Multiple bonds between main-group elements and transition metals: Part 157 [1]
Neutral and cationic *ansa*-metallocenes of niobium(V) and tantalum(V): synthesis, structures and stereochemical non-rigidity [2]

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Abstract

The metal amide route has been exploited to synthesize $\eta^5:\eta^1$- and $\eta^5:\eta^5$ *ansa*-metallocenes of pentavalent niobium and tantalum. Tris(dimethylamido)(2,6-diisopropylphenylimido)-niobium(V) **2a** and -tantalum(V) **2b** were found to be appropriate starting compounds to cleanly react with CH-acidic ligand precursors such as cyclopentadiene and 2,2-bis(cyclopentadienyl)propane. In the latter case, the novel *ansa*-metallocenes of formula $[C_5H_4-C(CH_3)_2-C_5H_4]M[=N(2,6-^iPr_2C_6H_3)][N(CH_3)_2]$ (**4a**, M = Nb; **4b**, M = Ta) result in high yields. While the hydrocarbon ligand adopts an $\eta^1:\eta^5$-coordination to the metals in the solid state (X-ray diffraction studies), a rapid $\eta^1:\eta^5-\eta^5:\eta^1$ equilibration occurs in solution. Complexes **4a,b** react promptly with $(CH_3)_3SiCl$, thus affording the *ansa*-metallocenes $[C_5H_4-C(CH_3)_2-C_5H_4]M[=N(2,6-^iPr_2C_6H_3)]Cl$ (**5a**, M = Nb; **5b**, M = Ta) quantitatively. The crystal structures of the niobium(V) and tantalum(V) chloro derivatives **5a,b** reveal a 'conventional' $\eta^5:\eta^5$-coordination for the chelating bis(cyclopentadienyl) ligand. Protonolysis of **4a,b** with $[NHMe_3][B(C_6H_5)_4]$ afforded the first cationic *ansa*-metallocenes $[C_5H_4-C(CH_3)_2-C_5H_4]M[=N(2,6-^iPr_2C_6H_3)][NH(CH_3)_2][B(C_6H_5)_4]$ (**6a**, M = Nb; **6b**, M = Ta) in high yields. The crystal structure of **6a** shows an $\eta^5:\eta^5$-coordination mode for the bis(cyclopentadienyl) ligand. The $^1J(C,H)$ coupling constants of the bis(cyclopentadienyl) ligand of the *ansa*-metallocenes **4a,b**, **5a,b** and **6a,b** are related to its hapticity, which is a result of the electronic properties of the metal center. © 1997 Elsevier Science S.A.

Keywords: Multiple bonds; Niobium (V); Tantalum (V)

1. Introduction

ansa-Metallocenes of the Group 4 elements have been investigated intensively in the last decade because of their implication in the stereospecific polymerization of α-olefins [2]. Although cyclopentadienyl complexes of the Group 5 elements $(\eta^5-C_5H_5)M(\eta^4-diene)(CH_3)_2$ (M = Nb, Ta) were found to catalyze ethylene polymerization [3], *ansa*-metallocene derivatives of these elements in high oxidation states are relatively rare and only one complex $[C_5H_4-C(CH_3)_2-C_5H_4]Nb(=N^tBu)(C_5H_5)$

was recently reported [4]. Furthermore, very little is known on *ansa*-metallocenes or *ansa*-functionalized cyclopentadienyl complexes other than those of Group 4 elements [5,6].

In the last decade, imido ligands have been employed increasingly in organometallic chemistry because of their capability to stabilize complexes in high-oxidation states [7,8] and for the wide reactivity of the metal–nitrogen multiple bond [9]. Recently, the d^0 imido complexes $(HBPz_3)V(=NR)Cl_2$ [10] and $Cr[=N(2,6-^iPr_2C_6H_3)]_2(CH_2C_6H_5)_2$ [11], which are in an isolobal relationship [12,13] with the above-mentioned cyclopentadienyl titanium catalysts, were found to induce olefin polymerization in the presence of MAO and $[C(C_6H_5)_3][B(C_6F_5)_4]$ respectively. On the other hand, the imido-vanadium(V) and -tantalum(V) complexes $M(=NSi^tBu_3)(R)(NHSi^tBu_3)_2$ (M = V, R = CH_3; M = Ta, R = C_6H_5) as well as the cationic, bent metallocene

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[1] Dedicated to Professor Gottfried Huttner on the occasion of his 60th birthday.
[2] For the preceding communication, no. 156 of this series, see Ref. [1].

$[\{\eta^5\text{-}C_5(CH_3)_5\}_2Ta(=N^tBu)]^+$ were shown to activate CH bonds of methane [14–16].
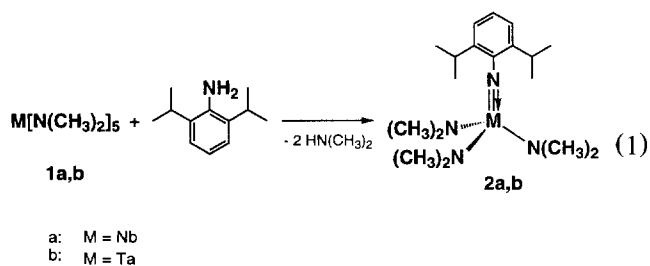
ansa-Bridged metallocenes of Group 4 elements have recently been obtained in high yields starting from the homoleptic amides and functionalized cyclopentadienes [17,18]. However, despite the fact that deprotonation of cyclopentadiene with amides has been known for 20 years, no transition metal cyclopentadienyl complexes other than that of Group 4 elements and the lanthanides [19] were thus obtained until recently [20,21].

We now report on the high-yield synthesis and structure of neutral and first cationic *ansa*-bis(cyclopentadienyl) complexes of niobium(V) and tantalum(V). They are stabilized by ancillary imido ligands (RN). We also report on the crystal structure of the tris(amido)imido niobium (V) complex Nb[= N (2,6-$^iPr_2C_6H_3$)][N(CH$_3$)$_2$]$_3$. This compound and the tantalum analogue seem to offer a general entry into the high-oxidation state chemistry of these elements.

2. Results and discussion

2.1. Tris(amido)imido complexes

The tris(amido)imido precursor complexes **2a,b** are prepared in 79% and 86% isolated yields respectively, from the reaction of the homoleptic amides M[N(CH$_3$)$_2$]$_5$ (M = Nb, Ta) **1a,b** with equimolar amounts of the primary amine NH$_2$(2,6-$^iPr_2C_6H_3$). A double deprotonation of the amine by two amido ligands occurs in this reaction (Eq. (1)).

M[N(CH$_3$)$_2$]$_5$ + [image: diisopropylaniline] $\xrightarrow{-2\,HN(CH_3)_2}$ [image: product structure] (1)

1a,b → **2a,b**

a: M = Nb
b: M = Ta

Although the α-hydrogen abstraction is considered a general method to prepare imido compounds [7], a low yield of the corresponding complex was obtained when **1b** was treated with t-butylamine [22,23]. With the aromatic amine NH$_2$(2,6-$^iPr_2C_6H_3$), however, the tris(amido)imido complexes **2a,b** of niobium(V) and tantalum(V) respectively were obtained in quantitative yields.

The tetracoordinated, thermally stable complexes react cleanly with CH-acidic compounds that effect extrusion of the dimethyl*amido* ligands; the latter are more reactive than the *imido* group. Furthermore, no con-

comitant redox side-reactions occur upon deprotonation of cyclopentadiene with complexes like **2a,b**, in sharp contrast with the behaviour of the homoleptic amides Nb[N(CH$_3$)$_2$]$_5$ [24], Cr(NEt$_2$)$_4$ [25] and Mo[N(CH$_3$)$_2$]$_4$ [20]. The niobium(IV) complex (C$_5$H$_5$)Nb[N(CH$_3$)$_2$]$_3$, reported by Lappert and coworkers [24], was isolated starting from Nb[N(CH$_3$)$_2$]$_5$ **1a** and cyclopentadiene, but there is only insufficient characterization of this compound. The reactions of **1a,b** and cyclopentadiene or C$_5$H$_5$–C(CH$_3$)$_2$–C$_5$H$_5$ were investigated in toluene and afforded mixtures of undefined products. The 'spectator imido ligand' of **2a,b** seems to favorably control the maintenance of high oxidation states in cyclopentadienyl complexes.

The crystal structure of **2a** is shown in Fig. 1, the crystal data are summarized in Table 1, while selected bond lengths and angles are given in Table 2.

The complex exhibits a molecular symmetry close to C_s. The Nb=N1 bond length, 1.794(2) Å and the Nb–N1–C7 angle of 167.4(2)° are similar to the data of compounds such as Nb(=NTol)(S$_2$CNEt$_2$)$_3$ (1.783(3) Å, 167.4(3)°) [26] and {Nb[=NP(C$_6$H$_5$)$_3$]Cl$_3$}$_2$(μ-Cl)$_2$ (1.776(8) Å, 171.1(6)°) [27]. The nitrogen atoms of the amido ligands are in a nearly planar environment. The planes of two amido ligands contain the Nb=N1 axis, while the third amido group is roughly perpendicular with regard to the other two. The Nb–N distances of 1.974(2), 1.979(2), and 2.023(2) Å are similar to those found in the homoleptic amido complex Nb[N(CH$_3$)$_2$]$_5$ **1a** (1.98(2) and 4 × 2.04(2) Å) [28]. Although the solid state study reveals two inequivalent amido ligands, the ^{1}H NMR spectrum of **2a** exhibits only one signal of the N(CH$_3$)$_2$ groups even at −90°C, indicating the ex-
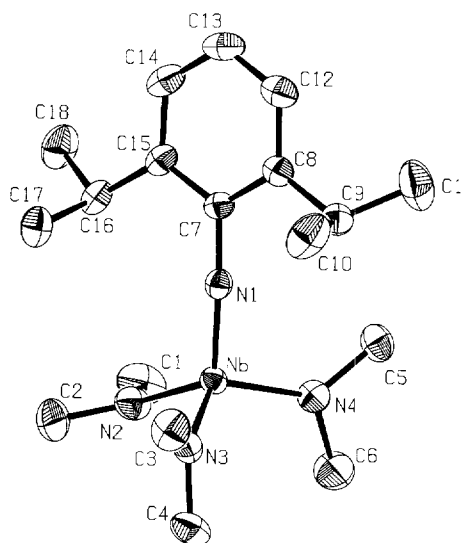

Fig. 1. Structure of tris(dimethylamido)(2,6-diisopropylphenylimido)-niobium(V) (**2a**) in the crystal. Ellipsoids are drawn at the 50% probability level. Hydrogen atoms are omitted for clarity.

pected facile rotation around the Nb–N bonds. Although the related compounds $M(=N^tBu)[N(CH_3)_2]_3$ (M = Nb, Ta), were isolated by Nugent and Harlow in relatively low yield, starting from $Li[NH^tBu]$, $Li[N(CH_3)_2]$ and MCl_5, the molecular parameters of $Ta(=N^tBu)[N(CH_3)_2]_3$ were not established with sufficient accuracy. In particular, the methyl groups of the N^tBu and $N(CH_3)_2$ ligands were disordered about the fixed threefold rotation axis [22].

2.2. Reaction of 2a,b with cyclopentadiene

Treatment of the complexes **2a,b** with cyclopentadiene in toluene affords the cyclopentadienyl derivatives **3a,b** in 81% and 69% isolated yields respectively, as a result of a deprotonation by a single amine ligand (Scheme 1).

The niobium complex **2a** reacts with cyclopentadiene at 60 °C, while the reaction with the tantalum congener **2b** occurs only at 90 °C. However, no bis(cyclopentadienyl) complexes form under these conditions, even with a threefold molar excess of cyclopentadiene. Complexes **3a,b** are thermally stable, but they are high air-sensitive. The $^1J(C,H)$ coupling constants of the cyclopentadienyl ligand of **3a,b** (172 Hz, Nb; 174 Hz, Ta) are similar to those of $(C_5H_5)Nb[=N(2,6-^iPr_2C_6H_3)][CH_2^tBu]X$ (X = Cl, Br, CH_2^tBu) (174–176 Hz) [29], suggesting a simple η^5-coordination mode for the C_5H_5 ligand.

Table 1
Crystallographic data for $Nb[=N(2,6-^iPr_2C_6H_3)][N(CH_3)_2]_3$ **2a**, $[\eta^5:\eta^1-C_5H_4-C(CH_3)_2-C_5H_4]M[=N(2,6-^iPr_2C_6H_3)][N(CH_3)_2]$ (M = Nb, Ta) **4a,b**, $[\eta^5:\eta^5-C_5H_4-C(CH_3)_2-C_5H_4]M[=N(2,6-^iPr_2C_6H_3)]Cl$ (M = Nb, Ta) **5a,b** and $[(\eta^5:\eta^5-C_5H_4-C(CH_3)_2-C_5H_4)Nb\{=N(2,6-^iPr_2C_6H_3)\}\{NH(CH_3)_2\}]^+[B(C_6H_5)_4]^-\cdot THF$ **6a**

	2a	4a	4b	5a	5b	6a
Crystal data						
Chemical formula	$C_{18}H_{35}N_4Nb$	$C_{27}H_{37}N_2Nb$	$C_{27}H_{37}N_2Ta$	$C_{25}H_{31}ClNNb$	$C_{25}H_{31}ClNTa$	$C_{55}H_{66}BN_2NbO$
Fw	400.41	482.51	570.55	473.89	561.93	874.86
Color	yellow	orange	yellow	yellow	yellow	red-brown
Crystal size (mm³)	0.51 × 0.43 × 0.38	0.39 × 0.38 × 0.31	0.46 × 0.30 × 0.10	0.43 × 0.36 × 0.17	0.38 × 0.30 × 0.25	0.84 × 0.64 × 0.46
Crystal system	triclinic	monoclinic	monoclinic	triclinic	triclinic	monoclinic
space group	$P\bar{1}$	$P2_1/n$	$P2_1/n$	$P\bar{1}$	$P\bar{1}$	$P2_1/n$
a (Å)	8.859(1)	10.003(1)	9.995(1)	9.562(2)	9.514(1)	10.0034(6)
b (Å)	10.655(1)	21.861(1)	21.869(2)	10.716(2)	10.719(1)	22.1516(6)
c (Å)	12.767(1)	11.531(1)	11.537(1)	11.403(2)	11.385(1)	23.8018(14)
α (deg)	70.47(1)			76.52(1)	76.44(1)	
β (deg)	85.49(1)	95.29(1)	95.23(1)	83.14(1)	83.16(1)	101.757(3)
γ (deg)	70.58(1)	79.97(1)	80.36(1)			
V (Å³)	1070.4(2)	2510.8(4)	2511.3(4)	1115.1(4)	1108.9(2)	5163.6(5)
Z	2	4	4	2	2	4
T (K)	173	223	223	173	173	163
ρ_{calcd} (g cm⁻³)	1.242	1.276	1.509	1.411	1.683	1.125
μ (cm⁻¹)	5.7	4.9	43.9	6.7	50.9	21.7
F_{000}	424	1016	1144	492	556	1856
Data collection						
λ (Å)	0.71073	0.71073	0.71073	0.71073	0.71073	1.54184
Scan method	imaging plate	imaging plate	imaging plate	ω	imaging plate	$\Theta-2\Theta$
Θ range (deg)	2.26 to 24.97	2.00 to 24.91	1.86 to 24.98	1.84 to 25.96	2.92 to 25.65	2.75 to 68.01
Data collected (h,k,l)	±10, ±12, ±15	±11, ±25, ±13	±11, ±25, ±13	+11, ±13, ±14	±11, ±13, ±13	−12, +26, ±28
Refinement [a]						
No. reflections collected	11965	18328	15269	4473	14986	9944
No. independent reflecntios	3446	4322	4298	4210	3850	9370
No. observed reflections	3446 (all data)	4322 (all data)	4298 (all data)	4210 (all data)	3850 (all data)	9370 (all data)
R_{int}	0.0273	0.0215	0.0435	0.0162	0.0425	0.0219
$R1$	0.0255	0.0295	0.0338	0.0233	0.0195	0.0336
$wR2$	0.0680	0.0649	0.0808	0.0551	0.0437	0.0803
GOF	1.070	1.072	1.088	1.057	1.067	1.053
$\Delta(\rho_{max/min})$ (e⁻ Å⁻³)	0.30, −0.38	+0.30, −0.38	+1.00, −1.87	+0.34, −0.64	+0.86, −1.14	+0.46, −1.07

[a] $R1 = \Sigma(\|F_o| - |F_c\|)/\Sigma|F_o|$; $wR2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$; $GOF = [\Sigma w(F_o^2 - F_c^2)^2/(NO - NV)]^{1/2}$; $w = $ SHELXL-93 weights.

Table 2
Selected bond lengths (Å) and bond angles (deg) for $Nb[=N(2,6-{}^iPr_2C_6H_3)][N(CH_3)_2]_3$ **2a**

Bond lengths			
Nb–N(1)	1.794(2)	N(2)–C(2)	1.453(4)
Nb–N(2)	2.023(2)	N(3)–C(3)	1.449(3)
Nb–N(3)	1.974(2)	N(3)–C(4)	1.457(4)
Nb–N(4)	1.979(2)	N(4)–C(5)	1.456(4)
N(1)–C(7)	1.389(3)	N(4)–C(6)	1.455(4)
N(2)–C(1)	1.451(4)		
Bond angles			
N(1)–Nb–N(2)	116.61(9)	C(1)–N(2)–C(2)	111.2(2)
N(1)–Nb–N(3)	108.09(9)	Nb–N(3)–C(3)	132.0(2)
N(2)–Nb–N(3)	105.06(9)	Nb–N(3)–C(4)	116.1(2)
N(2)–Nb–N(4)	105.46(9)	C(3)–N(3)–C(4)	111.8(3)
N(3)–Nb–N(4)	118.36(8)	Nb–N(4)–C(5)	128.3(2)
Nb–N(1)–C(7)	167.4(2)	Nb–N(4)–C(6)	120.6(2)
Nb–N(2)–C(1)	123.2(2)	C(5)–N(4)–C(6)	111.0(2)
Nb–N(2)–C(2)	123.4(2)		

2.3. η^5:η^1 ansa-Metallocenes

The tris(amido) complexes **2a,b** were treated with equimolar amounts of the diprotic ligand C_5H_5–$C(CH_3)_2$–C_5H_5 in toluene at 110 °C (Scheme 1). The new ansa-bis(cyclopentadienyl) complexes **4a,b** form quantitatively, as monitored by the ^{1}H NMR spectra, and were isolated as orange and yellow solids in 74% and 59% yields respectively. The products are readily soluble in n-heptane, thermally quite stable both in hydrocarbon solution and in the solid state, but extremely water-sensitive.

2.4. Crystal and molecular structure

The X-ray crystal structures of **4a,b** were determined. Perspective and perpendicular to the η^5-C_5H_4
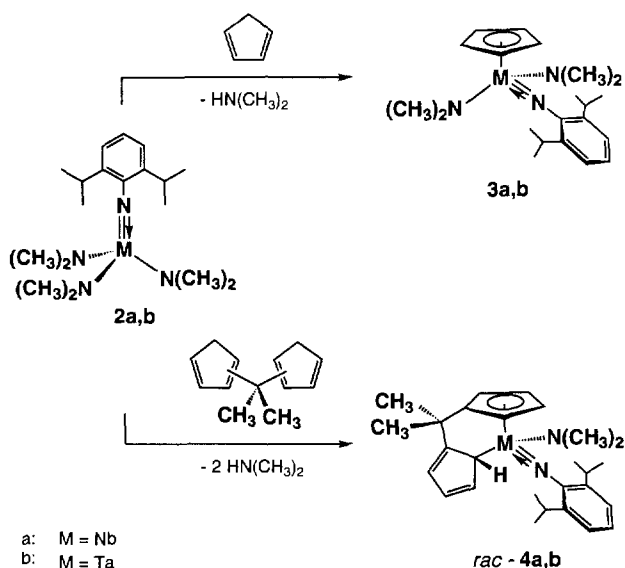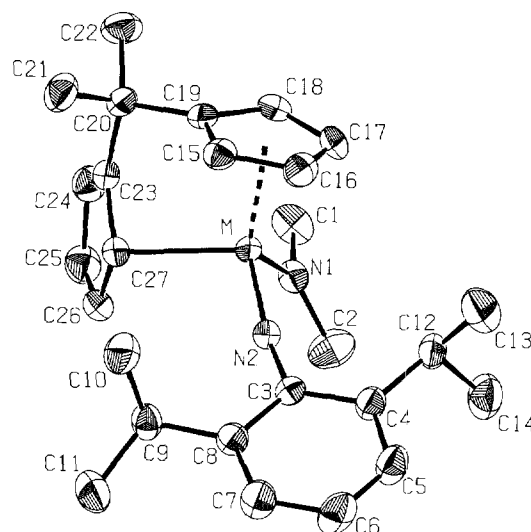
Fig. 2. ORTEP drawing of the crystal and molecular structure of the η^5:η^1 ansa-metallocenes **4a** (niobium) and **4b** (tantalum). Ellipsoids are drawn at the 50% probability level. Hydrogen atoms are omitted for clarity.

plane views of the compounds are shown in Figs. 2 and 3. The crystal data are summarized in Table 1, while selected bond lengths and angles are reported in Table 3.

The two complexes are isostructural in the solid state and almost identical in their molecular parameters. The metals are in pseudo-tetrahedral environments and are coordinated to an imido ligand, a dimethylamido group, and two cyclopentadienyl rings bonded in the η^5- and η^1-fashions. The M=N distances (1.786(2) Å, Nb; 1.793(4) Å, Ta) and the M=N–C angles, (167.4(1)°, Nb; 168.5(3)°, Ta) are close to those of the complex **2a**

Scheme 1.
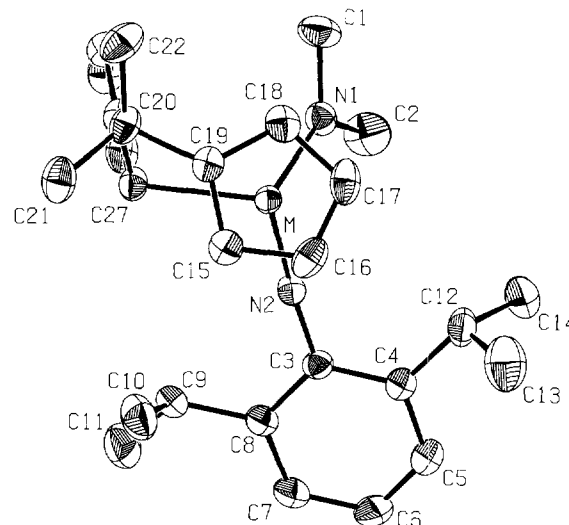
Fig. 3. Structural presentation of the η^5:η^1 ansa-metallocenes **4a,b** perpendicular to the plane of the η^5-coordinated cyclopentadienyl ring. Ellipsoids are drawn at the 50% probability level. Hydrogen atoms are omitted for clarity.

$(1.794(2)\,\text{Å}, 167.4(2)°)$. These data compare well with those of other imido-cyclopentadienyl complexes: $(\eta^5\text{-}C_5R_5)M[=N(2,6\text{-}^iPr_2C_6H_3)]Cl_2$ $(1.761(6)/1.780(5)\,\text{Å};$ $165.6(5)/171.4(5)°$; $M = Nb/R = H$, and $M = Ta/R = CH_3$ respectively) [30], $(\eta^5\text{-}C_5H_5)Nb[=N(2,6\text{-}^iPr_2C_6H_3)][CH_2{}^tBu]_2$ $(1.788(2)\,\text{Å}, 174.6(2)°)$ [29], $(\eta^5\text{-}C_5H_5)_2(\eta^1\text{-}C_5H_5)Nb(=N^tBu)$ $(1.756(3)\,\text{Å}, 176.8(3)°)$, $[\eta^5\text{-}C_5H_4Si(CH_3)_3]_2Nb(=NC_6H_5)Cl$ $(1.792(2)\,\text{Å}, 165.1(2)°)$, $[\eta^5\text{-}C_5(CH_3)_5]_2Ta(=NC_6H_5)H$ $(1.83(1)\,\text{Å}, 177.8(9)°)$ [31–33]. Metal–nitrogen bond lengths, M–N–C angles and MO calculations [34] suggest an M–N bond order between 2 and 3 for imido transition metal complexes. A Walsh diagram for the complex $(\eta^5\text{-}C_5H_5)_2Ta(=NC_6H_5)H$ shows that the minimal energy is obtained for a linear M=N–C arrangement with the phenyl group lying in the equatorial plane. Bending of the phenyl group at the N atom for θ between 180 and 160° or rotation round the N–C bond do not change significantly the total energy [34]. The $M-N(CH_3)_2$ distances amounting to $1.974(2)$, $1.966(3)\,\text{Å}$ in compounds **4a,b** compare well with those of **2a** $(1.974(2)–2.023(2)\,\text{Å})$ and of $Ta(=N^tBu)[N(CH_3)_2]_3$ $(1.99\,\text{Å})$ [22]. The nitrogen atoms are in a nearly planar environment with the largest deviation from the mean plane (M, N1, N2, C1, C2) of $0.005(2)$ and $0.009(3)\,\text{Å}$ for Nb and Ta respectively. The planes contain the M=N axes and this is consistent with the single-faced amido ligand acting as a 'compass' of the π-donor strength of the imido ligand in a tetrahedral environment [12]. The η^5-cyclo-

pentadienyl ligands of **4a,b** are oriented with one of the ring carbon atoms such that it approximately eclipses the M=N bond, in agreement with the strongly π-donating imido ligand [12]. The calculated $M-(\eta^5\text{-}C_5H_4R)_{cent}$ distances $2.149\,\text{Å}$ and $2.134\,\text{Å}$ (for $M = Nb$ and Ta respectively) are slightly shorter than those of $(\eta^5\text{-}C_5H_5)Nb[=N(2,6\text{-}^iPr_2C_6H_3)][CH_2{}^tBu]_2$ $(2.173\,\text{Å})$ [29] and $(\eta^5\text{-}C_5H_5)_2(\eta^1\text{-}C_5H_5)Nb(=N^tBu)$ $(2.217/2.208\,\text{Å})$ [31] for which compounds a significant destabilization of the metal–ring bonding has been proposed. As a matter of fact, the strongly π-donating imido ligand seems to be responsible for a trend towards an allyl/olefin-type coordination of the cyclopentadienyl group observed in a series of imido/cyclopentadienyl complexes of Group 5 metals [12]. The η^1-cyclopentadienyl ligands of **4a,b** are bent away from the imido ligands, in contrast to $[C_5H_4-C(CH_3)_2-C_5H_4]Nb(=N^tBu)(C_5H_5)$, with the angle between the M, the C27 and the ring center amounting to $111.5°$ and $114.2°$. The $M-C27(\eta^1)$ bond lengths of $2.291(2)$ and $2.251(4)\,\text{Å}$ show a slightly shorter tantalum–carbon distance than that of niobium, and this value is close to the M–C(alkyl) distances found in compounds: $(\eta^5\text{-}C_5H_5)_2(\eta^1\text{-}C_5H_5)Nb(=N^tBu)$, $2.330(2)\,\text{Å}$ [31]; $(\eta^5\text{-}C_5H_5)Nb(=N^tBu)(CH_3)(Cl)$, $2.193(5)\,\text{Å}$ [35]; $[\eta^5\text{-}C_5(CH_3)_5]Ta(CHPh)(CH_2Ph)_2$, $2.19(2)$ and $2.23(1)\,\text{Å}$ [36], $(\eta^5\text{-}C_5H_5)_2Ta(=CH_2)(CH_3)$, $2.25(1)\,\text{Å}$ [37], $Ta(=NSi^tBu_3)_2(py)_2(CH_3)$, $2.23(2)\,\text{Å}$ [15]. The M...C23 distances $(2.897(2)$, $2.911(4)\,\text{Å})$ are non-

Table 3

Selected bond lengths (Å) and bond angles (deg) for $[\eta^5{:}\eta^1\text{-}C_5H_4\text{-}C(CH_3)_2\text{-}C_5H_4]M[=N(2,6\text{-}^iPr_2C_6H_3)][N(CH_3)_2]$ (M = Nb, Ta) **4a,b**

	Nb	Ta		Nb	Ta
Bond lengths					
M–N(1)	1.974(2)	1.966(3)	C(16)–C(17)	1.406(3)	1.406(7)
M–N(2)	1.786(2)	1.793(4)	C(17)–C(18)	1.411(3)	1.409(6)
M–C(15)	2.457(2)	2.444(4)	C(18)–C(19)	1.411(3)	1.406(6)
M–C(16)	2.439(2)	2.421(5)	C(19)–C(20)	1.523(3)	1.523(6)
M–C(17)	2.434(2)	2.416(4)	C(20)–C(23)	1.520(3)	1.518(6)
M–C(18)	2.492(2)	2.481(4)	C(23)–C(24)	1.363(3)	1.368(6)
M–C(19)	2.491(2)	2.484(4)	C(23)–C(27)	1.463(3)	1.471(6)
M–C(27)	2.291(2)	2.251(4)	C(24)–C(25)	1.434(3)	1.435(6)
C(15)–C(16)	1.404(3)	1.409(6)	C(25)–C(26)	1.356(3)	1.361(6)
C(15)–C(19)	1.421(3)	1.418(6)	C(26)–C(27)	1.450(3)	1.469(6)
Bond angles					
N(1)–M–N(2)	102.13(7)	102.6(2)	C(19)–C(20)–C(21)	110.9(2)	111.1(4)
N(1)–M–C(27)	105.04(7)	104.0(1)	C(19)–C(20)–C(22)	110.7(2)	111.1(4)
N(2)–M–C(27)	102.78(7)	102.7(2)	C(19)–C(20)–C(23)	104.1(2)	104.1(3)
M–N(1)–C(1)	123.2(2)	123.9(3)	C(21)–C(20)–C(22)	109.3(2)	109.3(4)
M–N(1)–C(2)	126.7(2)	125.9(3)	C(21)–C(20)–C(23)	110.3(2)	109.9(4)
C(1)–N(1)–C(2)	110.1(2)	110.1(4)	C(22)–C(20)–C(23)	111.5(2)	111.3(4)
M–N(2)–C(3)	167.4(1)	168.5(3)	C(20)–C(23)–C(24)	130.3(2)	130.2(4)
C(16)–C(15)–C(19)	109.1(2)	109.0(4)	C(20)–C(23)–C(27)	121.7(2)	121.0(3)
C(15)–C(16)–C(17)	107.7(2)	107.2(4)	C(24)–C(23)–C(27)	107.7(2)	108.4(3)
C(16)–C(17)–C(18)	107.9(2)	108.3(4)	C(23)–C(24)–C(25)	109.1(2)	108.6(4)
C(17)–C(18)–C(19)	108.8(2)	108.7(4)	C(24)–C(25)–C(26)	108.9(2)	109.6(4)
C(15)–C(19)–C(18)	106.4(2)	106.7(4)	C(25)–C(26)–C(27)	108.6(2)	108.2(4)
C(15)–C(19)–C(20)	126.4(2)	126.1(4)	C(23)–C(27)–C(26)	105.6(2)	104.9(3)
C(18)–C(19)–C(20)	126.0(2)	126.1(4)			

bonding and represent the shortest $M-C(\eta^1-C_5H_4R)$ lengths. The C–C bond around the ring varies according to the diene structure: C27–C23, 1.463(3), 1.471(6); C23–C24, 1.363(3), 1.368(6); C24–C25, 1.434(3), 1.435(6); C25–C26, 1.356(3), 1.361(6); C26–C27, 1.450(3), 1.469(6) Å for M = Nb, Ta respectively. The largest deviation of the carbon atoms from a mean plane of the five-membered ring is 0.021(1) Å and 0.026(6) Å for Nb and Ta respectively.

The $\eta^1-C_5H_5$ coordination mode to transition metals has been known for a number of tetra- and tris(cyclopentadienyl) complexes such as $(\eta^5-C_5H_5)_3Zr(\eta^1-C_5H_5)$ [38], $(\eta^5-C_5H_5)_2M(\eta^1-C_5H_5)_2$ (M = Ti, Hf) [39] and $(\eta^5-C_5H_5)_2Mo(\eta^1-C_5H_5)(NO)$ [40]. However, bis(cyclopentadienyl) complexes are generally metallocenes, and few examples have been reported with a cyclopentadienyl ring coordinated in an η^1-fashion, e.g. $(\eta^5-C_5H_5)Cr(\eta^1-C_5H_5)(NO)_2$, $(\eta^5-C_5H_5)Mo(\eta^1-C_5H_5)(NO)[S_2CN(CH_3)_2]$ $(\eta^5-C_5H_5)Fe(\eta^1-C_5H_5)(CO)_2$, $(\eta^5-C_5H_5)Mn(\eta^1-C_5H_5)[(CH_3)_2N(CH_2)_2-N(CH_3)_2]$, $(\eta^5-C_5H_5)Pd(\eta^1-C_5H_5)(P^iPr_3)$ [41]. Only a few examples of ring-slippage [42] of an *ansa*-type bis(cyclopentadienyl) complex have been reported thus far, namely $[\eta^5:\eta^1-C_5H_4-Si(CH_3)_2-C_5H_4]_2Zr$ [17] and $[\eta^5:\eta^1-C_5H_4-C(CH_3)_2-C_5H_4)]Nb(=N^tBu)(C_5H_5)$ [4], related to the tetra- and tris-(cyclopentadienyl) complexes. Indenyl- or fluorenyl-derivatives often exhibit localized allyl–ene structures, for example $[\eta^5:\eta^3-C_5H_4-C(CH_3)_2-C_{13}H_9]HfCl_2$ and $[\eta^5:\eta^3-C_5H_4-C(CH_3)_2-C_{11}H_9)Zr(\mu-H)Cl]_2$ [43]. The ring-slippage of **4a,b** is not necessarily related to the strain of the short $C(CH_3)_2$ bridge. In this regard, it should be noted that the *ansa*-metallocenes $[\eta^5:\eta^5-C_5H_4-C(CH_3)_2-C_5H_4]MX_2$ (M = Ti, Zr; X = Cl, CH_3 [44] and M = Mo, X = H; M = W, X = Cl [6]) and $[\eta^5:\eta^5-C_5H_4-C(CH_3)_2-C_5H_4](\eta^5-C_5H_5)MCl$ (M = Zr, Hf) [45] exhibit the bis(cyclopentadienyl) ligand in an $\eta^5:\eta^5$-fashion [46], both in the solid state and in solution.

The η^5-cyclopentadienyl coordination was also determined for the formally 20e⁻ 'bent metallocene' imido complexes. Examples are $(\eta^5-C_5H_5)_2Zr(=N^tBu)(OC_4H_8)$ [47], $(\eta^5-C_5H_5)_2(\eta^1-C_5H_5)Nb(=N^tBu)$ [31], $[\eta^5-C_5(CH_3)_5]_2Ta(=NC_6H_5)H$ [33], $(\eta^5-C_5H_5)_2Mo(=N^tBu)$ and $[\{\eta^5-C_5H_4(CH_3)\}_2Mo(=N^tBu)(CH_3)]I$ [48].

Steric interactions between the cyclopentadienyl rings and the isopropyl groups of complexes **4a,b** are not likely to cause the monohapto coordination of one of the two cyclopentadienyl ring ligands. As a matter of fact, all the bis(cyclopentadienyl) complexes of niobium and tantalum of type $(C_5H_5)_2MX_n$ (X different from C_5H_5 and n = 2, 3) are 'bent metallocenes'. We tentatively assign the η^1-ring-slippage to the π-donation of the lone pairs of the linear imido ligand and the planar amido ligand to the metal center. If we regard the imido and amido ligands $N(2,6-^iPr_2C_6H_3)$ and $N(CH_3)_2$ as

respectively four- and three-electron ligands, then the complexes **4a,b** will attain an 18e⁻ configuration.

A structural examination of the complexes **4a,b** reveals the presence of two chiral centers, namely the metal and the carbon C27 atoms. The perspective view of Fig. 3 shows (S) and (R) configurations for the metal and carbon centers, with the $\eta^1-C_5H_5$ ligand being bent away from the metal, thus minimizing steric interactions. A racemic mixture $(S)(R) + (R)(S)$ of **4a,b** was established in the solid state, while the other two possible stereoisomers are obviously energetically unfavorable.

2.5. Structure in solution

The lack of symmetry of the complexes **4a,b** would render all atoms inequivalent, if the structure was retained in solution. The ^1H NMR spectra of the complex **4b** in toluene-d_8 exhibit one doublet and one septet for the isopropyl groups of the imido ligand, with a slight loss of resolution at $-80\,°C$. The $N(CH_3)_2$ ligand shows at $80\,°C$ a broad signal at $\delta = 2.88$ $(\Delta\nu_{1/2} \approx 25\,Hz)$ which disappears in the base line at $20\,°C$. Upon cooling to $-80\,°C$, the amido ligand shows up again with two sharp resonances at $\delta = 2.04$ and $3.58\,ppm$, corresponding to two non-equivalent methyl groups and indicating that rotation around the Ta–N axis is slow at this temperature on the NMR time scale. The ^1H spectra of the coordinated ligand $C_5H_4-C(CH_3)_2-C_5H_4$ at $80\,°C$ exhibit a structured, somewhat broad singulet at $\delta = 4.93\,ppm$ and three symmetric multiplets at $\delta = 5.44, 5.99, 6.17\,ppm$; while the two methyl groups are inequivalent. The proton resonances, consistent with a molecule of C_s symmetry on the NMR time scale, do not change substantially at low temperature, only suffering from a slight loss of proton peak resolution at $-80\,°C$ in toluene-d_8. The ^{13}C NMR spectrum of **4b** in C_6D_6 at $20\,°C$ shows five signals at $\delta = 89.1, 108.3, 112.8, 116.1, 144.8$ (*ipso* carbon) ppm for the C_5H_4 rings.

In order to distinguish between symmetric $\eta^n:\eta^n$ (n = 1, 3 and 5) coordination fashions and fast $\eta^5:\eta^1-\eta^1:\eta^5$ interchange of the $C_5H_4-C(CH_3)_2-C_5H_4$ ligand (Fig. 4), proton and carbon NMR parameters were assigned and compared with data reported in the literature.

The connectivity of the atoms within the two cyclopentadienyl rings, established through a $^{13}C,^1H$ correlation and proton DQF-COSY, 2D-NOESY experiments, is shown in Fig. 5.

The NMR data for an $\eta^1:\eta^1$-coordination (I) are not consistent with the different conceivable metallacycles. As a matter of fact, structures with a CH_2 fragment must be excluded on the basis of the coupled ^{13}C NMR spectra, while those with $CHC(CH_3)_2$ and CHTa groups should present a $^1J(C,H)$ in the range 120 to 130 Hz

(I)   (II)   (III)

C	$\delta\,^1$H	$\delta\,^{13}$C	^{1}J(C, H)
a		145.3	
b	5.51	108.3	166
c	6.08	113.2	167
d	6.28	116.1	171
e	5.01	89.4	156

δ [ppm], ^{1}J(C, H) [Hz], C_6D_6 70 ºC

Fig. 5. ^{1}H–^{13}C NMR chemical shifts and ^{1}J(C,H) coupling constants for the cyclopentadienyl ring of **4b**.
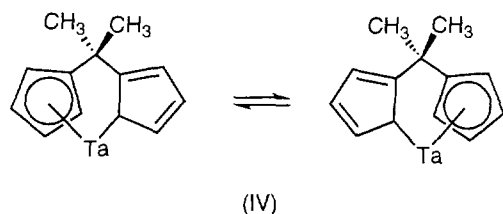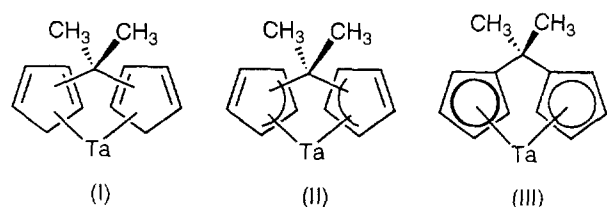

(IV)

Fig. 4. Conceivable coordination modes for the 2,2-bis(cyclopentadienyl)propane ligand of **4b**.

[36,49,50]. Finally, the structure with a $C(CH_3)_2Ta$ fragment should have two olefinic non-*ipso* carbons in the range of $\delta = 130$ to 140 ppm, as expected from the simple 'model complex' $(\eta^5\text{-}C_5H_5)_2(\eta^1\text{-}C_5H_5)Nb(=N^tBu)$ [31].

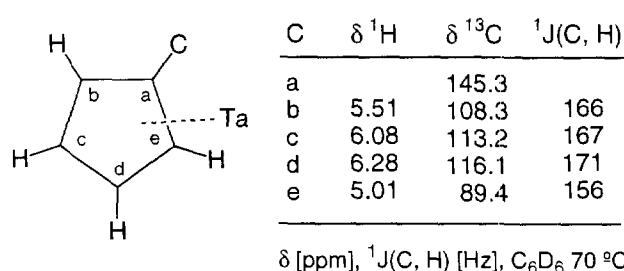The η^5:η^5-coordination (III) should imply four

^{1}J(C,H) in the range of 170 to 180 Hz, cf. the *ansa*-hafnocene complex $[\eta^5\text{:}\eta^5\text{-}C_5H_4\text{-}C(CH_3)_2\text{-}C_5H_4](\eta^5\text{-}C_5H_5)HfCl$ (172–178 Hz) and of the related tantalum complex **3b** (174 Hz).

Although η^3- and distorted η^5-coordination of the unsubstituted cyclopentadienyl ligand was established in the solid state for $(\eta^5\text{-}C_5H_5)(\eta^3\text{-}C_5H_5)W(CO)_2$ and $[\eta^5\text{-}C_5(CH_3)_5][\eta^3\text{-}C_5(CH_3)_5]Cr(CO)_2$ [51], no clear NMR evidence for this coordination mode in solution has ever been reported. Apparently, fast fluxional processes take place. We observe that many cyclopentadienyl complexes with an η^1-coordination in the solid state exhibit a single ^{1}H NMR resonance for this ligand even at low temperatures; examples are the complexes
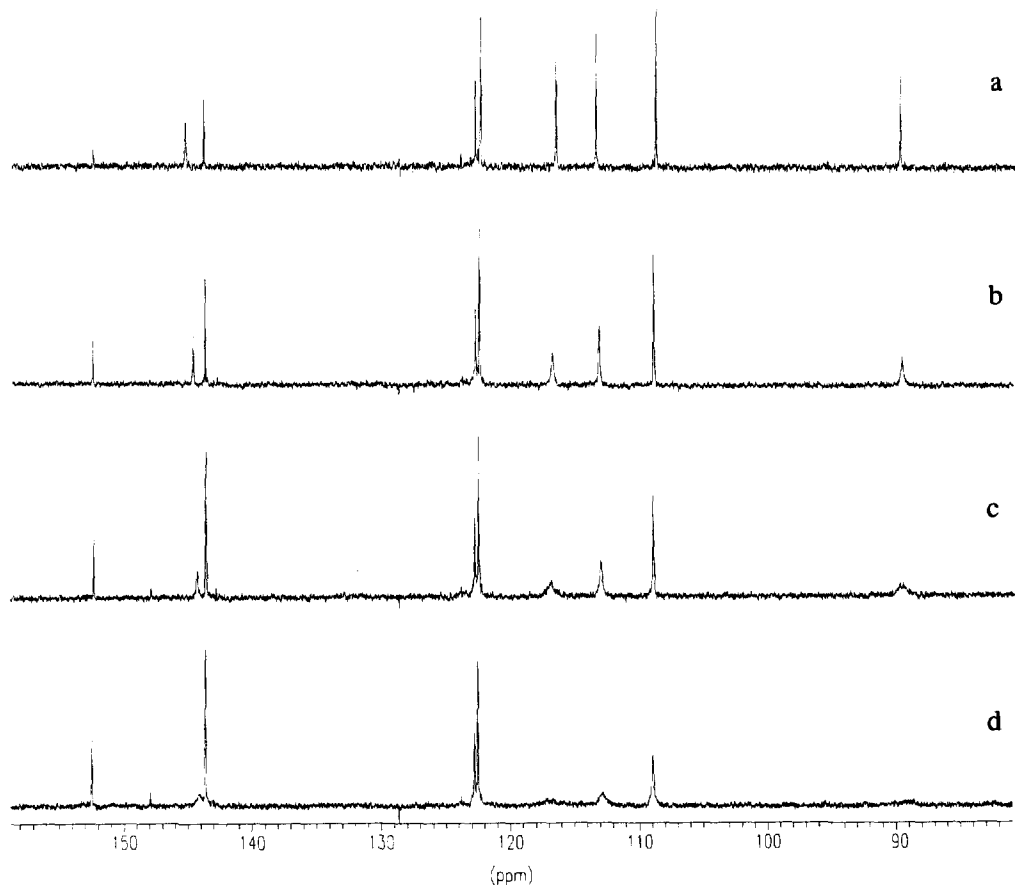

Fig. 6. Variable-temperature ^{13}C NMR spectra of the η^5:η^1 *ansa*-metallocene **4b** in the phenyl and cyclopentadienyl range (thf-d_8): (a) 20 °C; (b) –50 °C; (c) –80 °C; (d) –105 °C.
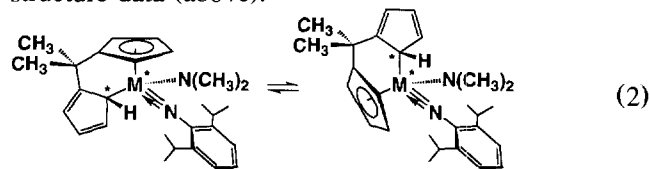
$(\eta^1\text{-}C_5H_5)Tc[=N(C_6H_5)]_3$, $(\eta^1\text{-}C_5H_5)Re(CO)_3[P(CH_3)_3]$ and $[(\eta^1\text{-}C_5H_5)Re(=N^tBu)_2]_2(\mu\text{-}C_5H_4)(\mu\text{-}O)$ [52]. The ^{13}C NMR parameters of η^3-allyl and η^3-indenyl complexes are discussed as follows. The middle carbon atom of the η^3-allyl ligand presents a lower field ^{13}C chemical shift and a higher $^1J(C,H)$ compared to the other two carbon atoms [53]. Examples of the Group V elements are the tantalum allyl complexes $[\eta^5\text{-}C_5(CH_3)_5]Ta(\eta^3\text{-}CH_2CHCH_2)_2$ $(^1J(C,H) = 170$ and $149\,Hz)$ and $[\eta^5\text{-}C_5(CH_3)_5]Ta[\eta^3\text{-}CH_2CHCH(C_6H_5)]_2$ $(^1J(C,H) = 168$ and 145, $151\,Hz)$ [54]. The ^{13}C chemical shift of the *ipso*-carbon atoms of the indenyl systems are quite sensitive to the hapticity of this ligand; in particular, a remarkably low-field shift ($\Delta\delta$ of 40–50 ppm) was observed changing from η^5- to η^3-coordination [55]. In the case of an η^3:η^3-coordination (II) two olefinic carbon atoms with $\delta > 130$ ppm [56] are expected for an allyl/olefin-type cyclopentadienyl ring. The presence of a small coupling constant $^1J(C,H)$ related to the carbon atom with a ^{13}C NMR high-field resonance and near to the *ipso*-carbon is difficult to interpret in terms of an allylic structure for which two small coupling constants $^1J(C,H)$ are expected. The lack of four multiplet proton signals in the ^1H NMR spectra suggests that the η^3:η^3-coordination is not present in the *ansa*-metallocenes **4a,b**.

Upon cooling of a thf-d_8 solution of **4b** to $-105\,°C$, the ^1H NMR spectra show a pronounced broadening of the signal at $\delta = 5.03$ ppm $(\Delta\nu_{1/2} \approx 30\,Hz)$, while the other three cyclopentadienyl protons are less affected $(\Delta\nu_{1/2} \approx 12\,Hz)$. Finally, the ^{13}C-$\{^1H\}$ NMR spectra at $20\,°C$ show sharp signals, while upon cooling only the cyclopentadienyl resonances broaden. At $-105\,°C$ the peaks at $\delta = 89.8$ and 116.6 ppm disappear in the base line, while the other three cyclopentadienyl signals are quite broad compared to the remaining four sharp phenyl carbon signals (Fig. 6).

We therefore propose that the η^5:η^1-coordination fashion is retained in solution, with a rapid η^5:η^1–η^5:η^1 interchange of the *ansa*-metallocene taking place even at low temperature. The slow exchange limit must be below $-100\,°C$. It is interesting to observe that the measured $^1J(C,H)$ values for the bis(cyclopentadienyl) ligand are in rather good agreement with those obtained as the main values of the corresponding coupling constants of **4b** and C_5H_6 [57], [3] taken as rough models for η^5- and η^1- (in parentheses) coordination: 156 (150), 166 (169), 167 (169) and 171 (172) Hz. During the

isomerization process, a reversible inversion of the configurations of the two chiral centers $(S)(R)$ and $(R)(S)$ occurs, while the other two stereoisomers seem not to be present in solution either (Eq. (2)), cf. the crystal structure data (above).
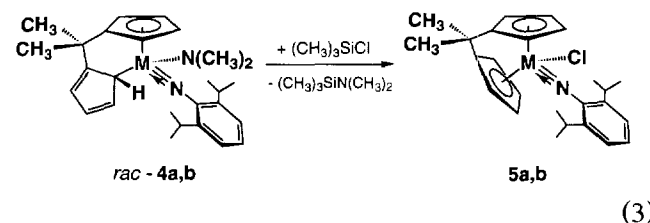

$$(2)$$

The low energy barrier of this process must be related to only small geometrical displacements of the cyclopentadienyl rings necessary to allow fluxionality. The $^1H$$^{13}C$-$\{^1H\}$ spectra of **4b** at different temperatures indicate that this complex is stereochemically non-rigid with a rather slow rotation of the amido ligand (Ta–N axis) compared to the free N–C rotation of the imido and the rapid η^5:η^1–η^1:η^5 isomerization exchange of the cyclopentadienyl ligands. It is to note that a rapid η^5:η^1–η^1:η^5 interchange between two functionalized cyclopentadienyl ligands was also observed in the case of the dinuclear complex $[\eta^5\text{-}C_5H_4\text{-}P(C_6H_5)_2]Pt_2[\eta^1\text{-}C_5H_4\text{-}P(C_6H_5)_2]_2(CH_3)_2$ [58].

The NMR spectra of niobium complex **4a** are rather similar to those of the tantalum congener **4b**. The ^1H NMR spectrum of **4a** in toluene-d_8 at $20\,°C$ exhibits three sharp resonances at $\delta = 5.39$, 5.44 and 6.06 ppm in a 1:1:2 ratio for the cyclopentadienyl protons, while at $+100\,°C$ four peaks are observed at $\delta = 5.38$, 5.46, 6.03 and 6.06 ppm. The amido ligand presents at $20\,°C$ one peak at $\delta = 2.84$ $(\Delta\nu_{1/2} \approx 14\,Hz)$, which broadens upon cooling, and at $-95\,°C$ two singlets at $\delta = 2.16$ and 3.46 ppm are observed. The ^{13}C NMR spectrum of the bis(cyclopentadienyl) ligand of **4a** at $20\,°C$ shows five signals at 90.0, 106.7, 112.5 and 114.0 ppm, with a $^1J(C,H) = 157$, 165, 167 and 170 Hz respectively, similar to the values of the Ta analog **4b**.

2.6. η^5:η^5 ansa-Metallocenes

Treatment of the complexes **4a,b** with chlorotrimethylsilane in toluene at low temperatures, affords the *ansa*-metallocene chlorides **5a,b**, in quantitative yield (Eq. (3)).

rac - **4a,b**   **5a,b**

$$(3)$$

The product $(CH_3)_3SiN(CH_3)_2$ and the excess of $(CH_3)_3SiCl$ are volatile enough to be removed easily

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[3] The $^1J(C,H)$ data for the $(\eta^1\text{-}C_5H_5)Ta$ fragment are not reported and are assumed equal to those of C_5H_6 (164, 169 and 126 Hz) [56]. Low accuracy is expected for the carbon atom bound to the metal, for which the value 126 Hz is in the range of tantalum alkyl complexes [36,50].
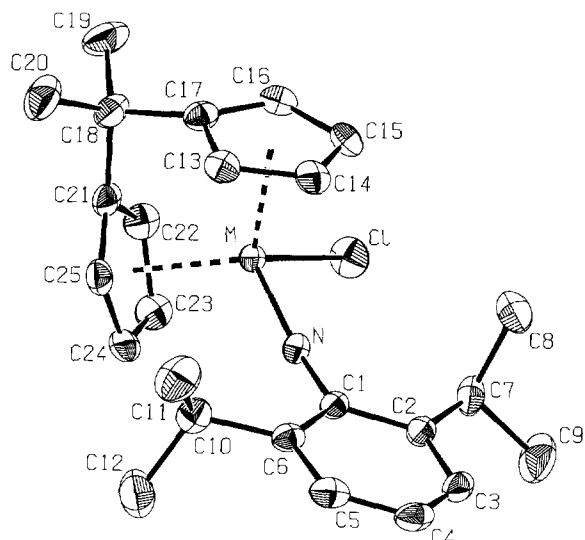
Fig. 7. ORTEP drawing of the crystal and molecular structure of the $\eta^5:\eta^5$ ansa-metallocenes **5a** (niobium) and **5b** (tantalum). Ellipsoids are drawn at the 50% probability level. Hydrogen atoms are omitted for clarity.

with the solvent at low pressure. The red and orange complexes **5a,b** are quite thermally stable and are not extremely air-sensitive in the solid state compared to the compounds **4a,b**.

An X-ray experiment was carried out on **5a,b** to clarify the coordination mode of the ligands. The niobium and tantalum complexes present similar crystal and molecular parameters. The metals are in a pseudo-tetrahedral environment and are coordinated to one

chloride, the imido ligand and the bis(cyclopentadienyl) ligand bonded in an $\eta^5:\eta^5$ mode (Fig. 7). Crystal data are reported in Table 1; selected bond lengths and angles are summarized in Table 4.

The M–Cl distances (2.433(1), Nb; 2.404(1) Å, Ta) are similar to that of $[\eta^5\text{-}C_5H_4Si(CH_3)_3]_2Nb(=NC_6H_5)Cl$ (2.453(1) Å) [32], but they are longer compared to those of the mono(cyclopentadienyl) complexes $(\eta^5\text{-}C_5H_5)Nb(=N\text{-}2,6\text{-}^iPr_2C_6H_3)Cl_2$ (2.338(2) Å), $(\eta^5\text{-}C_5Me_5)Ta(=N\text{-}2,6\text{-}^iPr_2C_6H_3)Cl_2$ (2.345(2) Å) [30]. The M=N distances (1.798(2), Nb; 1.799(2) Å, Ta) and the M–N–C angles (167.5(1), Nb; 168.3(2)°, Ta) are quite near to those of the related complexes **4a,b**. The $M\text{-}(\eta^5\text{-}C_5H_4R)_{cent}$ distances of the bis(cyclopentadienyl) ligand (C(13–17)/C(21–25); 2.156/2.178 Å, Nb; 2.140/2.168 Å, Ta) are similar to those of the complexes **4a,b** ((C15–19); 2.150 Å, Nb; 2.136 Å, Ta). The C(17,18,21) angles of the bridged carbon of **5a,b** (99.4(2)°, Nb; 99.0(2)°, Ta) are similar to those of $[\eta^5:\eta^5\text{-}C_5H_4\text{-}C(CH_3)_2\text{-}C_5H_4](\eta^5\text{-}C_5H_5)MCl]$ (99.4(2), Zr; 97.7(5), Hf) [45] but smaller than those of **4a,b** (C(19,20,23); 104.1(2)°, Nb; 104.1(3)°, Ta). If we regard the imido ligand as a four-electron donor, **5a,b** are formally $20e^-$ metallocene complexes, a class of compounds previously mentioned. The strong π-donor character of the amido ligand in **4a,b** compared to the chloride in **5a,b** is the cause of the η^1-coordination of one of the two cyclopentadienyl rings and this ring slippage is to be considered a purely electronic effect.

The ^1H and $^{13}C\text{-}\{^1H\}$ NMR spectra of **5a,b** show

Table 4

Selected bond lengths (Å) and bond angles (deg) for $[\eta^5:\eta^5\text{-}C_5H_4\text{-}C(CH_3)_2\text{-}C_5H_4]M[=N(2,6\text{-}^iPr_2C_6H_3)]Cl$ (M = Nb, Ta) **5a,b**

	Nb	Ta		Nb	Ta
Bond lengths					
M–Cl	2.433(1)	2.404(1)	C(13)–C(17)	1.436(3)	1.425(5)
M–N	1.798(2)	1.799(2)	C(14)–C(15)	1.393(3)	1.384(5)
M–C(13)	2.400(2)	2.381(3)	C(15)–C(16)	1.426(3)	1.425(5)
M–C(14)	2.475(2)	2.461(3)	C(16)–C(17)	1.402(3)	1.398(4)
M–C(15)	2.491(2)	2.480(3)	C(17)–C(18)	1.525(3)	1.531(5)
M–C(16)	2.501(2)	2.491(3)	C(18)–C(19)	1.535(3)	1.530(5)
M–C(17)	2.474(2)	2.460(3)	C(18)–C(20)	1.528(3)	1.516(5)
M–C(21)	2.499(2)	2.495(3)	C(18)–C(21)	1.528(3)	1.534(4)
M–C(22)	2.528(2)	2.521(3)	C(21)–C(22)	1.391(3)	1.389(4)
M–C(23)	2.510(2)	2.498(3)	C(21)–C(25)	1.441(3)	1.428(5)
M–C(24)	2.492(2)	2.473(3)	C(22)–C(23)	1.432(3)	1.425(5)
M–C(25)	2.404(2)	2.385(3)	C(23)–C(24)	1.385(3)	1.375(5)
N–C(1)	1.385(3)	1.390(4)	C(24)–C(25)	1.410(3)	1.405(4)
C(13)–C(14)	1.413(3)	1.414(4)			
Bond angles					
Cl–M–N	98.3(1)	98.1(1)	C(17)–C(18)–C(21)	99.4(2)	99.0(2)
M–N–C(1)	167.5(1)	168.3(2)	C(22)–C(21)–C(25)	106.5(2)	106.3(3)
C(14)–C(13)–C(17)	108.6(2)	108.6(3)	C(21)–C(22)–C(23)	108.6(2)	108.6(3)
C(13)–C(14)–C(15)	107.8(2)	107.8(3)	C(22)–C(23)–C(24)	108.4(2)	108.4(3)
C(14)–C(15)–C(16)	108.3(2)	108.3(3)	C(23)–C(24)–C(25)	107.8(2)	107.7(3)
C(15)–C(16)–C(17)	108.7(2)	108.6(3)	C(21)–C(25)–C(24)	108.5(2)	108.7(3)
C(13)–C(17)–C(16)	106.5(2)	106.6(3)			

four pseudo quartet resonances (C_5H_4), consistent with $\eta^5:\eta^5$-coordination in solution, in which the coupling constants $^nJ(H,H)$ are rather similar (2–3 Hz). The $^1J(C,H)$ of the bis(cyclopentadienyl) ligand of **5a,b** are between 171 and 178 Hz, in agreement with those of the $\eta^5:\eta^5$ ansa-hafnocene (172–178 Hz) [45]. These quantities are larger than those of the complexes **4a,b**, (156–171 Hz) and are to be considered diagnostic of the hapticity of the cyclopentadienyl ligand.

2.7. Cationic $\eta^5:\eta^5$ ansa-metallocenes

Cationic metallocene complexes of the titanium group are well-known highly active catalysts for olefin poly-

merization [59]. Neutral and cationic imido complexes of Group V metals have been found to activate carbon–hydrogen bonds of alcanes [14–16]. Protonolysis of alkyl and amido compounds with $[NHEt_3]^+$-$[B(C_6H_5)_4]^-$ represents an alternative route to prepare cationic complexes in high yield and under mild conditions [60], compared to the 'classical' heterolytic cleavage of metal–halogen bond with silver and thallium salts. Treatment of **4a,b** with an equimolar amount of $[NHMe_3]^+[B(C_6H_5)_4]^-$ in thf at low temperatures afforded the first cationic ansa-metallocenes of niobium and tantalum **6a,b** (Eq. (4)), which were isolated as dark red and pink orange microcrystalline powders in 90% and 73% yields respectively.

$$rac\text{-}\mathbf{4a,b} \qquad\qquad \mathbf{6a,b}$$

$$\tag{4}$$
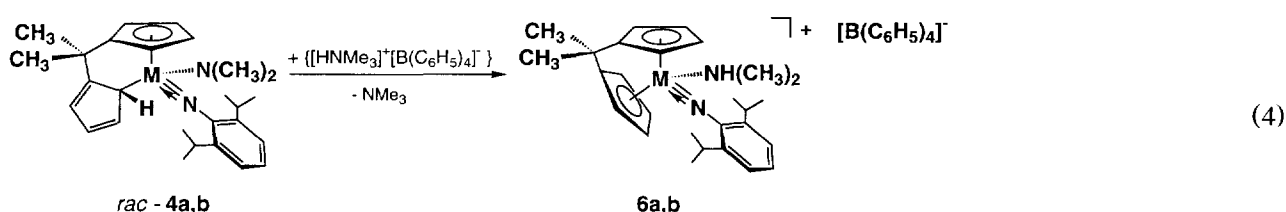
In the solid state the complexes **6a,b** are not extremely air-sensitive and are slowly hydrolyzed (1 h) in the air affording colorless oxides. The cationic compounds **6a,b** have quite good solubility in thf, but not in toluene or other hydrocarbons. No substitution of the coordinated dimethylamine with a thf molecule was observed dissolving **6a** or **6b** in thf after many hours at room temperature, suggesting that the dimethylamine is a better donor compared to the thf molecule.

The X-ray analysis of **6a** carried out on a single crystal obtained from a thf–n-heptane solution reveals cation–anion pairs. The $B(C_6H_5)_4$ anion presents the expected structural parameters, while a perspective view of the cation is shown in Fig. 8. Crystal data are reported in Table 1; selected bond lengths and angles of the cation are summarized in Table 5.

The niobium is coordinated to one dimethylamine, one linear imido and one $\eta^5:\eta^5$ bis(cyclopentadienyl) ligand. The Nb=N1 distance (1.803(2) Å), the Nb–N1–C1 angle (166.8(1)°) and the Nb–Cp$_{cent}$ distance ((C13–17); 2.156 Å and (C21–25); 2.181 Å) of **6a** are similar to those of chloro $\eta^5:\eta^5$ ansa-niobiocene **5a**. The N2 atom is in a pseudo tetrahedral environment with an Nb–N2 bond (2.266(2) Å) significantly longer than that of the amido ligand of $\eta^5:\eta^1$ ansa-niobiocene **4a** (1.974(2) Å). Similar steric properties of the anionic $N(CH_3)_2^-$ and neutral $N(CH_3)_2H$ ligands suggests that the ring cyclopentadienyl slippage observed in **4a** compared to **6a** can be considered as a result of electronic effects only.

Complex **6a**, like **5a,b**, will attain a 20e$^-$ configuration, although a slightly allyl–ene distortion of one

cyclopentadienyl ring was observed. In fact the dihedral angle between the planes C21–C22–C23–C24 and C21–C25–C24 is 4.5°, while the Nb–C distances range from 2.375(2) Å for the Nb–C25 bond to 2.558(2) Å for the Nb–C22 bond, as a result of the electronic flexibility of the cyclopentadienyl ligand.

The ^1H NMR spectra of **6a,b** present four pseudo quartets (C_5H_4) as observed for **5a,b**, one doublet at $\delta = 2.70$, 2.77 ppm and one septet at $\delta = 5.06$, 5.28 ppm (M = Nb, Ta, respectively) for the coordinated dimethylamine. The coupling constants $^1J(C,H)$ of the
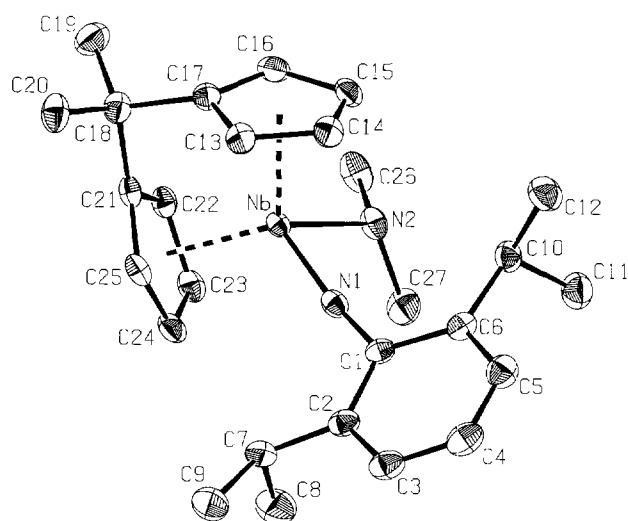

Fig. 8. ORTEP drawing of the crystal and molecular structure of the cationic niobium $\eta^5:\eta^5$ ansa-metallocene **6a**. Ellipsoids are drawn at the 50% probability level. Hydrogen atoms are omitted for clarity.

Table 5
Selected bond lengths (Å) and bond angles (deg) for [{η^5:η^5-
C_5H_4–C(CH$_3$)$_2$–C_5H_4)Nb{=N(2,6-^{i}Pr$_2$C$_6$H$_3$)}{NH(CH$_3$)$_2$}]$^+$-
[B(C$_6$H$_5$)$_4$]$^-$ **6a**

Bond lengths			
Nb–N(1)	1.803(2)	C(13)–C(14)	1.417(3)
Nb–N(2)	2.266(2)	C(13)–C(17)	1.426(3)
Nb–C(13)	2.394(2)	C(14)–C(15)	1.389(3)
Nb–C(14)	2.478(2)	C(15)–C(16)	1.427(3)
Nb–C(15)	2.490(2)	C(16)–C(17)	1.403(3)
Nb–C(16)	2.506(2)	C(21)–C(22)	1.388(3)
Nb–C(17)	2.471(2)	C(21)–C(25)	1.443(3)
Nb–C(21)	2.484(2)	C(22)–C(23)	1.428(3)
Nb–C(22)	2.558(2)	C(23)–C(24)	1.396(3)
Nb–C(23)	2.542(2)	C(24)–C(25)	1.414(3)
Nb–C(24)	2.486(2)	C(17)–C(18)	1.532(3)
Nb–C(25)	2.375(2)	C(18)–C(19)	1.525(3)
N(1)–C(1)	1.395(3)	C(18)–C(20)	1.524(3)
N(2)–C(26)	1.489(3)	C(18)–C(21)	1.532(3)
N(2)–C(27)	1.493(3)		

Bond angles			
N(1)–Nb–N(2)	91.70(7)	C(22)–C(21)–C(25)	107.3(2)
Nb–N(1)–C(1)	166.8(1)	C(21)–C(22)–C(23)	108.7(2)
Nb–N(2)–C(26)	118.2(1)	C(22)–C(23)–C(24)	108.1(2)
Nb–N(2)–C(27)	114.2(1)	C(23)–C(24)–C(25)	108.1(2)
C(26)–N(2)–C(27)	109.8(2)	C(21)–C(25)–C(24)	107.7(2)
C(14)–C(13)–C(17)	108.5(2)	C(17)–C(18)–C(19)	111.6(2)
C(13)–C(14)–C(15)	107.5(2)	C(17)–C(18)–C(20)	112.1(2)
C(14)–C(15)–C(16	108.8(2)	C(17)–C(18)–C(21)	97.7(2)
C(15)–C(16)–C(17)	108.0(2)	C(19)–C(18)–C(20)	109.8(2)
C(13)–C(17)–C(16)	107.1(2)		

bis(cyclopentadienyl) ligand of **6a,b** range from 174 to 178 Hz in agreement with those of **5a,b**.

3. Conclusion

ansa-Metallocenes of pentavalent niobium and tantalum are effectively stabilized by strong σ-/π-donor imido ligand RN, with R representing the sterically demanding 2,6-diisopropylphenyl. No redox reactions occur when the hydrocarbon ligands are introduced by deprotonation with an amide ligand of the precursor complex. The 'metal amide route' quite obviously is much more successful to enter new metallocenes of high-valent metals than the commonly employed metal halide route. The coordination mode of the *ansa*-ligands seems to be flexible in terms of the nature of the ancillary ligands. This is already seen by simple ligand exchange of chloro or dimethylamine vs. dimethylamido (**5a,b** or **6a,b** vs. **4a,b**). The observed η^5:η^1–η^1:η^5 isomerism holds promise for catalytic conversions at such metal centers since *ansa*-ligands can provide coordination sites by virtue of the geometrically rather undemanding 'ring slippage' fluxionality.

4. Experimental procedure

All operations were carried out in dry oxygen-free solvents (< 3 ppm H$_2$O, Karl Fischer titration control) and in a dry argon atmosphere (Schlenk tube and glovebox techniques). NMR spectra were measured with a Jeol-JMN-GX 400 and a Bruker DPX 400 FT-NMR spectrometer, mass spectra (CI, FAB) with a Varian-MAT 90 spectrometer. [NHMe$_3$]$^+$[B(C$_6$H$_5$)$_4$]$^-$ was purchased from Aldrich Chemicals, while Nb[N(CH$_3$)$_2$]$_5$, Ta[N(CH$_3$)$_2$]$_5$ and C$_5$H$_5$–C(CH$_3$)$_2$–C$_5$H$_5$ were prepared as reported in the literature [61].

Satisfactory microanalyses (C, H, N) have been obtained for all of the new compounds.

4.1. *Tris(dimethylamido)(2,6-diisopropylphenylimido) niobium(V) 2a*

A solution of freshly distilled 2,6-diisopropylaniline (0.580 g, 3.27 mmol) in 20 ml of toluene was added dropwise to a solution of Nb[N(CH$_3$)$_2$]$_5$ **1a** (1.025 g, 3.27 mmol) in 20 ml of toluene at −78 °C. The mixture was stirred at −78 °C for 30 min and was then allowed to attain room temperature within 2 h. The red-brown solution was gently heated within 2 h at 70 °C, then it was stirred 1 h at 80 °C and 1 h at 90 °C. Toluene was evaporated in vacuo, and the resulting orange oily residue was dissolved in a minimum amount of *n*-pentane (5 ml). The orange crystalline product **2a**, separated by keeping it at −78 °C, was filtered and dried under reduced pressure. Yield: 1.030 g (79%).

Spectroscopic data: ^{1}H NMR (400 MHz, C$_6$D$_6$, 25 °C, TMS): δ = 1.37 (d, 12 H; ^{3}J(H,H) = 7.0 Hz; CH(CH$_3$)$_2$), 3.13 (s, 18 H; N(CH$_3$)$_2$), 4.21 (sept, 2 H; ^{3}J(H,H) = 6.8 Hz; CH(CH$_3$)$_2$), 7.02 (t, 1 H; ^{3}J(H,H) = 7.5 Hz, *p*-C$_6$H$_3$), 7.16 (d, 2 H; ^{3}J(H,H) = 7.5 Hz, *m*-C$_6$H$_3$). ^{13}C{^{1}H} NMR (100.4 MHz, C$_6$D$_6$, 25 °C, TMS): δ = 24.1 (CH(CH$_3$)$_2$), 28.5 (CH(CH$_3$)$_2$), 46.2 (N(CH$_3$)$_2$), 122.6 (*m*-C$_6$H$_3$), 122.9 (*p*-C$_6$H$_3$), 142.2 (*o*-C$_6$H$_3$), 152.8 (*ipso*-C$_6$H$_3$). MS (CI): *m/z* (%) = 400.1 (100) [M^+], 355.1 (5) [M^+ − NH(CH$_3$)$_2$].

4.2. *Tris(dimethylamido)(2,6-diisopropylphenylimido) tantalum(V) 2b*

This synthesis was carried out as described above for the niobium congener. A solution of freshly distilled 2,6-diisopropylaniline (1.88 g, 10.6 mmol) in 20 ml of toluene was added dropwise to a solution of Ta[N(CH$_3$)$_2$]$_5$ **1b** (4.25 g, 10.6 mmol) in 30 ml of toluene at −78 °C. The mixture was stirred at −78 °C for 30 min and was then allowed to attain room temperature within 2 h. The yellow solution was gently heated within 2 h at 90 °C and it was stirred 2 h at 90 °C and 0.5 h at 110 °C. Toluene was evaporated in vacuo, and the resulting oily residue was dissolved in a minimum amount

of n-pentane (7 ml). The yellow product **2b**, separated by keeping it at $-78\,°C$, was filtered and dried under reduced pressure. Yield: 4.45 g (86%).

Spectroscopic data: ^1H NMR (400 MHz, C_6D_6, 25 °C, TMS): $\delta = 1.40$ (d, 12 H; $^3J(H,H) = 6.7$ Hz; CH(CH_3)$_2$), 3.15 (s, 18 H; N(CH_3)$_2$), 4.20 (sept, 2 H; $^3J(H,H) = 7.0$ Hz; CH(CH$_3$)$_2$), 7.02 (t, 1 H; $^3J(H,H) = 8.1$ Hz, p-C$_6H_3$), 7.24 (d, 2 H; $^3J(H,H) = 7.9$ Hz, m-C$_6H_3$). ^{13}C{^{1}H} NMR (100.4 MHz, C_6D_6, 25 °C, TMS): $\delta = 24.2$ (CH(CH_3)$_2$), 28.3 (CH(CH$_3$)$_2$), 45.2 (N(CH_3)$_2$), 121.9 (p-C$_6H_3$), 122.3 (m-C$_6H_3$), 142.7 (o-C$_6H_3$), 153.1 ($ipso$-C$_6H_3$). MS (CI): m/z (%) = 488.2 (100) [M^+], 444.2 (3) [M^+ − N(CH$_3$)$_2$].

4.3. Bis(dimethylamido)(2,6-diisopropylphenylimido)-(η^5-cyclopentadienyl)-niobium(V) 3a

Freshly distilled cyclopentadiene (250 mg, 3.78 mmol) was added dropwise to a solution of **2a** (540 mg, 1.35 mmol) in 10 ml of toluene at $-30\,°C$. The mixture was stirred 1 h at 20 °C and 1 h at 60 °C. Toluene was evaporated in vacuo, and the oily residue was dissolved in a minimum amount of n-pentane (3 ml) and re-precipitated by keeping it at $-78\,°C$. The orange product **3a** was filtered and dried under reduced pressure. Yield: 460 mg (81%).

Spectroscopic data: ^1H NMR (400 MHz, C_6D_6, 25 °C, TMS): $\delta = 1.29$ (d, 12 H; $^3J(H,H) = 6.7$ Hz; CH(CH_3)$_2$), 3.22 (s, 12 H; N(CH_3)$_2$), 4.11 (sept, 2 H; $^3J(H,H) = 7.0$ Hz; CH(CH$_3$)$_2$), 5.92 (s, 5 H; C_5H_5), 6.97 (t, 1 H; $^3J(H,H) = 7.3$ Hz, p-C$_6H_3$), 7.11 (d, 2 H; $^3J(H,H) = 7.3$ Hz, m-C$_6H_3$). ^{13}C{^{1}H} NMR (100.4 MHz, C_6D_6, 25 °C, TMS): $\delta = 24.7$ (CH(CH_3)$_2$), 27.4 (CH(CH$_3$)$_2$), 52.1 (N(CH_3)$_2$), 108.2 (d, $^1J(C,H) = 172$ Hz; C_5H_5), 122.9 (m-C$_6H_3$), 123.1 (p-C$_6H_3$), 143.0 (o-C$_6H_3$), 152.8 ($ipso$-C$_6H_3$). MS (CI): m/z (%) = 421.4 (100) [M^+], 378.4 (18) [M^+ + H − N(CH$_3$)$_2$].

4.4. Bis(dimethylamido)(2,6-diisopropylphenylimido)-(η^5-cyclopentadienyl)-tantalum(V) 3b

This synthesis was carried out as described above for the niobium congener. Freshly distilled cyclopentadiene (250 mg, 3.78 mmol) was added dropwise to a solution of **2b** (615 mg, 1.26 mmol) in 10 ml of toluene at $-30\,°C$. The mixture was stirred 1 h at 20 °C and 2.5 h at 90 °C. Toluene was evaporated in vacuo, and the oily residue was dissolved in a minimum amount of n-pentane (3 ml) and re-precipitated by keeping it at $-78\,°C$. The yellow product **3b** was filtered and dried under reduced pressure. Yield: 440 mg (69%).

Spectroscopic data: ^1H NMR (400 MHz, C_6D_6, 25 °C, TMS): $\delta = 1.31$ (d, 12 H; $^3J(H,H) = 6.7$ Hz; CH(CH_3)$_2$), 3.24 (s, 12 H; N(CH_3)$_2$), 4.07 (sept, 2 H; $^3J(H,H) = 6.7$ Hz; CH(CH$_3$)$_2$), 5.90 (s, 5 H; C_5H_5),

6.95 (t, 1 H; $^3J(H,H) = 7.3$ Hz, p-C$_6H_3$), 7.19 (d, 2 H; $^3J(H,H) = 7.3$ Hz, m-C$_6H_3$). ^{13}C{^{1}H} NMR (100.4 MHz, C_6D_6, 25 °C, TMS): $\delta = 24.8$ (CH(CH_3)$_2$), 27.1 (CH(CH$_3$)$_2$), 51.4 (N(CH_3)$_2$), 108.1 (d, $^1J(C,H) = 174$ Hz; C_5H_5), 122.2 (p-C$_6H_3$), 122.6 (m-C$_6H_3$), 143.2 (o-C$_6H_3$), 152.7 ($ipso$-C$_6H_3$). MS (CI): m/z (%) = 509.6 (100) [M^+].

4.5. (Dimethylamido)(2,6-diisopropylphenylimido)-[η^5:η^1-2,2-bis(cyclopentadienyl)propane] niobium(V) 4a

A solution of 2,2′-bis(cyclopentadienyl)propane (480 mg, 2.78 mmol) in 20 ml of toluene was added dropwise to a solution of **2a** (1092 mg, 2.72 mmol) in 10 ml of toluene at $-30\,°C$. The mixture was stirred 2 h at 20 °C and it was refluxed for 3 h. Toluene was evaporated in vacuo and the oily residue was dissolved in a minimum amount of n-pentane (6 ml) and re-precipitated by keeping it at $-78\,°C$. The orange product **4a** was filtered and dried under reduced pressure. Yield: 980 mg (74%).

Spectroscopic data: ^1H NMR (400 MHz, C_6D_6, 25 °C, TMS): $\delta = 1.31$ (d, 12 H; $^3J(H,H) = 7.0$ Hz; CH(CH_3)$_2$), 1.55 (s, 3 H; C(CH_3)$_2$), 1.58 (s, 3 H; C(CH_3)$_2$), 2.88 (s, 6 H; N(CH_3)$_2$), 4.04 (sept, 2 H; $^3J(H,H) = 7.0$ Hz; CH(CH$_3$)$_2$), 5.48 (s, 2 H; C_5H_4), 5.53 (s, 2 H; C_5H_4), 6.18 (s, 4 H; C_5H_4), 6.96 (t, 1 H; $^3J(H,H) = 7.5$ Hz, p-C$_6H_3$), 7.09 (d, 2 H; $^3J(H,H) = 7.5$ Hz, m-C$_6H_3$). ^{13}C{^{1}H} NMR (100.4 MHz, C_6D_6, 25 °C, TMS): $\delta = 24.4$ (CH(CH_3)$_2$), 25.2 (C(CH_3)$_2$), 28.1 (CH(CH$_3$)$_2$), 28.4 (C(CH_3)$_2$), 36.3 (C(CH$_3$)$_2$), 54.2 (N(CH_3)$_2$), 90.9, 106.7, 112.5, 114.0 ($^1J(C,H) = 157$, 165, 167, 170 Hz respectively; C_5H_4), 122.9 (m-C$_6H_3$), 123.8 (p-C$_6H_3$), 142.8 ($ipso$-C_5H_4), 143.2 (o-C$_6H_3$), 152.6 ($ipso$-C$_6H_3$). MS (CI): m/z (%) = 483.8 (14) [M^+ + H], 437.7 (100) [M^+ − NH(CH$_3$)$_2$].

4.6. (Dimethylamido)(2,6-diisopropylphenylimido)-[η^5:η^1-2,2-bis(cyclopentadienyl)propane] tantalum(V) 4b

This synthesis was carried out as described above for the niobium congener. A solution of 2,2′-bis(cyclopentadienyl)propane (138 mg, 0.800 mmol) in 13 ml of toluene was added dropwise to a solution of **2b** (338 mg, 0.802 mmol) in 6 ml of toluene at $-30\,°C$. The mixture was stirred 1 h at 20 °C and it was refluxed for 7 h. Toluene was evaporated in vacuo and the oily residue was heated at 100 °C for 1 h. The product was dissolved in a minimum amount of n-pentane (3 ml) and re-precipitated by keeping it at $-78\,°C$. The yellow product **4b** was filtered and dried under reduced pressure. Yield: 270 mg (59%).

Spectroscopic data: ^1H NMR (400 MHz, C_6D_6, 70 °C, TMS): $\delta = 1.32$ (d, 12 H; $^3J(H,H) = 7.3$ Hz;

CH(CH_3)$_2$), 1.49 (s, 3 H; C(CH_3)$_2$), 1.58 (s, 3 H; C(CH_3)$_2$), 2.93 (s, 6 H; N(CH_3)$_2$), 3.99 (sept, 2 H; ^3J(H,H) = 7.0 Hz; CH(CH$_3$)$_2$), 5.01 (s, 2 H; C$_5H_4$), 5.51 (m, 2 H; C$_5H_4$), 6.08 (m, 2 H; C$_5H_4$), 6.28 (m, 2 H; C$_5H_4$), 6.91 (t, 1 H; ^3J(H,H) = 7.6 Hz, p-C$_6H_3$), 7.15 (d, 2 H; ^3J(H,H) = 8.0 Hz, m-C$_6H_3$). ^{13}C{^{1}H} NMR (100.4 MHz, C$_6$D$_6$, 70 °C, TMS): δ = 24.4 (CH(CH_3)$_2$), 25.5 (C(CH_3)$_2$), 28.1 (CH(CH$_3$)$_2$), 29.4 (C(CH$_3$)$_2$), 36.4 (C(CH$_3$)$_2$), 53.3 (N(CH_3)$_2$), 89.4, 108.3, 113.2, 116.1 (^1J(C,H) = 156, 166, 167, 171 Hz respectively; C$_5$H$_4$), 122.4 (m-C$_6$H$_3$), 123.1 (p-C$_6$H$_3$), 143.7 (o-C$_6$H$_3$), 145.3 ($ipso$-C$_5$H$_4$), 152.2 ($ipso$-C$_6$H$_3$). MS (CI): m/z (%) = 570.6 (100) [M^+], 525.5 (46) [$M^+ - $ NH(CH$_3$)$_2$].

4.7. Chloro(2,6-diisopropylphenylimido)[η^5:η^5-2,2-bis(cyclopentadienyl)propane] niobium(V) 5a

A solution of freshly distilled (CH$_3$)$_3$SiCl (76 mg, 0.700 mmol) in 5 ml of toluene was added dropwise to an orange solution of **4a** (165 mg, 0.342 mmol) in 3 ml of toluene at −78 °C. The mixture was allowed to attain room temperature and it was stirred 2 h at 20 °C. Toluene was evaporated in vacuo and the resulting red oily residue was treated with a minimum amount of n-pentane (1 ml). The solvent was removed under reduced pressure and afforded a red crystalline product **5a** (154 mg, 95% yield).

Spectroscopic data: ^{1}H NMR (400 MHz, C$_6$D$_6$, 25 °C, TMS): δ = 1.00 (s, 3 H; C(CH_3)$_2$), 1.32 (s, 3 H; C(CH_3)$_2$), 1.33 (d, 12 H; ^3J(H,H) = 7.0 Hz; CH(CH_3)$_2$), 3.89 (sept, 2 H; ^3J(H,H) = 7.0 Hz; CH(CH$_3$)$_2$), 5.51 (pseudo q, 2 H; J(H,H) = 2 Hz; C$_5H_4$), 5.85 (pseudo q, 2 H; J(H,H) = 2 Hz; C$_5H_4$), 6.03 (pseudo q, 2 H; J(H,H) = 3 Hz; C$_5H_4$), 6.30 (pseudo q, 2 H; J(H,H) = 3 Hz; C$_5H_4$), 6.85 (t, 1 H; ^3J(H,H) = 7.5 Hz, p-C$_6H_3$), 7.06 (d, 2 H; ^3J(H,H) = 7.5 Hz, m-C$_6$H$_3$). ^{13}C{^{1}H} NMR (100.4 MHz, C$_6$D$_6$, 25 °C, TMS): δ = 22.1 (C(CH_3)$_2$), 24.1 (C(CH$_3$)$_2$), 24.4 (CH(CH_3)$_2$), 27.7 (CH(CH$_3$)$_2$), 36.4 (C(CH$_3$)$_2$), 95.4, 105.7, 115.4, 118.3 (^1J(C,H) = 171, 173, 177, 177 Hz respectively; C$_5$H$_4$), 122.6 (m-C$_6$H$_3$), 123.1 (p-C$_6$H$_3$), 139.8 ($ipso$-C$_5$H$_4$), 140.9 (o-C$_6$H$_3$), 154.5 ($ipso$-C$_6$H$_3$). MS (CI): m/z (%) = 472.7 (69) [M^+], 437.7 (6) [$M^+ - $ Cl], 297.6 (100).

4.8. Chloro(2,6-diisopropylphenylimido)[η^5:η^5-2,2-bis(cyclopentadienyl)propane] tantalum(V) 5b

This synthesis was carried out as described above for the niobium congener. A solution of freshly distilled (CH$_3$)$_3$SiCl (80 mg, 0.736 mmol) in 7 ml of toluene was added dropwise to a yellow solution of **4b** (167 mg, 0.292 mmol) in 3 ml of toluene at −40 °C. The mixture was allowed to attain room temperature and it was stirred 2 h at 20 °C and 0.5 h at 60 °C. Toluene was

evaporated in vacuo and the resulting orange oily residue was treated with a minimum amount of n-pentane (1 ml). The solvent was removed under reduced pressure and afforded an orange crystalline product **5b** (156 mg, 95% yield).

Spectroscopic data: ^{1}H NMR (400 MHz, C$_6$D$_6$, 25 °C, TMS): δ = 1.02 (s, 3 H; C(CH_3)$_2$), 1.28 (s, 3 H; C(CH_3)$_2$), 1.36 (d, 12 H; ^3J(H,H) = 7.0 Hz; CH(CH_3)$_2$), 3.84 (sept, 2 H; ^3J(H,H) = 7.0 Hz; CH(CH$_3$)$_2$), 5.53 (pseudo q, 2 H; J(H,H) = 2 Hz; C$_5H_4$), 5.84 (pseudo q, 2 H; J(H,H) = 3 Hz; C$_5H_4$), 5.90 (pseudo q, 2 H; J(H,H) = 2 Hz; C$_5H_4$), 6.13 (pseudo q, 2 H; J(H,H) = 3 Hz; C$_5H_4$), 6.81 (t, 1 H; ^3J(H,H) = 7.7 Hz, p-C$_6H_3$), 7.18 (d, 2 H; ^3J(H,H) = 7.7 Hz, m-C$_6$H$_3$). ^{13}C{^{1}H} NMR (100.4 MHz, C$_6$D$_6$, 25 °C, TMS): δ = 22.4 (C(CH_3)$_2$), 24.2 (C(CH$_3$)$_2$), 24.5 (CH(CH_3)$_2$), 27.4 (CH(CH$_3$)$_2$), 36.4 (C(CH$_3$)$_2$), 93.1, 104.5, 115.3, 116.8 (^1J(C,H) = 172, 174, 178, 178 Hz respectively; C$_5$H$_4$), 122.2 (m-C$_6$H$_3$), 125.2 (p-C$_6$H$_3$), 139.9 ($ipso$-C$_5$H$_4$), 140.3 (o-C$_6$H$_3$), 153.3 ($ipso$-C$_6$H$_3$). MS (CI): m/z (%) = 560.8 (72) [M^+], 385.6 (100).

4.9. (2,6-Diisopropylphenylimido)[η^5:η^5-2,2-bis(cyclopentadienyl)propane]-(dimethylamine) niobium(V) tetraphenylborate 6a

The complex **4a** (176 mg, 0.365 mmol) and [NHMe$_3$]$^+$[B(C$_6$H$_5$)$_4$]$^-$ (135 mg, 0.355 mmol) were cooled at −78 °C and thf (3 ml) was dropped in slowly. The dark-red mixture was stirred 30 min at −78 °C and was then allowed to attain room temperature within 1 h. The solution was stirred 1 h at 20 °C and upon addition of pentane (10 ml) a dark red powder precipitated. The product was filtered, washed with pentane and dried under reduced pressure. Yield: 256 mg (90%).

Spectroscopic data: ^{1}H NMR (400 MHz, thf-d_8, 25 °C, TMS): δ = 1.22 (d, 12 H; ^3J(H,H) = 7.0 Hz; CH(CH_3)$_2$), 1.60 (s, 3 H; C(CH_3)$_2$), 1.80 (s, 3 H; C(CH_3)$_2$), 2.70 (d, 6 H; ^3J(H,H) = 6.0 Hz; NH(CH_3)$_2$), 3.19 (sept, 2 H; ^3J(H,H) = 7.0 Hz; CH(CH$_3$)$_2$), 5.06 (sept, 1 H; ^3J(H,H) = 6.0 Hz; NH(CH$_3$)$_2$), 5.67 (pseudo q, 2 H; J(H,H) = 2 Hz; C$_5H_4$), 6.21 (pseudo q, 2 H; J(H,H) = 2 Hz; C$_5H_4$), 6.51 (pseudo q, 2 H; J(H,H) = 3 Hz; C$_5H_4$), 6.60 (pseudo q, 2 H; J(H,H) = 3 Hz; C$_5H_4$), 6.74 (t, 4 H; ^3J(H,H) = 7.0 Hz; p-C$_6H_5$), 6.88 (t, 8 H; ^3J(H,H) = 7.5 Hz; m-C$_6H_5$), 7.06 (d, 2 H; ^3J(H,H) = 7.5 Hz, m-C$_6H_3$), 7.31 (s, 8 H; o-C$_6H_5$). The ^{1}H NMR signal of p-C$_6H_3$ is covered by the B(C$_6$H$_5$)$_4$ resonances. ^{13}C{^{1}H} NMR (100.4 MHz, thf-d_8, 25 °C, TMS): δ = 22.9 (C(CH_3)$_2$), 23.3 (C(CH$_3$)$_2$), 24.7 (CH(CH_3)$_2$), 28.3 (CH(CH$_3$)$_2$), 37.8 (C(CH$_3$)$_2$), 49.1 (NH(CH_3)$_2$), 102.5, 104.5, 115.9, 117.5 (^1J(C,H) = 174, 174, 178, 174 Hz respectively; C$_5$H$_4$), 121.9 (p-C$_6H_5$), 123.8 (m-C$_6H_3$), 125.7 (m-C$_6H_5$), 126.0 (p-C$_6H_3$), 137.1 (o-C$_6H_5$), 140.1 ($ipso$-C$_5$H$_4$), 140.3

$(o\text{-}C_6H_3)$, 154.0 $(ipso\text{-}C_6H_3)$, 165.1 $(^1J(\text{C,B}) = 50\,\text{Hz}$; $ipso\text{-}C_6H_5)$. MS (FAB): m/z (%) = 483.6 (72) $[M^+]$, 438.5 (86) $[M^+ - \text{NH(CH}_3)_2]$.

4.10. (2,6-Diisopropylphenylimido)[η^5:η^5-2,2-bis(cyclopentadienyl)propane]-(dimethylamine) tantalum(V) tetraphenylborate 6b

This synthesis was carried out as described above for the niobium congener. The complex **4b** (103 mg, 0.180 mmol) and $[\text{NHMe}_3]^+[\text{B}(C_6H_5)_4]^-$ (67 mg, 0.177 mmol) were cooled at $-78\,^\circ\text{C}$ and thf (2 ml) was dropped in slowly. The yellow-orange mixture was stirred 30 min at $-78\,^\circ\text{C}$ and was then allowed to attain room temperature within 1 h. The orange solution was stirred 2 h at 20 °C, 5 min at 40 °C and upon addition of pentane (8 ml) a pink powder precipitated. The product was filtered, washed with pentane and dried under reduced pressure. Yield: 115 mg (73%).

Spectroscopic data: ^{1}H NMR (400 MHz, thf-d_8, 25 °C, TMS): $\delta = 1.26$ (d, 12 H; $^3J(\text{H,H}) = 6.5\,\text{Hz}$; CH(C$H_3$)$_2$), 1.65 (s, 3 H; C(C$H_3$)$_2$), 1.79 (s, 3 H; C(C$H_3$)$_2$), 2.77 (d, 6 H; $^3J(\text{H,H}) = 5.5\,\text{Hz}$; NH(C$H_3$)$_2$), 3.17 (sept, 2 H; $^3J(\text{H,H}) = 6.7\,\text{Hz}$; C$H$(CH$_3$)$_2$), 5.28 (sept, 1 H; $^3J(\text{H,H}) = 6.0\,\text{Hz}$; N$H$(CH$_3$)$_2$), 5.78 (pseudo q, 2 H; C$_5H_4$), 6.26 (pseudo q, 2 H; C$_5H_4$), 6.32 (pseudo q, 2 H; C$_5H_4$), 6.50 (pseudo q, 2 H; C$_5H_4$), 6.77 (t, 4 H; $^3J(\text{H,H}) = 6.8\,\text{Hz}$; $p\text{-}C_6H_5$), 6.90 (t, 8 H; $^3J(\text{H,H}) = 7.0\,\text{Hz}$; $m\text{-}C_6H_5$), 7.10 (d, 2 H; $^3J(\text{H,H}) = 7.5\,\text{Hz}$, $m\text{-}C_6H_3$), 7.32 (s, 8 H; $o\text{-}C_6H_5$). The ^{1}H NMR signal of $p\text{-}C_6H_3$ is covered by the B(C$_6$H$_5$)$_4$ resonances. ^{13}C{^{1}H} NMR (100.4 MHz, thf-d_8, 25 °C, TMS): $\delta = 23.3$ (C(CH_3)$_2$), 23.4 (C(CH_3)$_2$), 24.9 (CH(CH_3)$_2$), 28.0 (CH(CH$_3$)$_2$), 38.0 (C(CH$_3$)$_2$), 49.6 (NH(CH_3)$_2$), 100.1, 103.5, 115.3, 115.8 ($^1J(\text{C,H}) = 175, 175, 175, 177\,\text{Hz}$ respectively; C$_5$H$_4$), 122.0 ($p\text{-}C_6H_5$), 123.3 ($m\text{-}C_6H_3$), 124.9 ($p\text{-}C_6H_3$), 125.8 ($m\text{-}C_6H_5$), 137.0 ($o\text{-}C_6H_5$), 138.7 ($ipso\text{-}C_5H_4$), 140.8 ($o\text{-}C_6H_3$), 152.1 ($ipso\text{-}C_6H_3$), 165.0 ($^1J(\text{C,B}) = 49\,\text{Hz}$; $ipso\text{-}C_6H_5$). MS (FAB): m/z (%) = 571.7 (100) $[M^+]$, 526.6 (56) $[M^+ - \text{NH(CH}_3)_2]$.

4.11. X-ray crystallography

Suitable single crystals for an X-ray diffraction study were obtained by cooling concentrated solutions of the complex **2a** in n-pentane at $-78\,^\circ\text{C}$ and of the compounds **4a**, **4b**, **5a**, **5b** in n-heptane at $-30\,^\circ\text{C}$. Single crystals of ionic complex **6a** were obtained by slow diffusion of a thf-solution of **6a** in n-heptane at room temperature. All structures were solved by a combination of direct methods, difference-Fourier syntheses and least squares methods. Neutral atom scattering factors for all atoms and anomalous dispersion corrections for the non-hydrogen atoms were taken from the Interna-

tional Tables for X-ray Crystallography. All calculations were performed on a DEC 3000 AXP workstation with the STRUX-V system, including the programs PLATON-92, PLUTON-92, SIR-92 SHELXS-86 and SHELXL-93 [62].

4.11.1. Data collection, structure solution and data refinement for complexes 2a, 4a, 4b and 5b

A summary of the collection and refinement data are reported in Table 1. Preliminary examination and data collection were carried out on an imaging plate diffraction system (IPDS; Stoe & Cie) equipped with a rotating anode (Enraf Nonius FR591; 50 kV; 80 mA; 4.0 kW) and graphite monochromated Mo Kα radiation. The data collection was performed at 173 K (223, 223, and 173 K) within the Θ-range of $1.86 < \Theta < 25.65°$ with an exposure time of 3 min (2.5, 2.5, and 1.5 min) per image (either oscillation or rotation scan modes from $\varphi = 0.0°$ to 320° (220°, 240°, and 360°) with $\Delta\varphi = 1°$). A total number of 11 965 (18 328, 15 269, and 14 986) reflections were collected, from which a sum of 3446 (4322, 4298, and 3850) independent reflections remained and were used for all calculations. Data were corrected for Lorentz and polarization effects [63]. Corrections for intensity decay and/or absorption effects with the program DECAY [63] were applied for **2a** and **4b**. The unit cell parameters were obtained by least squares refinements of 1955 (1966, 1952, and 1853) reflections with the program CELL [63]. All 'heavy atoms' of the asymmetric unit were anisotropically refined. All hydrogen atoms were located in difference Fourier maps and refined isotropically for **2a**, **4a** and **5b**; for **4b** they were calculated in ideal positions (riding model). Full matrix least squares refinements were carried out by minimizing $\Sigma w(F_o^2 - F_c^2)^2$ with SHELXL weighting scheme and stopped at shift/err < 0.001. Further details of the crystal structure investigations are available on request from the Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, D-76344 Eggenstein-Leopoldshafen 2, on quoting the depository number CSD-405082 (CSD-405083, CSD-407067, CSD-407068), the names of the authors and the journal citation.

4.11.2. Structure solution and data refinement for complex 5a

Preliminary examination and data collection were carried out on an automatic four circle diffractometer (CAD4, Enraf Nonius) equipped with a sealed tube and graphite monochromated Mo Kα radiation. The data collection was performed at 173 K within the Θ-range of $1.84 < \Theta < 25.96°$, using the ω-scan method, maximal acquisition time 60 s for a single reflection. A total number of 4473 reflections were collected, from which a sum of 4210 independent reflections remained and

were used for all calculations. Data were corrected for Lorentz, polarization effects and intensity decay. Corrections for absorption effects and extinction were not necessary and were not applied. The unit cell parameters were obtained by least squares refinements of 25 high angle reflections [64]. All 'heavy atoms' of the asymmetric unit were anisotropically refined. All hydrogen atoms were located in difference Fourier maps and refined isotropically. Full matrix least squares refinements were carried out by minimizing $\Sigma w(F_o^2 - F_c^2)^2$ with SHELXL weighting scheme and stopped at shift/err < 0.001. Further details of the crystal structure investigation are available on request from the Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, D-76344 Eggenstein-Leopoldshafen 2, on quoting the depository number CSD-407069, the names of the authors and the journal citation.

4.11.3. Structure solution and data refinement for complex 6a

Preliminary examination and data collection were carried out on an automatic four circle diffractometer (CAD4, Enraf Nonius) equipped with a sealed tube and graphite monochromated $Cu K\alpha$ radiation. The data collection was performed at 163 K within the Θ-range of $2.75 < \Theta < 68.01°$, using the $\Theta-2\Theta$-scan method, maximal acquisition time 60 s for a single reflection. A total number of 9944 reflections were collected, from which a sum of 9370 independent reflections remained and were used for all calculations. Data were corrected for Lorentz, polarization effects, intensity decay and for disordered solvent syndrome [65]. Corrections for absorption effects and extinction were not necessary and were not applied. The unit cell parameters were obtained by least squares refinements of 25 high angle reflections [64]. All 'heavy atoms' of the asymmetric unit were anisotropically refined. All hydrogen atoms were located in difference Fourier maps and refined isotropically. Full matrix least squares refinements were carried out by minimizing $\Sigma w(F_o^2 - F_c^2)^2$ with SHELXL weighting scheme and stopped at shift/err < 0.001. Further details of the crystal structure investigation are available on request from the Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, D-76344 Eggenstein-Leopoldshafen 2, on quoting the depository number CSD-407070, the names of the authors and the journal citation.

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