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Journal of Organometallic Chemistry 554 (1998) 185–194

Journal of Organometallic Chemistry

Alkyl chloro, dialkyl and mixed alkyl derivatives of imido(pentamethylcyclopentadienyl) tantalum(V). X-ray crystal structure of [TaCp*Cp′Cl{N(2,6-$Me_2C_6H_3$)}], (Cp′ = η^5-$C_5H_4SiMe_3$][1]

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Received 22 September 1997

Abstract

[TaCp*Cl_2{N(2,6-$Me_2C_6H_3$)}] (Cp* = η^5-C_5Me_5) reacts with one equivalent of LiR (R = CH_2SiMe_3, CH_2CMe_2Ph, CH_2CMe_3, 2-(CH_2NMe_2)C_6H_4, $C_5H_4SiMe_3$) or 0.5 equivalents of $Mg(CH_2C_6H_5)_2(THF)_2$ to give the alkyl chloro complexes [TaCp*ClR{N(2,6-$Me_2C_6H_3$)}],(R = CH_2SiMe_3, **1**; CH_2CMe_2Ph, **2**; CH_2CMe_3, **3**; $CH_2C_6H_5$, **4**; 2-(CH_2NMe_2)C_6H_4, **5**; $C_5H_4SiMe_3$, **6**). When the same reaction was carried out with two equivalents of lithium or one equivalent of magnesium reagent, the corresponding dialkyl derivatives [TaCp*R_2{N(2,6-$Me_2C_6H_3$)}],(R = CH_2SiMe_3, **7**; CH_2CMe_2Ph, **8**; C_6H_5, **9**; $CH_2C_6H_5$, **10**; CH_2CMe_3, **11**) were obtained. The mixed alkyl derivatives [TaCp*MeR{N(2,6-$Me_2C_6H_3$)}], (R = CH_2SiMe_3, **12**; CH_2CMe_2Ph, **13**; C_6H_5, **14**; CH_2CMe_3, **15**; 2-(CH_2NMe_2)C_6H_4, **16**; $CH_2C_6H_5$, **17**; $C_5H_4SiMe_3$, **18**) have been prepared by treatment of solutions containing [TaCp*ClMe{N(2,6-$Me_2C_6H_3$)}] with one equivalent of lithium or 0.5 equivalents of magnesium reagent. All the new complexes were characterized by the usual IR and NMR spectroscopic methods. The crystal structure of **6** was determined by X-ray diffraction studies. Crystals of **6** are monoclinic, space group $P2_1/c$, with $Z = 4$ in a unit cell of dimensions $a = 12.597(3)$, $b = 11.338(2)$, $c = 18.297(4)$ Å and $\beta = 96.53(3)°$. The structure was solved from diffractometer data by a combination of direct and Fourier methods and refined by full-matrix least squares fit on the basis of 4846 observed reflections to R_1 and wR^2 values of 0.0224 and 0.0574, respectively.

Keywords: Tantalum; alkyl imido pentamethylcyclopentadienyl complexes

1. Introduction

High-valent early transition metal complexes containing cyclopentadienyl ligands and strong π-donor oxo and organoimido substituents are being intensively studied in relation to their many potential applications in catalytic and stoichiometric processes [1–3].

The isolobal relationship between the imido and the cyclopentadienyl ligands [4,5] allows the isoelectronic [MCp_2] group 4 and the [MCp(NR)] group 5 metal fragments to generate two groups of related complexes due to their similar stereochemical properties. The easy modification of the steric and electronic properties of the cyclopentadienyl ligand by the introduction of appropriate ring-substituents and also of the imido ligand by the modification of its alkyl moiety make this type of compound very versatile. For all these reasons a rich chemistry of imido group 5 metal complexes containing mono-functional [6,7], tetradentate triamidoamine [8,9] and cyclopentadienyl ligands in mono- [10–14] and di-cyclopentadienyltype [15–18] complexes has been reported in recent years. Protonated lithium amides [12]

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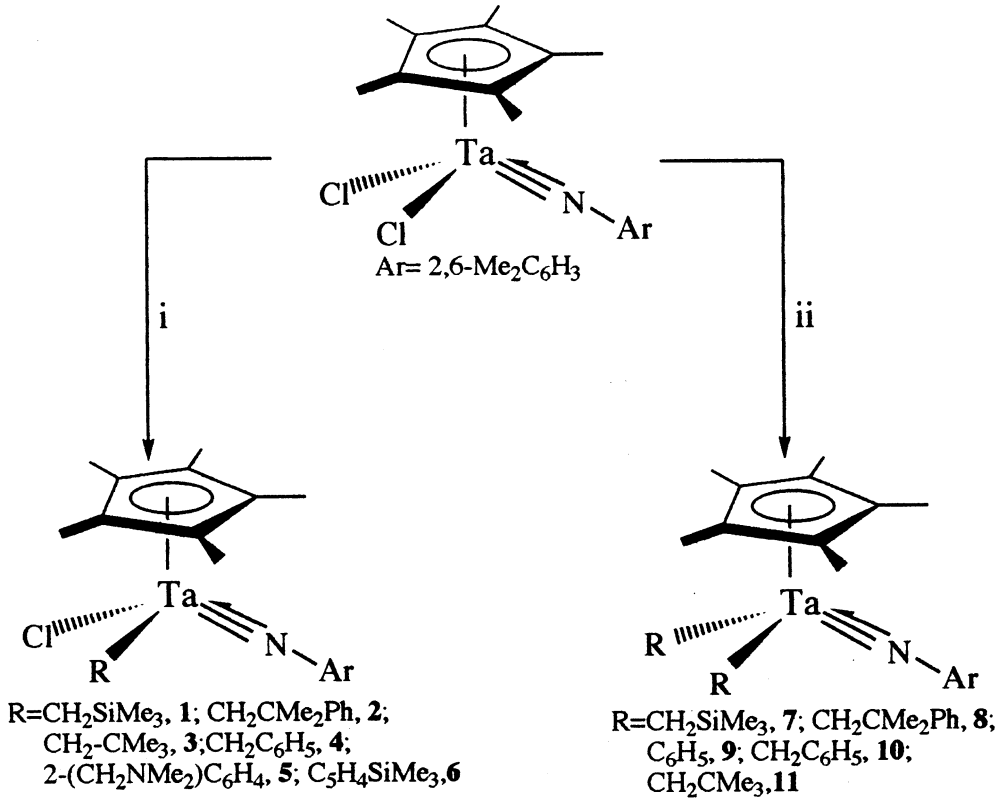
[1] Dedicated to Prof. P.M. Maitlis on the occasion of his 65th birthday.

[2] X-ray diffraction studies.

0022-328X/98/$19.00
PII S0022-328X(97)00724-9



Reagents and conditions:
i- 1 equiv LiR (R=CH_2SiMe_3, CH_2CMe_2Ph, CH_2CMe_3, 2-$(CH_2NMe_2)C_6H_4$, $C_5H_4SiMe_3$) or 1/2 equiv $Mg(CH_2C_6H_5)_2(THF)_2$, toluene or THF(**6**), 12 h, RT.
ii- 2 equiv LiR (R=CH_2SiMe_3, CH_2CMe_2Ph, C_6H_5, CH_2CMe_3) or 1 equiv $Mg(CH_2C_6H_5)_2(THF)_2$,toluene or n-hexane(**11**), 12 h, RT.

Scheme 1.

have been extensively used to generate the imido ligand but other synthetic strategies have also been applied such as those based on the deprotonation of cyclopentadiene by metal amides [10,15], β-hydrogen elimination of amides and amines coordinated to metal(III) compounds [16,18] and oxidation of metal(III) complexes with azides [17]. Related alkoxylimido and hydrazido(2-) derivatives have been reported [19–21] more recently.

Although the chemistry of imido pentamethylcyclopentadienyl tantalum halides is well established, the alkyl compounds are less known even though such complexes have significant potential applications. Following our recent work on the dichloro- and chloromethyl derivatives [Ta(η^5-C_5Me_5)Cl_2(NAr)], (Ar = 2,6-$Me_2C_6H_3$; 2,4,6-$Me_3C_6H_2$) [22], [Ta(η^5-C_5Me_5)XY{N(2,6-$Me_2C_6H_3$)}],(X = Y = Me; X = Cl, $OC_6H_3Me_2$, Y = Me) [23] we report herein a systematic study of the reactivity of monocyclopentadienyl arylimido tantalum complexes [Ta(η^5-C_5Me_5)XY{N(2,6-$Me_2C_6H_3$)}], (X = Y = Cl; X = Cl, Y = Me) towards alkylating reagents and the X-ray molecular structure of the [Ta(η^5-C_5Me_5)(η^5-$C_5H_4SiMe_3$) Cl{N(2,6-$Me_2C_6H_3$)}] complex.

2. Results and discussion

2.1. Alkyl chloro and dialkyl imido pentamethylcyclopentadienyl tantalum(V) compounds

The direct alkylation of [TaCp*Cl_2{N(2,6-$Me_2C_6H_3$)}] (Cp* = η^5-C_5Me_5) with an appropriate amount of the alkylating reagent leads to the formation of the half-sandwich alkyl chloro imido [TaCp*ClR{N(2,6-$Me_2C_6H_3$)}] (**1–6**) and dialkyl imido [TaCp*R_2{N(2,6-$Me_2C_6H_3$)}] (**7–11**) complexes, as shown in Scheme 1.

Treatment of the starting dichloro imido complex with one equivalent of LiPh gives a 1:1 mixture of

Table 1
Kinetic parameters of Berry pseudorotation for complexes **2**, **3** and **4**

Complex	log A	Ea	$\Delta H^{\#}$	$\Delta S^{\#}$	$\Delta G^{\#\,298\ K}$
		kcal mol^{-1}	kcal mol^{-1}	e.u.	kcal mol^{-1}
2 $R = CH_2CMe_2Ph$	12.2 ± 0.31	12.8 ± 0.39	12.8 ± 0.30	-2.5 ± 1.2	13.5
3 $R = CH_2CMe_3$	12.8 ± 0.12	12.9 ± 0.15	12.3 ± 0.16	-2.0 ± 0.5	12.9
4 $R = CH_2C_6H_5$	12.2 ± 0.30	12.8 ± 0.30	12.8 ± 0.25	-2.5 ± 1.1	12.0

chloro phenyl and diphenyl complexes, but the diphenyl complex **9** is the only product formed when two equivalents of LiPh are used in the reaction. Several attempts to prepare the bis-2-[(dimethylamino)methyl]phenyl imido compound were unsuccessful, probably due to steric factors, and in all cases a mixture of monoalkyl derivative **5** and the excess alkylating reagent were obtained.

All of the complexes **1–11** are soluble in aromatic and saturated hydrocarbons, chlorinated solvents, diethyl ether and tetrahydrofuran. They are air- and moisture-sensitive, and rigorously dried solvents and handling under dry inert atmosphere were found to be imperative for successful preparations.

The analytical, IR, and ^1H and $^{13}C\{^1H\}$ NMR spectroscopic data (Section 3) for compounds **1–11** are consistent with their formulation. The new imido complexes show the $\nu_{(Ta=N)}$ [13,24] IR absorption at ca. 1320 cm^{-1}.

The ^1H NMR spectra show an AB spin system for the α-CH_2 protons of the alkyl groups of complexes **1–4** with a chiral metal center, and of the α-CH_2 protons of complexes **7**, **8**, **10** and **11** with a prochiral metal center. In addition, the ^1H and $^{13}C\{^1H\}$ NMR spectra of **2** and **8** show the expected two resonances for the inequivalent methyl substituents of the β-CMe_2 groups. Complex **6** shows four proton and five carbon resonances for the silyl-substituted cyclopentadienyl ring.

The ^1H NMR spectra of complexes **2**, **3** and **4** in CD_2Cl_2 or $CDCl_3$ solutions at room temperature show slightly broad signals for the o-methyl(phenyl) groups of the imido ligand, whereas the $^{13}C\{^1H\}$ NMR spectrum of **3** displays a very broad signal for the same groups. The ^1H NMR study at variable temperature indicates typical dynamic behaviour involving the exchange of two equally populated signals [25,26]. The kinetic parameters of this dynamic process which were calculated using the ^1H DNMR data and DNMR5 program (see Table 1) are consistent with an intramolecular process (log $A \approx 12$). The free Gibbs energy ($\Delta G^{\#}$) found for complexes **2**, **3** and **4** depends on the steric requirement of the alkyl substituent and increases from the smallest ($R = CH_2C_6H_5$) to bulkiest substituent ($R = CH_2CMe_2Ph$). We suggest that this dynamic process does not take place by rotation around the Ta–N–C_i(aryl) axis hindered by the steric requirement of the pentamethylcyclopentadienyl and 2,6-dimethylphenyl groups, but involves in a Berry pseudorotation with negligible variation of $\Delta S^{\#}$ [27] in a solvated pentacoordinate species present in solution.

The 2-[(dimethylamino)methyl]phenyl ligand is able to form cyclometalated complexes [28] containing a five-membered chelate ring by coordination of the nitrogen to electron-deficient metal centers, leading to a distorted peudo-square pyramidal geometry as has been reported for similar alkylated tantalum compounds [29]. However the NMR data for complex **5** (Section 3) show that the Me_2N protons and carbons are equivalent, consistent with a singly coordinated aryl ligand with non-coordinated amine functionality.

Crystals of complex **6** suitable for X-ray diffraction studies were obtained by cooling its toluene solution to -40°C. An ORTEP drawing of **6** based on the X-ray structural analysis with the atomic labeling scheme is shown in Fig. 1. Selected bond distances and angles are given in Table 2.

The molecular structure of **6** shows a typical bent-metallocene geometry, with the chlorine atom and the imido group lying in the equatorial plane. Although the two cyclopentadienyl (Cp) rings are different the distance from the tantalum atom to both centroids is the same and the mean distance Ta–C does not show any significant difference (2.50 Å in Cp1 and 2.49 Å in Cp2). The equatorial plane is defined by Ta1, Cl1, N1 and C41. The two Cp centroids are equidistant from it with distances of 1.98 and 1.93 Å for Cp1 and Cp2, respectively. The angles between the equatorial plane and the mean Cp planes are also equivalent. All these features indicate that the bonding of both Cp rings to the metal centre is very similar. The Ta–N distance of 1.803(4) Å is very similar to those found in the closely related compounds $TaCp^*_2Cl$(=NPh), (Ta–N 1.799(4) Å) [18] and $TaCp^*_2H$(=NPh), (Ta–N 1.831(10) Å) [30]. Likewise, although slightly more closed, the Ta–N–

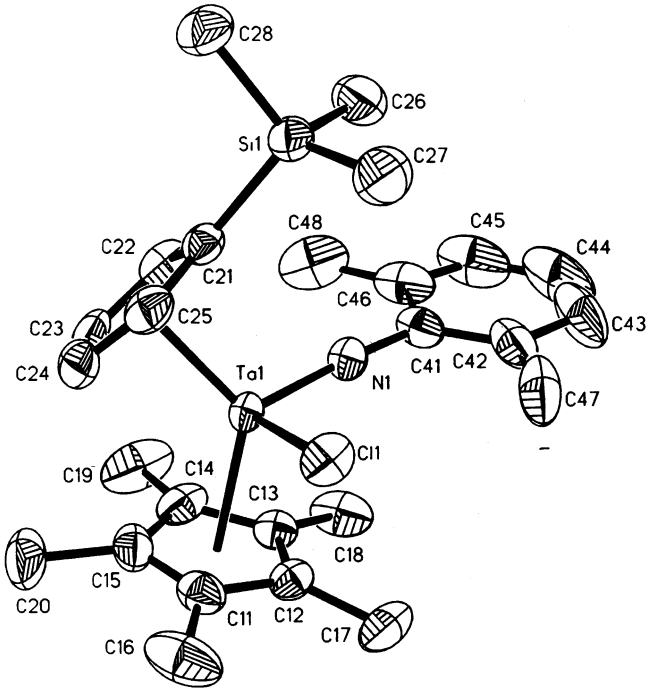


Fig. 1. ORTEP view of the molecular structure of [Ta(η^5-C_5Me_5)(η^5-$C_5H_4SiMe_3$)Cl{N(2,6-$Me_2C_6H_3$)}], **6**, with the atom-numbering scheme.

C41 angle of 174.6(3)° is almost linear. This disposition is in accordance with the MO explanation reported for complexes of this type [31] and is consistent with an 18-electron configuration at the metal centre and an sp hybridized nitrogen atom with a lone pair of electrons, involved in bonding with the phenyl substituent, centred on it. These data are consistent with a tantalum–nitrogen bond order of about 2. The phenyl ring occupies its sterically more favoured position fairly parallel to the equatorial plane at an angle of 15.4° with it, thus facilitating maximun overlap with the nitrogen centered p orbital.

One remarkable difference between our structure and the two structures previously reported is the situation of the ligands in the equatorial plane with respect to the Cp(centroid)–Ta–Cp(centroid) plane. In the reported compounds the imido nitrogen donor atom lies closer to this plane at 38 and 21° and the chloro and the hydrido ligands are located at 57 and 61°, respectively, whereas in complex **6** the chloro moiety is nearer to that plane, making an angle of 28.5° with it and the imido nitrogen is located at 53°, thus avoiding any unfavourable steric interaction with the $-SiMe_3$ ring-substituent located practically in that plane. The $SiMe_3$ fragment is bent away from the corresponding Cp plane and the Si atom is located at 0.28 Å from it. All of the Ta–Cl, C–C and C–Si distances are normal.

Table 2
Bond lengths [Å] and angles [°] for **6**

Ta(1)–N(1)	1.803(4)	Ta(1)–Cl(1)	2.426(1)
Ta(1)–C(14)	2.432(4)	Ta(1)–C(22)	2.433(5)
Ta(1)–C(23)	2.444(4)	Ta(1)–C(12)	2.487(4)
Ta(1)–C(13)	2.484(4)	Ta (1)–C(21)	2.506(4)
Ta(1)–C(25)	2.544(4)	Ta(1)–C(11)	2.559(5)
Ta(1)–C(24)	2.549(5)	Ta(1)–C(15)	2.570(5)
Si(1)–C(27)	1.847(6)	Si(1)–C(26)	1.849(6)
Si(1)–C(21)	1.873(5)	Si(1)–C(28)	1.863(5)
N(1)–C(41)	1.372(6)	Ta(1)–Cp(1)	2.202
Ta(1)–Cp(2)	2.190		
N(1)–Ta(1)–Cl(1)	98.5(1)	C(41)–N(1)–Ta(1)	174.6(3)
Cp(1)–Ta(1)–Cp(2)	126.2	Cp(1)–Ta(1)–Cl(1)	102.5
Cp(1)–Ta(1)–N(1)	110.1	Cp(2)–Ta(1)–Cl(1)	102.4
Cp(2)–Ta(1)–N(1)	112.3		

Cp(1) and Cp(2) are the centroids of the C_5Me_5 and $C_5H_4SiMe_3$, respectively.

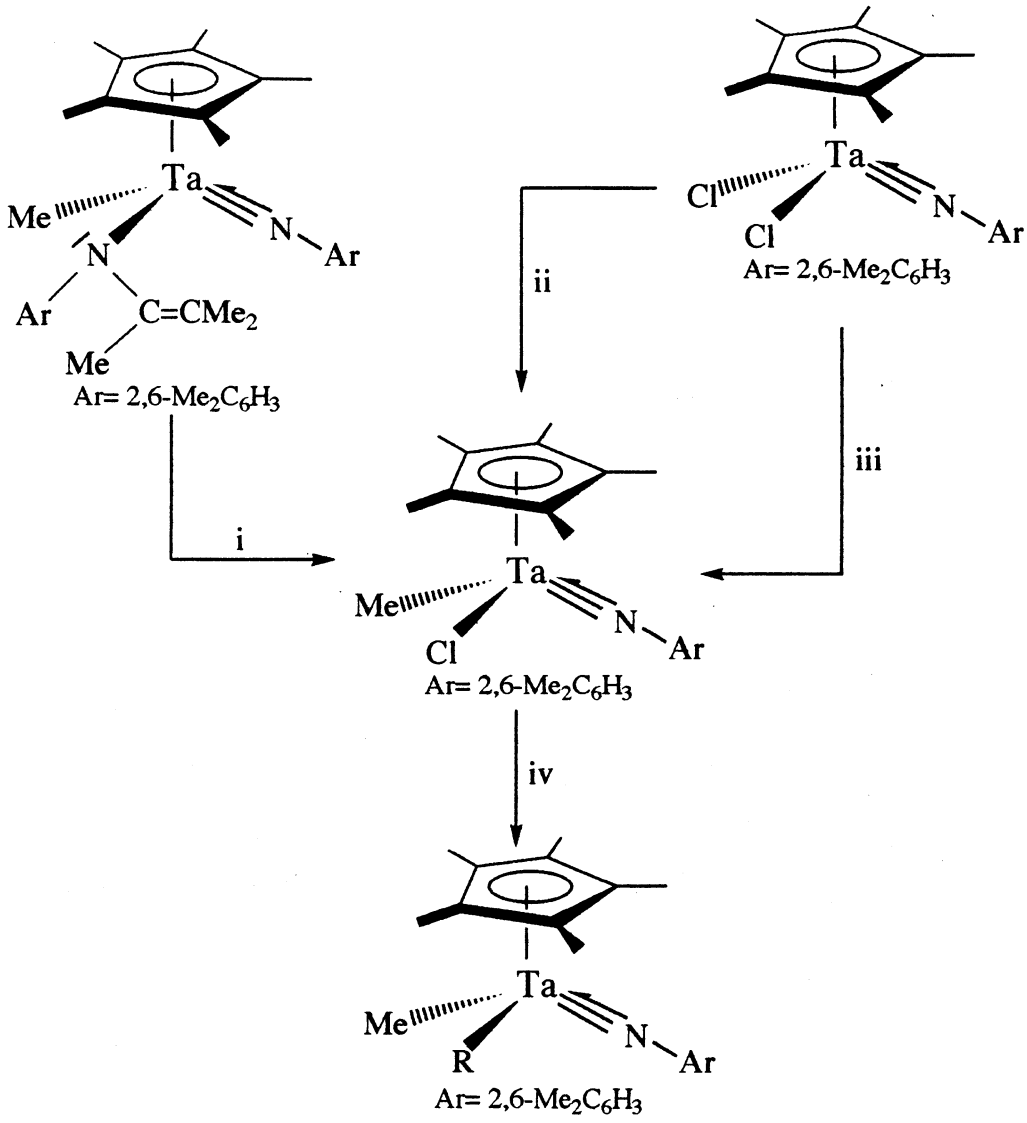
2.2. Alkyl methyl imido pentamethylcyclopentadienyl tantalum(V) compounds

When one equivalent of LiR or 0.5 equivalents of dibenzyl magnesium is added to a toluene solution of the starting chloro methyl imido complex, a yellow solution is obtained, which after manipulation affords the mixed alkylated complexes **12–18** in good yields, as shown in Scheme 2.

All of the complexes **12–18** are air- and moisture-sensitive, very soluble in alkanes, aromatic hydrocarbons and chlorinated solvents.

The structures of complexes **12–18** in the solid have not been determined but the compounds are assumed to be monomers, pseudotetrahedral and isostructural with other half-sandwich imido Group 5 metal derivatives [13,32]. Their formulation as mixed alkylated imido complexes is supported by analytical and spectroscopic data (Section 3) which show the behaviour expected for such chiral species.

The IR spectra of complexes **12–18** display a strong band at ca. 1326 cm^{-1} which can be assigned to the $\nu_{Ta=N}$ stretching vibration [13,24]. The ^1H and $^{13}C\{^1H\}$ NMR spectra of complexes **12–18** show the expected signals for the pentamethylcyclopentadienyl ring and also for the equivalent ortho-methyl phenyl imido groups except for complex **18** which shows two signals for both ortho-methylphenyl imido substituents due to slow rotation of the phenyl ring around the Ta–N–C_i(phenyl) axis. In addition, four



R=CH_2SiMe_3, **12**; CH_2CMe_2Ph, **13**; C_6H_5, **14**; CH_2CMe_3, **15**; 2-$(CH_2NMe_2)C_6H_4$, **16**; $CH_2C_6H_5$, **17**; $C_5H_4SiMe_3$, **18**

Reagents and conditions:
i- 1 equiv HCl (1M in OEt_2), toluene, -78°C, 20 min; RT, 2h
ii- 1 equiv [TaCp*Me_2{N(2,6-$Me_2C_6H_3$)}], toluene, 100°C, 72 h, sealed ampoule.
iii- 1 equiv $ZnMe_2$ (2M in toluene), toluene, RT, 12h.
iv- 1 equiv LiR (R=CH_2SiMe_3, CH_2CMe_2Ph, C_6H_5, CH_2CMe_3, 2-$(CH_2NMe_2)C_6H_4$, $C_5H_4SiMe_3$) or 1/2 equiv $Mg(CH_2C_6H_5)_2(THF)_2$,(R=$CH_2C_6H_5$), toluene or THF(**18**), RT, 12h.

Scheme 2.

and five resonances for the trimethylsilylcyclopentadienyl ring protons and carbons are observed. The α-CH_2 protons of the alkyl groups of complexes **12**, **13**, **15**, **16** and **17** appear as an AB spin system and in the case of **13** two resonances are observed for the inequivalent methyl substituents of the alkyl group.

3. Experimental section

3.1. General considerations

All manipulations were carried out under an atmosphere of argon using conventional Schlenk-tube and glove-box techniques.

Solvents were purified by distillation from an appropriate drying agent diethyl ether and tetrahydrofuran (Na/benzophenone), *n*-hexane (Na/K alloy) and toluene (Na).Reagent grade iodobenzene, Li^{n}Bu (1.6 M in hexanes) and $ZnMe_2$ (2 M in toluene) were purchased from Aldrich Chemical and were used without further purification. Alkyl lithium LiR (R = CH_2SiMe_3 [33], CH_2CMe_2Ph [33], CH_2CMe_3 [33], C_6H_5 [34], 2-$(CH_2NMe_2)C_6H_4$ [35], $C_5H_4SiMe_3$ [36]), benzyl magnesium $Mg(CH_2C_6H_5)_2(THE)_2$ [37] and the starting materials [TaCp*X_2{N(2,6-$Me_2C_6H_3$)}], (X = Cl [38], Me [23]), [TaCp*ClMe{N(2,6-$Me_2C_6H_3$)}] [23] and [TaCp*Me{N(2,6 - $Me_2C_6H_3$)}{N(2,6 - $Me_2C_6H_3$(CMe=CMe_2)}] [38] were prepared as described previously.

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

3.2. Synthesis of starting materials

Starting materials [TaCp*$Cl_{2-x}Me_x${N(2,6-$Me_2C_6H_3$)}] ($x = 0$ [38], 1 [23]) were recently prepared and described by our research group, but in the case of the chloro methyl imido derivative, we here report two new synthetic methods with better yield.

3.2.1. Method A

A mixture of equimolar amounts of [TaCp*Cl_2{N(2,6-$Me_2C_6H_3$)}](0.60 g, 1.18 mmol) and [TaCp*Me_2{N(2,6-$Me_2C_6H_3$)}] (0.55 g, 1.18 mmol) in toluene (25 ml) was heated at 100°C for 3 days in a sealed ampoule. After the ampoule was opened, the solution was evaporated to dryness and the residue washed with cold *n*-hexane (3 × 5 ml). The orange microcrystalline solid obtained was identified as [TaCp*ClMe{N(2,6-$Me_2C_6H_3$)}] by analytical and spectroscopic (IR, ^1H NMR) methods. The data coincide with those previously reported [7]. Yield 0.54 g (95%).

3.2.2. Method B

A 2 M solution of $ZnMe_2$ in toluene (0.70 ml, 1.38 mmol) was added at room temperature to a red solution of [TaCp*Cl_2{N(2,6-$Me_2C_6H_3$)}] (0.70 g, 1.38 mmol) in toluene (50 ml) and the mixture was stirred for 12 h. The solvent was removed in vacuo and the residue extracted into *n*-hexane (3 × 15 ml). The solution was filtered, concentrated to ca. 10 ml and cooled to −40°C to give the chloro methyl imido derivative as orange crystals. Yield 0.60 (90%).

3.3. Synthesis of [TaCp*ClR{N(2,6-$Me_2C_6H_3$)}] (R = CH_2SiMe_3, **1**; CH_2CMe_2Ph, **2**; CH_2–CMe_3, **3**; $CH_2C_6H_5$, **4**; 2-$(CH_2NMe_2)C_6H_4$, **5**; $C_5H_4SiMe_3$, **6**)

1–5. [TaCp*Cl_2{N(2,6-$Me_2C_6H_3$)}] (0.70 g, 1.38 mmol) and LiR (1.38 mmol; R = CH_2SiMe_3, 0.13 g; CH_2CMe_2Ph, 0.19 g; CH_2–CMe_3, 0.11 g; 2-$(CH_2NMe_2)C_6H_4$, 0.20 g) or $Mg(CH_2C_6H_5)_2(THF)_2$ (0.24 g, 1.38 mmol) were stirred in toluene (50 ml) at room temperature for 12 h. The resulting suspension was evaporated to dryness and the residue extracted into *n*-hexane (2 × 10 ml). Subsequently, the resulting solution was filtered, concentrated to ca. 10 ml and cooled to −40°C overnight to give **1–5** as yellow microcrystalline solids.

The data for **1** follow. Yield 0.64 g (70%). IR (Nujol mull, ν cm^{-1}): 1642 (w), 1327 (vs), 1241 (vs), 1095 (m), 1023 (m), 966 (m), 897 (m), 850 (m), 761 (m), 526 (w), 353 (m). ^1H NMR (δ ppm, in chloroform-d): 6.95 (d, 2H), 6.62 (t, 1H, $H_3C_6Me_2N$), 2.34 (s, 6H, $Me_2C_6H_3N$), 2.04 (s, 15H, C_5Me_5), 0.73$_{av}$ (AB, 2H, $^2J_{H-H}$ = 12.5 Hz, H_2CSiMe_3), 0.02 (s, 9H, Me_3SiCH_2). $^{13}C\{1H\}$ NMR (δ ppm, in chloroform-d): 152.33, 134.08, 122.00, 118.10 (C_i, C_p, C_o, C_m, $C_6H_3Me_2N$), 126.81 (C_5Me_5), 56.34 (CH_2SiMe_3), 19.02 ($Me_2C_6H_3N$), 11.27 (C_5Me_5), 1.95 (Me_3SiCH_2). Anal. Found: C, 47.55; H, 6.24; N, 2.62. $C_{22}H_{35}ClNSiTa$. Calc.: C, 47.35; H, 6.32; N, 2.51%.

The data for **2** follow. Yield 0.54 g (65%). IR (Nujol mull, ν cm^{-1}): 1590 (w), 1326 (vs), 1169 (m), 1096 (m), 1027 (m), 983 (m), 763 (s), 722 (m), 696 (m), 608 (w), 548 (w), 392 (w), 348 (s). ^1H NMR (δ ppm, in chloroform-d): 7.34 (d, 2H), 7.20 (t, 2H), 7.06 (t, 1H, $H_5C_6CMe_2CH_2$), 7.00 (d, 2H), 6.68 (t, 1H, $H_3C_6Me_2N$), 2.33 (br, 6H, $Me_2C_6H_3N$), 2.02 (s, 15H, C_5Me_5), 1.53 (s, 3H, H_2CCMe_2Ph), 1.46 (AB, 2H, $^2J_{H-H}$ = 14.5 Hz, H_2CCMe_2Ph), 1.43 (s, 3H, H_2CCMe_2Ph). $^{13}Cl\{^1H\}$ NMR (δ ppm, in chloroform-d): 155.20, 127.72, 127.00, 125.45 (C_i, C_o, C_p, C_m, $C_6H_5Me_2CCH_2$), 152.00, 128.20, 124.80, 122 20(C_i, C_p, C_o, C_m, $C_6H_3Me_2N$), 118.60 (C_5Me_5), 83.20(H_2CCMe_2Ph), 40.11 (H_2CCMe_2Ph), 33.26, 32.42 (H_2CCMe_2Ph), 19.00(br, $Me_2C_6H_3N$), 11.25 (C_5Me_5). Anal. Found: C, 55.94; H, 6.26; N, 2.38. $C_{28}H_{37}ClNTa$. Calc.: C, 55.68; H, 6.17; N, 2.32%.

The data for **3** follow. Yield 0.52 g (70%). IR (Nujol mull, ν cm^{-1}): 1587 (m), 1326 (vs), 1213 (s), l095 (s), 1022 (m), 984 (s), 760 (vs), 565 (m), 505 (w), 429 (m), 391 (m), 349 (vs). ^1H NMR (δ ppm, in chloroform-d): 6.97 (d, 2H), 6.65 (t, 1H, $H_3C_6Me_2N$), 2.37 (s, 6H, $Me_2C_6H_3N$), 2.20, 1.10 (AB, 2H, $^2J_{H-H}$ = 13.7 Hz, H_2C–CMe_3), 2.03 (s, 15H, C_5Me_5), 1.03 (s, 9H, Me_3C–CH_2). $^{13}C\{1H\}$ NMR (δ ppm, in chloroform-d): 152.20, 127.00, 122 04(C_i, C_p, C_m, $C_6H_3Me_2N$). 118.41

(C_5Me_5), 83.75(CH_2–CMe_3), 34.74 (Me_3C–CH_2), 33.70 (Me_3C–CH_2), 19.40 (br, $Me_2C_6H_3N$), 11.20 (C_5Me_5). Anal. Found: C, 54.92; H, 6.07; N, 2.46. $C_{27}H_{35}ClNTa$ Calc.: C, 54.97; H, 5.98; N, 2.37%.

The data for **4** follow. Yield 0.47 g (60%). IR (Nujol mull, ν cm^{-1}): 1591 (m), 1324 (vs), 1196 (m), 1096 (m), 1065 (m), 1027 (s), 984 (m), 895 (m), 794 (m), 760 (s), 749 (s), 692 (m), 546 (w), 393 (m), 347 (s), 228 (m). ^{1}H NMR (δ ppm, in chloroform-d): 7.20 (t, 1H), 7.08 (t, 2H), 7.00 (d, 2H, $H_5C_6CH_2$), 6.94(d, 2H), 6.64 (t, 1H, $H_3C_6Me_2N$), 3.08, 2.40 (AB, 2H, $^2J_{H-H} = 11$ Hz, $H_2CC_6H_5$), 2.36 (s, 6H, $Me_2C_6H_3N$), 2.03 (s, 15H, C_5Me_5) ^{13}C{1H} NMR (δ ppm, in chloroform-d): 152.35–122.33 (several phenyl for $C_6H_5CH_2$ and $C_6H_3Me_2N$), 117.01 (C_5Me_5), 62.00 (H_2C–C_6H_5), 19.20 ($Me_2C_6H_3N$), 11.24 (C_5Me_5). Anal. Found: C, 53.20; H, 5.45; N, 2.47. $C_{25}H_{31}ClNTa$ Calc.: C, 53.43; H, 5.56; N, 2.49%.

The data for **5** follow. Yield 0.58 g (70%). IR (Nujol mull, ν cm^{-1}): 1585 (w), 1407 (m), 1309 (vs), 1101 (m), 1019 (m), 981 (m), 845 (m), 761 (m), 740 (m), 516 (w), 331 (s). ^{1}H NMR (δ ppm, in chloroform-d): 7.66 (m, 1H), 7.05 [m, 3H, H_4C_6-2-(CH_2NMe_2)], 6.86 (d, 2H), 6.55 (t, 1H, $H_3C_6Me_2N$), 4.22, 3.46 [AB, 2H, $^2J_{H-H} =$ 14.1 Hz, 2-(CH_2NMe_2)C_6H_4], 2.66 [s, 6H, 2-(CH_2NMe_2)C_6H_4], 2.28 (s, 6H, $Me_2C_6H_3N$), 2.00 (s, 15H, C_5Me_5). ^{13}C{1H} NMR (δ ppm, in chloroform-d): 191.26 [C_i, H_4C_6-2-(CH_2NMe_2)], 144.60, 142.75 [C_o, H_4C_6-2-(CH_2NMe_2)]. 127.24 [H_4C_6-2-(CH_2NMe_2)] 126.02, 125.05 [C_m, H_4C_6-2-(CH_2NMe_2)], 153.92, 134.78, 123.20, 121.87 (C_i, C_p, C_m, C_o, $C_6H_3Me_2$), 119.66 (C_5Me_5), 72.94 [2-(CH_2NMe_2)C_6H_4], 50.73 [2-(CH_2NMe_2)C_6H_4] 20.30($Me_2C_6H_3N$), 12.37(C_5Me_5). Anal. Found: C, 53.52; H, 6.17; N, 4.70. $C_{27}H_{36}ClN_2Ta$. Calc.: C, 53.60; H, 6.00; N, 4.63%.

Compound **6**. A solution of $LiC_5H_4SiMe_3$ (0.28 g, 1.97 mmol) in 10 ml of THF was slowly added at room temperature to a stirred freshly prepared solution of [TaCp*Cl_2{N(2,6-$Me_2C_6H_3$)}] (1.00 g, 1.97 mmol) in 30 ml of THF. The mixture was stirred for 12 h to give an orange solution. Volatiles were removed in vacuo and the residue was extracted into toluene (3 × 20 ml). The resulting orange solution was filtered, the solvent evaporated to dryness and the orange solid washed with cold *n*-hexane (2 × 5 ml), dried in vacuo and identified as **6**.

The data for **6** follow. Yield 0.78 g (65%). IR (Nujol mull, ν cm^{-1}): 1584 (w), 1407 (m), 1323 (vs), 1243 (m), 1094 (m), 1022 (m), 959 (m), 838 (m), 801 (m), 752 (m), 727 (m), 324 (w). ^{1}H NMR (δ ppm, in chloroform-d): 6.90 (d, 1H), 6.80 (d,1H), 6.40 (t, 1H, $H_3C_6Me_2N$), 6.42 (m, 1H), 6.30 (m, 1H), 6.00 (m, 1H), 5.76 (m, 1H, $H_4C_5SiMe_3$), 2.32 (s, 3H, $Me_2C_6H_3N$), 2.00 (s, 15H, C_5Me_5), 0.064 (s, 9H, $Me_3SiC_5H_4$). ^{13}C{1H} NMR (δ ppm, in chloroform-d): 130.51 (C_i, $C_6H_3Me_2N$), 128.55 (C_1, $C_5H_4SiMe_3$), 127.04, 126.84 (C_m, $C_6H_3Me_2N$), 125.95, 120.60 ($C_{2,5}$, $C_5H_4SiMe_3$), 125.04, 120.95 (C_o, $C_6H_3Me_2N$), 118.76 (C_5Me_5), 118.70(C_p,$C_6H_3Me_2N$), 109.21, 105.23 ($C_{3,4}$, $C_5H_4SiMe_3$), 19.7, 18.8 ($Me_2C_6H_3N$), 12.00 (C_5Me_5), −0.44 ($Me_3SiC_5H_4$). Anal. Found: C, 51.12; H, 6.01; N, 2.30. $C_{26}H_{37}ClNSiTa$. Calc.: C, 51.35; H, 6.13; N, 2.30%.

3.4. Synthesis of [TaCpR_2{N(2,6-$Me_2C_6H_3$)}], (R = CH_2SiMe_3, **7**; CH_2CMe_2Ph, **8**; C_6H_5, **9**; $CH_2C_6H_5$, **10**; CH_2CMe_3, **11**)*

A solution of LiR (2.76 mmol; R = CH_2SiMe_3, 0.26 g; CH_2CMe_2Ph, 0.39 g; C_6H_5, 0.23 g; CH_2CMe_3, 0.21 g) or Mg ($CH_2C_6H_5)_2(THF)_2$ (0.48 g; 1.38 mmol) in toluene or *n*-hexane(**11**) (25 ml) was added at room temperature to a solution of [TaCp*Cl_2{N(2,6-$Me_2C_6H_3$)}] (0.70 g; 1.38 mmol) in toluene or *n*-hexane(**11**) (25 ml) and the mixture was stirred for 12 h. The solvent was removed in vacuo and the residue extracted into *n*-hexane (3 × 15 ml). The solution was concentrated to ca. 20 ml and cooled to −40°C to give **7–11** as brown (**7** ,**8**, **11**), red–orange (**9**) and yellow (**10**) microcrystalline solids.

The data for **7** follow. Yield 0.59 g (70%). IR (Nujol mull, ν cm^{-1}): 1588(m), 1320 (vs), 1243 (vs), 1159 (m), 1096 (m), 1025 (m), 965 (s), 908 (s), 850 (vs), 758 (vs), 683 (s), 523 (w), 471 (w), 348 (s). ^{1}H NMR (δ ppm, in chloroform-d): 6.96 (d, 2H), 6.62 (t, 1H, $H_3C_6Me_2N$), 2.33 (s, 6H, $Me_2C_6H_3N$), 1.49 (s, 15H, C_5Me_5), 0.40, −0.84 (AB, 4H, $^2J_{H-H} = 7.69$ Hz, H_2CSiMe_3), 0.021 (s, 18H, Me_3SiCH_2). ^{13}C{1H} NMR (δ ppm, in chloroform-d): 154.1 (C_i, $C_6H_3Me_2N$), 133.31 (C_p, $C_6H_3Me_2N$), 127.00 (C_5Me_5), 120.64 (C_m, $C_6H_3Me_2N$), 115.71 (C_o, $C_6H_3Me_2N$), 61.85 (CH_2SiMe_3), 20.01 ($Me_2C_6H_3N$), 11.22 (C_5Me_5), 2.50 (Me_3SiCH_2). Anal. Found: C, 51.42; H, 7.64; N, 2.41. $C_{26}H_{46}NSi_2Ta$. Calc.: C, 51.21; H, 7.60; N, 2.30%.

The data for **8** follow. Yield 0.68 g (70%). IR (Nujol mull, ν cm^{-1}): 1593 (s), 1317 (vs), 1162 (s), 1125 (m), 1099 (s), 1066 (s), 1028 (s), 980 (s), 761 (vs), 699 (vs), 550 (m), 345 (s). ^{1}H NMR (δ ppm, in chloroform-d): 7.20 (m, 10 H, $H_5C_6Me_2CCH_2$), 7.12 (d, 2H), 6.80 (t, 1H, $H_3C_6Me_2N$), 2.57 (s, 6H, $Me_2C_6H_3N$), 2.00 (s, 15H, C_5Me_5), 1.67 (s, 6H, Me_2PhCCH_2), 1.47 (s, 6H, Me_2PhCCH_2), 1.40, −0.25 (AB, 4H, $^2J_{H-H} = 13.2$ Hz, H_2CCMe_2Ph). ^{13}C{1H} NMR (δ ppm, in chloroform-d): 154.10 (C_i, $C_6H_3Me_2N$), 153.32 (C_i, $C_6H_5Me_2CCH_2$), 133.77 (C_p, $C_6H_5Me_2CCH_2$), 127.73 (C_o, $C_6H_5Me_2CCH_2$), 127.34 (C_m, $C_6H_5Me_2CCH_2$), 125.52 (C_5Me_5), 124.81 (C_m, $C_6H_3Me_2N$), 121.17 (C_p, $C_6H_3Me_2N$), 115.46 (C_o, $C_6H_3Me_2N$), 95.40 (CH_2CMe_2Ph), 42.80 (CH_2CMe_2Ph), 35.87, 32.20 (CH_2CMe_2Ph), 20.71 ($Me_2C_6H_3N$), 11.05 (C_5Me_5). Anal. Found: C, 64.92; H, 7.08; N, 2.03. $C_{38}H_{50}NTa$. Calc.: C, 65.04; H, 7.18; N, 2.00%.

The data for **9** follow. Yield 0.63 g (70%). IR (Nujol mull, ν cm^{-1}): 1586 (m), 1317 (vs), 1157 (m), 1095 (m), 1062 (m), 1020 (m), 985 (m), 761 (vs), 725 (vs), 698 (vs), 578 (m), 455 (m), 395 (m), 350 (s). ^{1}H NMR (δ ppm, in chloroform-d): 7.60 (d, 4H), 7.12 (t, 4H), 7.03 (t, 2H, H_5C_6), 6.82 (d, 2H), 6.53 (t, 1H, $H_3C_6Me_2N$), 2.28 (s, 6H, $Me_2C_6H_3N$), 1.93 (s, 15H, C_5Me_5). ^{13}C{1H} NMR (δ ppm, in chloroform-d): 153.64(C_i, $C_6H_3Me_2N$), 141.93 (C_i, C_6H_5), 130.15 (C_p, $C_6H_3Me_2N$), 128.80 (C_p, C_6H_5), 127.55 (C_o,C_6H_5), 127.01(C_5Me_5), 125.63 (C_m, C_6H_5), 121.50 (C_m, $C_6H_3Me_2N$), 114.87 (C_o, $C_6H_3Me_2N$), 20.01 ($Me_2C_6H_3$), 11.63 (C_5Me_5). Anal. Found: C, 64.84; H, 5.30; N, 2.11. $C_{35}H_{34}NTa$. Calc.: C, 64.71; H, 5.27; N, 2.15%.

The data for **10** follow. Yield 0.60 g (70%). IR (Nujol mull, ν cm^{-1}): 1588 (m), 1312 (vs), 1199 (m), 1096 (m), 1063 (m), 1028 (m), 980 (m), 799 (m), 741 (s), 693 (s), 533 (w), 502 (w), 443 (w), 362 (s). ^{1}H NMR (δ ppm, in chloroform-d): 7.09 (m, 8H), 6.80 (m, 2H, $H_5C_6CH_2$), 6.90 (d, 2H), 6.60 (t, 1H, $H_3C_6Me_2N$), 2.40, 1.45 (AB, 4H, $^2J_{H-H} = 12.45$ Hz, $H_2CC_6H_5$), 2.02 (s, 6H, $Me_2C_6H_3$), 1.97 (s, C_5Me_5). ^{13}C{1H} NMR (δ ppm, in chloroform-d): 152.86 (C_i, $C_6H_3Me_2N$), 147.42 (C_p, C_6H_5), 133.82 (C_i, C_6H_5), 128.16 (C_o,C_6H_5), 127.53 (C_5Me_5), 126.49 (C_m,C_6H_5), 122.58 (C_m, $C_6H_3Me_2N$), 121.02 (C_p, $C_6H_3Me_2N$), 115.56 (C_o, $C_6H_3Me_2N$), 74.25 ($CH_2C_6H_5$), 18.53 ($Me_2C_6H_3$), 10.56 (C_5Me_5). Anal. Found: C, 62.17; H, 6.18; N, 2.24. $C_{32}H_{38}NTa$. Calc.: C, 62.23; H, 6.20; N, 2.27%.

The data for **11** follow. Yield 0.56 g (70%).IR (Nujol mull, ν cm^{-1}): 1586 (w), 1308 (s), 1212 (m), 1098 (m), 1024 (m), 980 (m), 758 (s), 488 (m), 346 (m). ^{1}H NMR (δ ppm, in chloroform-d): 6.97 (d, 2H), 6.63 (t, 1H, $H_3C_6Me_2N$), 2.42 (s, 6H, $Me_2C_6H_3N$), 1.89 (s, 15H, C_5Me_5), 1.76, −0.62 (AB, 4H, $^2J_{H-H} = 13.04$ Hz, CH_2CMe_3), 1.07 (s, 9H, CH_2CMe_3). ^{13}C{1H} NMR (δ ppm, in chloroform-d): 154.23 (C_i, $C_6H_3Me_2N$), 133.53 (C_p, $C_6H_3Me_2N$), 127.15 (C_m, $C_6H_3Me_2N$), 120.80 (C_o, $C_6H_3Me_2N$), 115.12 (C_5Me_5), 96.97 (CH_2CMe_3), 35.68 (CH_2CMe_3), 34.41 (CH_2CMe_3), 20.36 ($Me_2C_6H_3N$), 11.00 (C_5Me_5). Anal. Found: C, 58.12; H, 7.87; N, 2.31.$C_{28}H_{46}NTa$. Calc.: C, 58.22; H, 8.03; N, 2.42.

*3.5. Synthesis of [TaCp*MeR{N(2,6-$Me_2C_6H_3$)}], (R = CH_2SiMe_3, **12**; CH_2CMe_2Ph, **13**; C_6H_5, **14**; CH_2–CMe_3, **15**; 2-$(CH_2NMe_2)C_6H_4$, **16**; $CH_2C_6H_5$, **17**; $C_5H_4SiMe_3$, **18**)*

12–17. In a standard vacuum line, LiR (1.44 mmol; R = CH_2SiMe_3, 0.13 g; CH_2CMe_2Ph, 0.20 g; C_6H_5, 0.12 g; CH_2–CMe_3, 0.11 g; 2-$(CH_2NMe_2)C_6H_4$, 0.20 g) or $Mg(CH_2C_6H_5)_2(THF)_2$ (0.25 g; 0.72 mmol) was added to a toluene (50 ml) solution of [TaCp*ClMe{N(2,6-$Me_2C_6H_3$)}] (0.70 g; 1.44 mmol) under rigorously anhydrous conditions and the reaction mixture stirred for 12 h. The resulting suspension was filtered, the solvent evaporated to dryness and the residue extracted into *n*-hexane (2 × 10 ml). The solution was concentrated to ca. 10 ml and cooled to −40°C to yield **12–17** as yellow microcrystalline solids.

The data for **12** follow. Yield 0.46 g (60%). IR (Nujol mull, ν cm^{-1}): 1588 (m). 1333 (vs), 1243 (vs), 1158 (m), 1096 (m), 1025 (m), 959 (s), 887 (s), 852 (vs), 758 (vs), 682 (s), 610 (m), 485 (m), 350 (s). ^{1}H NMR (δ ppm, in chloroform-d): 6.96 (d, 2H), 6.61 (t, 1H, $H_3C_6Me_2N$), 2.31 (s, 6H, $Me_2C_6H_3N$), 1.96 (s, 15H, C_5Me_5), 0.23, −0.14 (AB, 2H, $^2J_{H-H} = 11$ Hz, H_2CSiMe_3), 0.08 (s, 3H, Me–Ta), −0.03 (s, 9H, Me_3SiCH_2). ^{13}C{1H} NMR (δ ppm, in chloroform-d): 153.97, 133.65, 120.60, 115.88 (C_i, C_p, C_o, C_m, $C_6H_3Me_2N$), 126.73 (C_5Me_5), 60.97 (CH_2SiMe_3), 49.24 (Me–Ta), 19.23 ($Me_2C_6H_3N$), 11.05 (C_5Me_5), 2.26 (Me_3SiCH_2). Anal. Found: C, 51.30; H, 7.12; N, 2.58. $C_{23}H_{38}NSiTa$. Calc.: C, 51.38; H, 7.12; N, 2.60%.

The data for **13** follow. Yield 0.50 g (60%). IR (Nujol mull, ν cm^{-1}): 1587 (m), 1327 (vs), 1169 (m), 1095 (m), 1027 (m), 981 (m), 763 (s), 696 (m), 551 (w), 486 (m), 349 (m). ^{1}H NMR (δ ppm, in chloroform-d): 7.28 (d, 2H), 7. 17 (t, 2H), 7.05 (t, 1H, $H_5C_6CMe_2CH_2$), 7.00 (d, 2H), 6.66 (t, 1H, $H_3C_6Me_2N$), 2.30 (s, 6H, $Me_2C_6H_3N$), 1.92 (s, 15H, C_5Me_5), 1.49 (s, 3H, Me_2PhCCH_2), 1.44 (s, 3H, Me_2PhCCH_2), 0.91, 0.60 (AB, 2H, $^2J_{H-H} = 14.5$ Hz, H_2CCMe_2Ph), −0.30 (s, 3H, Me–Ta). ^{13}C{1H} NMR (δ ppm, in chloroform-d): 154.35 (C_i, $C_6H_3Me_2N$), 140.00 (C_i, $C_6H_5CMe_2CH_2$), 133.84 (C_o, $C_6H_3Me_2N$), 127.70 (C_m, $C_6H_5CMe_2CH_2$), 126.87 (C_m, $C_6H_3Me_2N$), 125.53 (C_o, $C_6H_5CMe_2CH_2$), 124.78 (C_p,$C_6H_5CMe_2CH_2$), 120.90 (C_p, $C_6H_3Me_2N$), 116.10 (C_5Me_5), 91.23 (CH_2CMe_2Ph), 50.99 (Me–Ta), 40.08 (CH_2CMe_2Ph), 35.60, 32.11 (CH_2CMe_2Ph), 19.48 ($Me_2C_6H_3N$), 10.97 (C_5Me_5). Anal. Found: C, 59.61; H, 6.97; N, 2.41. $C_{29}H_{40}NTa$ Calc.: C, 59.70; H, 6.91; N, 2.40%.

The data for **14** follow. Yield 0.46 g (60%). IR (Nujol mull, ν cm^{-1}): 1586 (m) 1328 (vs), 1158 (m), 1095 (m), 1066 (m), 1025 (m), 982 (m), 762 (s), 726 (s), 700 (m), 592 (m), 484 (m), 347 (s). ^{1}H NMR (δ ppm, in chloroform-d): 7.33 (d, 2H), 7.27 (t, 2H), 7.12 (t, 1H, H_5C_6), 6.97 (d, 2H), 6.62 (t, 1H, $H_3C_6Me_2N$), 2.45 (s, 6H, $Me_2C_6H_3N$), 1.94 (s, 15H, C_5Me_5), 0.69 (s, 3H, Me–Ta). ^{13}C{1H} NMR (δ ppm, in chloroform-d): 200.36 (C_i, C_6H_5), 153.90 (C_i, $C_6H_3Me_2N$), 135.18 (C_m, $C_6H_3Me_2N$), 134.36 (C_p, C_6H_5), 128.23 (C_o, $C_6H_3Me_2N$), 127.38 (C_m, C_6H_5), 126.92 (C_o, C_6H_5), 121.40 (C_p, $C_6H_3Me_2N$), 117.90 (C_5Me_5), 49.60 (Me–Ta), 19.75 ($Me_2C_6H_3N$), 11.14 (C_5Me_5). Anal. Found: C, 57.98; H, 4.38; N, 2.69. $C_{25}H_{32}NTa$. Calc.: C, 58.03; H, 4.30; N, 2.71%.

The data for **15** follow. Yield 0.45 g (60%). IR (Nujol mull, ν cm^{-1}): 1587 (m), 1324 (vs), 1261 (m), 1216 (m), 1158 (m), 1095 (m), 1025 (m), 982 (m), 803 (m), 758 (s), 532 (m), 471 (m), 349 (s), 253 (m). ^{1}H NMR (δ ppm, in

chloroform-d): 7.00 (d, 2H), 6.65 (t, 1H, $H_3C_6Me_2N$), 2.36 (s, 6H, $Me_2C_6H_3N$), 1.95 (s, 15H, C_5Me_5), 1.00 (s, 9H, Me_3CCH_2), 0.70, −0.015 (AB, 2H, $^2J_{H-H}=14.65$ Hz, H_2CCMe_3), 0.11 (s, 3H, Me–Ta). $^{13}C\{1H\}$ NMR (δ ppm, in chloroform-d): 153.87, 127.73, 126.84, 120.69 (C_i, C_p, C_o, C_m, $C_6H_3Me_2N$), 115.95 (C_5Me_5), 93.64 (CH_2CMe_3), 49.32 (Me–Ta), 34.84 (CH_2CMe_3), 33.66 (CH_2CMe_3), 20.10, 19.56 ($Me_2C_6H_3N$), 10.95 (C_5Me_5). Anal. Found: C, 55.27; H, 7.30; N, 2.64. $C_{24}H_{38}NTa$ Calc.: C, 55.27; H, 7.34; N, 2.68.

The data for **16** follow. Yield 0.57 g (60%). IR (Nujol mull, ν cm^{-1}): 1586 (m), 1317 (vs), 1165 (m), l099 (m), 1015 (m), 981 (s), 865 (m), 841 (s), 737 (s), 578 (m), 510 (m), 461 (m), 334 (m). ^1H NMR (δ ppm, in chloroform-d): 7.98 (m, 1H),7.11 (m, 1H), 7.03 [m, 2H, H_4C_6-2-(CH_2NMe_2)], 6.87 (d, 2H), 6.57 (t, 1H, $H_3C_6Me_2N$), 3.95, 3.36 [AB, 2H, $^2J_{H-H}=13.5$ Hz, H_4C_6-2-(CH_2NMe_2)], 2.35 [s, 6H, H_4C_6-2-(CH_2NMe_2)], 2.35 (s, 6H, $Me_2C_6H_3N$), 1.85 (s, 15H, C_5Me_5), 0.24 (s, 3H, Me–Ta). $^{13}C\{1H\}$NMR (δ ppm, in chloroform-d): 194.00[C_1, C_6H_4-2-(CH_2NMe_2)], 155.15 (C_i, $C_6H_3Me_2N$), 144.63, 144.26 [$C_{2,6}$, C_6H_4-2-(CH_2NMe_2)], 134.21 (C_p, $C_6H_3Me_2N$), 127.26 [C_4, C_6H_4-2-(CH_2NMe_2)]. 124.85, 124.56 [$C_{3,5}$, C_6H_4-2-(CH_2NMe_2)], 123.04(C_m, $C_6H_3Me_2N$), 120.10(C_o, $C_6H_3Me_2N$), 116.10 (C_5Me_5), 74.30 [C_6H_4-2-(CH_2NMe_2)], 50.00 [C_6H_4-2-(CH_2NMe_2)], 35.10 (Me–Ta), 20.48 ($Me_2C_6H_3N$), 11.87(C_5Me_5). Anal. Found: C, 61.97; H, 6.31; N, 4.28. $C_{28}H_{39}N_2Ta$ Calc.: C, 62.00; H, 6.27; N, 4.25.

The data for **17** follow. Yield 0.47 g (60%). IR (Nujol mull, ν cm^{-1}): 1585 (w), 1326 (vs), 1200 (w), 1165 (m), 1091 (m), 1024 (m), 979 (m), 795 (m), 755 (s), 691 (m), 497 (m), 455 (m), 352 (m). 1H NMR (δ ppm, in chloroform-d): 7.06 (d, 2H), 6.76 (t, 1H, $H_3C_6Me_2N$), 6.89 (vbr, 5H, $H_5C_6CH_2$), 3.17, 1.95 (AB, 2H, $^2J_{H-H}=$ 9.5 Hz, $H_2CC_6H_5$), 2.49 (s, 6H, $Me_2C_6H_3N$), 1.70 (s, 15H, C_5Me_5), −0.38 (s, 3H, Me–Ta). $^{13}C\{1H\}$NMR (δ ppm, in chloroform-d): 154.02 (C_i, $C_6H_3Me_2N$), 134.12 (C_i, $C_6H_5CH_2$), 132.70 (C_p, $C_6H_5CH_2$) 130.76 (C_o, $C_6H_3Me_2N$), 129.14 (C_m, $C_6H_5CH_2$), 126.82 (C_o, $C_6H_5CH_2$). 126.22 (C_m, $C_6H_3Me_2N$), 120.85 (C_p, $C_6H_3Me_2N$), 114.23 (C_5Me_5), 61.34 ($CH_2C_6H_5$), 33.58 (Me–Ta), 19.27 ($Me_2C_6H_3N$), 11.02 (C_5Me_5). Anal. Found: C, 57.72; H, 6.27; N, 2.56. $C_{26}H_{34}NTa$. Calc.: C, 57.67; H, 6.33; N, 2.58.

18. A solution of $LiC_5H_4SiMe_3$ (0.21 g; 1.44 mmol) in THF (10 ml) was added dropwisely at room temperature to a stirred orange solution of [TaCp*ClMe{N(2,6-$Me_2C_6H_3$)}] (0.70 g; 1.44 mmol) in THF (30 ml). The mixture was stirred for 12 h. Subsequently, the suspension was evaporated to dryness and the residue extracted into toluene (2×10 ml). The solution was concentrated to ca. 10 ml, *n*-hexane (5 ml) added and cooled to −40°C overnight to give a microcrystalline brown–orange solid identified as **18**.

The data for **18** follow. Yield 0.51 g (60%). IR (Nujol mull, ν cm^{-1}): 1585 (m), 1328 (vs), 1243 (vs), 1179 (m), 1094 (s), 1024 (s), 955 (s), 835 (s), 753 (s), 693 (s), 633 (s), 597 (m), 560 (m), 476 (m), 417 (s), 338 (vs), 253 (m). ^1H NMR (δ ppm, in chloroform-d): 6.85 (d, 1H), 6.74 (d, 1H), 6.32 (t, 1H, $H_3C_6Me_2N$), 6.10 (m, 1H), 6.07 (m, 1H), 6.04 (m, 1H), 5.24 (m, 1H, $H_4C_5SiMe_3$), 2.35 (s, 3H, $Me_2C_6H_3N$), 1.869 (s, 3H, $Me_2C_6H_3N$), 1.863 (s, 15H, C_5Me_5), 0.45 (s, 3H, Me–Ta), −0.09 (s, 9H, $Me_3SiC_5H_4$). $^{13}C\{1H\}$ NMR (δ ppm, in chloroform-d): 156.63 (C_i, $C_6H_3Me_2N$), 128.56 (C_1, $C_5H_4SiMe_3$), 126.82, 126.78 (C_m, $C_6H_3Me_2N$), 122.43 (C_5Me_5), 124.74, 117.55 (C_o, $C_6H_3Me_2N$), 116.93, 115.40 ($C_{2,5}$, $C_5H_4SiMe_3$), 114.49 (C_p, $C_6H_3Me_2N$), 106.11, 105.31 ($C_{3,4}$, $C_5H_4SiMe_3$), 19.54, 19.02 ($Me_2C_6H_3N$), 11.60 (C_5Me_5), 0.46 ($Me_3SiC_5H_4$). Anal. Found: C, 55.14; H, 6.83; N, 2.40. $C_{27}H_{40}NSiTa$ Calc.: C, 55.19; H, 6.86; N, 2.38.

Table 3
Crystal data and structure refinement for **6**

Empirical formula	$C_{26}H_{37}ClNSiTa$
Formula weight	608.06
Temperature (K)	293(2)
Wavelength (Å)	0.71073
Crystal system	Monoclinic
Space group	$P2_1/c$
Unit cell dimensions	
a (Å)	12.597(3)
b (Å)	11.338(2)
c (Å)	18.297(4)
α (°)	90
β (°)	96.53(3)
γ (°)	90
Volume (Å^3)	2596.3(10)
Z	4
d_{calc} (g cm^{-3})	1.556
Absorption coeffficient (mm^{-1})	4.395
$F(000)$	1216
Crystal size (mm)	$0.35\times0.33\times0.28$
θ range for data collection	3.17–24.98°
Index ranges	$-15<h<0$, $-13<k<0$, $-21<l<21$
Reflections collected	4846
Independent reflections	4546 ($R_{int}=0.0163$)
Observed reflections [$F>4\sigma(F)$]	3931
Absorption correction	Ψ Scan
Max. and min. transmission	0.278 and 0.238
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	4537/0/271
Goodness-of-fit on F^2	0.908
Final R indices [$I>2\sigma(I)$]	$R_1=0.0224$, $wR^2=0.0574$
R indices (all data)	$R_1=0.0422$, $wR^2=0.1382$
Weighting scheme (calc.)	$w=1/[\sigma^2(F_o^2)+(0.0365P)^2+6.4510P]$
where $P=(F_o^2+2F_c^2)/3$	
Largest difference peak and hole (e Å^{-3})	0.449 and −0.798

3.6. X-ray data collection, structure determination and refinement for compound **6**

Crystallographic and experimental details of the crystal structure determination are given in Table 3. A suitable crystal of complex **6** was mounted on an Enraf–Nonius CAD-4 automatic four-circle diffractometer with bisecting geometry, equipped with a graphite-oriented monochromator and Mo–K_α radiation ($\lambda = 0.71073$ Å). Data were collected at room temperature. Intensities were corrected for Lorentz and polarization effects in the usual manner. Absorption was corrected by Ψ scans technique (max. and min. transmission factors 0.278 and 0.238, respectively). No extinction correction was made.

The structure was solved by direct methods (SHELXS 90) [39] and refined by full-matrix least-squares against F^2 (SHELXL 93) [40]. All non-hydrogen atoms were refined anisotropically. In the last cycle of refinement, the hydrogen atoms were positioned geometrically and refined using a riding model with fixed thermal parameters.

Calculations were carried out on an ALPHA AXP (Digital) workstation.

4. Supplementary material available

Tables of positional parameters of all atoms (Table S1, 1 page), anisotropic displacement parameters expressions (Table S2, 1 page), complete bond distances and angles (Table S3, 1 page), hydrogen coordinates (Table S4, 1 page) and structure factors (Table S5, 11 pages) for complex **6** are available. Ordering information is given on any current masthead page.

Acknowledgements

We are grateful to DGICYT (Project PB-92-0178-C) and to Universidad de Alcalá (Project E001/97) for financial support of this research.

References

[1] W.A. Nugent, J.M. Mayer, Metal–Ligand Multiple Bonds, Wiley, New York, 1988.
[2] W.A. Nugent, B.L. Haymore, Coord. Chem. Rev. 31 (1980) 123.
[3] D.E. Wigley, Prog. Inorg. Chem. 42 (1994) 239.
[4] D.S. Williams, M.H. Schofield, R.R. Schrock, Organometallics 12 (1993) 4560.
[5] V.C. Gibson, J. Chem. Soc. Dalton Trans. (1994) 1607.
[6] S.G. Bott, D.M. Hoffman, S.P. Rangarajan, Inorg. Chem. 34 (1995) 4305.
[7] P.J. Stewart, A.J. Blake, P. Mountford, lnorg. Chem. 36 (1997) 1982.
[8] J.S. Freundlich, R.R. Schrock, W.M. Davis, J. Am. Chem. Soc. 118 (1996) 3643.
[9] J.S. Freundlich, R.R. Schrock, C.C. Cummins, W.M. Davis, J. Am. Chem. Soc. 116 (1994) 6476.
[10] W.A. Herrmann, W. Baratta, J. Organomet. Chem. 506 (1996) 357.
[11] V.C. Gibson, A.D. Poole, J. Chem. Soc. Chem. Commun. (1995) 2261.
[12] T.C. Baldwin, S.R. Huber, M.A. Bruck, D.E. Wigley, Inorg. Chem. 32 (1993) 5682.
[13] D.N. Williams, J.P. Mitchell, A.D. Poole, U. Siemeling, W. Clegg, D.C.R. Hockless, P.A. O'Neil, V.C. Gibson, J. Chem. Soc. Dalton Trans. (1992) 739.
[14] S. Schmidt, J. Sundermeyer, J. Organomet. Chem. 427 (1994) 127.
[15] W.A. Herrmann, W. Baratta, E. Herdtweck, Angew. Chem. Int. Ed. Engl. 35 (1996) 1951.
[16] A. Antiñolo, P. Espinosa, M. Fajardo, P. Gómez-Sal, C. López-Mardomingo, A. Martín, A. Otero, J. Chem. Soc. Dalton Trans. (1995) 1007.
[17] G. Proulx, R.G. Bergman, Organometallics 15 (1996) 684.
[18] D.M. Antonelli, W.P. Schaefer, G. Parkin, J.E. Bercaw, J. Organomet. Chem. 462 (1993) 213.
[19] M.L.H. Green, J.J. James, J.F. Sanders, J. Chem. Soc. Chem. Commun. (1996) 1343.
[20] M.L.H. Green, J.J. James, A.N. Chernega, J. Chem. Soc. Dalton Trans. (1997) 1719.
[21] M.L.H. Green, J.J. James, J.F. Sanders, J. Souter, J. Chem. Soc. Dalton Trans. (1997) 1281.
[22] M.V. Galakhov, M. Gómez, G. Jimenez, P. Royo, M.A. Pellinghelli, A. Tiripicchio, Organometallics 14 (1995) 1901.
[23] M. Gómez, P. Gómez-Sal, G. Jimenez, A. Martín, P. Royo, J. Sánchez-Nieves, Organometallics 15 (1996) 3579.
[24] D.C. Bradley, M.B. Hursthouse, A.J. Howes, A.N. de M. Jelfs, J.D. Runnacles, M. Thornton-Pett, J. Chem. Soc. Dalton Trans. (1991) 841.
[25] S. Abragam, The Principles of Nuclear Magnetism, Clarendon, Oxford, 1961.
[26] K.M. Jackman, F.A. Cotton, DNMR Spectroscopy, Academic Press, New York, 1975.
[27] (a) S.J. McLain, C.D. Wood, R.R. Schrock, J. Am. Chem. Soc. 101 (1979) 4558. (b) J.M. Mayer, C.J. Curtis, J.E. Bercaw, J. Am. Chem. Soc. 105 (1983) 2651. (c) P. Kubácek, R. Hoffman, Z.Havlas, Organometallics 1 (1982) 180. (d) I. de Castro, M.V. Galakhov, M. Gómez, P. Gómez-Sal, A. Martín, P. Royo, J. Organomet. Chem. 514 (1996) 51.
[28] G.R. Newkome, W.E. Puckett, V.K. Gupta, G.E. Kiefer, Chem. Rev. 86 (1986) 451 and references therein.
[29] I. de Castro, M.V. Galakhov, M. Gómez, P. Gómez-Sal, P. Royo, Organometallics 15 (1996) 1362.
[30] G. Parkin, A. van Asselt, D.J. Leahy, L. Whinnery, N.G. Hua, R.W. Quan, L.M. Henling, W.P. Schaefer, B.D. Santarsiero, J.E. Bercaw, lnorg. Chem. 31 (1992) 82.
[31] K.A. Jørgensen, Inorg. Chem. 32 (1993) 1521.
[32] J.-K.F. Buijink, A. Meetsma, J.H. Teuben, H. Kooijman, A.L. Speck, J. Organomet. Chem. 497 (1995) 161.
[33] C. Tessiers-Youngs, O.T. Beachley Jr., Inorg. Synth. 24 (1986) 95.
[34] LiPh was prepared in situ by reaction of iodobenzene C_6H_5I and *n*-butil lithium $LiBu^n$ in a 1:1 molar ratio at 0°C and using a n-pentane/n-hexane mixture as solvent.
[35] J.T.B.H. Jastrzebski, G. van Koten, Inorg. Synth. 26 (1989) 152.
[36] F. Jutzi, R. Sauer, J. Organomet. Chem. 50 (1973) 29.
[37] R.R. Schrock, J. Organomet. Chem. 122 (1976) 209.
[38] M.V. Galakhov, M. Gómez, G. Jimenez, P. Royo, M.A. Pellinghelli, A. Tiripicchio, Organometallics 14 (1995) 2843.
[39] G.M. Sheldrick, Acta Crystallogr. Sect. A 46 (1990) 467.
[40] G.M. Sheldrick, SHELXL 93, University of Gottingen, Germany, 1993.