Intramolecular Coupling Reaction of 1-Aza-1,3-butadiene Ligand and Iminoacyl Ligand Giving Amido−Imido Complexes of Tantalum

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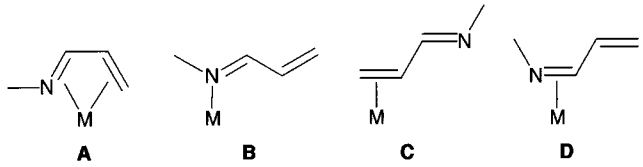
We have synthesized dibenzyl complexes of tantalum, Cp*Ta(CH_2Ph)$_2$(η^2-*C,N*-Ar-AD) (Ar-AD = 1-aryl-4-phenyl-1-aza-1,3-butadiene) (**1a**, Ar = Ph; **1b**, Ar = *o*-Tol), by the reaction of the corresponding dichloro complexes Cp*TaCl_2(η^4-*supine*-Ar-AD) (**2a**, Ar = Ph; **2b**, Ar = *o*-Tol) with Mg(CH_2Ph)$_2$ in toluene, and their reaction with 1 equiv of XylNC (Xyl = 2,6-dimethylphenyl) afforded amido−imido complexes, Cp*Ta(=NAr){N(Xyl)C(CH_2Ph)=CHCH=CHPh}(CH_2Ph) (**5a**, Ar = Ph; **5b**, Ar = *o*-Tol). These complexes were characterized by spectral data and crystallographic studies. The mechanism for the formation of the mixed amido−imido complexes was elucidated by NMR measurement, which detected an iminoacyl complex, Cp*Ta(η^2-Ph-AD){C(=NXyl)CH_2Ph}(CH_2Ph) (**3a**).

Introduction

Chemical transformations of organic compounds using organometallic compounds in catalytic and stoichiometric reactions have been investigated intensively.[1−3] Although many examples of intramolecular coupling reactions of organic functional groups bound to transition metals have been reported, few studies for group 5 metals have been conducted.[4−14] We have recently reported that group 5 metal complexes containing nitrogen-substituted 1,3-diene ligands such as 1,4-diaza-1,3-butadiene (DAD) and 1-aza-1,3-butadiene (AD) not only showed versatile coordination modes (Chart 1 for the AD ligand) but also exhibited unique reactivity, depending on the substituents on the ligand as well as on the metal center.[15−18] As an extension of our continuous interest in these chemistries, in this contribution

Chart 1



we report a unique intramolecular coupling reaction between an AD ligand and an iminoacyl ligand bound to a Cp*Ta moiety; reaction of isonitrile with dibenzyl complexes of tantalum bearing an η^5-C_5Me_5 (Cp*) and a 1-aryl-4-phenyl-1-aza-1,3-butadiene (Ar-AD) afforded amido−imido complexes. The X-ray structures of the starting dibenzyl complexes and the mixed amido−imido complex and the mechanism of the coupling reaction are also described.

Results and Discussion

Dibenzyl complexes of tantalum, Cp*Ta(CH_2Ph)$_2$(η^2-*C,N*-Ar-AD) (**1a**, Ar = Ph; **1b**, Ar = *o*-Tol), were prepared by the reaction of the corresponding dichloro complexes Cp*TaCl_2(η^4-*supine*-Ar-AD) (**2a**, Ar = Ph; **2b**, Ar = *o*-Tol) with Mg(CH_2Ph)$_2$ in toluene.[17] The alkylation altered the η^4-coordination mode of the Ar-AD ligand to a η^2-one. The structures of **1a** and **1b** were determined by X-ray analyses, and selected bond distances and angles are summarized in Table 1. The molecular structures of **1a** and **1b** are presented in Figures 1 and 2, respectively, which show three-legged piano stool geometry around the tantalum center. The AD ligand of **1a** and **1b** coordinated in an η^2-C=N mode

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Table 1. Selected Bond Lengths and Angles for 1a and 1b

	1a	1b
Bond Distances (Å)		
Ta−N	1.956(9)	1.941(5)
Ta−C(2)	2.15(1)	2.167(8)
Ta−C(6)	2.20(1)	2.253(8)
Ta−C(7)	2.19(1)	2.218(8)
N−C(2)	1.40(1)	1.42(1)
C(2)−C(3)	1.48(2)	1.46(1)
C(3)−C(4)	1.33(2)	1.32(1)
Ta−CCP[a]	2.166	2.149
Bond Angles (deg)		
C(2)−Ta−C(6)	109.2(5)	106.0(3)
C(2)−Ta−C(7)	115.5(5)	119.7(3)
N−Ta−C(2)	39.5(4)	39.8(3)
Ta−N−C(2)	77.8(7)	78.7(5)
Ta−C(2)−N	62.7(6)	61.5(4)
Ta−C(2)−C(3)	123.1(8)	130.9(6)
N−C(2)−C(3)	117(2)	119.3(7)
C(2)−C(3)−C(4)	127(1)	127.1(8)
C(3)−C(4)−C(6)	127(1)	127.1(9)
Ta−N−C(5)	156.7(8)	155.5(7)
C(2)−N−C(5)	123(1)	125.3(7)

[a] CCP: the centroid of the cyclopentadienyl ring.

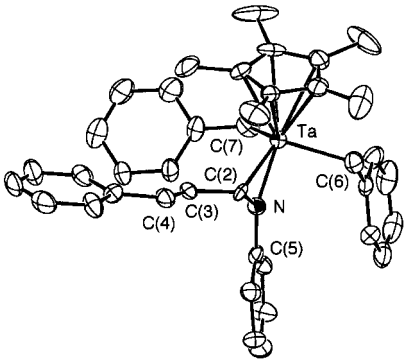


Figure 1. Molecular structure of **1a** with the labeling scheme.

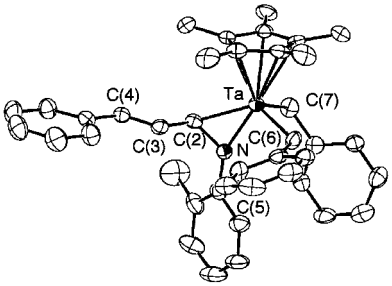


Figure 2. Molecular structure of **1b** with the labeling scheme.

to the tantalum atom, in contrast to the reported η^4-coordination mode found for some 1-aza-1,3-diene complexes of late transition metals as well as for the dichloro complexes **2**.[17] The nitrogen atom of azatantalacyclopropane was oriented away from the Cp* ligand, while that of a related tantalum−imine complex, $Cp^*TaMe_2(\eta^2\text{-}Me_2C{=}N(C_6H_3Me_2\text{-}2,6))$, was reported to point upward to the Cp* ligand.[11]

One equivalent of XylNC (Xyl = 2,6-dimethylphenyl) reacted with the dibenzyl complexes **1a** and **1b** in toluene at room temperature to give amido−imido complexes $Cp^*Ta(=NAr)\{N(Xyl)C(CH_2Ph){=}CHCH{=}CHPh\}(CH_2Ph)$ (**5a**, Ar = Ph; **5b**, Ar = *o*-Tol), respectively (Scheme 1). The ^{1}H NMR spectrum of **5a** showed

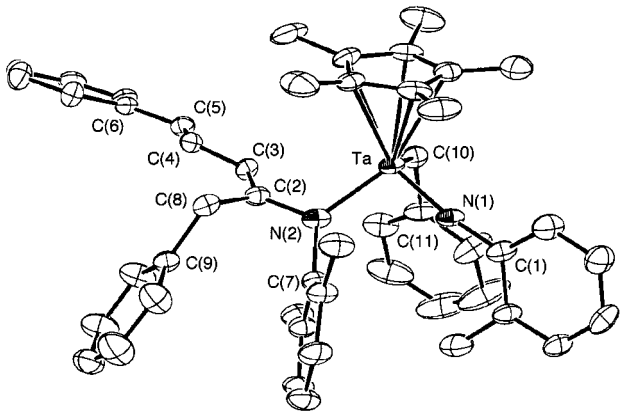
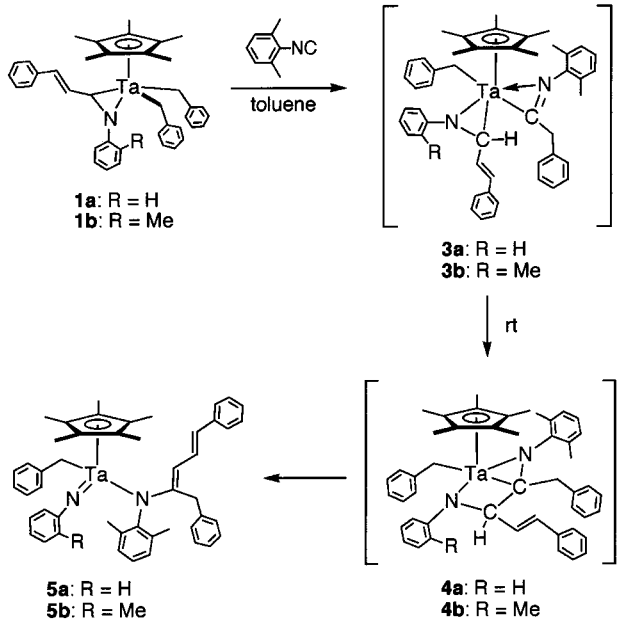


Figure 3. Molecular structure of one of two crystallographically independent molecules of **5b** showing the labeling scheme.

Scheme 1



two sets of ABq signals; one set of the proton signals (δ 2.54 and δ 2.81) is due to the benzyl group bound to the tantalum atom, while the other (δ 3.02 and δ 3.81) is assignable to the benzylic protons of the migrated benzyl group. Similar spectral data were observed for **5b**. These ^{1}H NMR spectral data were not able to rule out the other possible species **3**; however, the ^{13}C NMR spectra ruled out **3** because of no signal assignable to the iminoacyl carbon of **3**. The amido−imido structure of **5** was confirmed by the X-ray analysis of **5b** (Figure 3). The selected bond distances and angles of **5b** are shown in Table 2. The short bond distances (1.772(7) and 1.767(6) Å) of Ta−N(1) and the linear arrangement (171.5(6)° and 174.1(8)°) of Ta−N(1)−C(1) indicate that a Ta=N bond has triple-bond character,[19−23] while the distance (2.030(7) Å) of Ta−N(2) is slightly longer than

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Table 2. Selected Bond Lengths and Angles for 5b[a]

	molecule I	molecule II
	Bond Distances (Å)	
Ta−N(1)	1.772(7)	1.767(6)
Ta−N(2)	2.030(7)	2.019(9)
Ta−C(10)	2.216(9)	2.204(10)
N(2)−C(2)	1.42(1)	1.45(1)
	Bond Angles (deg)	
N(1)−Ta−N(2)	100.3(3)	99.8(3)
N(1)−Ta−C(10)	97.9(3)	98.8(3)
N(2)−Ta−C(10)	108.7(3)	100.1(3)
Ta−N(1)−C(1)	171.5(6)	174.1(8)
Ta−N(2)−C(7)	127.1(5)	120.7(5)
Ta−N(2)−C(2)	120.5(5)	127.2(7)
C(2)−N(2)−C(7)	112.3(7)	111.6(9)
Ta1−C(10)−C(11)	121.9(6)	125.9(6)

[a] Two independent molecules (I and II) of **5b** crystallized in the asymmetric unit.

those (ca. 1.93−1.98 Å) found for a typical Ta−N(alkylamido) bond,[24−32] but is comparable to a Ta−N(arylamido) bond,[28,33,34] presumably due to a contribution of π conjugation in the dienamido moiety.

We proposed the reaction mechanism as outlined in Scheme 1: the first step of the reaction is the insertion of XylNC into a Ta−C(benzyl) bond to give **3**, whose iminoacyl moiety can react with the C^2 atom of the AD ligand, leading to bicyclometallacycles **4**. Since the intermediate species **4** includes a four-membered skeleton, metathesis-type reaction cleaved the Ta−C and C^2−N(AD) bonds and spontaneously formed the C=C bond to give **5**. This mechanism was confirmed by detecting an iminoacyl complex Cp*Ta(η^2-Ph-AD)-{C(=NXyl)CH_2Ph}(CH_2Ph) (**3a**) by NMR measurement. The ^{1}H NMR spectrum of **3a** indicated that the Ph-AD ligand of **3a** kept the η^2-*C*,*N*-coordination mode; the H^2 proton of the Ph-AD ligand was observed at δ 2.65, comparable to that (δ 3.07) of **1a**, and showed two kinds of benzyl groups; one benzyl group binds to the tantalum atom and the other is adjacent to a quaternary carbon. Moreover, the direct evidence was the signal of the iminoacyl carbon (δ 251.2), the chemical shift value of which is in good accordance with that (δ 220−248) reported for some η^2-iminoacyl complexes of tantalum.[7,9,12−14,35−38] Complex **3a** was thermally unstable and gradually converted to **5a** at room temperature. Royo et al. already reported the same type of insertion reaction of XylNC into an imine complex, Cp*TaMeCl(η^2-Me_2C=NXyl) to give an amido−imido complex, Cp*TaCl(NXyl)(N(Xyl)C(Me)=C(Me)$_2$),[12] for which two possible pathways were proposed without alternative judgment: one is the same as Scheme 1, and the other involves the insertion of isonitrile into an azametallacyclopropane. We additionally carried out the reaction of the dichloro complex **2a** with XylNC and found that the replacement of the Ph-AD ligand by the isonitrile predominantly gave Cp*$TaCl_2$(CNXyl)$_3$ (**6**),[39] in sharp contrast to the reported insertion reaction of isonitrile into an azametallacyclopropane moiety of the imine complex Cp*$TaCl_2$(η^2-Me_2C=NAr), giving the imido complex Cp*$TaCl_2$(NAr).[12]

In summary, we have demonstrated the flexibility of the coordination mode of the AD ligand bound to the tantalum center and the unique intramolecular coupling reaction between the imine moiety of the AD ligand and the iminoacyl group on the tantalum center, resulting in the selective formation of the amido−imido complexes through intramolecular metathesis reaction. We are exploring the coordination flexibility and the unique reactivity of the AD and related heterosubstituted diene ligands.

Experimental Section

General Procedure. All manipulations involving air- and moisture-sensitive organometallic compounds were carried using 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. Complex Cp*$TaCl_4$ was prepared according to the literature.[40] Complexes **1a** and **2a** were prepared according to the literature.[17]

The ^{1}H (500, 400, 300, and 270 MHz) and ^{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*$TaCl_2$(*o*-Tol-AD) (2b). A mixture of Cp*$TaCl_4$ (892 mg, 1.95 mmol), 1-(*o*-methylphenyl)-4-diphenyl-1-aza-1,3-butadiene (992 mg, 1.52 mmol), aluminum (73.0 mg, 2.69 mmol), and $HgCl_2$ (5 mg) in THF (30 mL) was stirred at room temperature for 12 h. After insoluble products were separated 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 **2b** as purple crystalline solids, which were washed with hexane (10 mL). Complex **2b** (922 mg) was obtained in 78% yield, mp 115−117 °C (dec). ^{1}H NMR (400 MHz, C_6D_6, 35 °C): δ 1.63 (d, $^3J_{H-H}$ = 7.8 Hz, 1H, H^4), 1.75 (s,

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3H, CH_3), 1.89 (s, 15H, C_5Me_5), 6.01 (dd, $^3J_{H-H}$ = 5.3 and 7.8 Hz, 1H, H^3), 6.06 (d, $^3J_{H-H}$ = 5.3 Hz, 1H, H^2), 7.01 (d, 1H, 3-C_6H_4), 7.02 (t, 1H, 4-C_6H_4), 7.02 (t, 1H, *p*-Ph), 7.12 (t, 2H, 5-C_6H_4), 7.32 (d, 2H, *m*-Ph), 7.32 (s, 2H, *o*-Ph), 7.70 (d, 1H, 6-C_6H_4). ^{13}C NMR (100 MHz, C_6D_6, 35 °C): δ 12.0 (q, $^1J_{C-H}$ = 128 Hz, C_5Me_5), 18.0 (q, $^1J_{C-H}$ = 127 Hz, CH_3), 81.9 (d, $^1J_{C-H}$ = 135 Hz, C^4), 117.0 (d, $^1J_{C-H}$ = 187 Hz, C^2), 117.3 (d, $^1J_{C-H}$ = 165 Hz, C^3), 122.5 (s, C_5Me_5), 125.5 (d, $^1J_{C-H}$ = 160 Hz, 6-C_6H_4), 125.7 (d, $^1J_{C-H}$ = 158 Hz, *p*-Ph), 126.6 (d, $^1J_{C-H}$ = 158 Hz, 5-C_6H_4), 127.1 (d, $^1J_{C-H}$ = 158 Hz, *m*-Ph), 127.2 (d, $^1J_{C-H}$ = 156 Hz, *o*-Ph), 129.3 (d, $^1J_{C-H}$ = 158 Hz, *m*-Ph), 130.1 (d, $^1J_{C-H}$ = 158 Hz, 3-C_6H_4), 135.4 (s, 2-C_6H_4), 142.2 (s, *ipso*-Ph), 147.8 (s, 1-C_6H_4). Anal. Calcd for $C_{26}H_{30}Cl_2NTa$: C, 51.33; H, 4.97; N, 2.30. Found: C, 51.10; H, 5.30; N, 2.07.

Preparation of Cp*Ta(CH_2Ph)$_2$(*o*-Tol-AD) (1b). To a solution of **2b** (700 mg, 1.15 mmol) in toluene (15 mL) at −20 °C was added a suspension of Mg(CH_2Ph)$_2$ (1.5 equiv, 357 mg, 0.669 mmol) in toluene (5 mL). The reaction mixture was allowed to warm to room temperature and stirred for 1 h. After all volatiles were removed under reduced pressure, the resulting solid was extracted with hexane (80 mL). The extract was concentrated in vacuo, followed by washing with hexane (1 mL), to give yellow crystalline solids **1b** (612 mg, 74% yield), mp 125−127 °C (dec). ^{1}H NMR (400 MHz, C_6D_6, 35 °C): δ 1.71 (s, 15H, C_5Me_5), 1.85 (s, 2H, Ta-CH_2Ph), 2.25 (d, $^2J_{H-H}$ = 11.1 Hz, 1H, Ta-CH_2Ph), 2.42 (s, 3H, Ar-CH_3), 2.50 (d, $^2J_{H-H}$ = 11.1 Hz, 1H, Ta-CH_2Ph), 3.49 (d, $^3J_{H-H}$ = 7.8 Hz, 1H, H^2), 6.24 (d, $^3J_{H-H}$ = 15.6 Hz, 1H, H^4), 6.66 (dd, $^3J_{H-H}$ = 7.8 and 15.6 Hz, 1H, H^3), 6.87 (t, 1H, *p*-Ph), 6.89 (d, 1H, 6-C_6H_4), 6.93 (d, 2H, *o*-Ph), 6.96 (t, 1H, *p*-Ph), 6.98 (t, 1H, *p*-Ph), 7.01 (t, 1H, 5-C_6H_4), 7.02 (d, 1H, 3-C_6H_4), 7.04 (t, 1H, 4-C_6H_4), 7.04 (d, 2H, *o*-Ph), 7.05 (t, 2H, *m*-Ph), 7.19 (t, 2H, *m*-Ph), 7.20 (d, 2H, *o*-Ph), 7.21 (t, 2H, *m*-Ph). ^{13}C NMR (100 MHz, C_6D_6, 35 °C): δ 11.1 (q, $^1J_{C-H}$ = 127 Hz, C_5Me_5), 21.0 (q, $^1J_{C-H}$ = 126 Hz, Ar-CH_3), 76.7 (t, $^1J_{C-H}$ = 119 Hz, Ta-CH_2Ph), 79.8 (t, $^1J_{C-H}$ = 119 Hz, Ta-CH_2Ph), 82.0 (d, $^1J_{C-H}$ = 160 Hz, C^2), 116.9 (s, C_5Me_5), 123.3 (d, $^1J_{C-H}$ = 162 Hz, 6-C_6H_4), 123.8 (d, $^1J_{C-H}$ = 158 Hz, *p*-Ph), 123.9 (d, $^1J_{C-H}$ = 159 Hz, *p*-Ph), 124.5 (d, $^1J_{C-H}$ = 159 Hz, 4-C_6H_4), 124.9 (d, $^1J_{C-H}$ = 154 Hz, C^4), 126.2 (d, $^1J_{C-H}$ = 158 Hz, *p*-Ph), 126.2 (d, $^1J_{C-H}$ = 158 Hz, *o*-Ph), 126.6 (d, $^1J_{C-H}$ = 160 Hz, 5-C_6H_4), 127.9 (d, $^1J_{C-H}$ = 159 Hz, *m*-Ph), 128.0 (d, $^1J_{C-H}$ = 159 Hz, *m*-Ph), 128.5 (d, $^1J_{C-H}$ = 159 Hz, *m*-Ph), 129.2 (d, $^1J_{C-H}$ = 158 Hz, *o*-Ph), 129.9 (d, $^1J_{C-H}$ = 159 Hz, *o*-Ph), 130.0 (s, 2-C_6H_4), 131.9 (d, $^1J_{C-H}$ = 157 Hz, 3-C_6H_4), 138.5 (s, *ipso*-Ph), 138.8 (d, $^1J_{C-H}$ = 147 Hz, C^3), 145.4 (s, *ipso*-Ph), 147.0 (s, *ipso*-Ph), 154.6 (s, 1-C_6H_4). The 2D ^{1}H−^{1}H NOESY spectrum indicates neighboring protons in the molecule, e.g., (C_5Me_5 and H^2), (C_5Me_5 and H^3), (C_5Me_5 and H^4), (C_5Me_5 and CH_2Ph), (C_5Me_5 and *o*-Ph of AD), (C_5Me_5 and *o*-Ph of CH_2Ph), (CH_2Ph and *o*-Ph of CH_2Ph), (Me and 3-C_6H_4), (H^2 and H^4), (H^2 and H^3), (H^3 and H^4), and so on. IR (KBr): ν(C=C)/cm^{-1} 1590 (s) and ν(C=N)/cm^{-1} 1495 (s). Anal. Calcd for $C_{40}H_{44}NTa$: C, 66.75; H, 6.16; N, 1.95. Found: C, 66.64; H, 6.24; N, 2.02.

Synthesis of TaCp*(η^2-Ph-AD){C(=N-2,6-$Me_2C_6H_3$)-CH_2Ph}CH_2Ph (3a). Complex **1a** (48 mg, 0.068 mmol) and 2,6-dimethylphenylisocyanide (XylNC; 8.9 mg, 0.068 mmol) were dissolved in 0.6 mL of C_6D_6 in a 5 mm NMR tube. The NMR tube was sealed under reduce pressure, and then ^{1}H NMR was measured immediately. The spectrum showed formation of **3a** with a small amount of a second migration product, **5a**. ^{1}H NMR (C_6D_6, 35 °C): δ 1.10 (s, 3H, Me), 1.71 (s, 15H, C_5Me_5), 1.88 (s, 3H, Me), 2.14 (d, $^2J_{H-H}$ = 11.7 Hz, 1H, Ta-CH_2Ph), 2.65 (d, $^3J_{H-H}$ = 8.1 Hz, 1H, H^2), 3.80 (d, $^2J_{H-H}$ = 11.7 Hz, 1H, Ta-CH_2Ph), 4.06 (d, $^2J_{H-H}$ = 16.6 Hz, 1H, CH'_2Ph), 4.31 (d, $^2J_{H-H}$ = 16.6 Hz, 1H, CH'_2Ph), 6.28 (d, 1H, *m*-xyl), 6.47 (dd, $^3J_{H-H}$ = 8.1 and 15.6 Hz, 1H, H^3), 6.65 (m, 3H, *m*- and *p*-Ph), 6.70 (d, $^3J_{H-H}$ = 15.6 Hz, 1H, H^4), 6.70 (m, 2H, *m*- and *p*-xyl), 6.80 (d, 2H, *o*-Ph), 6.89 (m, 3H, *m*- and *p*-Ph), 6.01 (t, 1H, *p*-Ph), 7.05 (d, 2H, *o*-Ph), 7.22 (t, 2H, *m*-Ph), 7.34 (d, 2H, *o*-Ph), 7.37 (t, 2H, *m*-Ph), 7.86 (d, 2H, *o*-Ph). ^{13}C NMR (toluene-d_8, 5 °C): δ 10.8 (q, $^1J_{C-H}$ = 127 Hz, C_5Me_5), 19.2 (q, $^1J_{C-H}$ = 128 Hz, Me), 19.8 (q, $^1J_{C-H}$ = 128 Hz, Me), 41.9 (t, $^1J_{C-H}$ = 127 Hz, *C*H_2Ph), 47.4 (d, $^1J_{C-H}$ = 155 Hz, C^2), 49.5 (t, $^1J_{C-H}$ = 120 Hz, *C*H_2Ph), 112.1 (s, C_5Me_5), 120.1−155.8 (aromatic and olefinic carbons), 251.2 (s, N=*C*(CH_2Ph)$_2$).

Preparation of TaCp*(=NPh){N(2,6-$Me_2C_6H_3$)C(CH_2-Ph)=CHCH=CHPh}(CH_2Ph) (5a). To a solution of **1a** (125 mg, 0.177 mmol) in toluene (2.0 mL) was added a solution of XylNC (23 mg, 0.177 mmol) in toluene (2.0 mL) at −25 °C. The reaction mixture was allowed to warm to room temperature and further stirred for 12 h at room temperature. After removal of the solvent under reduced pressure, the resulting solid was washed with hexane (1.2 mL) to give analytically pure yellow microcrystals of **5a** (115 mg), in 78% yield, mp 190−194 °C (dec). ^{1}H NMR (C_6D_6, 35 °C): δ 1.61 (s, 3H, Me), 1.95 (s, 15H, C_5Me_5), 2.48 (s, 3H, Me), 2.54 (d, $^2J_{H-H}$ = 12.2 Hz, 1H, Ta-CH_2Ph), 2.81 (d, $^2J_{H-H}$ = 12.2 Hz, 1H, Ta-CH_2Ph), 3.02 (d, $^2J_{H-H}$ = 14.9 Hz, 1H, CH_2Ph), 3.81 (d, $^2J_{H-H}$ = 14.9 Hz, 1H, CH_2Ph), 5.97 (d, $^3J_{H-H}$ = 10.7 Hz, 1H, H^2), 6.33 (d, 2H, *o*-Ph), 6.50 (d, 1H, *m*-xyl), 6.71 (d, $^3J_{H-H}$ = 15.6 Hz, 1H, H^4), 6.76 (t, 1H, *p*-Ph), 6.76 (t, 1H, *p*-xyl), 6.81 (d, 2H, *o*-Ph), 6.89 (t, 1H, *p*-Ph), 6.89 (m, 3H, *m*- and *p*-Ph), 7.01 (d, 1H, *m*-xyl), 7.01 (t, 1H, *p*-Ph), 7.10 (t, 1H, *p*-Ph), 7.10 (t, 2H, *m*-Ph), 7.12 (t, 2H, *m*-Ph), 7.22 (t, 2H, *m*-Ph), 7.32 (dd, $^3J_{H-H}$ = 10.7 and 15.6 Hz, 1H, H^3), 7.43 (d, 2H, *o*-Ph), 7.50 (d, 2H, *o*-Ph). ^{13}C NMR (C_6D_6, 35 °C): δ 12.0 (q, $^1J_{C-H}$ = 127 Hz, C_5Me_5), 18.5 (q, $^1J_{C-H}$ = 127 Hz, Me), 21.9 (q, $^1J_{C-H}$ =126 Hz, Me), 38.2 (t, $^1J_{C-H}$ = 126 Hz, *C*H_2Ph), 59.7 (t, $^1J_{C-H}$ = 119 Hz, Ta-*C*H_2Ph), 116.2 (d, $^1J_{C-H}$ = 163 Hz, C^2), 117.0 (s, C_5Me_5), 122.3 (d, $^1J_{C-H}$ = 158 Hz, *p*-xyl), 123.2 (d, $^1J_{C-H}$ = 157 Hz, *p*-Ph), 125.2 (d, $^1J_{C-H}$ = 157 Hz, *p*-Ph), 125.6 (d, $^1J_{C-H}$ = 157 Hz, *o*-Ph), 126.0 (d, $^1J_{C-H}$ = 156 Hz, *p*-Ph), 126.4 (d, $^1J_{C-H}$ = 157 Hz, *o*-Ph), 127.0 (d, $^1J_{C-H}$ = 147 Hz, C^3), 127.3 (d, $^1J_{C-H}$ = 159 Hz, *p*-Ph), 127.9 (d, $^1J_{C-H}$ = 159 Hz, *m*-xyl), 128.0 (d, $^1J_{C-H}$ = 158 Hz, *m*-Ph), 128.0 (d, $^1J_{C-H}$ = 158 Hz, *m*-Ph), 128.0 (d, $^1J_{C-H}$ = 158 Hz, *m*-Ph), 128.6 (d, $^1J_{C-H}$ = 157 Hz, *o*-Ph), 129.0 (d, $^1J_{C-H}$ = 158 Hz, *m*-Ph), 129.2 (d, $^1J_{C-H}$ = 159 Hz, *m*-xyl), 129.7 (d, $^1J_{C-H}$ = 155 Hz, *o*-Ph), 130.1 (d, $^1J_{C-H}$ = 156 Hz, C^4), 132.5 (s, *o*-xyl), 136.4 (s, *o*-xyl), 138.2 (s, *ipso*-Ph on C^4), 138.6 (s, N*C*(CH_2Ph)=), 149.2 (s, ipso-Ph of Ta-CH_2Ph), 151.9 (s, ipso-Ph of CH_2Ph), 152.5 (s, *ipso*-xyl), 156.0 (s, *ipso*-Ph on N). IR (KBr): 1578, 1481, 1349, 1264, 1120, 1095, 1026, 803, 751, 692. UV (cyclohexane): λ_{max} 302 nm (ϵ 1.9 × 10^4) and λ_{max} 364 nm (ϵ 1.7 × 10^4). FAB-MS: *m*/*z* 837 (M^+), 746 [($M - CH_2Ph)^+$, base peak]. Anal. Calcd for $C_{48}H_{51}N_2Ta$: C, 68.89; H, 6.14; N, 3.35. Found: C, 68.53; H, 6.41; N, 3.33.

Preparation of TaCp*{=N(2-MeC_6H_4)}{N(2,6-$Me_2C_6H_3$)-C(CH_2Ph)=CHCH=CHPh}(CH_2Ph) (5b). A solution of **1b** (200 mg, 0.278 mmol) and XylNC (36.5 mg, 0.278 mmol) in toluene (2.0 mL) was stirred overnight. After removal of all volatiles under reduced pressure, the resulting solids were rinsed with hexane (1.2 mL) to give analytically pure yellow crystals of **5b** (213 mg, 0.250 mmol, 90% yield), mp 220−202 °C (dec). ^{1}H NMR (C_6D_6, 35 °C): δ 1.68 (s, 3H, Me), 1.94 (s, 15H, C_5Me_5), 2.02 (s, 3H, Me(xyl)), 2.49 (s, 3H, Me(xyl)), 2.72 (d, $^2J_{H-H}$ = 12.7 Hz, 1H, Ta-CH_2Ph), 2.98 (d, $^2J_{H-H}$ = 14.6 Hz, 1H, Ta-CH_2Ph), 3.05 (d, $^2J_{H-H}$ = 12.9 Hz, 1H, CH_2Ph), 3.86 (d, $^2J_{H-H}$ = 14.6 Hz, 1H, CH_2Ph), 6.04 (d, $^3J_{H-H}$ = 10.5 Hz, 1H, H^2), 6.45 (d, 1H, *m*-xyl), 6.68 (t, 1H, *p*-xyl), 6.71 (d, $^3J_{H-H}$ = 15.3 Hz, 1H, H^4), 6.74 (d, 1H, 4-C_6H_4), 6.78 (t, 1H, 5-C_6H_4), 6.79 (d, 2H, *o*-Ph), 6.89 (d 1H, *m*-xyl), 6.0.89 (d, 2H, *m*-Ph), 6.89 (t, 1H, *p*-Ph), 7.00 (d, 1H, 3-C_6H_4), 7.11 (t, 2H, *m*-Ph), 7.11 (d, 2H, 6-C_6H_4), 7.23 (t, 2H, *m*-Ph), 7.36 (dd, $^3J_{H-H}$ = 10.5 and 15.3 Hz, 1H, H^3), 7.45 (d, 2H, *o*-Ph), 7.47 (d, 2H, *o*-Ph). ^{13}C NMR (C_6D_6, 35 °C): δ 11.8 (q, $^1J_{C-H}$ = 127 Hz, C_5Me_5), 18.2 (q, $^1J_{C-H}$ = 127 Hz, Me), 18.8 (q, $^1J_{C-H}$ =127 Hz, Me(xyl)), 22.0 (q, $^1J_{C-H}$ = 126 Hz, Me(xyl)), 38.2 (t, $^1J_{C-H}$ = 125 Hz, *C*H_2Ph), 58.2 (t, $^1J_{C-H}$ = 118 Hz, Ta-*C*H_2Ph), 158.4 (d, $^1J_{C-H}$ = 158 Hz, C^2), 117.1 (s, C_5Me_5), 122.6 (d, $^1J_{C-H}$ = 158 Hz, 4-C_6H_4), 123.5 (d, $^1J_{C-H}$ = 158 Hz, *p*-Ph), 125.3 (d, $^1J_{C-H}$ = 159 Hz, *p*-xyl), 125.3 (d, $^1J_{C-H}$ = 157 Hz, *p*-Ph), 125.9 (d, $^1J_{C-H}$ = 159 Hz, *p*-Ph), 126.4 (d, $^1J_{C-H}$ = 160 Hz, *o*-Ph), 126.8 (d,

Table 3. Crystal Data and Data Collection Parameters of 1a and 1b

	1a
formula	$C_{39}H_{42}NTa$
fw	705.72
cryst syst	monoclinic
space group	$P2_1/n$ (#14)
a, Å	16.065(4)
b, Å	10.998(4)
c, Å	19.730(5)
α, deg	
β, deg.	112.61(2)
γ, deg	
V, Å^3	3218(1)
Z	4
no. of reflns for cell determ (2*θ* range)	25 (20−30°)
D_{calcd}, g/cm^{-3}	1.456
F(000)	1424.00
μ [Mo Kα], cm^{-1}	34.37
diffractometer	AFC-7R
T, K	296(1)
cryst size, mm	0.20 × 0.17 × 0.13
scan type	*ω*−2*θ*
scan speed, deg/min	16
scan width, deg	1.10 + 0.30 tan *θ*
$2\theta_{min}$, $2\theta_{max}$, deg	5.0, 55.0
unique data (R_{int})	6580 (0.127)
no. of obsns	4218
no. of variables	370
R1, wR2 (all data)	0.140, 0.107
R, R_w	0.040, 0.043 ($I > 3.0\sigma(I)$)
GOF on *F*^{2}	1.01
Δ, e Å^{-3}	2.67, −3.95
	1b
formula	$C_{40}H_{44}NTa$
fw	719.74
cryst syst	monoclinic
space group	$P2_1/c$ (#14)
a, Å	9.504(3)
b, Å	17.511(4)
c, Å	20.263(8)
α, deg	
β, deg.	100.58(4)
γ, deg	
V, Å^3	3315(1)
Z	4
no. of reflns for cell determ (2*θ* range)	25 (20−30°)
D_{calcd}, g/cm^{-3}	1.442
F(000)	1456.00
μ [Mo Kα], cm^{-1}	33.38
diffractometer	AFC-7R
T, K	296(1)
cryst size, mm	0.58 × 0.25 × 0.12
scan type	*ω*−2*θ*
scan speed, deg/min	32
scan width, deg	1.57 + 0.30 tanq
$2\theta_{min}$, $2\theta_{max}$, deg	5.0, 55.0
unique data (R_{int})	7977 (0.083)
no. of obsns	7718
no. of variables	379
R1, wR2 (all data)	0.126, 0.080
R, R_w	0.037, 0.037 ($I > 3.0\sigma(I)$)
GOF on *F*^{2}	1.22
Δ, e Å^{-3}	2.53, −2.70

$^1J_{C-H}$ = 148 Hz, C^3), 127.0 (d, $^1J_{C-H}$ = 155 Hz, 5-C_6H_4), 127.3 (d, $^1J_{C-H}$ = 156 Hz, 6-C_6H_4), 127.9 (d, $^1J_{C-H}$ = 157 Hz, *m*-xyl), 127.9 (d, $^1J_{C-H}$ = 158 Hz, *m*-Ph), 128.1 (d, $^1J_{C-H}$ = 158 Hz, *m*-Ph), 128.2 (d, $^1J_{C-H}$ = 156 Hz, *o*-Ph), 129.0 (d, $^1J_{C-H}$ = 158 Hz, *m*-Ph), 129.2 (d, $^1J_{C-H}$ = 157 Hz, *m*-xyl), 130.0 (d, $^1J_{C-H}$ = 156 Hz, 3-C_6H_4), 130.1 (d, $^1J_{C-H}$ = 152 Hz, C^4), 130.7 (d, $^1J_{C-H}$ = 155 Hz, *o*-Ph), 132.6(s, *o*-xyl), 133.5 (s, 2-C_6H_4), 136.2 (s, *o*-xyl), 138.2 (s, *ipso*-Ph on C^4), 138.7 (s, N*C*(CH_2Ph)═), 148.4 (s, ipso-Ph of Ta-CH_2Ph), 152.0 (s, ipso-Ph of CH_2Ph), 152.0 (s, *ipso*-xyl), 154.3 (s, *ipso*-Ph on N). IR (KBr): 1614, 1591, 1475, 1448, 1330, 1264, 1181, 1121, 1096, 1029, 967, 747, 693 cm^{-1}. FAB-MS: *m/z* 851 (M^+), 760 ($M - CH_2Ph)^+$. Anal. Calcd for $C_{49}H_{53}N_2Ta$: C, 69.16; H, 6.28; N, 3.29. Found: C, 69.00; H, 6.20; N, 3.29.

Table 4. Crystal Data and Data Collection Parameters of 5b

formula	$C_{98}H_{106}N_4Ta_2$
fw	1701.84
cryst syst	triclinic
space group	$P\bar{1}$ (No. 2)
a, Å	21.211(1)
b, Å	21.695(1)
c, Å	10.7573(5)
α, deg	95.316(2)
β, deg	94.598(2)
γ, deg	118.338(1)
V, Å^3	4055.0(4)
Z	2
no. of reflns for cell determ (2*θ* range)	36105(3.8−55.0°)
D_{calcd}, g/cm^{-3}	1.394
F(000)	1736.00
μ[Mo Kα], cm^{-1}	27.42
diffractometer	R-AXIS-RAPID
T, K	213(1)
cryst size, mm	0.10 × 0.10 × 0.08
no. of images	101
total oscillation angles (deg)	300.0
exposure time (min per deg)	7.50
$2\theta_{min}$, $2\theta_{max}$, deg	3.8, 55.0
no. of reflns measured (total)	47396
no. of reflns measured (unique)	18354 (R_{int} = 0.054)
no. of variables	1018
R1, wR2 (all data)	0.112, 0.147
R ($I > 2.0\sigma(I)$)	0.063
GOF on *F*^{2}	1.22
Δ, e Å^{-3}	7.45, −7.74

Crystallographic Data Collections and Structure Determination of 1a, 1b, and 5b. The X-ray diffraction studies was sealed in glass capillaries under an argon atmosphere The crystals of complexes **1a** and **1b** were mounted on a Rigaku AFC-7R four-circle diffractometer for data collection using Mo Kα (graphite monochromated, $\lambda = 0.71069$) radiation, and the crystals of complex **5b** were mounted on a Rigaku R-AXIS Rapid imaging plate diffractometer for data collection using Mo Kα (graphite monochromated, $\lambda = 0.71069$) radiation. Relevant crystal and data statistics are summarized in Table 3 (**1a** and **1b**) and Table 4 (**5b**). The unit cell parameters and the orientation matrix at 23 °C were determined by a least-squares fit to 2*θ* values of 25 strong higher reflections for complexes **1a** and **1b**. In the case of the AFC-7R four-circle diffractometer, an empirical absorption correction was applied on the basis of azimuthal scans and the data were corrected for Lorentz and polarization effects. In the case of the R-AXIS Rapid imaging plate diffractometer, a symmetry-related absorption correction using the program ABSCOR[41] was applied. The data were corrected for Lorentz and polarization effects.

The structures of complex **1a** and **1b** were solved by a direct method (SHELXS 86)[42] and refined by the full-matrix least-squares method. The structure of complex **5b** was solved by a direct method (SHELXS-97)[43] and expanded using Fourier techniques (DIRDIF94).[44] Two independent molecules of **5b** crystallized in the asymmetric unit. Measured nonequivalent reflections were used for the structure determination. In the subsequent refinement, the function $\sum w(|F_o| - |F_c|)^2$ was

(41) Higashi, T. *Program for Absorption Correction*; Rigaku Corporation: Tokyo, Japan, 1995.
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(43) Sheldrick, G. M. *Program for the Solution of Crystal Structures*; University of Göttingen: Germany, 1997.
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minimized, where $|F_o|$ and $|F_c|$ are the observed and calculated structure factor amplitudes, respectively. The agreement indices are defined as $R1 = \sum(||F_o| - |F_c||)/\sum|F_o|$ and $wR2 = [\sum w(F_o^2 - F_c^2)^2/\sum(wF_o^4)]^{1/2}$. 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.

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Supporting Information Available: Tables giving crystallographic data for complexes **1a**, **1b**, and **5b**. This material is available free of charge via the Internet at http://pubs.acs.org.

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