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Synthesis and characterization of titanium and tantalum complexes with di(2-pyridyl)amine (dpa): Molecular structures of Cp*TaCl₃(dpa) and Ti(NMe₂)₂(dpa)₂

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Abstract

The new titanium complex Cp*TiMe₂(dpa) (**1**) (Cp* = η⁵-C₅Me₅; dpa = di(2-pyridyl)amide) has been synthesized by reaction of Cp*TiMe₃ with Hdpa. Reaction of Cp*TiCl₃ or Cp*TaCl₄ with Lidpa renders Cp*TiCl₂(dpa) (**2**) or Cp*TaCl₃(dpa) (**3**), respectively. On the other hand, Ti(NMe₂)₄ reacts with Hdpa to yield Ti(NMe₂)₂(dpa)₂ (**4**). The molecular structures of **3** and **4** have been established by X-ray diffraction methods.
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1. Introduction

The development of new ancillary ligands such as alkoxides or amides has been vital to the discovery of new metal-mediated organic transformations. In this context, nitrogen donor ligands are a versatile approach since proper substitution patterns allow suitable combinations of electronic and steric properties. Titanium amide complexes have been shown to stabilize reactive species such as methylidene ligands [1] and are precursors for polymerization of α-olefins [2]. Of particular interest has been the finding of supporting ligands in which hard base donors are coordinated to metals so as to enforce a cis arrangement of the reactive ligands bearing nitrogen donor atoms. In this field, metal complexes including diamido [3], β-diketiminate [4], aminotroponiminate [5], amidinate [6], and guanidinate [7] ligands have been studied.

We are especially interested in complexes supported by the anion of di(2-pyridyl)amine, dpa (**I**). The chemistry of complexes supported by this anion has attracted much attention due not only to their structural and chemical properties [8] but also to their unusual coordination modes [9]. The studies regarding the coordination behaviour of this ligand have been mainly focussed on the synthesis of compounds of late transition metals [10]. We report here the synthesis of the first complexes of titanium and tantalum with di-2-pyridylamide as a ligand. We have chosen titanium and tantalum in order to

compare the bonding behaviour of the ligand with early transition metals of different electronic and steric requirements.

2. Results and discussion

The reaction of Cp*TiMe$_3$ with Hdpa in a 1:1 ratio in pentane at room temperature, yields the orange crystalline complex Cp*TiMe$_2$(dpa) (**1**) in 62% yield. Complex **1** is highly air sensitive, and soluble in pentane, toluene or THF. It has been characterized by the usual spectroscopic techniques. The ^{1}H NMR spectrum at room temperature displays two singlet signals at 1.03 and 1.72 ppm assigned to the methyl groups bound to the titanium atom and to the Cp* ligand, respectively. Besides, it shows four multiplet signals at 6.24, 7.03, 7.28 and 7.70 ppm attributable to the protons of the two equivalent pyridyl fragments. This spectroscopic data of compound **1** indicate that both pyridyl groups are in the same chemical environment and would be in agreement with the coordination of the dpa ligand to the metal through the central N atom of the amide fragment as it is shown in Scheme 1.

However, the spectroscopic data could also be in agreement with a bidentate coordination of the ligand to the metal. A fast interchange of the nitrogen atoms of both pyridyl moieties in the co-ordination sphere of the titanium would make them equivalent. In order to establish this point, we have carried out a variable temperature ^{1}H NMR study. In fact, at 193 K the ^{1}H NMR spectrum shows that the pyridyl rings are in different chemical environments. Besides, the spectrum shows a singlet corresponding to the Cp* ligand a two singlet signals assigned to the methyl groups bonded to the titanium atoms. With these data, we propose that at low temperature the dpa ligand is bonded to the titanium atom as an bidentate aminopyridinate group. At high temperature the quick interchange of the two nitrogen atoms in the coordination sphere of the titanium makes both pyridyl groups equivalent while at low temperature interchange is slow and the pyridyl moieties as well as the methyl groups bonded to the titanium centre are in

different chemical environments (see Scheme 2). The coalescence temperature was found at 207 K and the calculated value by means of the two site exchange equation [11] for $\Delta G^\#$ is 10.0(1) kcal mol^{-1}.

Complex **1** reacts with xylylisocyanide, in C$_6$D$_6$ at room temperature, to give a mixture of unidentified compounds.

Compound **2** is readily synthesized through a metathesis reaction of 2 molar equivalent of Lidpa and Cp*TiCl$_3$ (Scheme 3). The reaction of Lidpa and Cp*TiCl$_3$ in a 1:1 molar ratio renders also complex **2** but in lower yield (39%). Complex **2** is a dark red, air sensitive solid, very soluble in toluene or THF and less soluble in pentane or Et$_2$O. The ^{1}H NMR spectrum of complex **2** shows four broad signals at 6.21, 6.98, 7.06 and 7.61 ppm with relative integration of two protons each. The broadness of these signals could be indicative of a fluxional process at this temperature.

To clarify this point a ^{1}H VTNMR experiment was carried out. This showed that, at 233 K, the ^{1}H NMR spectrum shows a singlet signal corresponding to the Cp* ligand and eight multiplet signals attributable to the pyridyl groups proton atoms as it would be expected if the ligand is bonded to the metal centre in a bidentate fashion through the central nitrogen atom and one of the two pyridyl nitrogen atoms, that is as an aminopyridinate group. Upon rising the temperature, interchange of the nitrogen atoms of both pyridyl rings in the co-ordination sphere of the titanium atom becomes quicker and both pyridyl groups convert equivalent. The coalescence
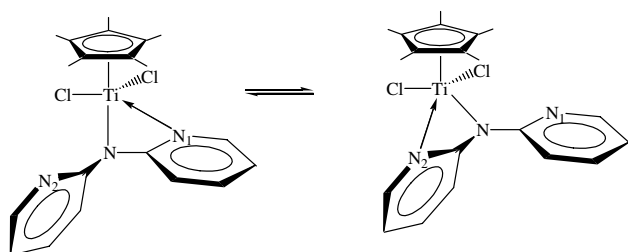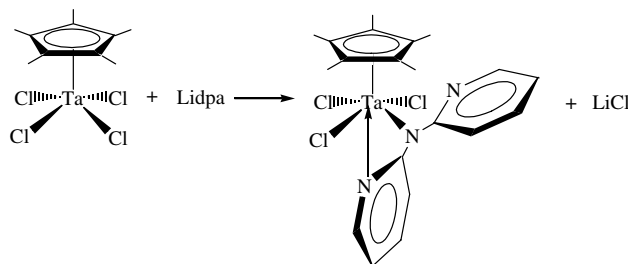
Scheme 2.

1

Scheme 1.

2
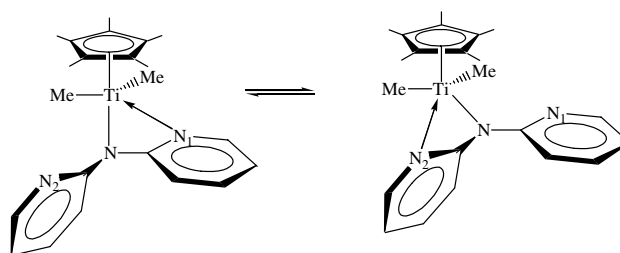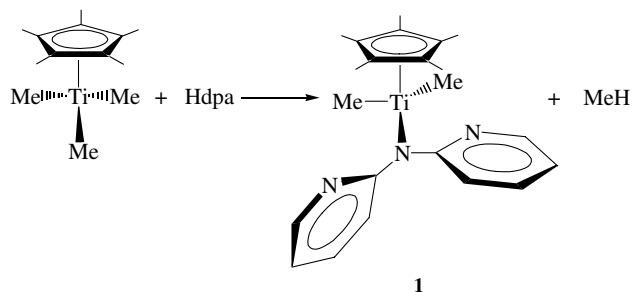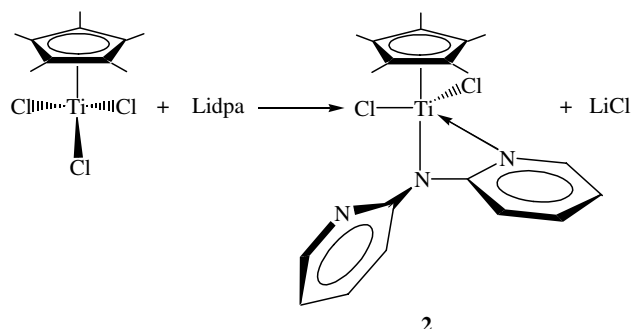
Scheme 3.

Scheme 4.

Scheme 5.

temperature was 285 K and the calculated value [11] of $\Delta G^{\#} = 13.4(1)$ kcal mol^{-1} (see Scheme 4).

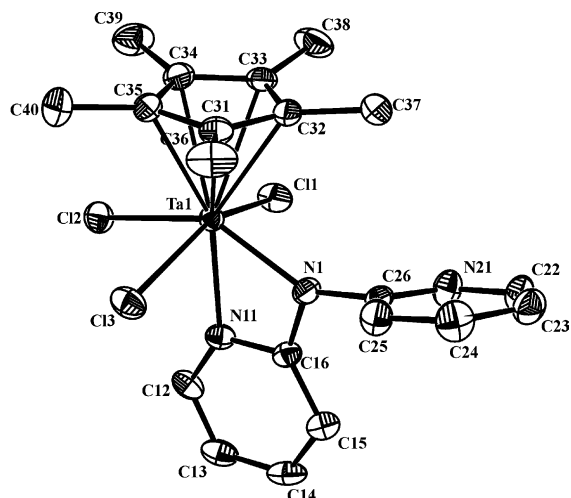In an analogous way, Cp*TaCl$_4$ reacts with two molar equivalent of Lidpa to yield the tantalum derivative

Fig. 1. Perspective ORTEP drawing of the molecular structure of complex 3.

3. When the reaction is carried out in a 1:1 molar ratio complex **3** is also obtained as the only identified compound but the yield is somewhat lower (61%). Complex **3** is isolated as orange crystals which are highly air sensitive, soluble in toluene or THF and less soluble in pentane. It has been fully characterized by NMR and IR spectroscopy, single-crystal X-ray diffraction, and by

Table 1
Crystal data and structure refinement for **3** and **4**

	3	4
Empirical formula	C$_{20}$H$_{23}$Cl$_3$N$_3$Ta	C$_{24}$H$_{28}$N$_8$Ti · 0.5C$_4$H$_{10}$O
Formula weight	592.71	513.50
T (K)	293(2)	180(2)
λ (Å)	0.71073	0.71073
Crystal system	Monoclinic	Triclinic
Space group	$P2_1/n$	$P\bar{1}$
a (Å)	15.596(5)	9.2063(8)
b (Å)	8.820(5)	10.7209(7)
c (Å)	16.721(5)	13.548(1)
α (°)		90.018(4)
β (°)	112.820(5)	98.915(3)
γ (°)		100.033(4)
V (Å^3)	2120.1(15)	1300.3(2)
Z	4	2
D_{calc} (g/cm^3)	1.857	1.311
Absorption coefficient (cm^{-1})	5.573	3.62
$F(000)$	1152	542
Crystal size (mm^3)	0.3 × 0.2 × 0.1	0.32 × 0.19 × 0.19
Index ranges	$-20 \leqslant h \leqslant 18, 0 \leqslant k \leqslant 11, 0 \leqslant l \leqslant 22$	$-11 \leqslant h \leqslant 11, -12 \leqslant k \leqslant 13, -16 \leqslant l \leqslant 16$
Reflections collected	10189	11054
Independent reflections (R_{int})	5121 (0.0016)	5109 (0.0410)
Completeness to $\theta = 428.02°$ (%)	99.8	99.9
Maximum and minimum transmission	0.6541 and 0.1830	0.9344 and 0.8930
Data/restraints/parameters	5121/0/244	5109/0/333
Goodness-of-fit on F^2	1.077	1.086
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0316, wR_2 = 0.0746$	$R_1 = 0.0504, wR_2 = 0.1271$
R indices (all data)	$R_1 = 0.0511, wR_2 = 40.0823$	$R_1 = 0.0745, wR_2 = 0.1554$
Largest difference in peak and hole (e Å^{-3})	0.592 and −0.939	0.537 and −0.444

elemental analysis. The ^{1}H NMR spectrum of complex **3** shows one singlet signal at δ 2.16 ppm, which is assigned to the methyl groups of the Cp* ring. On the other hand, it shows eight multiplet signals corresponding to the pyridyl rings protons, indicating that in solution there are two different chemical environments for the pyridyl groups. All these data suggest that the bis(2-pyridyl)amide ligand is co-ordinated to the tantalum atom in a bidentate manner (Scheme 5).

In order to confirm this proposal, crystals of **3** were grown from a toluene-pentane solution. The molecular structure (Fig. 1) confirms the proposal based on the spectroscopic data. The most important bond distances and angles are summarized in Table 2. The X-ray diffraction study shows complex **3** to be a monomer, in which the tantalum atom adopts a pseudo-octahedral co-ordination geometry. The dpa ligand is bonded to the tantalum atom as an aminopyridinato group.

Two of the nitrogen atoms in the dpa ligand, the amido N(1) atom and the pyridyl N(11) atom, are chelated to Ta(1). The Ta(1)–N(1) (amido) bond length (2.070(4)

Å) is shorter than that of Ta(1)–N(11) (pyridyl, 2.226(4) Å) and both of them are within the normal range of the Ta–N bond lengths [12]The C(16)–N(1)–Ta(1), C(16)–N(11)–Ta(1) and C(1)–Ta(1)–Cl(3) (99.3(3)°, 92.9(3)° and 152.91(5)°, respectively) angles are comparable to those found in other tantalum aminidate complexes [13].

Finally, compound **4** was obtained in 73% yield by the reaction of Ti(NMe$_2$)$_4$ with two molar equivalents of Hdpa in toluene. The ^{1}H and ^{13}C NMR spectra show that, in solution at room temperature, all pyridyl groups are equivalent. The ^{1}H NMR spectrum shows a singlet signal at 3.19 ppm assigned to the methyls groups of the dimethylamide ligands and a set of pyridyl resonances at 6.23, 7.16, 7.87 and 7.99 ppm. The ratio of the integrals is consistent with the proposed stoichiometry (Scheme 6).

In order to establish the coordination mode of the dpa ligand to the titanium atom, complex **4** has been characterized by an X-ray diffraction study. X-ray quality crystals were grown by cooling down to −23 °C a saturated solution of **4**, in Et$_2$O. Fig. 2 shows an ORTEP diagram of the molecule and the most important bond distance and angles are in Table 2. The titanium centre

Table 2
Bond lengths (Å) and angles (°) for **3** and **4**

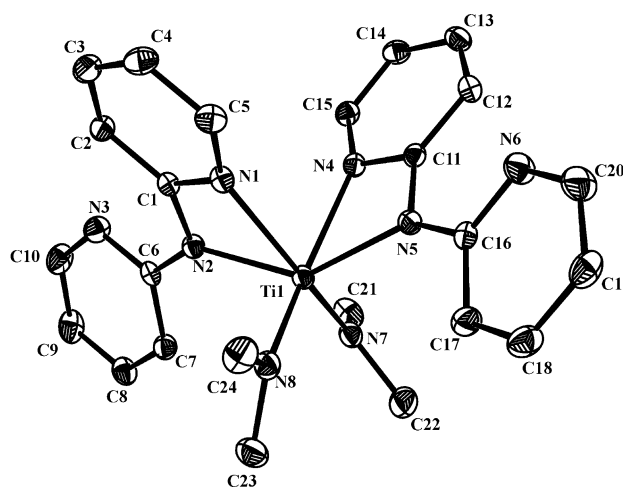| Complex **3**		Complex **4**	
Bond lengths (Å)			
Ta(1)–N(1)	2.070(4)	Ti(1)–N(7)	1.894(2)
Ta(1)–N(11)	2.226(4)	Ti(1)–N(8)	1.906(2)
Ta(1)–Cl(2)	2.4141(15)	Ti(1)–N(2)	2.129(2)
Ta(1)–Cl(1)	2.4223(17)	Ti(1)–N(5)	2.129(2)
Ta(1)–C(35)	2.443(5)	Ti(1)–N(1)	2.203(2)
Ta(1)–Cl(3)	2.4470(15)	Ti(1)–N(4)	2.205(2)
Ta(1)–C(34)	2.469(6)	N(2)–C(1)	1.367(4)
Ta(1)–C(31)	2.471(5)	N(2)–C(6)	1.378(3)
Ta(1)–C(32)	2.499(5)	N(5)–C(11)	1.373(3)
Ta(1)–C(33)	2.506(5)	N(5)–C(16)	1.387(3)
Ta(1)–C(16)	2.660(5)	N(7)–C(21)	1.457(4)
N(1)–C(16)	1.370(7)	N(7)–C(22)	1.457(4)
N(1)–C(26)	1.421(7)	N(8)–C(23)	1.456(4)
		N(8)–C(24)	1.457(4)
Bond angles (°)			
N(1)–Ta(1)–N(11)	60.9(2)	N(7)–Ti(1)–N(8)	102.9(1)
N(1)–Ta(1)–Cl(2)	142.4(1)	N(7)–Ti(1)–N(2)	99.6(1)
N(11)–Ta(1)–Cl(2)	81.5(1)	N(8)–Ti(1)–N(2)	101.7(1)
N(1)–Ta(1)–Cl(1)	87.8(1)	N(7)–Ti(1)–N(5)	102.7(1)
N(11)–Ta(1)–Cl(1)	77.5(1)	N(8)–Ti(1)–N(5)	102.91(9)
Cl(2)–Ta(1)–Cl(1)	84.52(6)	N(2)–Ti(1)–N(5)	141.88(9)
N(1)–Ta(1)–Cl(3)	86.0(1)	N(7)–Ti(1)–N(1)	156.8(1)
N(11)–Ta(1)–Cl(3)	76.4(1)	N(8)–Ti(1)–N(1)	94.0(1)
Cl(2)–Ta(1)–Cl(3)	84.45(6)	N(2)–Ti(1)–N(1)	61.01(9)
Cl(1)–Ta(1)–Cl(3)	152.91(5)	N(5)–Ti(1)–N(1)	88.58(9)
C(16)–N(1)–C(26)	116.4(4)	N(7)–Ti(1)–N(4)	90.5(0)
C(16)–N(1)–Ta(1)	99.3(3)	N(8)–Ti(1)–N(4)	161.4(1)
C(26)–N(1)–Ta(1)	144.2(3)	N(2)–Ti(1)–N(4)	88.41(9)
C(12)–N(11)–C(16)	121.6(5)	N(5)–Ti(1)–N(4)	61.06(8)
C(12)–N(11)–Ta(1)	145.5(4)	N(1)–Ti(1)–N(4)	77.16(9)
C(16)–N(11)–Ta(1)	92.9(3)	C(1)–N(2)–Ti(1)	97.0(2)
		C(6)–N(2)–Ti(1)	138.6(2)
		C(11)–N(5)–Ti(1)	97.2(2)
		C(16)–N(5)–Ti(1)	138.3(2)
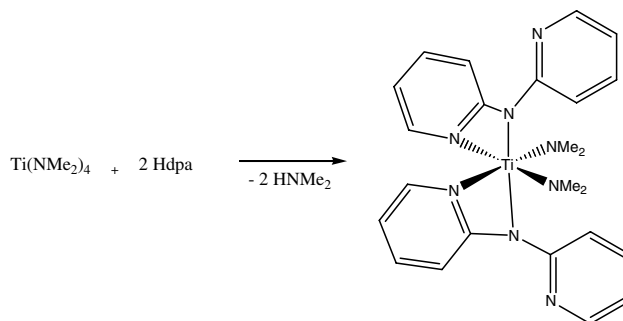
Scheme 6.

Fig. 2. Perspective ORTEP drawing of the molecular structure of complex **4**.
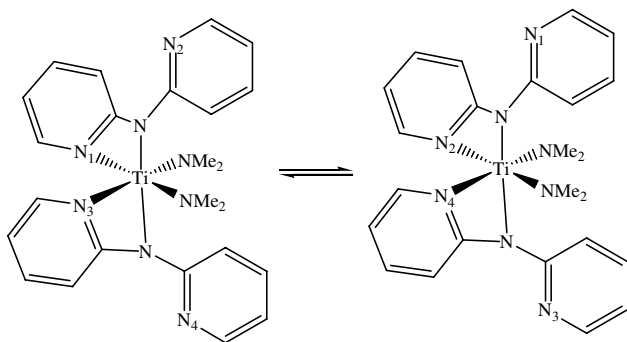
Scheme 7.

has a distorted octahedral geometry. Six nitrogen atoms define the coordination sphere of the metal. The dpa ligands are bonded to the titanium in an aminopyridinato fashion [14]. The distorted octahedral geometry is, probably, due to the small bite angles of the of the ligand (N(2)–Ti(1)–N(1), 61.01(9)° and N(5)–Ti(1)–N(4), 61.06(8)°).

The Ti(1)–N(2) and Ti(1)–N(5) bond distances (2.129(2) Å) are close to the observed bond lengths from the pyridyl nitrogen atoms to the metal centre Ti(1)–N(1) and Ti(1)–N(4) 2.203(2) and 2.205(2) Å, respectively. On the other hand, Ti(1)–N(7) and Ti(1)–N(8) bond distances (1.894(2) and 1.906(2) Å, respectively) are significantly shorter than those reported above but are within the range expected for titanium amide complexes [15].

We can see that while ^1H and ^{13}C NMR spectra of complex **4** show that in solution, at room temperature, both pyridyl rings of the dpa ligand are equivalent, the X-ray molecular structure determination reveals that in the solid state one of the two pyridyl ring in each dpa ligand is coordinated to the titanium atom. This could mean that in solution, at room temperature, interchange between the two nitrogen atoms in the coordination sphere of the titanium centre is rapid (see Scheme 7).

To confirm this proposal we have carried out an VT ^1H NMR study. It shows that at 198 K interchange is slow and the spectrum shows two different sets of signals for the pyridyl rings protons while at room temperature interchange is fast in the NMR time scale and all the four pyridyl moieties become equivalent. The coalescence temperature was found at 248 K and the estimate the value for $\Delta G^{\#}$ is 11.1(1) kcal mol^{-1}.

3. Conclusion

In conclusion, new complexes of the groups 4 and 5 transition metals containing one cyclopentadienyl ligand and one bis(2-pyridyl)amide spectator ligand have been prepared. We have seen that the ligand is

bonded to the metal centre in a chelate fashion in an analogous way to that an aminopyridinato groups, although a fluxional behaviour for this ligand has been found and it was studied by VT NMR spectroscopy. Further investigations on the synthesis of new complexes of early transition elements with this ligand are being conducted in our laboratory.

4. Experimental

The preparation and handling of described compounds was performed with rigorous exclusion of air and moisture under nitrogen atmosphere using standard vacuum line and Schlenk techniques. All solvents were dried and distilled under a nitrogen atmosphere.

The following reagents were prepared by the literature procedures: Ti(NMe$_2$)$_4$ [16], Cp*TiCl$_3$ [17], Cp*TiMe$_3$ [18], Cp*TaCl$_4$ [19].

^1H and ^{13}C NMR spectra were recorded on 200 Mercury Varian Fourier Transform spectrometer. Trace amounts of protonated solvents were used as references, and chemical shifts are reported in units of parts per million relative to SiMe$_4$.

IR spectra were recorded in the region 4000–400 cm^{-1} with a Nicolet Magna-IR 550 spectrophotometer.

4.1. Preparation of 1

A solution of Cp*TiMe$_3$ (0.505 g, 2.21 mmol) and Hdpa (0.379 g, 2.21 mmol) in 5 mL of pentane was stirred at room temperature for 2 h. After filtration, the solution was concentrated to approximately 4 mL, followed by storage at −30 °C overnight, yielding 0.520 g (62%) of an orange crystalline solid, which was characterized as **1**. IR (cm^{-1}): 1586 (vs), 1533 (s), 1241 (m), 1149 (s), 990 (m), 598 (w), 525 (m), 499 (m). ^1H NMR (toluene-d$_8$, 291 K): δ 0.99 (s, 6H, Me), 1.77 (s, 15H, Cp*), 6.29 (m, 2H, Py), 7.06 (m, 2H, Py), 7.28 (m, 2H, Py), 7.73 (m, 2H, Py). ^1H NMR (toluene-d$_8$, 193 K): 0.96 (s, 3H, Me), 1.18 (s, 3H, Me), 1.63 (s, 15H, Cp*), 5.88 (m, 1H, Py), 6.37 (m, 1H, Py), 6.76 (m, 1H, Py), 6.83 (m, 1H, Py), 6.95 (m, 2H, Py), 7.73 (m, 1H, Py), 8.27 (m, 1H, Py). $^{13}C\{^1H\}$ NMR: 12.3 (s, Cp*), 69.6 (s, Ti-Me), 114.4 (s, Cp*), 113.8 (s, C–H), 124.4 (s, C–H), 138.6 (s, C–H), 144.9 (s, C–H), 162.4 (s, C$_{ipso}$). Anal. Calc. for C$_{22}$H$_{29}$N$_3$Ti: C, 68.95; H, 7.57; 10.96. Found: C, 68.56; H, 7.20; N, 11.10%.

4.2. Preparation of 2

A solution of Cp*TiCl$_3$ (0.720 g, 2.48 mmol) and Lidpa (0.880 g, 4.96 mmol) in 8 mL of toluene was stirred at room temperature for 1 h. After filtration, the complex **2** was recrystallized by slow diffusion of pentane into the solution, yielding a black crystalline solid (0.543 g,

52%). IR (cm^{-1}): 1646 (w), 1553 (w), 1295 (s), 1142 (w), 857 (d), 764 (s), 532 (d), 433 (m). ^{1}H NMR (toluene-d$_8$, 338 K): δ 1.87 (s, 15H, Cp*), 6.39 (m, 2H, Py), 7.07 (m, 2H, Py), 7.65 (m, 2H, Py), 8.04 (m, 2H, Py). ^{1}H NMR (toluene-d$_8$, 233 K): 1.99 (s, 15H, Cp*), 6.07 (m, 1H, Py), 6.58 (m, 1H, Py), 6.84 (m, 1H, Py), 7.20 (m, 1H, Py), 7.50 (m, 1H, Py), 7.73 (m, 1H, Py), 7.96 (m, 1H, Py), 8.33 (m, 1H, Py). ^{13}C{^{1}H} NMR: 13.8 (s, Cp*), 111.8 (s, C–H), 116.2 (s, C–H), 134.0 (s, Cp*), 137.3 (s, C–H), 147.9 (s, C–H), 160.6 (s, C$_{ipso}$). Anal. Calc. for C$_{20}$H$_{23}$Cl$_2$N$_3$Ti: C, 56.62; H, 5.46; N, 9.90. Found: C, 56.44; H, 5.49; N, 9.47%.

4.3. Preparation of 3

A solution of Cp*TaCl$_4$ (0.173 g, 0.38 mmol) and Lidpa (0.134 g, 0.76 mmol) in 4 mL of toluene was stirred at room temperature for 1 h. After filtration, the complex **3** was recrystallized by slow diffusion of pentane into the solution, yielding red crystals (0.171 g, 77%). IR (cm^{-1}): 1593 (s), 1560 (s), 1275 (m), 1222 (m), 1142 (m), 1023 (m), 857 (s), 779 (s), 499 (m). ^{1}H NMR (C$_6$D$_6$, rt): δ 2.16 (s, 15H, Cp*), 5.46 (m, 1H, Py), 6.04 (m, 1H, Py), 6.50 (m, 1H, Py), 6.59 (m, 1H, Py), 6.85 (m, 1H, Py), 6.97 (m, 1H, Py), 8.32 (m, 1H, Py), 8.97 (m, 1H, Py). ^{13}C{^{1}H} NMR: 12.6 (s, Cp*), 107.0 (s, C–H), 114.9 (s, Cp*), 120.9 (s, C–H), 121.7 (s, C–H), 130.0 (s, C–H), 137.6 (s, C–H), 140.3 (s, C–H), 142.0 (s, C–H), 149.3 (s, C–H). Anal. Calc. for C$_{20}$H$_{23}$Cl$_3$N$_3$Ta: C, 40.52; H, 3.88; N, 7.09. Found: C, 40.09; H, 3.66; N, 7.09%.

4.4. Preparation of 4

A solution of Ti(NMe$_2$)$_4$ (0.490 g, 2.18 mmol) and Hdpa (0.748 g, 4.37 mmol) in 8 mL of toluene was stirred at room temperature for 1 h. After this, the solvent was removed under vacuum and the residue washed with pentane (8 mL) to yield an orange solid, which was characterized as complex **4**. Yield: 0.751 g (73%). IR (cm^{-1}): 1593 (vs), 1308 (m), 1241 (m), 1142 (m), 1003 (w), 943 (s), 645 (m), 579 (m), 532 (s), 415 (s). ^{1}H NMR (toluene-d$_8$, 291 K): δ 3.22 (s, 12 H), 6.26 (m, 4H, Py), 7.17 (m, 4H, Py), 7.86 (m, 4H, Py), 7.99 (m, 4H, Py). ^{1}H NMR (toluene-d$_8$, 198 K): δ 3.07 (s, 12 H), 5.74 (m, 2H, Py), 6.55 (m, 2H, Py), 6.91 (m, 2H, Py), 7.28 (m, 6H, Py), 8.49 (m, 2H, Py), 8.64 (m, 2H, Py). ^{13}C{^{1}H} NMR: 46.5 (s, Me-N), 113.8 (s, C–H), 114.4 (s, C–H), 137.6 (s, C–H), 145.0 (s, C–H), 162.4 (s, C$_{ipso}$). Anal. Calc. for C$_{24}$H$_{28}$N$_8$Ti: C, 60.50; H, 5.92; N, 23.52. Found: C, 60.10, H, 5.87; N, 23.10%.

4.5. X-ray crystallographic structure determination

Crystals of **3** were examined at 293 K on a Nonius-Mach3 diffractometer and crystals of **4** were examined at 180 K on a Bruker-Nonius X8 APEXII CCD area-detector diffractometer, both with a graphite monochromated Mo Kα radiation ($\lambda = 0.71073$ Å). Table 1 summarized the crystal data, data collection and refinement parameters for both compounds.

The structures were solved by the direct methods using the SIR-92 computer program [20], completed by subsequent difference Fourier syntheses, and refined by full-matrix least-squares procedures (SHELXL-97) [21] on F^2. All non-hydrogen atoms were refined with anisotropic thermal parameters. The hydrogen atoms were placed using a "riding model" and included in the refinement at calculated positions.

5. Supplementary material

Crystallographic data for the structural analysis of **3** and **4** have been deposited with the Cambridge Crystallographic Data Centre, CCDC Nos. 275275–275276. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44 1223 336033; e-mail: deposit@ccdc.cam.ac.uk or www: http//www.ccdc.cam.ac.uk).

References

[1] L. Scoles, R. Minhas, R. Duchateau, J. Jubb, S. Gambarotta, Organometallics 13 (1994) 4978.
[2] (a) Y. Yoshida, J. Saito, M. Mitani, Y. Takagi, S. Matsui, S. Ishii, T. Nakano, N. Kashiwa, T. Fujita, Chem. Commun. (2002) 1298;
(b) R.R. Schrock, R. baumann, S.M. Reid, J.T. Goodman, R. Stumpf, W.M. Davis, Organometallics 18 (1999) 3649.
[3] (a) R. Kempe, Angew. Chem. Int. Ed. 39 (2000) 468;
(b) R. Baumann, R. Stumpf, W.M. Davis, L.C. Liang, R.R. Schrock, J. Am. Chem. Soc. 121 (1999) 7822;
(c) L. Gade, Chem. Commun. (2000) 173.
[4] L. Kakaliou, W.J. Scanlon, B. Qian, S.W. Baek, M.R. Smith, D.H. Motry, Inorg. Chem. 38 (1999) 5964.
[5] (a) D.P. Steinhuebel, S.J. Lippard, Organometallics 18 (1999) 109;
(b) P.W. Roesky, Chem. Soc. Rev. 29 (2000) 335.
[6] (a) J.R. Hagadorn, J. Arnold, Inorg. Chem. 36 (1997) 2928;
(b) J.R. Hagadorn, J. Arnold, J. Am. Chem. Soc. 118 (1996) 893;
(c) H.W. Roesky, B. Meller, M. Noltemeyer, H.G. Schmidt, U. Scholz, G.M. Sheldrick, Chem. Ber. 121 (1988) 1403;
(d) P.J. Stewart, A.J. Blake, P. Mountford, Inorg. Chem. 36 (1977) 3616;
(e) R. Kempe, P. Arndt, Inorg. Chem. 35 (1996) 2644.

[7] S.M. Mullins, A.P. Duncan, R.G. Bergman, J. Arnold, Inorg. Chem. 40 (2001) 6952.

[8] R. Clérac, F.A. Cotton, L.M. Daniels, K.R. Dunbar, C.A. Murillo, X. Wang, Inorg. Chem. 40 (2001) 1256.

[9] J.A. Cabeza, I. del Río, S. García-Granda, V. Riera, M. Suárez, Organometallics 21 (2002) 2540.

[10] (a) E.C. Yang, M.C. Cheng, M.S. Tsai, S.M. Peng, J. Chem. Soc., Chem. Commun. (1994) 2377;
(b) F.A. Cotton, L.M. Daniels, G.T. Jordan, Chem. Commun. (1997) 421;
(c) F.A. Cotton, L.M. Daniels, G.T. Jordan, C.A. Murillo, J. Am. Chem. Soc. 119 (1997) 10377;
(d) F.A. Cotton, C.A. Murillo, X. Wang, J. Chem. Soc., Dalton Trans. (1999) 3327;
(e) J.T. Sheu, C.C. Lin, I. Chao, C.C. Wang, S.M. Peng, J. Chem. Soc., Chem. Commun. (1996) 315;
(f) R. Clérac, F.A. Cotton, L.M. Daniels, K.R. Dunbar, C.A. Murillo, I. Pascual, Inorg. Chem. 39 (2000) 748.

[11] R.J. Abrahams, J. Fisher, P. Loftus, Introduction to NMR Spectroscopy, Wiley, New York, 1988.

[12] (a) L.D. Brown, J.A. Ibers, J. Am. Chem. Soc. 98 (1976) 2796;
(b) E. Pfeiffer, K. Olie, Cryst. Struct. Commun. (1975) 605;

(c) M. Corbett, B.F. Hoskins, J. Am. Chem. Soc. 89 (1967) 1530;
(d) J.M. Decker, S.J. Geib, T.Y. Meyer, Organometallics 18 (1999) 4417.

[13] F. Schrumpf, H.W. Roesky, T. Subrahmanyan, M. Noltemeyer, Z. Anorg. Allg. Chem. 583 (1990) 124.

[14] M. Talja, M. Klinga, M. Polamo, E. Aitola, M. Leskelä, Inorg. Chim. Acta 358 (2005) 1061.

[15] E. Hollink, P. Wei, D.W. Stephan, Can. J. Chem. 82 (2004) 1634.

[16] D.C. Bradley, I.M. Thomas, J. Chem. Soc. (1960) 3857.

[17] (a) A.M. Cardoso, R.J.H. Clark, S.J. Moorhouse, J. Chem. Soc., Dalton Trans. (1980) 1156;
(b) G. Hidalgo, M. Mena, F. Palacios, P. Royo, R. Serrano, J. Organomet. Chem. 340 (1988) 37.

[18] M. Mena, Ph.D. Thesis, 1988, Universidad de Alcalá.

[19] R.J. Burt, J. Chatt, G.J. Leigh, J.H. Teuben, A. Whesterhof, J. Organomet. Chem. 129 (1977) C33.

[20] A. Altomare, G. Cascarano, C. Giacovazzo, A. Guagliardi, J. Appl. Crystallogr. 26 (1993) 343–350.

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