; N, 14.95. Found: C, 44.05; H, 6.56; N 14.83%.

Synthesis of [MTp*Cl(CH_2SiMe_3)(N*t*Bu)] (M=Nb **4a**, Ta **4b**).

Under rigorously anhydrous conditions, a toluene (30 mL) solution of [MTp*Cl_2(N*t*Bu)] (0.31 g; M=Nb 0.58 mmol; Ta 0.50 mmol) was placed in an ampoule and treated with a 1M diethyl ether solution of $MgCl(CH_2SiMe_3)$ (M=Nb 0.70 mL, 0.60 mmol; Ta 0.55 mL, 0.55 mmol) and then sealed. The mixture was stirred during 8 (Nb) and 11 (Ta) days at 70 and 90ºC, respectively. After the ampoule was opened, the solvent was evaporated to dryness and the residue extracted with hexane (3 x 10 mL). The solution was filtered, concentrated to ca. 10 mL and cooled at –40°C overnight giving **4a** and **4b** as green (M=Nb) and brown (M=Ta) microcrystalline solids, respectively.

4a. Yield 0.15 g (44%). IR (KBr, $\bar{\nu}$ cm^{-1}): 3431 (m), 2962 (s), 2546 (m), 1544 (s), 1448 (s), 1413 (m), 1365 (m), 1240 (s), 1209 (s), 1069 (m), 1040 (m), 850 (m), 648 (w), 551 (w), 464 (d), 418 (w). ^{1}H NMR (δ ppm, C_6D_6): 5.64(m, 1H, Tp*$_{ax}$), 5.48(m, 1H, Tp*$_{eq2}$) 5.31(m, 1H, Tp*$_{eq1}$, 3,5-Me_2C_3**H**N_2), 4.64(q, 1H, J_{B-H}=130.9 Hz, B**H**), 4.08, 0.32(AB, 2H, $^2J_{H-H}$=11.37 Hz, Nb-C**H**$_2$SiMe$_3$), 2.76(m, 3H, Tp*$_{ax}$), 2.63(m, 3H, Tp*$_{eq1}$), 2.60(m, 3H, Tp*$_{eq2}$, 3,**5**-**Me**$_2C_3HN_2$), 2.19(m, 3H, Tp*$_{ax}$), 2.05(m, 3H, Tp*$_{eq2}$), 1.93(m, 3H, Tp*$_{eq1}$, **3**,5-**Me**$_2C_3HN_2$), 1.65(s, 9H, NC**Me**$_3$), -0.12(s, 9H, Nb-CH_2Si**Me**$_3$). ^{13}C{^{1}H} NMR (δ ppm, C_6D_6): 152.4(Tp*$_{ax}$), 151.8(Tp*$_{eq1}$), 151(Tp*$_{eq2}$, C_3, 3,5-Me_2**C**$_3HN_2$), 145.0(Tp*$_{eq2}$), 145.1(Tp*$_{eq1}$), 143.2(Tp*$_{ax}$, C_5, 3,5-Me_2**C**$_3HN_2$), 108.1(Tp*$_{ax}$), 106.9(Tp*$_{eq2}$), 106.6(Tp*$_{eq1}$, C_4, 3,5-Me_2**C**$_3HN_2$), 68.6(N**C**Me$_3$), 67(Nb-**C**H$_2$SiMe$_3$), 30.9(NC**Me**$_3$), 17.4(Tp*$_{eq2}$),

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16.3(Tp*$_{eq1}$), 15.9(Tp*$_{ax}$, 3,**5**-**Me**$_2$C$_3$HN$_2$), 12.7(Tp*$_{eq2}$), 12.6(Tp*$_{eq1}$), 12.4(Tp*$_{ax}$, **3**,5-**Me**$_2$C$_3$HN$_2$), 2.5(Nb-CH$_2$Si**Me**$_3$). ^{15}N NMR (δ ppm, C$_6$D$_6$): 29.9(**N**CMe$_3$), -112.5(Tp*$_{ax}$), -118.9(Tp*$_{eq2}$), -121.3(Tp*$_{eq1}$, **N**2-Nb), -156.9(Tp*$_{eq2}$), -157.2(Tp*$_{eq1}$), -157.3(Tp*$_{ax}$, **N**1-B). Anal. Calcd. for C$_{23}$H$_{42}$N$_7$BClSiNb (583.894): C, 47.31; H, 7.25; N, 16.79. Found: C, 47.32; H, 7.20; N, 16.67%.

4b. Yield 0.15 g (45%). IR (KBr, $\bar{\nu}$ cm^{-1}): 3440 (w), 2960 (vs), 2552 (w), 1545 (s), 1448 (s), 1416 (s), 1363 (m), 1260 (vs), 1210 (vs), 1071 (vs), 1041 (s), 911 (m), 851 (s), 728 (m), 426 (w). ^{1}H NMR (δ ppm, C$_6$D$_6$): 5.62(m, 1H, Tp*$_{ax}$), 5.47(m, 1H, Tp*$_{eq2}$), 5.32(m, 1H, Tp*$_{eq1}$, 3,5-Me$_2$C$_3$**H**N$_2$), 4.59(q, 1H, J_{B-H}=131.43 Hz, B**H**), 2.75(s, 3H, Tp*$_{ax}$), 2.67(s, 3H, Tp*$_{eq1}$), 2.66(s, 3H, Tp*$_{eq2}$, 3,**5**-**Me**$_2$C$_3$HN$_2$), 2.70, 0.20(AB, 2H, $^2J_{H-H}$=12.30 Hz, Ta-C**H**$_2$SiMe$_3$), 2.14(s, 3H, Tp*$_{ax}$), 1.99(s, 3H, Tp*$_{eq2}$), 1.90(s, 3H, Tp*$_{eq1}$, **3**,5-**Me**$_2$C$_3$HN$_2$), 1.66(s, 9H, NC**Me**$_3$), -0.03(s, 9H, Ta-CH$_2$Si**Me**$_3$). ^{13}C{^{1}H} NMR (δ ppm, C$_6$D$_6$): 152.9(Tp*$_{ax}$), 152.6(Tp*$_{eq1}$), 152.1(Tp*$_{eq2}$, C$_3$, 3,5-Me$_2$**C**$_3$HN$_2$), 145.3(Tp*$_{eq2}$), 145(Tp*$_{eq1}$), 143(Tp*$_{ax}$, C$_5$, 3,5-Me$_2$**C**$_3$HN$_2$), 108.3(Tp*$_{ax}$), 107.7(Tp*$_{eq2}$), 107.1(Tp*$_{eq1}$, C$_4$, 3,5-Me$_2$**C**$_3$HN$_2$), 65.7(N**C**Me$_3$), 59.6(Ta-**C**H$_2$SiMe$_3$), 32.65(NC**Me**$_3$), 17.8(Tp*$_{eq2}$), 16.8(Tp*$_{eq1}$), 16.2(Tp*$_{ax}$, 3,**5**-**Me**$_2$C$_3$HN$_2$), 12.7(Tp*$_{eq2}$), 12.3(Tp*$_{eq1}$), 12.3(Tp*$_{ax}$, **3**,5-**Me**$_2$C$_3$HN$_2$), 3.7(Ta-CH$_2$Si**Me**$_3$). ^{15}N NMR (δ ppm, C$_6$D$_6$): 4(**N**CMe$_3$), -113.9(Tp*$_{ax}$), -117.3(Tp*$_{eq2}$), -121.5(Tp*$_{eq1}$, **N**2-Ta), -155.3(Tp*$_{eq2}$), -157.4(Tp*$_{eq1}$), -157.5(Tp*$_{ax}$, **N**1-B). Anal. Calcd. for C$_{23}$H$_{42}$N$_7$BClSiTa (671.936): C, 41.11; H, 6.30; N, 14.59. Found: C, 41.05; H, 6.26; N, 14.39%.

Synthesis of [MTp*Cl(CH$_2$CMe$_2$Ph)(N*t*Bu)] (M=Nb **5a**, Ta **5b**)

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$MgCl(CH_2CMe_2Ph)$ (0.5M in diethyl ether; M=Nb, 0.82 mL, 0.53 mmol; Ta, 1.00 mL, 0.53 mmol) was added to a stirred toluene (25 mL) solution of [$MTp^*Cl_2(N\textit{t}Bu)$] (M=Nb, 0.20 g, 0.37 mmol; Ta, 0.27 g, 0. 44 mmol). The mixture was stirred during 5 h (Nb) or 11 days (Ta) at room temperature and 90ºC, respectively. The resulting suspension was filtered, the solvent concentrated to dryness and the residue extracted with hexane (3 x 15 mL). The solution was concentrated to ca. 5 mL and cooled overnight to –40°C giving **5a** and **5b** as orange microcrystalline solids.

5a. Yield 0.13 g (55%). IR (KBr, $\bar{\nu}$ cm^{-1}): 3454 (w), 2966 (m), 2915 (m), 2548 (w), 1544 (f), 1446 (s), 1416 (s), 1366 (s), 1233 (s), 1202 (s), 1068 (s), 1041 (m), 852 (w), 799 (m), 700 (m), 643 (w), 466 (w). ^{1}H NMR (δ ppm, C_6D_6): 7.36(m, 2H, H_o), 7.22(m, 2H, H_m), 7.00(m, 1H, H_p, $\mathbf{H}_5C_6Me_2CCH_2$-Nb), 5.63(m, 1H, Tp^*_{ax}), 5.45(m, 1H, Tp^*_{eq2}), 5.30(m, 1H, Tp^*_{eq1}, 3,5-$Me_2C_3\mathbf{H}N_2$), 4.65(q, 1H, $J_{B\text{-}H}$=119.67 Hz, B**H**), 4.67, 0.98(AB, 2H, $^2J_{H\text{-}H}$=11.4 Hz, Nb-C$\mathbf{H}_2CMe_2Ph$), 2.72(m, 3H, Tp^*_{ax}), 2.64(m, 3H, Tp^*_{eq1}), 2.12(m, 3H, Tp^*_{eq2}, 3,**5**-$\mathbf{Me}_2C_3HN_2$), 2.20(m, 3H, Tp^*_{ax}), 2.08(m, 3H, Tp^*_{eq2}), 1.92(m, 3H, Tp^*_{eq1}, **3**,5-$\mathbf{Me}_2C_3HN_2$), 1.61(s, 9H, NC$\mathbf{Me}_3$), 1.41(s, 3H), 1.06(s, 3H, Nb-$CH_2C\mathbf{Me}_2Ph$). $^{13}C\{^1H\}$ NMR (δ ppm, C_6D_6): 152.7(Tp^*_{ax}), 152(Tp^*_{eq2}), 151.8(Tp^*_{eq1}, C_3, 3,5-$Me_2\mathbf{C}_3HN_2$), 145.1(Tp^*_{eq2}), 145(Tp^*_{eq1}), 143.3(Tp^*_{ax}, C_5, 3,5-$Me_2\mathbf{C}_3HN_2$), 130-125.5(several phenyl, $H_5\mathbf{C}_6Me_2CCH_2$-Nb), 108.2(Tp^*_{ax}), 107(Tp^*_{eq2}), 106.6(Tp^*_{eq1}, C_4, 3,5-$Me_2\mathbf{C}_3HN_2$), 97.6(Nb-$\mathbf{C}H_2CMe_2Ph$), 68.9(N$\mathbf{C}Me_3$), 44.2(Nb-$CH_2\mathbf{C}Me_2Ph$), 35.5, 30.48(Nb-$CH_2C\mathbf{Me}_2Ph$), 30.7(NC$\mathbf{Me}_3$), 17.2(Tp^*_{eq2}), 16.9(Tp^*_{eq1}), 15.7(Tp^*_{ax}, 3,**5**-$\mathbf{Me}_2C_3HN_2$), 12.9(Tp^*_{eq2}), 12.7(Tp^*_{ax}), 12.5(Tp^*_{eq1}, **3**,5-$\mathbf{Me}_2C_3HN_2$). ^{15}N NMR (δ ppm, C_6D_6): 32.2(**N**CMe_3), -112(Tp^*_{ax}), -118(Tp^*_{eq2}), -121.5(Tp^*_{eq1}, **N**2-Nb), -156.8(Tp^*_{ax}),

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-156.9(Tp*$_{eq2}$), -157.3(Tp*$_{eq1}$, **N**1-B). Anal. Calcd. for $C_{29}H_{44}N_7BClNb$ (629.89): C, 55.30; H, 7.04; N, 15.57. Found: C, 55.53; H, 6.95; N, 15.27%.

5b. Yield 0.13 g (42%). IR (KBr, $\bar{\nu}$ cm^{-1}): 3429 (s), 2962 (s), 2922 (s), 2549 (m), 1544 (f), 1446 (s), 1362 (s), 1258 (s), 1209 (s), 1072 (s), 1034 (s), 799 (s), 699 (w), 648 (w), 466 (w). ^{1}H NMR (δ ppm, C_6D_6): 7.46(m, 2H, H_o), 7.17(m, 2H, H_m), 7.00(m, 1H, H_p, **H**$_5$C$_6$Me$_2$CCH$_2$-Ta), 5.55(m, 1H, Tp*$_{ax}$), 5.46(m, 1H, Tp*$_{eq2}$), 5.33(m, 1H, Tp*$_{eq1}$, 3,5-Me$_2$C$_3$**H**N$_2$), 4.57(q, 1H, J_{B-H}=120.45 Hz, B**H**), 3.11, 1.08(AB, 2H, $^2J_{H-H}$=14.8 Hz, Ta-C**H**$_2$CMe$_2$Ph), 2.70(m, 3H, Tp*$_{ax}$), 2.66(m, 3H, Tp*$_{eq1}$), 2.42(m, 3H, Tp*$_{eq2}$, 3,**5**-**Me**$_2$C$_3$HN$_2$), 2.10(s, 3H, Tp*$_{ax}$), 1.98(m, 3H, Tp*$_{eq2}$), 1.89(m, 3H, Tp*$_{eq1}$, **3**,5-**Me**$_2$C$_3$HN$_2$), 1.81(s, 3H), 1.54(s, 3H, Ta-CH$_2$C**Me**$_2$Ph), 1.61(s, 9H, NC**Me**$_3$). ^{13}C{^{1}H} NMR (δ ppm, C_6D_6): 153.4(Tp*$_{ax}$), 152.9(Tp*$_{eq2}$), 152.7(Tp*$_{eq1}$, C_3, 3,5-Me$_2$**C**$_3$HN$_2$), 145.7(Tp*$_{eq2}$), 144.8(Tp*$_{eq1}$), 143(Tp*$_{ax}$, C_5, 3,5-Me$_2$**C**$_3$HN$_2$), 131-125.5(several phenyl, H$_5$**C**$_6$Me$_2$CCH$_2$-Ta), 107.9(Tp*$_{ax}$), 107.3(Tp*$_{eq2}$), 107(Tp*$_{eq1}$, C_4, 3,5-Me$_2$**C**$_3$HN$_2$), 91.4(Ta-**C**H$_2$CMe$_2$Ph), 66(N**C**Me$_3$), 42.1(Ta-CH$_2$**C**Me$_2$Ph), 35.7, 32.3(Ta-CH$_2$C**Me**$_2$Ph), 32.4(NC**Me**$_3$), 16.8(Tp*$_{eq2}$), 16.4(Tp*$_{eq1}$), 15.4(Tp*$_{ax}$, 3,**5**-**Me**$_2$C$_3$HN$_2$), 12.2(Tp*$_{eq2}$), 11.9(Tp*$_{ax}$), 11.8(Tp*$_{eq1}$, **3**,5-**Me**$_2$C$_3$HN$_2$). ^{15}N NMR (δ ppm, C_6D_6): 4.2(**N**CMe$_3$), -113.2(Tp*$_{ax}$), -115.8(Tp*$_{eq2}$), -122.6(Tp*$_{eq1}$, **N**2-Ta), -156.1(Tp*$_{eq2}$), -157.4(Tp*$_{eq1}$), -157.5(Tp*$_{ax}$, **N**1-B). Anal. Calcd for $C_{29}H_{44}N_7BClTa$ (717.932): C, 48.52; H, 6.18; N, 13.63. Found: C, 48.33; H, 6.09; N, 13.54%.

Synthesis of [MTp*Me$_2$(N*t*Bu)] (M=Nb **6a**, Ta **6b**)

Under rigorously anhydrous conditions, a 3M solution of MgClMe in THF (M=Nb 0.40 mL, 1.16 mmol; Ta 0.30 mL, 0.90 mmol) was added at room temperature to a solution of

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[MTp*Cl_2(N*t*Bu)] (M=Nb 0.31 g, 0.58 mmol; Ta 0.25 g, 0.41 mmol) in toluene (30 mL), and the reaction mixture was stirred (M=Nb 8 h, r.t.; Ta 11 days, 90°C). The suspension was removed by filtration and the resulting solution was evaporated to dryness. The residue was extracted with hexane (3 x 10 mL) and the solution concentrated to ca. 10 mL and cooled to -40°C overnight to give **6a** and **6b** as white microcrystalline solid.

6a.Yield 0.25 g (80%). IR (KBr, $\bar{\nu}$ cm^{-1}): 3135(w), 2966(vs), 2928(vs), 2852(s), 2542(m), 2470(w), 2362(m), 1546(vs), 1448(vs), 1416(s), 1382(s), 1366(s), 1250(vs), 1203(vs), 1168(m), 1135(m), 1069(vs), 1041(vs), 983(m), 909(m), 889(w), 852(m), 814(s), 795(vs), 775(s), 753(m), 697(vs), 666(m), 650(vs), 579(w), 555(s), 528(s), 472(vs). ^{1}H NMR (δ ppm, C_6D_6): 5.55(m, 1H, 3,5-Me_2C_3**H**N_2, Tp*$_{ax}$), 5.41(s, 2H, 3,5-Me_2C_3**H**N_2, Tp*$_{eq1}$, Tp*$_{eq2}$), 4.62(q, 1H, J_{B-H}=117.5 Hz, B**H**), 2.56(m, 6H, **3**,5-**Me**$_2C_3HN_2$, Tp*$_{eq1}$, Tp*$_{eq2}$), 2.41(m, 3H, **3**,5-**Me**$_2C_3HN_2$, Tp*$_{ax}$), 2.28(m, 3H, 3,**5**- **Me**$_2C_3HN_2$, Tp*$_{ax}$), 2.02(m, 6H, **3**,5-**Me**$_2C_3HN_2$, Tp*$_{eq1}$, Tp*$_{eq2}$), 1.78(s, 9H, NC**Me**$_3$), 1.08(s, 6H, Nb**Me**$_2$). ^{13}C{^{1}H} NMR (δ ppm, C_6D_6): 151.7(C_3, 3,5-Me_2**C**$_3HN_2$, Tp*$_{ax}$), 150.2(C_3, 3,5-Me_2**C**$_3HN_2$, Tp*$_{eq1}$, Tp*$_{eq2}$), 144.4(C_5, 3,5-Me_2**C**$_3HN_2$, Tp*$_{eq1}$, Tp*$_{eq2}$), 143.1(C_5, 3,5-Me_2**C**$_3HN_2$, Tp*$_{ax}$), 107.1(C_4, 3,5-Me_2**C**$_3HN_2$, Tp*$_{ax}$), 105.7(C_4, 3,5-Me_2**C**$_3HN_2$, Tp*$_{eq1,}$ Tp*$_{eq2}$), 66.7(N**C**Me_3), 46.9(Nb**Me**$_2$), 31.4(NC**Me**$_3$), 15.4(**3**,5-**Me**$_2C_3HN_2$, Tp*$_{eq1}$, Tp*$_{eq2}$), 14.4(**3**,5-**Me**$_2C_3HN_2$, Tp*$_{ax}$), 12.5(3,**5**- **Me**$_2C_3HN_2$, Tp*$_{ax}$), 12.4(3,**5**- **Me**$_2C_3HN_2$, Tp*$_{eq1}$, T`p*$_{eq2}$). ^{15}N NMR (δ ppm, C_6D_6): 5(**N**CMe_3), -107(Tp*$_{ax}$), -115(Tp*$_{eq1}$, Tp*$_{eq2}$, **N**2-Nb), -156(Tp*$_{ax}$), -155(Tp*$_{eq1}$, Tp*$_{eq2}$, **N**1-B). Anal. Calcd. for $C_{21}H_{37}N_7BNb$ (491.293): C, 51.34; H, 7.59; N, 19.95. Found: C, 51.64; H, 7.44; N, 19.45%.

6b.Yield 0.15 g (65%). IR(KBr, $\bar{\nu}$ cm^{-1}): 3427(s), 2959(s), 2923(s), 2541(m), 1545(m), 1448(m), 1380(m), 1269(s), 1206(s), 1069(s), 1041(s), 797(s), 649(w), 528(w), 478(w). ^{1}H

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NMR (δ ppm, C_6D_6): 5.74(m, 1H, 3,5-$Me_2C_3\mathbf{H}N_2$, Tp*$_{ax}$), 5.40(m, 2H, 3,5-$Me_2C_3\mathbf{H}N_2$, Tp*$_{eq2}$,Tp*$_{eq1}$), 4.67(q, 1H, J_{B-H}=128 Hz, B**H**), 2.62(m, 6H, Tp*$_{eq1}$, Tp*$_{eq2}$), 2.44(m, 3H, Tp*$_{ax}$, 3,**5**-$\mathbf{Me}_2C_3HN_2$), 2.22(m, 3H, Tp*$_{ax}$), 1.97(m, 6H, **3**,5-$\mathbf{Me}_2C_3HN_2$, Tp*$_{eq2}$, Tp*$_{eq1}$), 1.77(s, 9H, NC$\mathbf{Me}_3$), 0.80(s, 6H, Ta$\mathbf{Me}_2$). $^{13}C\{^1H\}$ NMR (δ ppm, C_6D_6): 151.9(Tp*$_{ax}$), 151.4(Tp*$_{eq2}$, Tp*$_{eq1}$, C_3, 3,5-$Me_2\mathbf{C}_3HN_2$), 144.7(Tp*$_{eq1}$, Tp*$_{eq2}$), 142.7(Tp*$_{ax}$, C_5, 3,5-$Me_2\mathbf{C}_3HN_2$), 107.6(Tp*$_{ax}$), 106.3(Tp*$_{eq2}$, Tp*$_{eq1}$, C_4, 3,5-$Me_2\mathbf{C}_3HN_2$), 65.3(N**C**Me_3), 52.5(Ta$\mathbf{Me}_2$), 33(NC$\mathbf{Me}_3$), 15.9(Tp*$_{eq2}$, Tp*$_{eq1}$), 14.8(Tp*$_{ax}$, 3,**5**-$\mathbf{Me}_2C_3HN_2$), 12.1(Tp*$_{eq1}$, Tp*$_{eq2}$), 12(Tp*$_{ax}$, **3**,5-$\mathbf{Me}_2C_3HN_2$). ^{15}N NMR (δ ppm, C_6D_6): -15(**N**CMe_3), -112(Tp*$_{ax}$), -117(Tp*$_{eq2}$), -123(Tp*$_{eq1}$, **N**2-Ta), -156(Tp*$_{ax}$), -157(Tp*$_{eq1}$,Tp*$_{eq2}$, **N**1-B). Anal. Calcd. for $C_{21}H_{37}N_7BTa$ (579.335): C, 43.54; H, 6.44; N, 16.92. Found: C, 43.64; H, 6.74; N, 16.71%.

Reaction of [MTp*Cl_2(N*t*Bu)] (M=Nb, Ta) **with MgClMe**.

In a typical experiment, a solution of [MTp*Cl_2(N*t*Bu)] (M=Nb, 0.01 g, 0.018 mmol; Ta, 0.01 g, 0.016 mmol) in C_6D_6 (0.70 mL) was placed into a NMR valved tube and then, under rigorously anhydrous conditions, was treated with a 3M in THF solution of MgClMe (M=Nb, 7 μL, 0.018 mmol; Ta, 5 μL, 0.016 mmol). The reaction was monitorized by ^1H NMR spectroscopy and the results to different reaction conditions (time, temperature) were as follows:

i-30 m, r.t.: M=Nb, a mixture of [NbTp*Cl_2(N*t*Bu)], [NbTp*ClMe(N*t*Bu)] **7a** and [NbTp*Me_2(N*t*Bu)] **6a**; M=Ta, a mixture of [TaTp*Cl_2(N*t*Bu)] and MgClMe.

ii-24 h, 60°C: M=Nb, a mixture of [NbTp*Cl_2(N*t*Bu)], 4(**7a**):1(**6a**); M=Ta, a mixture of [TaTp*Cl_2(N*t*Bu)] (57%), MgClMe (20%), **7b** (5%) and **6b** (18%).

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iii-7 days, 60°C, M=Nb, **7a** (88%) as major specie; 7 days, 100°C, M=Ta, a mixture of **7b** (20%) and **6b** (45%).

Reaction between [MTp*Cl_2(N*t*Bu)] and [MTp*Me_2(N*t*Bu)] (M=Nb **6a**, Ta **6b**).

A solution of [MTp*Cl_2(N*t*Bu)] (M=Nb, 0.01 g, 0.018 mmol; Ta, 0.01 g, 0.016 mmol) in C_6D_6 (0.70 mL) was placed into a valved NMR tube and then, under rigorously anhydrous conditions, was added a solution of [NbTp*Me_2(N*t*Bu)] (M=Nb **6a**, 0.009 g, 0.018 mmol; Ta **6b**, 0.009 g, 0.016 mmol) in C_6D_6 (0.50 mL). The mixture was shaked at room temperature and monitorized by ^{1}H NMR spectroscopy. The results to different reactions conditions (time, temperature) were as follows:

i-15 m, r.t.: M=Nb, small amount of **7a**; M=Ta, no changes were observed.

ii-8 days, 60°C: M=Nb, a mixture of **7a** (88%), **6a** (2%) and [NbTp*Cl_2(N*t*Bu)] (10%); M=Ta, no changes were observed.

iii-28 days, 100°C, M=Ta, a mixture of **7b** (70%), **6b** (5%) and [TaTp*Cl_2(N*t*Bu)] (25%).

The chlorido methyl imido derivatives [MTp*ClMe(N*t*Bu)] (M=Nb **7a**, Ta **7b**) were only characterized by NMR spectroscopy.

7a: ^{1}H NMR (δ ppm, C_6D_6): 5.66(m, 1H, Tp*$_{ax}$), 5.41(m, 1H, Tp*$_{eq2}$), 5.33(m, 1H, Tp*$_{eq1}$, 3,5-Me_2C_3**H**N_2), 4.68(q, 1H, J_{B-H}=119.67 Hz, B**H**), 2.69(m, 3H, Tp*$_{ax}$), 2.61(m, 3H, Tp*$_{eq1}$), 2.56(m, 3H, Tp*$_{eq2}$, 3,**5-Me**$_2C_3HN_2$), 2.18(m, 3H, Tp*$_{ax}$), 1.98(m, 3H, Tp*$_{eq2}$), 1.97(m, 3H, Tp*$_{eq1}$, **3**,5- **Me**$_2C_3HN_2$), 1.67(s, 9H, NC**Me**$_3$), 1.66(s, 3H, Nb**Me**). ^{13}C{^{1}H} NMR (δ ppm, C_6D_6): 152.2(Tp*$_{ax}$), 151.8(Tp*$_{eq1}$), 150.5(Tp*$_{eq2}$, **C**$_3$, 3,5-Me_2**C**$_3HN_2$), 145.3(Tp*$_{eq1}$), 144.6(Tp*$_{eq2}$), 142.5(Tp*$_{ax}$, **C**$_5$, 3,5-Me_2**C**$_3HN_2$), 107.7(Tp*$_{ax}$), 106.7(Tp*$_{eq2}$), 106.6(Tp*$_{eq1}$, **C**$_4$, 3,5-Me_2**C**$_3HN_2$), 68.8(N**C**Me_3), 50(Nb**Me**), 30.7(NC**Me**$_3$),

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16.2(Tp*$_{eq2}$), 16(Tp*$_{eq1}$), 15(Tp*$_{ax}$, 3,**5-Me**$_2$C$_3$HN$_2$), 12.6(Tp*$_{eq2}$), 12.3(Tp*$_{ax}$), 12.1(Tp*$_{eq1}$, **3**,5-**Me**$_2$C$_3$HN$_2$). ^{15}N NMR (δ ppm, C_6D_6): 27(**N**CMe$_3$), -112(Tp*$_{ax}$), -119(Tp*$_{eq2}$), -121(Tp*$_{eq1}$, **N**2-Ta), -155(Tp*$_{ax}$), -156(Tp*$_{eq2}$), -157(Tp*$_{eq1}$, **N**1-B).

7b: ^{1}H NMR (δ ppm, C_6D_6): 5.74(m, 1H, Tp*$_{eq2}$), 5.72(m, 1H, Tp*$_{eq1}$), 5.71(m, 1H, Tp*$_{ax}$, 3,5-Me$_2$C$_3$**H**N$_2$), 4.68(q, 1H, J_{B-H}=119.67 Hz, B**H**), 2.55(m, 3H, Tp*$_{eq2}$), 2.49(m, 3H, Tp*$_{eq1}$), 2.37(m, 3H, Tp*$_{ax}$, 3,**5-Me**$_2$C$_3$HN$_2$), 2.30(m, 3H, Tp*$_{eq2}$), 2.25 (m, 3H, Tp*$_{eq1}$), 2.24(m, 3H, Tp*$_{ax}$, **3**,5- **Me**$_2$C$_3$HN$_2$), 1.44(s, 9H, NC**Me**$_3$), 0.60(s, 3H, Ta**Me**). ^{13}C{^{1}H} NMR (δ ppm, C_6D_6): 152.8(Tp*$_{eq2}$), 152.6(Tp*$_{eq1}$), 152.5(Tp*$_{ax}$, **C**$_3$, 3,5-Me$_2$**C**$_3$HN$_2$), 145.7(Tp*$_{ax}$), 145.4(Tp*$_{eq1}$), 143.3(Tp*$_{eq2}$, **C**$_5$, 3,5-Me$_2$**C**$_3$HN$_2$), 108.4(Tp*$_{ax}$), 106.9(Tp*$_{eq1}$), 106.8(Tp*$_{eq2}$, **C**$_4$, 3,5-Me$_2$**C**$_3$HN$_2$), 65.3(N**C**Me$_3$), 51.5(Ta**Me**), 32(NC**Me**$_3$), 16.5(Tp*$_{eq2}$), 16.2(Tp*$_{eq1}$), 14.9(Tp*$_{ax}$, 3,**5-Me**$_2$C$_3$HN$_2$), 13(Tp*$_{ax}$), 12.9(Tp*$_{eq1}$), 12.6(Tp*$_{eq2}$, **3**,5-**Me**$_2$C$_3$HN$_2$). ^{15}N NMR (δ ppm, C_6D_6): 3(**N**CMe$_3$), -115(Tp*$_{ax}$), -118(Tp*$_{eq2}$), -121(Tp*$_{eq1}$, **N**2-Ta), -156(Tp*$_{ax}$, Tp*$_{eq1}$), -157(Tp*$_{eq2}$, **N**1-B).

Crystal Structure Determination for Compounds 1b, **2a**/**2b**, **3a**/**3b**, **4a** and **5a**/**5b**.

Suitable monocrystals of the compounds were obtained by slow crystallization from a hexane saturated solutions at -30°C. A summary of crystal data, data collection, and refinement parameters for the structural analysis is given in Table 4. Crystals were glued to a glass fiber using an inert polyfluorinated oil and mounted in the N_2 stream in a Bruker-Nonius Kappa-CCD 4 diffractometer with area detector and data were collected using graphite-monochromated Mo-Kα radiation (λ=0.71073 Å) at low temperature (200K). Data for compound **1b** were collected with an exposure time of 380 s per frame (three sets; 143 frames; omega scans 2.0° scan-width), compound **2a** with an exposure time of 199 s per

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frame (four sets; 275 frames; phi/omega scans 2.0º scan-width), compound **2b** with an exposure time of 120 s per frame (six sets; 317 frames; phi/omega scans 2.0º scan-width), compound **3a** with an exposure time of 30 s per frame (four sets; 203 frames; omega scans 2.0º scan-width), compound **3b** with an exposure time of 27 s per frame (three sets; 208 frames; phi/omega scans 1.8º scan-width), compound **4a** with an exposure time of 70 s per frama (four sets; 822 frames; phi/omega scans 0.7º scan-width), compound **5a** with an exposure time of 57 s per frame (two sets; 159 frames; phi/omega scans 1.9º scan-width) and compound **5b** with an exposure time of 20 s per frame (four sets; 279 frames; phi/omega scans 2.0º scan-width). Raw data were corrected for Lorenz and polarization effects.

Structures were solved by direct methods, completed by the subsequent difference Fourier techniques and refined by full-matrix least squares on F^2 (SHELXL-97).[26] Anisotropic thermal parameters were used in the last cycles of refinement for the non hydrogen atoms in both structures. Hydrogen atoms were included from geometrical calculations and refined using a riding model in most of the cases; some of them were located in the Fourier difference maps. All the calculations were made using the WINGX system.[27]

In the case of the compounds **2a** and **2b** some remaining electronic density due to disordered solvent molecules were found in the difference Fourier map but it was not possible to get a chemically sensible model for it, so the Squeeze procedure[28] was used to remove its contribution to the structure factors and in the compound **4a**, some rest of

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electronic density was modelated as ½ hexane disordered molecule for asymmetric unit of the unit cell.

Crystallographic data (excluding structure factors) for the reported structures in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC 902489 for **1b**, 902490 for **2a**, 902491 for **2b**, 902492 for **3a**, 902493 for **3b**, 902494 for **4a**, 902495 for **5a** and 902496 for **5b**. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif.

Table 4. Crystal data structure refinement for alkyl chlorido imido complexes **1b-5b.**

Complex	**1b**	**2a**	**2b**	**3a**	**3b**	**4a**	**5a**	**5b**
Molecular Formula	$C_{21}H_{36}N_7BClTa$	$C_{26}H_{38}N_7BClNb$	$C_{26}H_{38}N_7BClTa$	$C_{24}H_{42}N_7BClNb$	$C_{24}H_{42}N_7BClTa$	$C_{23}H_{42}N_7BClSiNb \cdot 1/4\ C_6H_{14}$	$C_{29}H_{44}N_7BClNb$	$C_{29}H_{44}N_7BClTa$
Molecular Weight	613.78	587.80	675.84	567.82	655.86	605.44	629.89	717.93
Temperature K	200(2)	200(2)	200(2)	200(2)	200(2)	200(2)	200(2)	200(2)
Wawelength Å	0.71073	0.71073	0.71073	0.71069	0.71073	0.71073	0.71073	0.71073
Crystal system, space group	Triclinic, P_{-1}	Triclinic, P_{-1}	Triclinic, P_{-1}	Monoclinic, $P_{21/n}$	Monoclinic, $P_{21/n}$	Monoclinic, $P_{21/n}$	Monoclinic, $P_{21/n}$	Triclinic, P_{-1}
Unit cell dimensions	a=11.2722(12)Å α=96.485(9)° b=14.845(3)Å β=94.684(8)° c=15.7278(14)Å γ=94.906(12)°	a=10.6170(13)Å α=96.911(11)° b=11.2000(9)Å β=97.518(12)° c=14.3110(15)Å γ=107.041(9)°	a=10.7131(10)Å α=96.882(5)° b=11.1795(10)Å β=97.911(5)° c=14.3633(7)Å γ=107.181(7)°	a=10.6587(12)Å b=14.113(6)Å β=114.993(14)° c=20.728(4)Å	a=10.5914(16)Å b=14.0905(14)Å β=95.365(9)° c=18.9936(19)Å	a=9.9978(7)Å b=38.529(5)Å β=98.009(7)° c=17.280(2)Å	a=11.820(15)Å b=20.044(11)Å β=105.81(8)° c=13.824(11)Å	a=10.7974(7)Å α=83.471(5)° b=11.6980(7)Å β=89.385(6)° c=13.9965(11)Å γ=63.341(4)°
Volume $Å^3$	2594.3(6)	1590.3(3)	1604.3(2)	2826.1(14)	2822.2(6)	6591.5(12)	3151(5)	1568.07(19)
Z, Calculated density $mg \cdot m^{-3}$	4, 1.577	2, 1.228	2, 1.399	4, 1.335	4, 1.544	8, 1.220	4, 1.328	2, 1.521
Absortion coefficient mm^{-1}	4.361	0.487	3.534	0.545	4.015	0.506	0.497	3.620

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F(000)	1224	612	676	1192	1320	2548	1320	724
Crystal size mm	0.39x0.28x0.25	0.15x0.1x0.1	0.3x0.3x0.2	0.3x0.2x0.2	0.7x0.3x0.2	0.4x0.2x0.1	0.5x0.4x0.4	0.35x0.3x0.25
Theta range for data collection (□)	3.06 to 25.18	3.21 to 27.40	3.21 to 27.50	3.08 to 26.05	3.09 to 27.52	3.07 to 26.80	3.06 to 25.03	3.32 to 27.50
Limiting indices	-13<=h<=13 -17<=k<=17 -18<=l<=18	-13<=h<=13 -14<=k<=14 -18<=l<=18	-13<=h<=13 -14<=k<=14 -18<=l<=18	-12<=h<=11 -14<=k<=17 -25<=l<=25	-13<=h<=13 -18<=k<=18 -24<=l<=23	-12<=h<=12 -48<=k<=48 -21<=l<=21	-14<=h<=14 -22<=k<=23 -16<=l<=16	-14<=h<=14 -14<=k<=15 -18<=l<=18
Reflections collected/ unique	15305/9026 [R(int)=0.1005]	13551/7195 [R(int)=0.0665]	37885/7230 [R(int)=0.1321]	15126/5349 [R(int)=0.2398]	19594/6432 [R(int)=0.0818]	41498/13770 [R(int)=0.1379]	16190/5518 [R(int)=0.1079]	13499/7132 [R(int)=0.0289]
Completeness to theta (%)	96.7	99.2	98.1	95.9	99.1	97.7	99.2	99.2
Absorption correction	Semi-empirical from equivalents	Semi-empirical from equivalents	Semi-empirical from equivalents	Semi-empirical from equivalents	Semi-empirical from equivalents	Semi-empirical from equivalents	None	Semi-empirical from equivalents
Max. and min. transmission	0.208 and 0.162	1.123 and 0.761	0.276 and 0.213	1.024 and 0.696	0.086 and 0.136	0.658 and 0.766		0.254 and 0.214
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data/restraints /parameters	9026/0/559	7195/0/325	7230/0/329	5549/0/311	6432/0/311	13770/0/637	5518/0/364	7132/0/364
Goodness-of-fit on F^2	0.957	0.905	1.144	0.831	1.017	0.994	1.067	0.835
Final R indices [$I>2\sigma(I)$]	R1=0.0628, wR2=0.1289	R1=0.0697, wR2=0.1816	R1=0.0496, wR2=0.1152	R1=0.0755, wR2=0.1389	R1=0.0498, wR2=0.1018	R1=0.0710, wR2=0.1545	R1=0.0673, wR2=0.1402	R1=0.0290, wR2=0.0621
R indices (all data)	R1=0.1416, wR2=0.1592	R1=0.1408, wR2=0.2268	R1=0.597, wR2=0.1236	R1=0.1959, wR2=0.1954	R1=0.0987, wR2=0.1196	R1=0.1781, wR2=0.1897	R1=0.1106, wR2=0.1573	R1=0.0461, wR2=0.0685
Largest diff. peak and hole ($e \cdot Å^{-3}$)	2.715 and -1.267	1.261 and -1.290	1.824 and -2.496	0.990 and -1.019	2.061 and -2.488	1.074 and -0.537	1.261 and -0.757	2.217 and -1.226

$R1 = \Sigma||F_0|-|F_c||/[\Sigma|F_0|]$; $wR2 = \{[\Sigma w(F_0^2 - F_c)^2] / [\Sigma w(F_0^2)^2]\}^{1/2}$.

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Electronic supplementary information (ESI) available

Additional NMR spectroscopy data: Dbppste cc spectrum (ESI-1) and ROESYAD (mixR=500 ms) (ESI-2) spectrum of the complex **3a** in C_6D_6 at 25°C.

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Alkyl Chlorido Hydridotris(3,5-dimethylpyrazolyl)borate Imido Niobium and Tantalum(V) Complexes: Synthesis, Conformational States of Alkyl Groups in Solid and Solution, X-Ray Diffraction and Multinuclear Magnetic Resonance Spectroscopy Studies.

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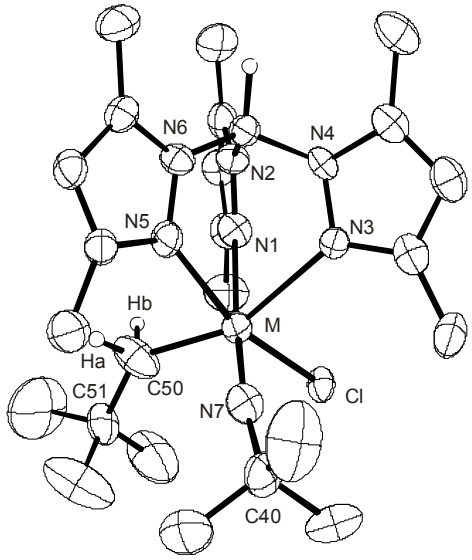
Summary

This article include the synthesis of a series of new alkyl imido hydridotris(3,5-dimethylpyrazolyl)borate Niobium and Tantalum complexes which have been characterized by a complete multinuclear NMR spectroscopic studies and also, the crystal structures of some of them were resolved by diffraction methods.



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