

1-Aza-1,3-butadiene complexes of tantalum: preparation and alkylation of $\text{TaCl}_2(\eta^5\text{-C}_5\text{Me}_5)(\eta^4\text{-1-aza-1,3-butadiene})$

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Dedicated to Professor Fausto Calderazzo on the occasion of his 70th birthday and for his contribution in organometallic and inorganic chemistry.

Abstract

We have synthesized half-metallocene 1-aza-1,3-butadiene (abbr. AD) complexes of tantalum and have demonstrated the unique coordination mode and reactivity of the AD ligand. Treatments of a dimeric complex $[\text{TaCl}_2\text{Cp}^*]_2$ (**2**) (Cp^* = pentamethylcyclopentadienyl) with one equivalent of 1,4-diphenyl-1-aza-1,3-butadiene (abbr. Ph-AD) and 1-*p*-methoxyphenyl-4-phenyl-1-aza-1,3-butadiene (abbr. *p*-MeOC₆H₄-AD) afforded purple complexes of the formula $\text{TaCl}_2\text{Cp}^*(\text{supine-}\eta^4\text{-AD})$ (**3**: AD = Ph-AD; **4**: AD = *p*-MeOC₆H₄-AD), whose formulation and supine- η^4 -coordination mode with a contribution of $\eta^1\text{-N-}\eta^3$ -allyl canonical form were elucidated by their combustion analysis and NMR spectroscopy along with the X-ray crystal structure determination for the complex **3**. Reaction of **3** with one equivalent of MgMe_2 gave a dimethyl complex $\text{TaMe}_2\text{Cp}^*(\text{supine-}\eta^4\text{-Ph-AD})$ (**6**) in 96% yield, whereas the methylation reaction using MeLi or MeMgX did not afford **6**. Benzoylation of **3** and **4** using one equivalent of $\text{Mg}(\text{CH}_2\text{Ph})_2$ in toluene led to the formation of dibenzyl complexes $\text{Ta}(\text{CH}_2\text{Ph})_2\text{Cp}^*(\eta^2\text{-C,N-AD})$ (**9**: AD = Ph-AD; **11**: AD = *p*-MeOC₆H₄-AD) in modest yield, while reaction of **3** with 0.5 equivalent of $\text{Mg}(\text{CH}_2\text{Ph})_2$ gave a monobenzylated complex $\text{TaCl}(\text{CH}_2\text{Ph})\text{Cp}^*(\text{supine-}\eta^4\text{-Ph-AD})$ (**13**). When complex **3** reacted with one equivalent of $\text{Mg}(\text{CH}_2\text{Ph})_2$ in THF, we obtained a product mixture of **9** and a metallacyclic tantalum-carbene complex **10**. Similarly, reaction of **4** with $\text{Mg}(\text{CH}_2\text{Ph})_2$ in THF gave **11** and a metallacyclic tantalum-carbene complex **12**. The carbene complexes **10** and **12** might be respectively derived from nascent benzylidene species, $\text{Ta}(\text{=CHPh})\text{Cp}^*(\eta^4\text{-AD})$ (**14**: AD = Ph-AD; **15**: AD = *p*-MeOC₆H₄-AD), which may abstract the H⁴ proton of the AD ligand. © 2000 Elsevier Science S.A. All rights reserved.

Keywords: Tantalum; 1-Aza-1,3-butadiene; Half sandwich complex; Crystal structure; Alkylidene complex

1. Introduction

Metallocene complexes of early transition metals have attracted much interest owing to their potential applicability as catalysts of various organic reactions as well as polymerization, and as source of versatile materials [1,2]. Half-metallocene complexes, in which one Cp ligand of the metallocene is replaced by different kinds of ancillary ligand, are another attracting system that are more flexible and feasible in design of the desired catalyst system. We have been interested in the half-metallocene complexes of niobium and tantalum and we have chosen diene as the ancillary ligand. The

diene complexes having ‘ $\text{M}(\eta^5\text{-C}_5\text{R}_5)(\eta^4\text{-1,3-diene})$ ’ fragments are isoelectronic and isolobal to Group 4 metallocene fragments ‘ MCp_2 ’, which are 14 electron species. We had found not only that these metallocene-like fragments stabilized various reactive species such as benzyne [3] similar to the corresponding metallocene complexes of Group 4 metals, but also that *cis*-dialkyl derivatives were catalyst precursors for the living polymerization of ethylene [4–6] and the stereoselective ROMP of norbornene [7–9]. We recently have reported that 1,4-diaza-1,3-butadiene ligands [10,11] coordinated to the half-metallocene fragment of niobium and tantalum exhibited unique coordination features [12,13].

As an extension of our continuous synthesis of half-metallocene complexes of Group 5 metals, we have synthesized 1-aza-1,3-butadiene (abbr. AD) complexes

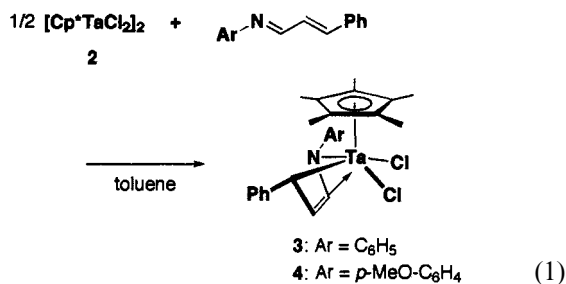
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of tantalum, whose structure and alkylation reactions are reported comparing with the precedent AD complexes of titanium and zirconium [14–18].

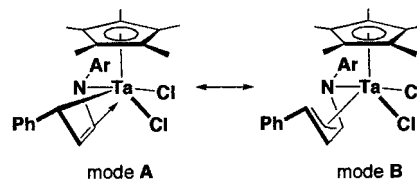
2. Results and discussion

2.1. Synthesis and characterization of dichloro-AD complexes of tantalum

Simple reduction of a tetrachloro compound of tantalum, TaCl_4Cp^* (**1**) (Cp^* = pentamethylcyclopentadienyl), by using lithium dispersion in the presence of 1,4-diphenyl-1-aza-1,3-butadiene (abbr. Ph-AD) gave an unidentified mixture of products. We thus chose a stepwise synthetic route starting from a dinuclear Ta(III) complex, $[\text{TaCl}_2\text{Cp}^*]_2$ (**2**) [19,20], which can be readily derived from the amalgam reduction of the complex **1**. When the toluene solution of **2** was treated with two equivalents of Ph-AD, the deep green colour of **2** faded out and a purple complex $\text{TaCl}_2\text{Cp}^*(\text{supine-}\eta^4\text{-Ph-AD})$ (**3**) was formed in quantitative yield, monitored by the $^1\text{H-NMR}$ spectrum, and **3** was isolated in modest yield (Eq. (1)). Similarly, reaction of **2** with two equivalents of 1-*p*-methoxyphenyl-4-phenyl-1-aza-1,3-butadiene (abbr. *p*-MeOC₆H₄-AD) in toluene afforded a purple complex $\text{TaCl}_2\text{Cp}^*(\text{supine-}\eta^4\text{-}p\text{-MeOC}_6\text{H}_4\text{-AD})$ (**4**) in 81% yield.

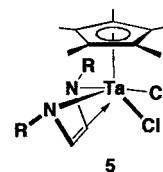


These complexes are air- and moisture-sensitive both in solution and as solids. The formulation and structure of **3** and **4** was revealed by elemental analyses and NMR spectroscopy along with a single crystal X-ray analysis of **3** (vide infra). The $^1\text{H-NMR}$ spectra of **3** and **4** in benzene-*d*₆ show signals due to the AD ligand and the Cp* ligand in an exact 1:1 ratio. Noteworthy is that the terminal H⁴ proton of the AD ligand displays a doublet resonance at much lower-field shift (δ 4.38–5.01), almost the olefinic region, compared with the corresponding signal found for the σ^2 , π -Ph-AD complexes of titanocene (δ 0.66–1.67) [16] and zirconocene (δ 0.94–1.55) [15], and even for the typical η^4 -Ph-AD complexes of late transition metals (δ 2.12–3.45) [21–24]. Thus, this chemical shift value of the H⁴ proton strongly suggests that a Ta–C⁴ bond does not have a σ -bond character, but that there is a π -bonding be-



Scheme 1.

tween the tantalum atom and the C⁴ atom. The chemical shift value (δ 4.09–4.53) of the inner H² proton of the AD ligand is higher-field shifted compared with that (δ 6.00–6.09) of the inner protons found for the η^4 -1,4-diaza-1,3-butadiene ligand of tantalum complexes $\text{TaCl}_2\text{Cp}^*(\text{supine-}\eta^4\text{-R}_2\text{-DAD})$ (**5**) ($\text{R}_2\text{-DAD}$ = 1,4-R₂-1,4-diaza-1,3-butadiene) [12,13,25], while the chemical shift value (δ 6.67–6.79) of the inner H³ proton of the AD ligand is comparable with that (δ 7.09) of the corresponding inner protons found for 1,3-butadiene coordinated in supine- η^4 -fashion to ‘ TaCl_2Cp^* ’ moiety [26]; both H² and H³ chemical shift values of **3** and **4** indicate that the inner carbon atoms of the AD ligand interact in π -bonding with the metal center. Thus, the AD ligand of **3** and **4** proves to have a significant contribution of a $\eta^1\text{-N-}\eta^3\text{-allyl}$ canonical form (Scheme 1, mode B).



For half-metallocene complexes, two conformations of the *s-cis*- η^4 -1-aza-1,3-diene ligand, i.e. supine and prone, in the direction of the cyclopentadienyl ligand are possible. Fig. 1 shows a crystal structure of **3**; the direction of the Ph-AD ligand of **3** points toward the Cp* ligand (supine conformation). The complex **3** adopts four-legged piano-stool geometry comprised of the Cp* ligand as a cap and two chloride atoms, one

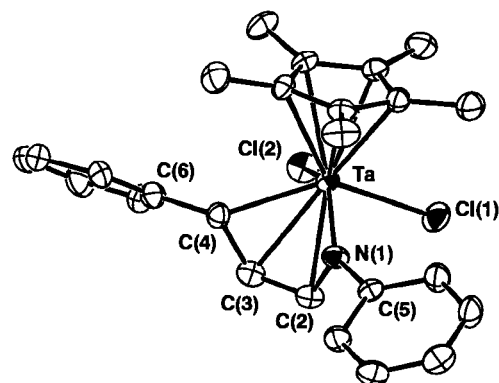


Fig. 1. Molecular Structure of **3** with the labeling scheme.

Table 1
Selected bond distances and angles for complexes **3**

Bond distance (Å)			
Ta–N(1)	2.010(7)	Ta–C(2)	2.364(8)
Ta–C(3)	2.437(9)	Ta–C(4)	2.312(8)
Ta–Cl(1)	2.457(2)	Ta–Cl(2)	2.443(2)
N(1)–C(2)	1.41(1)	N(1)–C(5)	1.42(1)
C(2)–C(3)	1.39(1)	C(3)–C(4)	1.41(1)
C(4)–C(6)	1.50(1)	Ta–CCP ^a	2.105
Bond angles (°)			
N(1)–Ta–C(4)	78.7(3)	Cl(1)–Ta–Cl(2)	80.85(8)
N(1)–Ta–Cl(1)	87.8(2)	C(4)–Ta–Cl(2)	84.2(2)
N(1)–C(2)–C(3)	115.0(8)	C(2)–C(3)–C(4)	122.9(8)
Ta–N(1)–C(2)	85.4(5)	Ta–N(1)–C(5)	150.4(6)
C(2)–N(1)–C(5)	116.7(7)	Ta–C(4)–C(3)	77.7(5)
Ta–C(4)–C(6)	136.5(6)	C(3)–C(4)–C(6)	120.0(8)
Fold angle ^b	103.8(3)		

^a CCP: centroid of cyclopentadienyl ring.

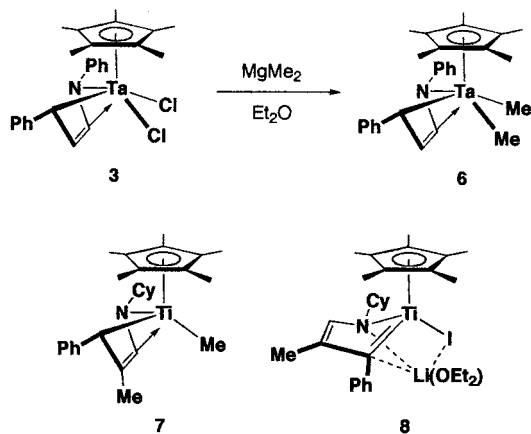
^b Fold angle: dihedral angle between the N(1)–Ta–C(4) plane and N(1)–C(2)–C(3)–C(4) plane.

C(4) atom, and one N(1) atom as four legs. Selected bond distances and angles for **3** are listed in Table 1. The distance [2.010(7) Å] of Ta–N(1) is comparable with that [2.000(4)–2.045(5) Å] found for the complexes **5** [13], which are definitely shorter than Ta–amine bonds [27] but are longer than Ta–imido bonds [28]. The distance [2.312(8) Å] of Ta–C(4) bond is slightly shorter than that [2.364(8) Å] of the Ta–C(2) bond and is much shorter than that [2.437(9) Å] of the Ta–C(3). The Ta–C(2) and Ta–C(3) bond distances are shorter than the corresponding Ta–C_{inner} distances [2.451(7)–2.48(2) Å] of the R₂DAD ligand for **5** [13]. The fold angle [103.8(3)°] between the planes defined by the atoms Ta, N(1), C(4) and N(1), C(2), C(3), C(4) is narrower than the corresponding fold angle (120.06–121.35°) found for **5** [13]; hence these three Ta–C bonds are short enough for the metal to make the π -bonding interaction with these three carbons. These findings suggest that the AD ligand coordinates to the tantalum atom with the contribution of the η^1 -N- η^3 -allyl canonical form (Scheme 1, mode B). The asymmetric environment on the tantalum atom results in the different Ta–Cl bonds; the Ta–Cl(1) distance (2.457(2) Å) *trans* to C(4) is slightly longer than the Ta–Cl(2) distance [2.443(2) Å] *trans* to N(1). The N(1)–C(2) [1.41(1)], C(2)–C(3) [1.39(1) Å] and C(3)–C(4) [1.41(1) Å] bonds are almost the same within standard deviation, being in contrast to the long–short–long alternation found for 1,3-butadiene ligand bound to early transition metals [26].

2.2. Alkylation of dichloro-AD complexes of tantalum

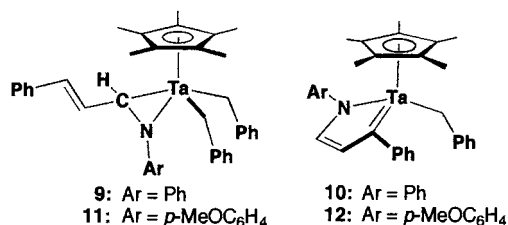
Treatment of **3** with one equivalent of MgMe₂ in diethyl ether resulted in the formation of a dimethyl complex TaMe₂Cp*(supine- η^4 -Ph-AD) (**6**) in 96%

yield (Eq. 2). Complex **6** can also be derived from one-pot reaction of **1** with two equivalents of Li metal, one equivalent of Ph-AD, and one equivalent of MgMe₂, though the chemical yield was poor (12%). In the case of methylation using MeLi or MeMgX, the reaction gave a complicated mixture including low valent tantalum species and **6**. The methyl complex **6** was thermally stable both in solution and as solids, being in sharp contrast to the reported stability of the methyl analogy of titanium, TiMeCp(supine- η^4 -CyN=CHCMe=CHPh) (**7**), which gradually decomposed via α -hydrogen elimination to give a metallacyclic titanium–carbene complex **8** [18]. The ¹H-NMR spectrum of **6** in benzene-*d*₆ exhibited two singlet signals due to two magnetically non-equivalent Ta–CH₃ protons at δ 0.10 and 0.14. The ¹H and ¹³C-NMR spectral data for the Ph-AD ligand of **6** are quite similar to those of **3**; the terminal H⁴ proton resonance (δ 4.91) of the Ph-AD ligand of **6** is also shifted to much lower-field compared with the related η^4 -Ph-AD complexes of transition metals [21–24]. The H³ proton resonances appear at the olefinic region (δ 6.43), and the resonance of imine–H² proton is observed in higher field (δ 3.84). The *J*_{C–H} values (168 Hz for C², 155 Hz for C³, 149 Hz for C⁴) for the skeleton of the AD ligand are comparable to those in **3**. Thus, it is likely assumed that the Ph-AD ligand of **6** also adopts the supine- η^4 -coordination mode with the contribution of the η^1 -N- η^3 -allyl canonical form.



Benzylation of the dichloro complexes **3** and **4** gave several interesting tantalum complexes having the AD ligand, depending on the reaction conditions, i.e. stoichiometry and solvent. When the reaction of **3** with one equivalent of Mg(CH₂Ph)₂ in toluene afforded a dibenzyl complex Ta(CH₂Ph)₂Cp*(η^2 -C,N-Ph-AD) (**9**) in quantitative yield. In contrast to the reaction carried out in toluene solution, the same reaction in THF led to the mixture of **9** (77%) and a metallacyclic tantalum–carbene complex **10** (23%), whose structure is similar to **8**, monitored by ¹H-NMR spectroscopy. The complex **10** could not be isolated due to the contamina-

tion with **9**; hence its structure is based on the comparison of its $^1\text{H-NMR}$ spectrum with that of **8** [18].

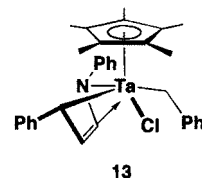


The ^1H and $^{13}\text{C-NMR}$ spectra of **9** in benzene-*d*₆ clearly indicate a rare $\eta^2\text{-C,N}$ -imine coordination mode of the AD ligand; some late transition metals have been reported to favor $\eta^2\text{-C,C-AD}$ or $\eta^1\text{-N-AD}$ coordination modes [29]. The H² proton resonance appears in a higher-field (δ 3.07) and the C² resonance of the Ph-AD ligand appears at δ 77.6 (159 Hz), both chemical shift values clearly indicating that the C=N moiety is bound in η^2 -fashion to the tantalum atom [13,26,30–32]. The H³ and H⁴ proton resonances in THF-*d*₈ are observed in olefinic region [δ 6.35 (dd, H³) and 6.25 (d, H⁴) with a trans coupling constant (16.1 Hz)] and the C=C double bond of the AD ligand is free from coordination. Two benzylic proton resonances are observed as two ABq-type signals. In the $^{13}\text{C-NMR}$ spectrum of **9**, two signals due to the two non-equivalent benzylic carbons are displayed at δ 78.5 and 80.2 with a normal coupling constants (118 and 121 Hz, respectively) for $J_{\text{C-H}}$, the chemical shift values which are comparable to those of the known benzyl complexes of tantalum, e.g. Ta(CH₂Ph)₂Cp*(η^4 -butadiene) (δ 70.6, 117 Hz) [9], Ta(CH₂Ph)₂(=CHPh)Cp* (δ 71.8, 120 Hz) [33], TaCl₂(CH₂Ph)₂Cp* (δ 97.3, 123 Hz) [33], TaCl₂(CH₂CMe₃)(CH₂Ph)Cp (*cis*-isomer: δ 96, 126 Hz; *trans*-isomer: δ 98.6, 128 Hz) [34], and TaCl₃(CH₂Ph)₂(PMe₃)₂ (δ 82; 133 Hz) [35], except for the highly shielded complex of Ta(=CHPh)(CH₂Ph)Cp₂ (δ 28.2, 123 Hz) [36].

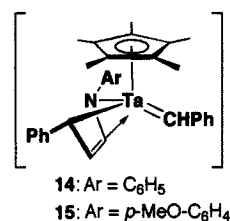
Reaction of **4** with Mg(CH₂Ph)₂ gave the same result, producing a dibenzyl complex **11** in toluene and the mixture of **11** and a metallacyclic tantalum-carbene complex **12** in THF. The complex **11** was isolated in 43% yield, while **12** was spectroscopically characterized. Thus, the complexes **10** and **12** are second metallacyclic carbene complexes that are derived from the α -hydrogen abstraction of the AD ligand.

When the amount of Mg(CH₂Ph)₂ was reduced to half, a monobenzylated complex TaCl(CH₂Ph)Cp*(supine- η^4 -Ph-AD) (**13**) in THF was obtained in 13% yield. The complex **13** was characterized by NMR spectroscopy as well as combustion analysis. The NOESY experiment allowed us to predict that **13** has the supine- η^4 -Ph-AD ligand and that the benzyl group is *trans* to the C⁴ atom. The H⁴ resonance (δ 2.93) of Ph-AD in **13** is upfield-shifted compared with that of **3**, and is comparable to that of η^4 -Ph-AD complexes of

late transition metals [21–24], indicating an η^4 -coordination mode of the Ph-AD ligand in **13**. This upfield-shift of the H⁴ resonance is reasonable by considering the steric hindrance of benzyl group; the steric bulkiness weakens Ta–N and Ta–H² bonds, conversely strengthens Ta–H³ and Ta–H⁴ bonds. The ABq benzylic protons (δ 1.80 and 2.02) are comparable to those of **9**.



During the dibenylation of **3** and **4** in toluene producing **9** and **11** respectively, the transformation from the supine- η^4 -AD coordination mode to the $\eta^2\text{-C,N}$ -imine one took place. The dibenylation of these complexes in THF afforded metallacyclic carbene complexes **10** and **12**, respectively, in addition to **9** and **11**. Bulky substituents on the nitrogen atoms of the DAD ligand was reported to control whether the coordination mode is η^4 or η^2 [12,13,25]. Thus, it is likely assumed that, for **9** and **11**, the congestion due to the two benzyl groups resulted in less bulky η^2 -coordination mode. On the other hand, in order to release the congestion of two benzyl groups, the η^4 -complexation might enforce the formation of nascent benzyldiene species such as **14** and **15** (two rotamers, *anti*- or *syn*-one, are possible), which abstract the H⁴ proton of their AD ligand to give the metallacyclic carbene complexes **10** and **12**, respectively. In contrast, the dimethylation and monobenylation did not cause the change of the conformation mode of the AD ligand. Thus, we have demonstrated that the AD ligand is not only the geometrically flexible one but also is the unique source of the cyclic carbene complexes.



3. Experimental

All manipulations involving air- and moisture-sensitive organometallic compounds were carried using the standard Schlenk techniques under argon. Hexane, THF, and toluene were dried and deoxygenated by distillation over sodium benzophenone ketyl under air-

gon. Benzene- d_6 and THF- d_8 were distilled from Na/K alloy and thoroughly degassed by trap-to-trap distillation before use. 1-Aza-1,3-butadiene ligands were prepared according to the known method, in which those were prepared by treating cinnamaldehyde with one equivalent of aniline or *p*-anisidine in EtOH at room temperature. Complexes TaCl₄Cp* (**1**) [37] and a low-valent tantalum complex, [Cp*TaCl₂]₂ (**2**) [19,20], were prepared according to the literature. The ether free dialkyl magnesium compounds were prepared according to the literature [38].

The ¹H (500, 400, 300, and 270 MHz), ¹³C (125, 100, 75, and 68 MHz) NMR spectra were measured on a Varian Unity Inova-500, a JEOL JNM-AL400, a Varian Mercury-300, or a JEOL GSX-270 spectrometer. When benzene- d_6 was used as the solvent, the spectra were referenced to the residual solvent protons at δ 7.20 in the ¹H-NMR spectra and to the residual solvent carbons at δ 128.0 in the ¹³C-NMR spectra. Assignments for ¹H and ¹³C-NMR peaks for some of the complexes were aided by 2D ¹H–¹H COSY, 2D ¹H–¹H NOESY, and 2D ¹H–¹³C COSY spectra, respectively. Other spectra were recorded by the use of the following instruments: IR, JASCO FT/IR-230; UV–vis spectra, JASCO V-570; elemental analyses, Perkin Elmer 2400. All melting points were measured in sealed tubes under argon atmosphere and were not corrected.

3.1. Preparation of TaCl₂Cp*(Ph–AD) (**3**)

To a sodium amalgam (0.5%; Na: 248 mg, 10.8 mol) in toluene (10 ml) was added a suspension of **1** (2.46 g, 5.37 mmol) in toluene (20 ml) at –30°C, and then was added a solution of 1,4-diphenyl-1-aza-1,3-butadiene in toluene (10 ml). The reaction mixture was allowed to warm to room temperature and then was further stirred for 5 h at room temperature. The red–brown solution was separated from the resulting salt and mercury by centrifugation and the solution was cooled at –20°C for 24 h to give purple crystals of **3** (1.89 g, 3.18 mmol, 59% yield); m.p. (dec.) 115–118°C. Alternatively, the reaction of [Cp*TaCl₂]₂ (**2**) with Ph–AD afforded the complex **3** in quantitative yield. ¹H-NMR (400 MHz, C₆D₆, 35°C): δ 1.84 (s, 15H, C₅Me₅), 4.09 (d, ³J_{H–H} = 6.8 Hz, 1H, H²), 5.01 (d, ³J_{H–H} = 13.7 Hz, 1H, H⁴), 6.79 (dd, ³J_{H–H} = 6.8 and 13.7 Hz, 1H, H³), 6.90 (t, 1H, *p*-Ph on N), 6.96 (t, 1H, *p*-Ph on C⁴), 7.21 (t, 2H, *m*-Ph on C⁴), 7.23 (t, 2H, *m*-Ph on N), 7.27 (d, 2H, *o*-Ph on C⁴), 7.40 (d, 2H, *o*-Ph on N). The 2D ¹H–¹H NOESY spectrum indicate neighboring protons in the molecule, e.g. H³-(*o*-Ph on C⁴), H⁴-(*o*-Ph on C⁴), H²-(*o*-Ph on N), (*o*-Ph on N)–(*m*-Ph on N), and so on. ¹³C-NMR (100 MHz, C₆D₆, 35°C): δ 11.6 (q, ¹J_{C–H} = 127 Hz, C₅Me₅), 86.7 (br d, C²), 113.2 (br d, C⁴), 122.4 (s, C₅Me₅), 123.5 (d, ¹J_{C–H} = 160 Hz, *o*-Ph on N), 124.3 (d, ¹J_{C–H} = 159

Hz, *p*-Ph on N), 126.4 (d, ¹J_{C–H} = 158 Hz, *p*-Ph on C⁴), 127.4 (d, ¹J_{C–H} = 159 Hz, *o*-Ph on C⁴), 128.1 (d, ¹J_{C–H} = 157 Hz, *m*-Ph on C⁴), 129.0 (d, ¹J_{C–H} = 157 Hz, *m*-Ph on N), 134.7 (d, ¹J_{C–H} = 167 Hz, C³), 138.9 (s, *ipso*-Ph on C⁴), 151.3 (s, *ipso*-Ph on N). IR (KBr): ν (C=C)/cm^{–1} 1593 (s) and ν (C=N)/cm^{–1} 1488 (s). UV (toluene) λ_{\max} = 396 nm (ϵ = 1.8 × 10³). Anal. Calc. for C₂₅H₂₈Cl₂NTa: C, 50.52; H, 4.75; N, 2.36%. Found: C, 50.43; H, 4.73; N, 2.17%.

3.2. Preparation of TaCl₂Cp*(*p*-MeOC₆H₄–AD) (**4**)

Complex **2** (151 mg, 0.194 mmol) and 1-(*p*-methoxyphenyl)-4-diphenyl-1-aza-1,3-butadiene (92.3 mg, 0.389 mmol) was dissolved in toluene (10 ml) at room temperature. After the reaction mixture was stirring for 24 h, the colour of the solution changed from green to red–brown. The resulting solution was cooled at –20°C for 24 h to give purple crystals of **4** (197 mg, 0.316 mmol, 81% yield), m.p. (dec.) 89–95°C. ¹H-NMR (400 MHz, C₆D₆, 35°C): δ 1.89 (s, 15H, C₅Me₅), 3.37 (s, 3H, OCH₃), 4.38 (d, 1H, H⁴), 4.53 (d, 1H, H²), 6.67 (dd, 1H, H³), 6.81 (m, 2H, *m*-C₆H₄), 7.06 (t, 1H, *p*-Ph), 7.24 (t, 2H, *m*-Ph), 7.27 (m, 2H, *o*-C₆H₄), 7.32 (d, 2H, *o*-Ph). The 2D ¹H–¹H NOESY spectrum indicate neighboring protons in the molecule, e.g. H³-(*o*-Ph), H⁴-(*o*-Ph), H²-(*o*-C₆H₄), (*o*-C₆H₄)-(*m*-C₆H₄), and so on. ¹³C-NMR (100 MHz, C₆D₆, 35°C): δ 11.7 (q, ¹J_{C–H} = 128 Hz, C₅Me₅), 55.1 (q, ¹J_{C–H} = 143 Hz, OCH₃), 93.3 (br, C⁴), 106.9 (br, C²), 114.3 (d, ¹J_{C–H} = 159 Hz, *m*-C₆H₄), 122.2 (s, C₅Me₅), 125.1 (d, ¹J_{C–H} = 160 Hz, *o*-C₆H₄), 126.2 (d, ¹J_{C–H} = 158 Hz, *p*-Ph), 127.8 (d, ¹J_{C–H} = 157 Hz, *o*-Ph), 128.5 (d, ¹J_{C–H} = 159 Hz, *m*-Ph), 131.7 (br, C³), 139.6 (s, *ipso*-Ph), 144.2 (s, *ipso*-C₆H₄), 157.6 (s, *p*-C₆H₄). IR (KBr): ν (C=C)/cm^{–1} 1596 (s) and ν (C=N)/cm^{–1} 1507 (s). UV (toluene) λ_{\max} = 381 nm (ϵ = 3.2 × 10³). Anal. Calc. for C₂₆H₃₀Cl₂NOTa: C, 50.02; H, 4.84; N, 2.24%. Found: C, 49.97; H, 4.85; N, 2.06%.

3.3. Preparation of TaMe₂Cp*(Ph–AD) (**6**)

To a solution of **3** (226 mg, 0.380 mmol) in diethyl ether (10 ml) cooled at –78°C was added a solution of MgMe₂ (1.2 equivalent, 0.456 mmol) in diethyl ether (10 ml) via syringe. The reaction mixture was allowed to warm to room temperature. After the reaction mixture was further stirred for 2 h at room temperature, all volatiles were removed under reduced pressure. The resulting residue was extracted with hexane (100 ml). The solution was evaporated to dryness, and then the residue was washed with hexane (1 ml) to afford **6** as yellow microcrystals in 96% yield (201 mg, 0.364 mmol), m.p. (dec.) 90–98°C. ¹H-NMR (400 MHz, C₆D₆, 35°C): δ 0.10 (s, 3H, Ta–CH₃), 0.14 (s, 3H, Ta–CH₃), 1.66 (s, 15H, C₅Me₅), 3.84 (d, ³J_{H–H} = 5.1

Hz, 1H, H²), 4.91 (d, ³J_{H-H} = 13.9 Hz, 1H, H⁴), 6.43 (dd, ³J_{H-H} = 5.1 and 13.9 Hz, 1H, H³), 6.99 (t, 1H, *p*-Ph on C⁴), 7.00 (t, 1H, *p*-Ph on N), 7.07 (d, 2H, *o*-Ph on C⁴), 7.20 (t, 2H, *m*-Ph on C⁴), 7.40 (t, 2H, *m*-Ph on N), 7.46 (d, 2H, *o*-Ph on N). The 2D ¹H–¹H NOESY spectrum indicate neighbouring protons in the molecule, e.g. H³–(*o*-Ph on C⁴), H⁴–(*o*-Ph on C⁴), H²–(*o*-Ph on N), (*o*-Ph on N)–(*m*-Ph on N), and so on. ¹³C-NMR (100 MHz, C₆D₆, 35°C): δ 11.0 (q, ¹J_{C-H} = 127 Hz, C₅Me₅), 46.0 (q, ¹J_{C-H} = 119 Hz, Ta–CH₃), 50.7 (q, ¹J_{C-H} = 120 Hz, Ta–CH₃), 83.8 (d, ¹J_{C-H} = 168 Hz, C²), 109.0 (d, ¹J_{C-H} = 149 Hz, C⁴), 115.5 (s, C₅Me₅), 121.3 (d, ¹J_{C-H} = 159 Hz, *p*-Ph on N), 121.8 (d, ¹J_{C-H} = 156 Hz, *o*-Ph on N), 125.3 (d, ¹J_{C-H} = 155 Hz, *p*-Ph on C⁴), 126.1 (d, ¹J_{C-H} = 156 Hz, *o*-Ph on C⁴), 128.1 (d, ¹J_{C-H} = 158 Hz, *m*-Ph on C⁴), 129.4 (d, ¹J_{C-H} = 157 Hz, *m*-Ph on N), 130.7 (d, ¹J_{C-H} = 155 Hz, C³), 139.8 (s, *ipso*-Ph on C⁴), 152.9 (s, *ipso*-Ph on N). IR (KBr): ν(C=C)/cm⁻¹ 1601 (s) and ν(C=N)/cm⁻¹ 1508 (s). Anal. Calc. for C₂₇H₃₄N₂Ta: C, 58.29; H, 6.19; N, 2.53%. Found: C, 58.29; H, 6.47; N, 2.61%.

3.4. Preparation of Ta(CH₂Ph)₂Cp*(Ph-AD) (9)

To a solution of **3** (200 mg, 0.337 mmol) in toluene (15 ml) was added a suspension of Mg(CH₂Ph)₂ (83.4 mg, 0.404 mmol) in toluene (4.0 ml) at –20°C. The mixture was allowed to warm to room temperature and stirred for 1 h. After removal of the solvent the resulting solid was extracted with hexane (80 ml). The extract was concentrated in vacuo, and the residue was washed with hexane (1 ml) to give **9** (228 mg, 0.323 mmol) as yellow microcrystals in 96% yield, m.p. (dec.) 153–155°C. ¹H-NMR (400 MHz, C₆D₆, 35°C): δ 1.56 (d, ²J_{H-H} = 12.0 Hz, 1H, Ta–CH₂), 1.68 (s, 15H, C₅Me₅), 2.02 (d, ²J_{H-H} = 11.2 Hz, 1H, Ta–CH₂), 2.28 (d, ²J_{H-H} = 12.0 Hz, 1H, Ta–CH₂), 2.83 (d, ²J_{H-H} = 11.2 Hz, 1H, Ta–CH₂), 3.07 (d, ³J_{H-H} = 6.3 Hz, 1H, H²), 6.45 (d, ³J_{H-H} = 6.3 Hz, 1H, H³), 6.45 (s, 1H, H⁴), 6.74 (d, 2H, *o*-Ph), 6.77 (t, 1H, *p*-Ph), 6.88 (m, 1H, *p*-Ph), 6.92 (t, 1H, *p*-Ph), 6.97 (t, 2H, *m*-Ph), 7.01 (m, 1H, *p*-Ph), 7.05 (d, 2H, *o*-Ph), 7.14 (t, 2H, *m*-Ph), 7.21 (m, 2H, *o*-Ph), 7.21 (m, 2H, *m*-Ph), 7.25 (m, 2H, *o*-Ph), 7.25 (m, 2H, *m*-Ph). The 2D ¹H–¹H NOESY spectrum indicate neighbouring protons in the molecule, e.g. C₅Me₅–H², and so on. ¹³C-NMR (100 MHz, C₆D₆, 35°C): δ 11.0 (q, ¹J_{C-H} = 127 Hz, C₅Me₅), 77.6 (d, ¹J_{C-H} = 159 Hz, C²), 78.5 (t, ¹J_{C-H} = 118 Hz, Ta–CH₂), 80.2 (t, ¹J_{C-H} = 121 Hz, Ta–CH₂), 116.7 (s, C₅Me₅), 121.1 (d, ¹J_{C-H} = 159 Hz, *p*-Ph), 121.8 (d, ¹J_{C-H} = 159 Hz, *o*-Ph), 123.8 (d, ¹J_{C-H} = 158 Hz, *p*-Ph), 124.0 (d, ¹J_{C-H} = 156 Hz, *p*-Ph), 126.1 (d, ¹J_{C-H} = 157 Hz, *m*-Ph), 126.5 (d, ¹J_{C-H} = 157 Hz, *p*-Ph), 126.8 (d, ¹J_{C-H} = 155 Hz, C⁴), 127.8 (d, ¹J_{C-H} = 158 Hz, *m*-Ph), 128.2 (d, ¹J_{C-H} = 158 Hz, *m*-Ph), 128.7 (d, ¹J_{C-H} = 157 Hz, *o*-Ph), 129.2 (d, ¹J_{C-H} = 158 Hz, *m*-Ph), 129.4 (d, ¹J_{C-H} = 156 Hz, *o*-

Ph), 129.8 (d, ¹J_{C-H} = 157 Hz, *o*-Ph), 138.2 (s, *ipso*-Ph), 138.3 (d, ¹J_{C-H} = 152 Hz, C³), 145.2 (s, *ipso*-Ph), 145.8 (s, *ipso*-Ph), 155.3 (s, *ipso*-Ph). IR (KBr): ν(C=C)/cm⁻¹ 1601 (s) and ν(C=N)/cm⁻¹ 1491 (s). Anal. Calc. for C₃₉H₄₂N₂Ta: C, 66.38; H, 6.00; N, 1.98%. Found: C, 66.22; H, 6.03; N, 1.88%.

When this reaction was carried out in THF, the other complex **10** was formed and characterized by the ¹H-NMR spectrum (THF-*d*₈).

10: ¹H-NMR (400 MHz, THF-*d*₈, 35 °C): δ 0.54 (d, ²J_{H-H} = 12.5 Hz, 1H, Ta–CH₂), 0.84 (d, ²J_{H-H} = 12.5 Hz, 1H, Ta–CH₂), 1.97 (s, 15H, C₅Me₅), 4.90 (d, ³J_{H-H} = 3.4 Hz, 1H, CH=CH), 5.62 (d, ³J_{H-H} = 3.4 Hz, 1H, CH=CH), 6.6–7.3 (m, 20H, aromatic protons).

3.5. Preparation of Ta(CH₂Ph)₂Cp*(*p*-MeOC₆H₄-AD) (11)

Similar treatment of **4** (144 mg, 0.230 mmol) with Mg(CH₂Ph)₂ afforded complex **11** (72.3 mg, 0.0983 mmol) as yellow micro crystals in 43% yield, m.p. (dec.) 131–134°C. ¹H-NMR (400 MHz, C₆D₆, 35°C): δ 1.53 (d, ²J_{H-H} = 11.6 Hz, 1H, Ta–CH₂), 1.70 (s, 15H, C₅Me₅), 2.01 (d, ²J_{H-H} = 10.8 Hz, 1H, Ta–CH₂), 2.28 (d, ²J_{H-H} = 11.6 Hz, 1H, Ta–CH₂), 2.81 (d, ²J_{H-H} = 10.8 Hz, 1H, Ta–CH₂), 3.11 (d, 1H, H²), 3.38 (s, 3H, OCH₃), 6.48 (s, 1H, H⁴), 6.49 (d, 1H, H³), 6.78 (d, 2H, *o*-Ph), 6.79 (t, 1H, *p*-Ph), 6.85 (d, 2H, *m*-C₆H₄), 6.92 (t, 1H, *p*-Ph), 7.00 (t, 2H, *m*-Ph), 7.02 (t, 1H, *p*-Ph), 7.06 (d, 2H, *o*-Ph), 7.15 (t, 2H, *m*-Ph), 7.16 (d, 2H, *o*-C₆H₄), 7.21 (d, 2H, *o*-Ph), 7.25 (t, 2H, *m*-Ph). The 2D ¹H–¹H NOESY spectrum indicate neighbouring protons in the molecule, e.g. C₅Me₅–H², and so on. ¹³C-NMR (100 MHz, C₆D₆, 35°C): δ 11.0 (q, ¹J_{C-H} = 127 Hz, C₅Me₅), 55.0 (q, ¹J_{C-H} = 143 Hz, OCH₃), 77.1 (d, ¹J_{C-H} = 162 Hz, C²), 78.0 (t, ¹J_{C-H} = 118 Hz, Ta–CH₂), 79.8 (t, ¹J_{C-H} = 120 Hz, Ta–CH₂), 114.7 (d, ¹J_{C-H} = 157 Hz, *m*-C₆H₄), 116.7 (s, C₅Me₅), 122.7 (d, ¹J_{C-H} = 158 Hz, *o*-C₆H₄), 123.7 (d, ¹J_{C-H} = 159 Hz, *p*-Ph), 123.8 (d, ¹J_{C-H} = 157 Hz, *p*-Ph), 126.0 (m, ¹J_{C-H} = 155 Hz, *p*-Ph), 126.5 (d, ¹J_{C-H} = 158 Hz, *p*-Ph), 126.5 (d, ¹J_{C-H} = 154 Hz, C⁴), 128.1 (d, ¹J_{C-H} = 158 Hz, *m*-Ph), 128.2 (d, ¹J_{C-H} = 158 Hz, *m*-Ph), 128.7 (d, ¹J_{C-H} = 158 Hz, *o*-Ph), 129.3 (d, ¹J_{C-H} = 156 Hz, *o*-Ph), 129.8 (d, ¹J_{C-H} = 156 Hz, *o*-Ph), 138.3 (s, *ipso*-Ph), 138.9 (d, ¹J_{C-H} = 151 Hz, C³), 145.4 (s, *ipso*-Ph), 146.0 (s, *ipso*-C₆H₄), 149.5 (s, *ipso*-Ph), 154.8 (s, *p*-C₆H₄). IR (KBr): ν(C=C)/cm⁻¹ 1597 (s) and ν(C=N)/cm⁻¹ 1510 (s). Anal. Calc. for C₄₀H₄₄NOTa: C, 65.30; H, 6.03; N, 1.90%. Found: C, 64.81; H, 6.31; N, 2.04%.

When this reaction was carried out in THF, the other complex **12** was formed and characterized by the ¹H-NMR spectrum (THF-*d*₈): **12**: ¹H NMR (400 MHz, THF-*d*₈, 35°C): δ 0.55 (d, ²J_{H-H} = 12.4 Hz, 1H, Ta–CH₂), 0.82 (d, ²J_{H-H} = 12.4 Hz, 1H, Ta–CH₂), 1.97 (s, 15H, C₅Me₅), 3.37 (s, 3H, OCH₃), 4.87 (d, ³J_{H-H} = 3.4

H_z, 1H, CH=CH), 5.57 (d, ³J_{H-H} = 3.4 Hz, 1H, CH=CH), 6.6–7.2 (m, 20H, aromatic protons).

3.6. Preparation of TaCl(CH₂Ph)Cp*(Ph-AD) (13)

A solution of Mg(CH₂Ph)₂ (0.377 mmol) in THF (10 ml) was added to a solution of **3** (374 mg, 0.629 mmol) in THF (10 ml) at –78°C. The reaction mixture was allowed to warm to room temperature, and then was stirred at room temperature for 6 h. The resulting solution was cooled at –20°C for 24 h to give red–purple crystals of **13** (51.2 mg, 0.0788 mmol, 13% yield), m.p. (dec.) 149–152°C. ¹H-NMR (400 MHz, C₆D₆, 35°C): δ 1.76 (s, 15H, C₅Me₅), 1.80 (d, ²J_{H-H} = 11.2 Hz, 1H, CH₂Ph), 2.02 (d, ²J_{H-H} = 11.2 Hz, 1H, CH₂Ph), 2.93 (d, 1H, H⁴), 4.88 (d, 1H, H²), 6.13 (dd, ³J_{H-H} = 5.4 and 10.3 Hz, 1H, H³), 6.88 (t, 1H, *p*-Ph of CH₂Ph), 6.95 (d, 2H, *o*-Ph on N), 6.96 (t, 1H, *p*-Ph on N), 7.03 (t, 1H, *p*-Ph on C⁴), 7.17 (t, 2H, *m*-Ph on N), 7.19 (t, 2H, *m*-Ph of CH₂Ph), 7.26 (t, 2H, *m*-Ph on C⁴), 7.27 (d, 2H, *o*-Ph on C⁴), 7.32 (d, 2H, *o*-Ph of CH₂Ph). The ¹H-NMR spectrum of **13** exhibited signals due to one equivalent of THF as a solvated molecule. The 2D ¹H–¹H NOESY spectrum indicate neighbouring protons in the molecule, e.g. H³-(*o*-Ph on C⁴), H⁴-(*o*-Ph on C⁴), H²-(*o*-Ph on N), H²-(*o*-Ph on CH₂Ph), and so on. ¹³C-NMR (100 MHz, C₆D₆, 35°C): δ 11.8 (q, ¹J_{C-H} = 128 Hz, C₅Me₅), 62.1 (br, CH₂Ph), 78.4 (br, C⁴), 103.0 (br, C²), 119.4 (s, C₅Me₅), 122.8 (d, ¹J_{C-H} = 158 Hz, *p*-Ph of CH₂Ph), 124.0 (d, ¹J_{C-H} = 155 Hz, *o*-Ph on N), 124.8 (d, ¹J_{C-H} = 155 Hz, *p*-Ph on N), 125.2 (d, ¹J_{C-H} = 157 Hz, *p*-Ph on C⁴), 126.1 (br, C³), 127.5 (d, ¹J_{C-H} = 158 Hz, *m*-Ph of CH₂Ph), 127.6 (d, ¹J_{C-H} = 158 Hz, *o*-Ph on C⁴), 128.1 (d, ¹J_{C-H} = 157 Hz, *o*-Ph of CH₂Ph), 128.2 (d, ¹J_{C-H} = 158 Hz, *m*-Ph on C⁴), 128.9 (d, ¹J_{C-H} = 158 Hz, *m*-Ph on N), 140.5 (s, *ipso*-Ph on C⁴), 149.6 (s, *ipso*-Ph on N), 152.9 (s, *ipso*-Ph of CH₂Ph). UV (toluene) λ_{max} = 521 nm (ε = 1.0 × 10³). IR (KBr): ν(C=C)/cm⁻¹ 1592 (s) and ν(C=N)/cm⁻¹ 1485 (s). Anal. Calc. for C₃₂H₃₅ClNTa(C₄H₈O): C, 59.88; H, 6.00; N, 1.94%. Found: C, 59.81; H, 6.04; N, 2.07%.

3.7. Crystallographic data collections and structure determination of **3**

The single crystal suitable for X-ray measurements was obtained by recrystallization of **3** from a mixture of toluene and hexane. The X-ray diffraction studies was sealed in glass capillaries under an argon atmosphere, and then each crystal of complexes was mounted on a Rigaku AFC-7R four-circle diffractometer for data collection using Mo–K_α (graphite monochromated, λ = 0.71069) radiation. Relevant crystal and data statistics are summarized in Table 2.

The unit cell parameters and the orientation matrix at 23°C were determined by a least-squares fit to 2θ values of 25 strong higher reflections for all complexes. Three standard reflections were chosen and monitored every 150 reflections. An empirical absorption correction was applied on the basis of azimuthal scans. The data was corrected for Lorentz and polarization effects.

The structure of complex **3** was solved by a direct method (SHELXS 86) [39] and refined by the full-matrix least squares method. Measured non-equivalent reflections were used for the structure determination. In the subsequent refinement, the function Σω(|F_o| – |F_c|)² was minimized, where |F_o| and |F_c| are the observed and calculated structure factor amplitudes, respectively. The agreement indices are defined as R₁ = Σ(|F_o| – |F_c||)/Σ|F_o| and wR₂ = [Σω(F_o² – F_c²)²/Σ(ωF_o⁴)]^{1/2}. The positions of all non-hydrogen atoms for all complexes were found from a difference Fourier electron density map and refined anisotropically. All hydrogen atoms were placed in calculated positions (C–H = 0.95 Å) and kept fixed. All calculations were performed using the TEXSAN crystallographic software package, and illustrations were drawn with ORTEP.

Table 2
Crystal data and data collection parameters of **3**

Complex	3
Formula	C ₂₅ H ₂₈ NCl ₂ Ta
Formula weight	594.36
Crystal system	Monoclinic
Space group	P2 ₁ /a (# 14)
a (Å)	17.210(9)
b (Å)	8.477(6)
c (Å)	18.013(6)
β (°)	103.88(3)
V (Å ³)	2551(2)
Z	4
Number of reflections for cell determination (2θ range)	20 (25–30°)
D _{calc.} (g cm ⁻³)	1.547
F(000)	1168.00
μ [Mo–K _α] (cm ⁻¹)	35.21
T (K)	296(1)
Crystal size (mm)	0.50 × 0.25 × 0.15
Scan type	ω – 2θ
Scan speed (° min ⁻¹)	16
Scan width (°)	1.26 + 0.30 tan θ
2θ _{min} , 2θ _{max} (°)	5.0, 55.0
Unique data (R _{int})	6248 (0.025)
Number of observations	5830
Number of variables	263
R ₁ , wR ₂ (all data)	0.090, 0.123
Goodness-of-fit on F ²	2.09
Δ (e Å ⁻³)	3.52, –1.34

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