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Half-Metallocene 1-Aza-1,3-butadiene Complexes of Tantalum: Auxiliary Ligand Effects on Controlling Coordination Modes of 1-Aza-1,3-butadiene Ligand

Yutaka Matsuo, Kazushi Mashima,* and Kazuhide Tani

Department of Chemistry, Graduate School of Engineering Science, Osaka University, Toyonaka, Osaka 560-8531

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We prepared some half-metallocene complexes of tantalum bearing *ortho*-substituted aryl derivatives of 1-aza-1,3-butadiene ligand. The coordination mode of the 1-aza-1,3-diene (abbr. AD) ligand highly depended on the substituent(s) on the aryl group of the AD ligand and also on the metal center. The number of methyl substituents on the aryl group of the AD ligand differentiated two coordination modes: one methyl substituent, $TaCl_2Cp^*(\eta^4$-*supine*-*o*-Tol-AD) (**1**) (Cp^* = pentamethylcyclopentadienyl; *o*-Tol-AD = 1-(2-methylphenyl)-4-phenyl-1-aza-1,3-butadiene), favored an η^4-*supine*-coordination mode, while two methyl substituents, $TaCl_2Cp^*(\eta^2$-*C*,*N*-Xyl-AD) (**5**) (Xyl-AD = 2,6-dimethylphenyl-4-phenyl-1-aza-1,3-butadiene), adopted an η^2-*C*,*N*-imine coordination fashion. Furthermore, the preferential coordination mode of the AD ligand was delicately affected by the substituent(s) on the tantalum center. Dialkylation of **1** led to the formation of TaR_2Cp^*(*o*-Tol-AD) (**6**: R = Me; **8**: R = CH_2Ph) in the dimethyl complex **6**. The equilibrium between η^4-coordination mode and η^2-*C*,*N*-coordination one was observed and the latter mode was thermally more feasible in solution and as solid state, and the *o*-Tol-AD ligand predominantly coordinated in an η^2-*C*,*N*-imine fashin to the tantalum center of **8**. In contrast, the monobenzylation of **1** did not change the η^4-*supine* coordination mode, giving a monobenzyl complex $Cp^*TaCl(CH_2Ph)(\eta^4$-*supine*-*o*-Tol-AD) (**9**). The dibenzyl complex **8** gradually turned to a benzylidene complex $Ta(=CHPh)Cp^*(\eta^4$-*supine*-*o*-Tol-AD) (**10**) on heating at 70 °C with the change of the coordination mode from η^2 to η^4. Introduction of a 1,3-butadiene ligand to the metal center gave a mixed-ligand complex $TaCp^*(\eta^2$-*C*,*N*-*o*-Tol-AD)(η^4-*s*-*cis*-1,3-butadiene) (**12**), in which the metal center adopted an η^2-*C*,*N*-fashion.

Nitrogen substituted 1,3-diene ligands such as 1,4-diaza-1,3-butadiene (abbr. DAD) and 1-aza-1,3-butadiene (abbr. AD) have been utilized as unique and versatile supporting ligands for the late transition metals;[1–3] however, these ligands have only recently been utilized for early transition metals. These hetero-diene ligands are of perticular interest recently in view of their versatile, flexible coordination to the metal center as described in Chart 1, and their ability to stabilize various catalyst precursors for polymerization as well as organic reactions.[4] In half-metallocene complexes of group 4[5–11] and group 5 metals,[12–18] the nitrogen substituted diene ligands not only coordinated in a *cis*-fashion to the metal center with large contribution of a metallacyclopent-3-ene canonical form, the form **B** in Chart 1, but also have two conformations, *supine* or *prone*, relative to the cyclopentadienyl ligand.[19] We already reported synthesis and reactions of half-metallocene complexes bearing 1-phenyl-1-aza-1,3-butadiene (abbr. Ph-AD) and its *para*-substituted derivatives.[15,20] As an extension of our syntheses of these half-metallocene complexes of group 5 metals, herein we report some tantalum complexes bearing *ortho*-substituted aryl AD ligands, whose coordination mode can be controlled depending on substituent(s) on aryl group of the AD ligand and on the metal center.

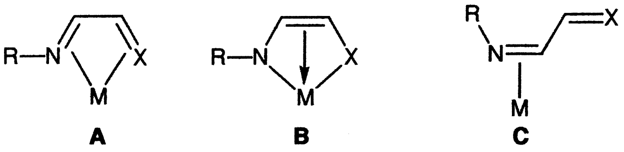


Chart 1. X = CHR (AD), X = NR (DAD).

Results and Discussion

Synthesis and Characterization of Dichloro Complexes of Tantalum Having *ortho*-Substituted Aryl-AD Ligands. A dichloro complex, $TaCl_2Cp^*(\eta^4$-*supine*-*o*-Tol-AD) (**1**) (*o*-Tol-AD) = 1-(2-methylphenyl)-4-phenyl-1-aza-1,3-butadiene) has been prepared by the reduction of $TaCl_4Cp^*$ (**2**) (Cp^* = pentamethylcyclopentadienyl) in THF using aluminum activated by catalytic amounts of $HgCl_2$ in the presence of *o*-Tol-AD.[20] Alternatively, the reaction of $[TaCl_2Cp^*]_2$ (**3**), which was derived from the amalgam reduction of the complex **2**,[21,22] with 2 equiv of *o*-Tol-AD in C_6D_6 afforded the purple dichloro complex **1** (Eq. 1). The structure of **1** was already characterized by spectroscopic date,[20] and was further determined by a crystallographic study (Fig. 1); the structure is the same as that of $TaCl_2Cp^*(\eta^4$-*supine*-Ph-AD) (**4**).[15] Selected bond distances and angles for **1** are listed in Table 1. The AD ligand of **1** coordinates in an η^4-fashion to the tantalum atom and the direction of the AD ligand points toward the Cp^* ligand, a *supine* conformation, whose coordination mode and structural features are essentially the same as those found for the Ph-AD complex **4**.[15] The methyl substituent of the AD ligand occupied the location outside of two *ortho*-positions of the phenyl group

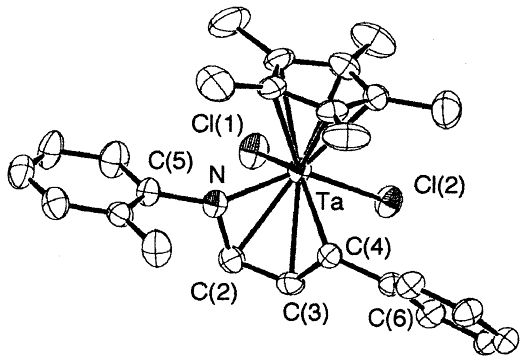


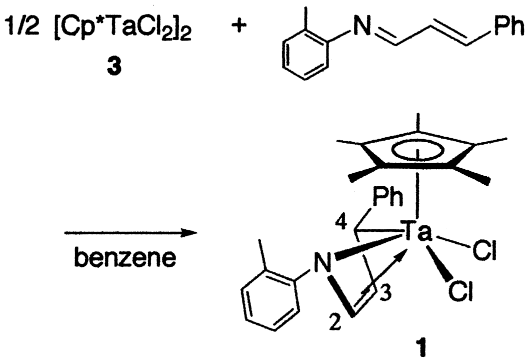
Fig. 1. Molecular structure of **1** with the labeling scheme. Hydrogen atoms are omitted for clarity.

Table 1. Selected Bond Distances and Angles for Complex **1**

Bond distance (Å)	
Ta–N	1.992(3)
Ta–C(2)	2.372(4)
Ta–C(3)	2.444(3)
Ta–C(4)	2.309(3)
Ta–Cl(1)	2.4663(9)
Ta–Cl(2)	2.4338(9)
N–C(2)	1.402(5)
N–C(5)	1.447(4)
C(2)–C(3)	1.379(5)
C(3)–C(4)	1.433(5)
C(4)–C(6)	1.494(4)
Ta–CCP[a]	2.112
Bond angles (deg)	
N–Ta–C(4)	78.7(1)
Cl(1)–Ta–Cl(2)	80.63(3)
N–Ta–Cl(1)	88.93(8)
C(4)–Ta–Cl(2)	82.79(8)
N–C(2)–C(3)	116.4(3)
C(2)–C(3)–C(4)	120.8(3)
Ta–N–C(2)	86.8(2)
Ta–N–C(5)	147.7(2)
C(2)–N–C(5)	118.0(3)
Ta–C(4)–C(3)	77.7(2)
Ta–C(4)–C(6)	134.6(2)
C(3)–C(4)–C(6)	119.9(3)
fold angle[b]	104.5(3)

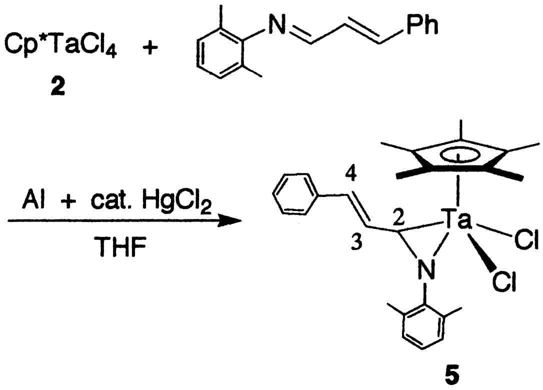
a) CCP: Centroid of cyclopentadienyl ring.
b) fold angle: Dihedral angle between the N–Ta–C(4) plane and N–C(2)–C(3)–C(4) plane.

bound to the nitrogen atom. The bond distance (1.992(3) Å) of Ta–N is comparable to that of Ta–N(amido)[23–26] and that (2.010(7) Å) of **4**,[15] but longer than that of Ta–N(imido).[27] The N–C(2) (1.402(5) Å), C(2)–C(3) (1.379(5) Å), and C(3)–C(4) (1.433(5) Å) bond lengths are alternated in a long-short-long sequence as expected for early-transition metal diene complexes, to which a contribution of a 1-metallacyclo-3-pentene canonical structure is dominant. The fold angle (104.5(3)°) between the best planes defined by atoms Ta, N, C(4) and N, C(2), C(3), C(4) is narrower than the corresponding fold angle (120.06–121.35°) found for some DAD complexes of tantalum,[14] indicating that the interaction of the C(2)–C(3) bond with the tantalum atom of **1** is much stronger than that of the DAD complexes. The dissymmetric environment around the tantalum atom made two Ta–Cl bonds different; the distance (2.4663(9) Å) of Ta–Cl(1) *trans* to C(4) is slightly longer than that (2.4338(9) Å) of Ta–Cl(2) *trans* to the nitrogen atom. The narrow angle (78.7(1)°) of N–Ta–C(4) is attributed to the constrained geometry of the 5-membered pukered structure of **1**.



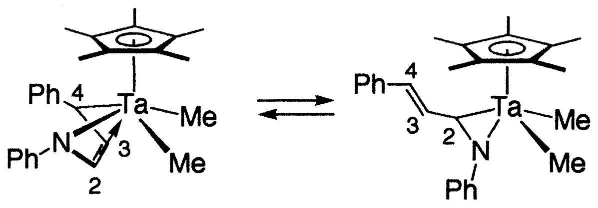
(1)

When 2,6-dimethylphenyl-4-phenyl-1-aza-1,3-butadiene ligand (abbr. Xyl-AD) was used, an η^2-*C*,*N*-imine complex $TaCl_2Cp^*(\eta^2$-*C*,*N*-Xyl-AD$)$ (**5**) was obtained in 18% yield by the reduction of **2** by Al/$HgCl_2$ (cat.) in the presence of Xyl-AD (Eq. 2). The second methyl group at the other *ortho*-position of the aryl group bound to the nitrogen atom prevented the η^4-coordination. The AD ligand of **5** thus coordinated in an η^2-*C*,*N*-fashion (Chart 1, **C**) to the tantalum center as confirmed by NMR spectroscopy; the H^2 proton appeared at higher-field (δ 2.08), while the signals due to the H^3 and H^4 protons were observed in olefinic region (δ 6.14 and 5.99, respectively).



(2)

Dimethylation of Dichloro-AD Complexes of Tantalum. Treatment of **1** with 1 equiv of $MgMe_2$ in diethyl ether afforded a dimethyl complex, $TaMe_2Cp^*$(*o*-Tol-AD) (**6**) in 90% yield (Eq. 3). The ^1H NMR spectrum of **6** in benzene-d_6 exhibited two singlet signals due to two magnetically nonequivalent Ta-CH_3 protons at δ −0.82 and 0.07, and additionally displayed a terminal H^4 proton resonance at δ 2.10 and H^2 and H^3 proton resonances at the olefinic region (δ 5.66 and 5.96, respectively). These spectral data suggest that the complex **6** adopts the *supine*-η^4-coordination mode as observed for the complex **1**, being in sharp contrast to the η^2-*C*,*N*-coordination mode in solid state (vide infra). The equilibrium between η^4-coordination



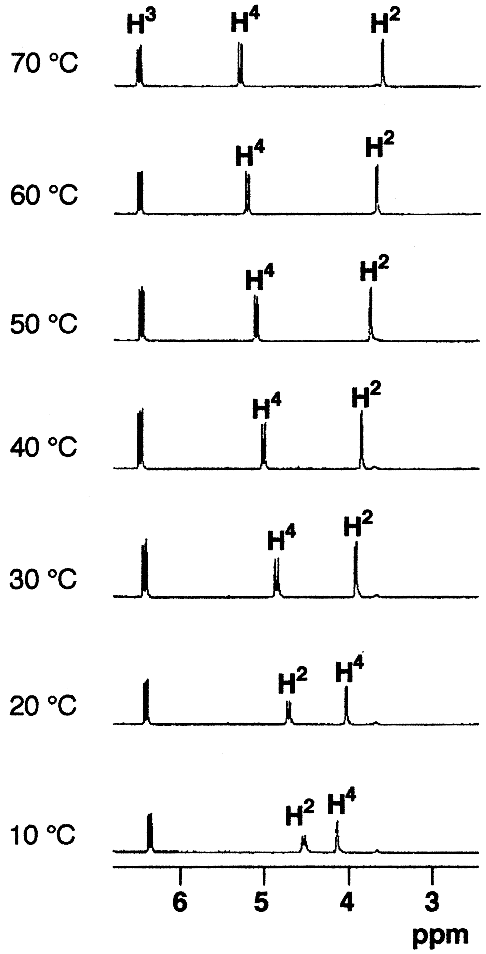


Fig. 2. The variable temperature–NMR spectra of **7** in C_6D_6.

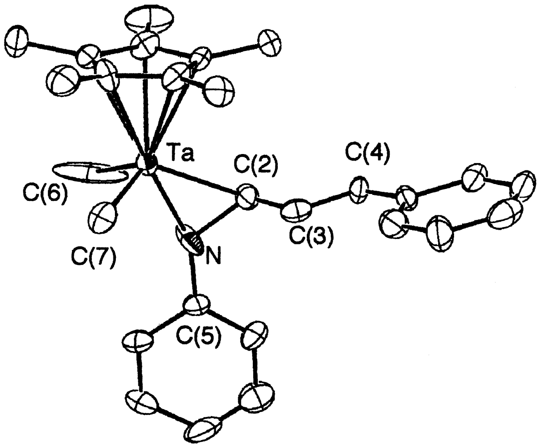


Fig. 3. Molecular structure of **7** with the labeling scheme. Hydrogen atoms are omitted for clarity.

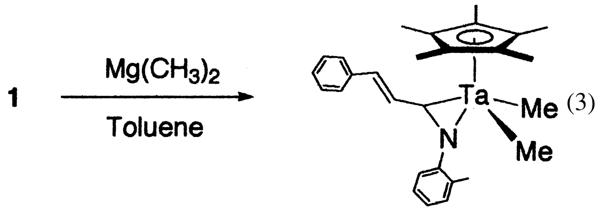
Table 2. Selected Bond Distances and Angles for Dimethyl Complex **7**

Bond distance (Å)	
Ta–N	1.91(1)
Ta–C(2)	2.19(1)
Ta–C(6)	2.07(2)
Ta–C(7)	2.03(3)
N–C(2)	1.48(2)
C(2)–C(3)	1.48(12)
C(3)–C(4)	1.33(2)
Ta–CCP[a)]	2.159
Bond angles (deg)	
C(2)–Ta–C(6)	111.8(6)
C(2)–Ta–C(7)	108.7(8)
N–Ta–C(2)	41.7(4)
Ta–N–C(2)	79.2(7)
Ta–C(2)–N	59.1(7)
Ta–C(2)–C(3)	123.4(10)
N–C(2)–C(3)	122(1)
C(2)–C(3)–C(4)	125(1)
C(3)–C(4)–C(6)	126(1)
Ta–N–C(5)	158.3(10)
C(2)–N–C(5)	122(1)
Sum of around N[b)]	359.5

a) CCP: Centroid of cyclopentadienyl ring.

b) Sun of around N: {Ta–N–C(2)} + {Ta–N–C(5)} + {C(2)–N–C(5)}.

mode and η^2-*C*,*N*-coordination one was observed in the ^{1}H NMR spectra (10–70 °C) of the complex **6** and its phenyl derivative $TaMe_2Cp^*(Ph\text{-}AD)$ (**7**)[15] (Fig. 2); the signal of H^2 of both complexes was observed in higher field at higher temperature, while the signal of H^4 was observed in lower field at higher temperature. In order to make the structrure of the dimethyl complexes clear by a crystallographic study, we tried to crystallize **6**; however, we were not able to obtain good crystals of **6**, but crystals of **7** were found to be suitable for X-ray analysis. Figure 3 clearly shows that the dimethyl complex **7** has the η^2-*C*,*N*-coordination mode as expected from the variable temperature NMR spectra. Selected bond distances and angles are summarized in Table 2. The tantalum center adopts a three-legged piano stool geometry comprised of a η^5-Cp* ligand, two carbon atom of the methyl ligands, and the C=N moiety of the Ph-AD ligand. The C=N moiety is perpendicular to the cyclopentadienyl ring. The direction of the nitrogen atom of C=N moiety points away from the Cp* ligand. This direction is opposite to the structure of tantalum-imine complex $TaMe_2Cp^*(\eta^2\text{-}C,N\text{-}2,6\text{-}Me_2C_6H_3\text{–}N{=}CMe_2)$ reported by Royo et al., in which the carbon atom of the imine ligand is *trans* to Cp* ligand.[28] The bond distance (1.91 Å) of Ta–N is comparable to those of typical Ta–N(dialkylamido) distances (ca. 1.93–1.96 Å).[25,26] The bond distance (2.19 Å) of Ta–C(2) is consistent with a single bond, suggesting that the Ta–N–C(2) moiety forms an azatantalacyclopropane structure.



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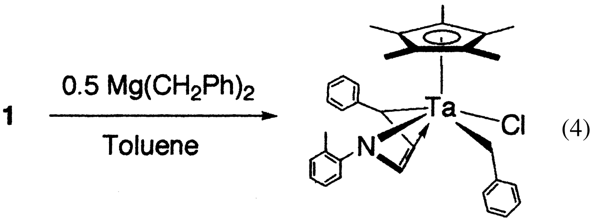
(3)

Synthesis and Characterization of Benzyl and Benzylidene Complexes. We already reported the benzylation of the complex **1**, giving a dibenzyl complex, Cp*Ta(CH_2Ph)$_2$-(η^2-*C*,*N*-*o*-Tol-AD) (**8**).[20] During the benzylation, the coordination mode of the AD ligand turned from η^4 to η^2, as observed in the methylation of **1**, and hence this transformation can be mainly attributed to the steric effect of alkyl groups bound to the tantalum center. A similar reaction of **5** with Mg(CH_2Ph)$_2$ resulted in a complicated mixture, from which no products could be isolated. Thus, the stability of dibenzyl complex sensitively depends on the substituent of the AD ligand.

In contrast, a monobenzyl complex Cp*TaCl(CH_2Ph)(η^4-*supine*-*o*-Tol-AD) (**9**), which was obtained in 77% yield by the reaction of **1** with a half equivalent of Mg(CH_2Ph)$_2$ in toluene (Eq. 4), kept the *supine*-η^4-coordination mode of **1**. The complex **9** was characterized by NMR spectroscopy as well as combustion analysis. The chemical shiftvalues of an outer proton (δ 2.05 for H^4) and inner protons (δ 5.39 for H^2 and 5.86 For H^3) of the *o*-Tol-AD ligand of **9** are comparable to those found for **1** and AB*q* resonances due to TaCH_2Ph appeared at δ 1.63 and 2.11 with a coupling constant of 10.5 Hz. The NOESY experiment indicated that complex **9** has a *supine*-η^4-*o*-Tol-AD ligand and that the benzyl group is trans to the C^4 atom.



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(4)

The dibenzyl complex **8** gradually released toluene via α-hydrogen abstraction followed by reductive elimination to give the corresponding benzylidene complex Ta(=CHPh)CP*(η^4-*supine*-*o*-Tol-AD) (**10**) on heating at 70 °C (Eq. 5). This benzylidene complex **10** was not thermally stable and decomposed during any attempted isolation, and hence **10** was characterized in solution by NMR spectroscopy; the ^{1}H NMR spectrum of **10** exhibited a characteristic α-benzylidene proton signal in a downfield (δ 8.14), suggesting the presence of a single rotamer. The 2D ^{1}H–^{1}H NOESY measurement clearly revealed that the methyl signal of the Cp* ligand can be correlated to the α-benzylidene proton, indicating that the phenyl group of the benzylidene moiety pointed in the direction opposite to the Cp* ligand, an *anti*-rotamer. In the ^{13}C NMR spectrum, the benzylidene carbon atom of **10** appeared at δ 243.4 with a coupling constant $^1J_{C\text{–}H}$ = 123 Hz. One notable feature was the change of the coordination mode of the AD ligand from the η^2-fashion to the η^4-*supine*-one, as confirmed by NMR spectroscopy. In the ^{1}H NMR spectrum of **10**, a signal due to H^4 appeared at higher-field (δ 1.62), while the H^2 and H^3 resonances were displayed at lower-field (δ 6.03 for H^2 and 5.17 for H^3). The selective formation of the benzylidene complex **10** is in sharp contrast to the formation fo metallacyclic carbene complex **11** (Chart 2) on the thermolysis of a bis(benzyl) complex bearing a Ph-AD ligand.[15]

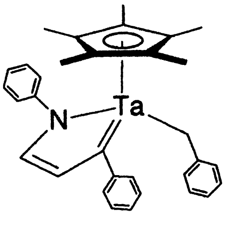

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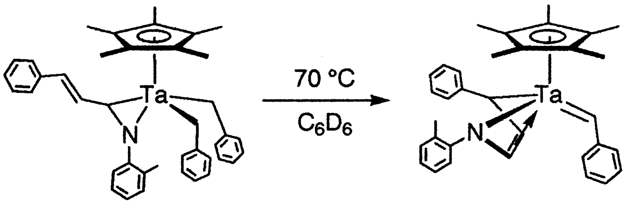
Chart 2.



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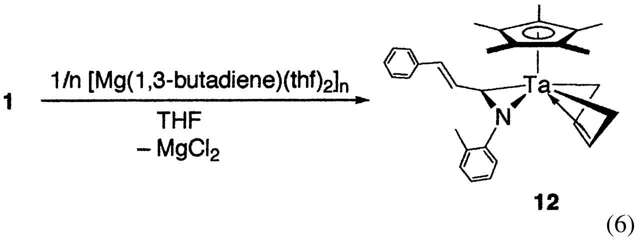
(5)

Synthesis of AD–Butadinene Complex of Tantalum. Introduction of a 1,3-butadiene ligand to the metal center led to a mixed-ligand complex TaCp*(η^2-*C*,*N*-*o*-Tol-AD)(η^4-*s*-*cis*-1,3-butadiene) (**12**) (Eq. 6). Treatment of **1** with a slight excess of the butadiene-megnesium addust [Mg(1,3-butadiene)(thf)$_2$]$_n$ in THF gave the mixed-ligand complex **12** as yellow microcrystals in 23% yield. This complex was found to be air- and moisture-sensitive and thermally unstable even in solid state. The ^{1}H NMR spectrum of **12** exhibited one set of signals due to both butadiene and AD ligands in an exact 1:1 integral ratio. The AD ligand was found to coordinate to the metal center in an η^2-*C*,*N*-fashion; the H^2 proton of the AD ligand was observed at a higher field (δ 1.76) than that found for the dichloro complex having the η^4-*supine*-AD ligand. The H^3 and H^4 protons were observed in the olefinic region (δ 4.24 and δ 7.09), the chemical shift values were comparable to those of the dibenzyl complex **8**. The butadiene ligand adopts an η^4-*supine*-*s*-*cis* conformation as judged by NMR spectroscopy; the signals of six kinds of butadiene protons were observed at δ −2.13, −1.07, 0.73, 1.89, 4.13, and 5.66. Based on the observed dissymmetric pattern of the butadiene protons, it is likely that an η^2-imino moiety coordinated in the plane bisecting the Cp* and the 1,3-butadiene ligands.



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(6)

Experimental

All maniqulations involving air- and moisture-sensitive organometallic compounds were carried out using the standard Schlenk techniques under argon. Hexane, THF, and toluene were dried and deoxygenated by distillation over sodium benzophenone ketyl under argon. Benzene-d_6 and THF-d_8 were distilled from Na/K alloy and thoroughly degassed by trap-to-trap distillation before use. Complexes **1**,[20] **2**,[29] **3**,[21,22] **7**,[15] and **8**[20] were prepared according to the literature.

The ^{1}H (500, 400, 300, and 270 MHz), ^{13}C (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 ^{1}H NMR spectra and to the residual solvent carbons at δ 128.0 in the ^{13}C NMR spectra. Assignments for ^{1}H and ^{13}C NMR peaks for some of the complexes were aided by 2D ^{1}H–^{1}H COSY, 2D ^{1}H–^{1}H NOESY, and 2D ^{1}H–^{13}C 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.

Preparation of Cp*TaCl$_2$(η^4-*supine-o*-Tol-AD) (1). The reaction of **3** (10 mg, 13 µmol) with two equiv of 1-(2-methylphenyl)-4-diphenyl-1-aza-1,3-butadiene (5.7 mg, 26 µmol) in C_6D_6 quantitatively afforded a purple solution of **1**, whose spectral data (^{1}H and ^{13}C) are superimposed with the reported data for **1.**

Preparation of Cp*TaCl$_2$(η^2-*C*,*N*-Xyl-AD) (5). A mixture of **2** (752 mg, 1.64 mmol), 1-(2,6-dimethylphenyl)-4-diphenyl-1-aza-1,3-butadiene (406 mg, 1.72 mmol), aluminum (61 mg, 2.26 mmol), and HgCl$_2$ (5 mg) in THF (40 mL) was stirred at room temperature for 12 h. After insoluble products were seperated by centrifugation, all volatiles were removed under reduced pressure. The resulting solid was extracted with toluene (80 mL, 6 times). The extract was concentrated under reduced pressure to give **5** as purple crystalline solids, which were then washed with hexane (10 mL) and dried in vacuo. Purple microcrystals of **5** (112 mg) were obtained in 18% yield, mp 108–113 °C (dec). ^{1}H NMR (400 MHz, C_6D_6, 35 °C): δ 1.69 (s, 3H, CH$_3$), 1.85 (s, 15H, C$_5$Me$_5$), 2.08 (br, 1H, H^2), 2.57 (s, 3H, CH$_3$), 5.99 (br, H^4), 6.14 (br, 1H, H^3), 6.8–7.4 (br m, 8H, aromatic protons). Anal. Calcd For $C_{27}H_{32}Cl_2NTa$: C, 52.10; H, 5.18; N, 2.25%. Found: C, 52.00; H, 5.23; N, 2.26%.

Preparation of Cp*TaMe$_2$(*o*-Tol-AD) (6). To a solution of **1** (731 mg, 1.20 mmol) in diethylether (10 mL) at 78 °C was added a solution of MgMe$_2$ (1.5 equiv, 98 mg, 1.80 mmol) in diethyl ether (10 mL) via a syringe. The reaction mixture was allowed to warm to room temperature. After the reaction mixture was 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 concentrated to precipitate yellow crystals, which were then washed with hexane to give **6** (610 mg, 90% yield), mp 92–97 °C (dec). ^{1}H NMR (400 MHz, C_6D_6, 35 °C): δ −0.82 (s, 3H, Ta-CH$_3$ *trans* to N), 0.07 (s, 3H, Ta-CH$_3$ *trans* to C), 1.67 (s, 15H, C$_5$Me$_5$), 1.85 (s, 3H, Ar-CH$_3$), 2.10 (d, $^3J_{H\text{–}H}$ = 8.8 Hz, 1H, H^4), 5.66 (d, $^3J_{H\text{–}H}$ = 4.9 Hz, 1H, H^2), 5.96 (dd, $^3J_{H\text{–}H}$ = 4.9 and 8.8 Hz, 1H, H^3), 6.96 (d, 1H, 6-C$_6$H$_4$), 7.00 (t, 1H, 4-C$_6$H$_4$), 7.03 (t, 1H, *p*-Ph), 7.06 (d, 1H, 3-C$_6$H$_4$), 7.08 (d, 2H, *o*-Ph), 7.09 (t, 1H, 5-C$_6$H$_4$), 7.31 (t, 2H, *m*-Ph). ^{13}C NMR (100 MHz, C_6D_6, 35 °C): δ 11.1 (q, $^1J_{C\text{–}H}$ = 127 Hz, C$_5$*Me*$_5$), 18.3 (q, $^1J_{C\text{–}H}$ = 126 Hz, Ar-*C*H$_3$), 26.6 (q, $^1J_{C\text{–}H}$ = 120 Hz, Ta-CH$_3$ *trans* to C), 35.3 (q, $^1J_{C\text{–}H}$ = 120 Hz, Ta-CH$_3$ *trans* to N), 69.7 (d, $^1J_{C\text{–}H}$ = 137 Hz, C^4), 107.7 (d, $^1J_{C\text{–}H}$ = 181 Hz, C^2), 114.4 (d, $^1J_{C\text{–}H}$ = 158 Hz, C^3), 115.1 (s, *C*$_5$Me$_5$), 123.1 (d, $^1J_{C\text{–}H}$ = 158 Hz, *p*-Ph), 123.5 (d, $^1J_{C\text{–}H}$ = 158 Hz, 6-C$_6$H$_4$), 125.3 (d, $^1J_{C\text{–}H}$ = 160 Hz, 4-C$_6$H$_4$), 126.3 (d, $^1J_{C\text{–}H}$ = 160 Hz, 5-C$_6$H$_4$), 126.9 (d, $^1J_{C\text{–}H}$ = 157 Hz, *m*-Ph), 127.6 (d, $^1J_{C\text{–}H}$ = 157 Hz, *m*-Ph), 130.5 (d, $^1J_{C\text{–}H}$ = 157 Hz, 3-C$_6$H$_4$), 134.9 (s, 2-C$_6$H$_4$), 143.9 (s, *ipso*-Ph), 150.0 (s, 1-C$_6$H$_4$). The 2D ^{1}H–^{1}H NOESY spectrum indicates neighboring protons in the molecule, e. g. (H^2 and Ta-CH$_3$ *trans* to C), (H^3 and Ta-CH$_3$ *trans* to N), (6-C$_6$H$_4$ and Ta-CH$_3$ *trans* to C), (*o*-Ph and Ta-CH$_3$ *trans* to N), (C$_5$Me$_5$ and 6-C$_6$H$_4$), (C$_5$Me$_5$ and *o*-Ph), (C$_5$Me$_5$ and H^4), (*o*-Ph and H^4), (3-C$_6$H$_4$ and Ar-CH$_3$), (H^3 and H^4), and so on. IR (KBr): ν(C=C)/cm^{-1} 1605 (s) and ν(C=N)/cm^{-1} 1510 (s). Anal. Calcd For $C_{28}H_{36}ClNTa$: C, 59.26; H, 6.39; N, 2.47%. Found: C, 59.00; H, 6.69; N, 2.32%.

Preparation of Cp*TaCl(CH$_2$Ph)(*o*-Tol-AD) (9). To a solution of **1** (678 mg, 1.11 mmol) in toluene (10 mL) was added a solution of Mg(CH$_2$Ph)$_2$ (0.6 equiv, 113 mg, 0.669 mmol) in toluene (10 mL). The reaction mixture was allowed to warm to room temperature, and than was stirred at room temperature for 6 h. The resulting solution was cooled at −20 °C for 24 h to give reddish-purple crystals of **9** (513 mg, 77% yield), mp 150–153 °C (dec). ^{1}H NMR (400 MHz, C_6D_6, 35 °C): δ 1.63 (d, $^2J_{H\text{–}H}$ = 10.5 Hz, 1H, Ta-C*H*$_2$Ph), 1.65 (s, 3H, Ar-CH$_3$), 1.76 (s, 15H, C$_5$*Me*$_5$), 2.05 (d, $^3J_{H\text{–}H}$ = 9.0 Hz, 1H, H^4), 2.11 (d, $^2J_{H\text{–}H}$ = 10.5 Hz, 1H, Ta-C*H*$_2$Ph), 5.39 (d, $^3J_{H\text{–}H}$ = 4.9 Hz, 1H, H^2), 5.86 (dd, $^3J_{H\text{–}H}$ = 4.9 and 9.0 Hz, 1H, H^3), 6.90 (t, 1H, *p*-Ph of CH$_2$Ph), 6.96 (d, 1H, 3-C$_6$H$_4$), 7.00 (t, 1H, 4-C$_6$H$_4$), 7.04 (t, 1H, *p*-Ph of AD), 7.12 (t, 1H, 5-C$_6$H$_4$), 7.24 (t, 2H, *m*-Ph of CH$_2$Ph), 7.25 (d, 2H, *o*-Ph of AD), 7.29 (t, 2H, *m*-Ph of AD), 7.31 (d, 1H, 6-C$_6$H$_4$), 7.55 (d, 2H, *o*-Ph of CH$_2$Ph). ^{13}C NMR (100 MHz, C_6D_6, 35 °C): δ 11.7 (q, $^1J_{C\text{–}H}$ = 128 Hz, C$_5$*Me*$_5$), 18.1 (q, $^1J_{C\text{–}H}$ = 128 Hz, Ar-*C*H$_3$), 55.7 (t, $^1J_{C\text{–}H}$ = 123 Hz, Ta-*C*H$_2$Ph), 75.7 (d, $^1J_{C\text{–}H}$ = 133 Hz, C^4), 114.1 (d, $^1J_{C\text{–}H}$ = 189 Hz, C^2), 118.2 (d, $^1J_{C\text{–}H}$ = 162 Hz, C^3), 119.2 (s, *C*$_5$Me$_5$), 122.4 (d, $^1J_{C\text{–}H}$ = 158 Hz, *p*-Ph of CH$_2$Ph), 124.7 (d, $^1J_{C\text{–}H}$ = 157 Hz, *p*-Ph of AD), 125.5 (d, $^1J_{C\text{–}H}$ = 160 Hz, 6-C$_6$H$_4$), 126.0 (d, $^1J_{C\text{–}H}$ = 163 Hz, 5-C$_6$H$_4$), 126.5 (d, $^1J_{C\text{–}H}$ = 160 Hz, 4-C$_6$H$_4$), 127.2 (d, $^1J_{C\text{–}H}$ = 157 Hz, *m*-Ph of AD), 127.2 (d, $^1J_{C\text{–}H}$ = 157 Hz, *m*-Ph of CH$_2$Ph), 128.0 (d, $^1J_{C\text{–}H}$ = 157 Hz, *o*-Ph of CH$_2$Ph), 128.5 (d, $^1J_{C\text{–}H}$ = 157 Hz, *o*-Ph of AD), 130.9 (d, $^1J_{C\text{–}H}$ = 160 Hz, 3-C$_6$H$_4$), 134.9 (s, 2-C$_6$H$_4$), 141.7 (s, *ipso*-Ph of AD), 147.9 (s, *ipso*-Ph of CH$_2$Ph), 154.9 (s, 1-C$_6$H$_4$). The 2D ^{1}H–^{1}H NOESY spectrum indicates neighboring protons in the molecule, e. g. (C$_5$Me$_5$ and *o*-Ph of AD), (C$_5$Me$_5$ and 6-C$_6$H$_4$), (H$_4$ and *o*-Ph of AD), (H^2 and *o*-Ph of CH$_2$Ph), (H^3 and *o*-Ph of AD), (Me and 3-C$_6$H$_4$), (Ta-C*H*$_2$Ph and 6-C$_6$H$_4$), and so on. IR (KBr): ν(C=C)/cm^{-1} 1594 (s) and ν(C=N)/cm^{-1} 1483 (s). Anal. Calcd For $C_{33}H_{37}ClNTa$: C, 59.69; H, 5.62; N, 2.11%. Found: C, 59.93; H, 5.72; N, 2.11%.

Synthesis of Cp*Ta(=CHPh)(*o*-Tol-AD) (10). Complex **8** (10 mg, 0.016 mmol) was dissolved in 0.58 mL of C_6D_6 in a 5-mm NMR tube. The solution was heated to 70 °C for 7 h, and ^{1}H NMR was measured. The spectrum showed the formation of **10** along with the signal due to toluene (protons of methyl group: δ 2.16). ^{1}H NMR (400 MHz, C_6D_6, 35 °C): δ 1.62 (d, $^3J_{H\text{–}H}$ = 6.8 Hz, 1H, H^4), 1.75 (s, 3H, Me), 1.79 (s, 15H, C$_5$Me$_5$), 5.17 (dd, $^3J_{H\text{–}H}$ = 5.1 and 6.8 Hz, 1H, H^3), 6.03 (d, $^3J_{H\text{–}H}$ = 5.1 Hz, 1H, H^2), 6.8–7.4 (m, 14H, aromatic protons), 8.14 (s, 1H, Ta=C*H*Ph). ^{13}C NMR (100 MHz, C_6D_6, 35 °C): δ 11.5 (q, $^1J_{C\text{–}H}$ = 127 Hz, C$_5$*Me*$_5$), 18.0 (q, $^1J_{C\text{–}H}$ = 125 Hz, Me), 68.8 (d, $^1J_{C\text{–}H}$ = 138 Hz,

Table 3. Crystal Data and Data Collection Perameters of Dichloro Complex **1**

Formula	$C_{29}H_{36}Cl_2NTa$
Solvent molecules	0.5 cyclohexane per **1**
Formula weight	650.46
Crystal system	monoclinic
Space group	$P2_1/a$ (No. 14)
a/Å	15.3639(8)
b/Å	9.4285(5)
c/Å	17.9859(9)
β/deg	99.781(2)
V/Å^3	2567.5(2)
Z	4
No. of refl. for cell detn. (2θ range)	22672 (5.1–55.0°)
D_{calcd}/g cm^{-3}	1.683
F(000)	1296.00
μ[Mo $K\alpha$]/cm^{-1}	40.01
Diffractometer	R-AXIS-RAPID
T/K	213(1)
Crystal size/mm	0.26×0.20×0.12
No. of images	55
Total oscillation angles/deg	222.0
Exposure time/min deg^{-1}	1.00
$2\theta_{min}$, $2\theta_{max}$/deg	5.1, 55.0
No. of refl. measured (Total)	24114
No. of refl. measured (Unique)	5884 (R_{int} = 0.039)
No. of variables	298
$R1$, w$R2$ (all data)	0.042, 0.060
$R(I > 2.0\sigma(I))$	0.027
GOF on F^2	1.03
Δ, e/Å^{-3}	1.06, −1.35

Table 4. Crystal Data and Data Collection Perameters of Dimethyl Complex **7**

Formula	$C_{27}H_{34}NTa$
Formula weight	553.52
Crystal system	triclinic
Space group	$P\bar{1}$ (No. 2)
a/Å	10.961(9)
b/Å	13.701(8)
c/Å	8.69(1)
α/deg	94.96(8)
β/deg	103.62(8)
γ/deg	70.03(5)
V/Å^3	1192(1)
Z	2
No. of refl. for cell detn. (2θ range)	25 (20–3°)
D_{calcd}/g cm^{-3}	1.542
F(000)	552.00
μ[Mo $K\alpha$]/cm^{-1}	46.15
diffractometer	AFC-7R
T/K	296(1)
Crystal size, mm	0.24×0.20×0.16
Scan type	ω–2θ
Scan speed/deg min^{-1}	32
Scan width/deg	1.84 + 0.30 tanθ
$2\theta_{min}$, $2\theta_{max}$/deg	5.0, 55.0
Unique data (R_{int})	5481 (0.085)
No. of observations	5468
No. of variables	262
$R1$, w$R2$ (all data)	0.195, 0.149
R, R_w	0.061, 0.062 ($I > 3.0\sigma(I)$)
GOF on F^2	2.09
Δ, e/Å^{-3}	4.95, −7.21

C^4), 105.5 (d, $^1J_{C-H}$ = 181 Hz, C^2), 110.0 (d, $^1J_{C-H}$ = 163 Hz, C^3), 113.7 (s, C_5Me_5), 122–131 (m, $^1J_{C-H}$ =155–160 Hz, aromatic carbons), 134.2 (s, 2-C_6H_4), 145.9 (s, *ipso*-Ph), 149.0 (s, *ipso*-Ph), 151.7 (s, *ipso*-Ph), 243.4 (d, $^1J_{C-H}$ = 123 Hz, Ta=CHPh).

Preparation of Cp*Ta(*o*-Tol-AD)(1,3-butadiene) (12). A solution of [Mg(1,3-butadiene)(thf)$_2$] (1.45 mmlo) in THF (15 mL) was added to a solution of **1** (880 mg, 1.45 mmol) in THF (15 mL) at −78 °C. The reaction mixture was allowed to warm to room temperature, and than was stirred at room temperature for 12 h. After removal of the solvent the resulting solid was extracted with hexane (60 mL × 2). The extract was dried in vacuo, and the residue was washed with hexane (1 mL) to give **12** (198 mg) as yellow microcrystals in 23% yield. ^{1}H NMR (400 MHz, C_6D_6, 35 °C; δ −2.13 (t, 1H, CH$_2$= (anti)), −1.07 (t, 1H, CH$_2$= (anti)), 0.73 (t, 1H, CH$_2$= (syn)), 1.74 (s, 3H, Me), 1.76 (d, 1H, H^2), 1.89 (t, 1H, CH$_2$= (syn)), 1.91 (s, 15H, C_5Me_5), 4.13 (m, 1H, =CH–), 4.24 (d, 1H, H^3), 5.66 (m, 1H, =CH–), 7.09 (d, 1H, H^4), 6.3–7.4 (aromatic protons). Elemental analysis did not give any satisfactory result due to the thermal instability of **12**.

Crystallographic Data Collections and Structure Determination of 1 and 7. The X-ray diffraction studies were carried on in sealed glass capillaries under an argon atmosphere. A crystal of complex **7** was mounted on a Rigaku AFC-7R four-circle diffractometer for data collection using Mo $K\alpha$ (graphite monochromated, λ = 0.71069) radiation and a crystal of **1** was mounted on a Rigaku R-AXIS Rapid imaging plate diffractometer for data collection using Mo $K\alpha$ (graphite monochromated, λ = 0.71069) radiation. Relevant crystal and data statistics are summarized in Tables 3 and 4. In the case of AFC-7R four-circle diffractometer, an empirical absorption correction was applied on the basis of azimuthal scans and the data was corrected for Lorentz and polarization effects. In the case of R-AXIS Rapid imaging plate diffractometer, a symmetry-related absorption correction using the program ABSCOR[30] was applied. The data was corrected for Lorentz and polarization effects.

The structure of **7** was solved by a direct method (SHELXS 86)[31] and refined by the full-matrix least squares method. The structure of **1** was solved by heavy-atom Petterson method (PATTY-94)[32] and expanded using Fourier techniques (DIRDIF94).[32] Measured non-equivalent reflections were used for the structure determination. In the subsequent refinement, the function $\Sigma\omega(|F_o| - |F_c|)^2$ was minimized, where $|F_o|$ and $|F_c|$ are the observed and calculated structure factor amplitudes, respectively. The agreement indices are defined as $R1 = \Sigma(||F_o| - |F_c||)/\Sigma|F_o|$ and $wR2 = [\Sigma\omega(F_o^2 - F_c^2)^2/\Sigma(\omega F_o^4)]^{1/2}$. The positions of all non-hydrogen stoms for all complexes were found from a difference Fourier electron density maps and were 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. The CIF date for the two crystals are deposited as Document No. 75025 at the Office of the Editor of Bull. Chem. Soc. Jpn. Crystallographic data have been deposited at the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK and copies can be obtained on requrest, free of charge, by quoting the publication citation and the deposition nimbners 179143 and 179144.

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