Synthesis, Characterization, and Reactions of a Half-Metallocene Benzylidene Complex of Tantalum Bearing 2,3-Dimethyl-1,3-butadiene and Pentamethylcyclopentadienyl Ligands

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A half-metallocene benzylidene complex of tantalum, Ta(CHPh)Cp*(η^4-*supine*-2,3-dimethyl-1,3-butadiene) (**1**), was prepared by treating $TaCl_2$Cp*(η^4-*supine*-2,3-dimethyl-1,3-butadiene) (**2**) with $Mg(CH_2Ph)_2$ in toluene. The structure of **1** was determined by X-ray analysis, indicating the syn rotamer of the Ta═CHPh moiety; the Ph group points upward toward the Cp* ligand. The coordinatively unsaturated 16-electron complex **1** reacted with some unsaturated organic molecules (ethylene, cyclopentene, and *tert*-butyl cyanide), an alcohol, and an amine. The cycloaddition of ethylene and cyclopentene gave rise to metallacyclobutanes. The addition of *tert*-butyl cyanide to **1** afforded an imido tantalum complex, Ta(NC(^{t}Bu)═CHPh)Cp*(η^4-*supine*-2,3-dimethyl-1,3-butadiene) (**6**), which was derived from the metathesis reaction of a nascent 2-aza-1-tantalacyclobut-2-ene intermediate. Protonolysis of **1** by addition of methanol and *p*-methoxyaniline gave a methoxy benzyl complex, Ta(CH_2Ph)(OCH_3)Cp*(η^4-*supine*-2,3-dimethyl-1,3-butadiene) (**7**), and an amido benzyl complex, Ta(CH_2Ph)($NHC_6H_4OCH_3$)Cp*(η^4-*supine*-2,3-dimethyl-1,3-butadiene) (**8**), respectively. Upon heating at 60 °C, complex **8** was converted to an imido butenyl complex, Ta(CH_2Ph)(NC_6H_4-OCH_3)(η^1-2,3-dimethyl-2-butene)Cp* (**9**). Structures of the amido complex **8** and the imido complexes **6** and **9** were determined by X-ray analysis.

Introduction

Since Schrock initiated study of the chemistry of alkylidene complexes of niobium and tantalum,[1−7] various alkylidene complexes of early transition metals have been prepared using different kinds of supporting ligands.[8−28] Some of these alkylidene complexes have been applied as catalysts for olefin metathesis reactions, including ring-opening metathesis polymerization of cyclic olefins, and as reagents for alkene formation from carbonyl compounds.[7,8,24,29−31] We have been interested in the chemistry of half-metallocene−diene complexes of group 5 metals, in view of their isoelectronic analogy to that of the metallocene complexes of group 4 metals.[32−35] Some alkylidene tantalum metallocene and

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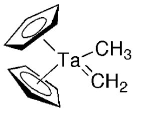
half-metallocene complexes such as $Ta(CH_2)(CH_3)Cp_2$ (**A**) and a dibenzyl benzylidene complex (**B**) have been investigated.[5,6] We have already reported benzylidene complexes of tantalum bearing 1,3-butadiene (**C**) and *o*-xylidene (**D**) ancillary ligands and their catalytic activity in the stereoselective ring-opening metathesis polymerization of norbornene.[36−38] In the present paper, we describe the synthesis of a new benzylidene diene complex of tantalum. The introduction of 2,3-dimethyl-1,3-butadiene (abbreviated DMBD) to half-metallocene complexes of tantalum has enabled us to isolate the phosphine-free benzylidene complex Ta(CHPh)Cp*(η^4-*supine*-DMBD) (**1**; Cp* = pentamethylcyclopentadienyl). We also report the reactivity of the complex **1** with various unsaturated organic compounds and protic substrates.



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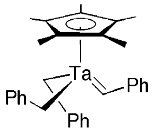

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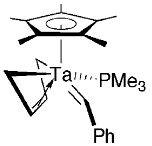

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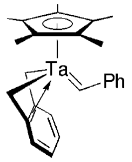

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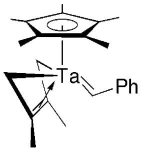

1

Results and Discussion

Complex **1** was prepared in 49% yield by the reaction of $TaCl_2Cp^*$(η^4-*supine*-DMBD) (**2**) with 1 equiv of $Mg(CH_2Ph)_2$ in toluene. α-Hydrogen abstraction of one of the two benzyl groups of an intermediate dibenzyl complex followed by the release of toluene proceeded spontaneously to give **1**. This is in sharp contrast to the analogous 1,3-butadiene complex $TaCl_2Cp^*$(η^4-*supine*-1,3-butadiene), which reacted with $Mg(CH_2Ph)_2$ in toluene to afford the corresponding dibenzyl complex, and the coordination of PMe_3 was required to stabilize the corresponding benzylidene complex **C** upon thermolysis.[36,38] The reaction of $TaCl_4Cp$ with 2 equiv of (2,3,3-trimethylallyl)magnesium bromide followed by the addition of $Mg(CH_2Ph)_2$ in THF in the presence of HMPA afforded the dibenzyl complex $Ta(CH_2Ph)_2Cp$(η^4-*supine*-DMBD) (**3**). The observed difference in reactivity might be attributed to the steric congestion around the metal center and the increased electron-donor character induced by the methyl groups on the ligand. The most characteristic feature of **1** is the stereochemistry of the Ta═CHPh moiety, which was found to be a syn rotamer, as evident from NMR spectroscopy and X-ray analysis: the phenyl group points upward toward the Cp* ligand. The ^1H NMR spectrum of **1** displayed a singlet resonance at δ 5.88 due to C*H*Ph, and the ^{13}C NMR spectrum showed a signal at δ 242.8 due to the benzylidene carbon with a rather small J_{C-H} coupling constant (90 Hz).

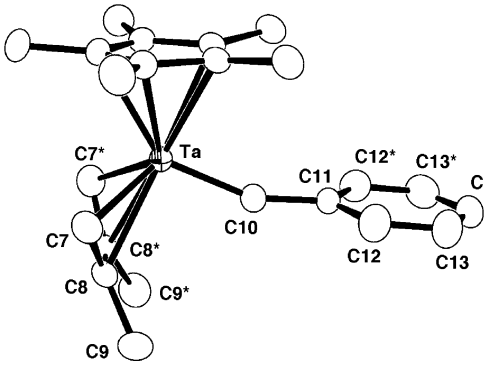

Figure 1. ORTEP view of **1** showing 50% probability displacement ellipsoids. Hydrogen atoms are omitted for clarity.

Table 1. Selected Bond Distances (Å) and Angles (deg) of 1[a]

Ta−C10	1.962(4)	Ta−C7	2.198(3)
Ta−C8	2.433(3)	C7−C8	1.454(5)
C8−C8*	1.395(7)	C8−C9	1.508(5)
C10−C11	1.461(5)		
C10−Ta−C7	114.24(12)	C7−Ta−C7*	84.12(19)
Ta−C10−C11	158.1(3)		

[a] An asterisk indicates that atoms are generated by the symmetry transformations *x*, $-y + {}^1/_2$, *z*.

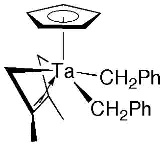

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Figure 1 shows the discrete structure of **1**, and selected bond distances and angles are listed in Table 1. The DMBD ligand coordinated in an η^4-supine fashion to the tantalum atom. It is noteworthy that the Ta═CHPh moiety in **1** adopts a syn geometry, the same as that found for **B** and **D**. The two methyl groups on the diene ligand enhance the σ-bond character of the Ta−C bond, favoring a metallacyclopentene form. The interaction between the double bond and vacant d orbital of the tantalum atom might be weakened, and hence the α-agostic interaction between C*H*Ph and the same vacant d-orbital controls the orientation of the Ph group. The short bond distance (1.962(4) Å) of Ta−C10 and the large angle (158.1(3)°) of Ta−C10−C11 indicated the

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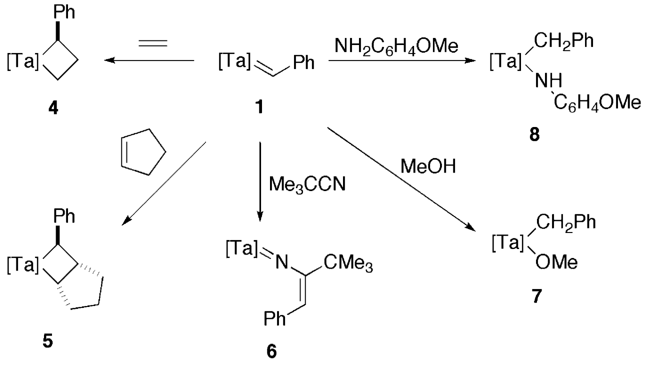
Scheme 1



[Ta] = TaCp*(DMBD)

presence of an α-agostic interaction between Ta and H_α, as is evident from the small J_{C-H} coupling constant. The Ta−C10 bond distance is shorter than that (2.044(8) Å) found for **C**[36] but is longer than those found for **D** (1.925(9) Å)[38] and **B** (1.883(14) Å).[6] The long−short−long bond alternation (C7−C8 = C7*−C8* = 1.454(5) Å and C8−C8* = 1.395(7) Å) of the diene unit and the obtuse fold angle (108.2(2)°) between the plane of the diene carbons and the plane of C7, Ta, and C7* are the consequence of the large contribution of η^2-2σ-metallacyclo-3-pentene, as found for early-transition-metal−diene complexes;[39] thus, the bond distance of Ta−C7 (2.198(3) Å) is longer than that (2.433(3) Å) of Ta−C8.

Scheme 1 shows some reactions of the 16-electron, coordinatively unsaturated complex **1**. Ethylene and cyclopentene reacted with **1** to give tantalacyclobutanes **4** and **5**, respectively. In the ^{1}H NMR spectra, we observed dissymmetric signals due to the DMBD ligand. The resonance due to the β-hydrogen of the metallacyclobutanes appeared at rather high field (δ 1.45 for **4** and 0.20 for **5**), as typically observed for such four-membered metallacycles.[37,38] These complexes are stable at room temperature but decompose at elevated temperature (60−80 °C). In the case of norbornene, no identifiable product was detected due to ROMP of the monomer, though the activity was very low and only a trace amount of poly(norbornene) was obtained.[36,38]

Treatment of **1** with 1 equiv of *tert*-butyl cyanide in toluene resulted in the formation of the imido complex **6**, whose formulation and structure were revealed by spectral data, combustion analysis, and an X-ray study. An azametallacyclobutene is anticipated as an intermediate, whose metathesis reaction would lead to the formation of **6**. The molecular structure of **6** is shown in Figure 2, clearly indicating the *Z* stereochemistry of the C=C bond. Selected bond distances and angles of **6** are listed in Table 2. The diene unit is normal in its η^4-supine-s-cis coordination to the tantalum atom: the fold angle between the planes defined by the diene carbons and C11, Ta, and C14 is 107.5(2)°. The short Ta−N bond distance (1.824(3) Å) and the large Ta−N−C17 angle (173.5(2)°) are consistent with a Ta−N imido fragment. However, the bond distance of Ta−N in **6** is much longer than those found for some tantalum−imido complexes such as Ta(NPh)Cl$_3$(thf)(PEt$_3$) (1.765(5) Å),[40] [Ta(NC$_6$H$_4$CMe$_3$-2)Cl$_4$(py)]$^-$ (1.779(5) Å),[41] and Ta(NC$_6$H$_3$(^{i}Pr)$_2$-2,6)(MeC(2-C$_5$H$_4$N)(CH$_2$NSiMe$_3$)$_2$) (1.808(2) Å)[42] and some half-metallocene imido complexes (1.772(5)−1.793(4) Å).[28,43−48] This might be attributed to the interaction of a π-orbital of the nitrogen atom with a π-orbital of the C17−C18 double bond (1.366(5) Å), weakening the π-donation from the nitrogen atom to the metal center.

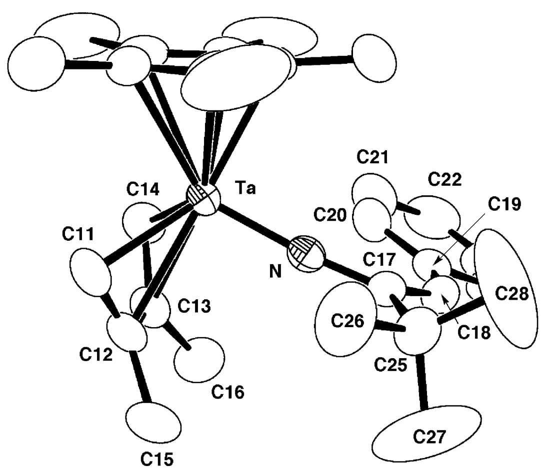


Figure 2. ORTEP view of **6** showing 50% probability displacement ellipsoids. Hydrogen atoms are omitted for clarity.

Table 2. Selected Bond Distances (Å) and Angles (deg) of 6

Ta−N	1.824(3)	Ta−C14	2.192(4)
Ta−C11	2.205(4)	Ta−C12	2.422(4)
Ta−C13	2.443(4)	N−C17	1.361(4)
C11−C12	1.445(7)	C12−C13	1.390(7)
C12−C15	1.514(6)	C13−C14	1.469(6)
C13−C16	1.514(6)	C17−C18	1.366(5)
C17−C25	1.562(5)	C18−C19	1.454(5)
C25−C28	1.473(7)	C25−C27	1.521(7)
C25−C26	1.521(6)		
Ta−N−C17	173.5(2)	Ta−C11−C12	80.2(2)
Ta−C12−C13	74.2(2)	Ta−C12−C11	63.8(2)
Ta−C12−C15	128.0(3)	Ta−C13−C12	72.6(2)
Ta−C13−C14	62.4(2)	Ta−C13−C16	126.9(3)
Ta−C14−C13	81.1(2)		
N−C17−C18	125.1(3)	N−C17−C25	116.9(3)
C11−C12−C13	122.8(4)	C11−C12−C15	117.4(5)
C13−C12−C15	118.8(5)	C12−C13−C14	121.0(4)
C12−C13−C16	121.5(4)	C14−C13−C16	115.7(4)
C18−C17−C25	118.0(3)	C17−C18−C19	132.0(3)

Protonolysis of **1** with 1 equiv of methanol in toluene proceeded readily to give the corresponding benzyl

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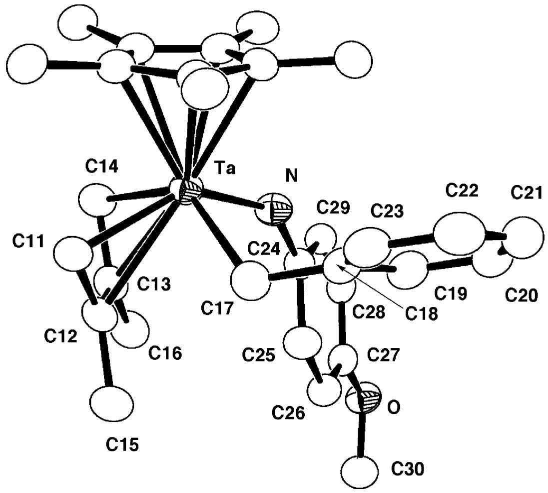
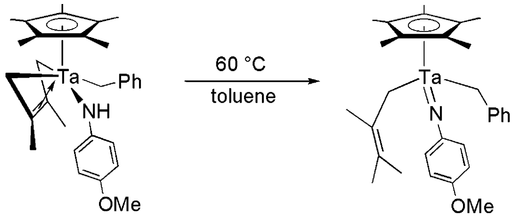


Figure 3. ORTEP view of **8** showing 50% probability displacement ellipsoids. Hydrogen atoms are omitted for clarity.

methoxy complex Ta(OMe)(CH_2Ph)Cp*(η^4-*supine*-DMBD) (**7**) in quantitative yield. The ^1H NMR spectrum of **7** displayed a singlet at δ 3.42 due to methoxy protons and an AB quartet (δ 1.84 and 2.17 with $J = 12.2$ Hz) due to the benzyl group along with dissymmetric signals of the DMBD ligand, owing to the coordination of methoxy and benzyl ligands to the tantalum atom.

Similarly, treatment of **1** with 1 equiv of *p*-methoxyaniline in toluene at −78 °C quantitatively afforded the amido tantalum complex **8**, which can be isolated below −10 °C. At room temperature **8** gradually turned into the imido tantalum complex **9**, and the conversion was complete at elevated temperature (eq 1). The proton of the nitrogen atom of **8**, whose signal in the ^1H NMR spectrum was observed at δ 1.73, migrated to the DMBD ligand, instead of the benzyl group, and thus **9** has 2,3-dimethyl-2-butenyl and benzyl ligands. This selective migration is due to the general tendency that a diene ligand bound to an early transition metal has a σ-bonding nature and a metallacyclo-3-pentene structure; hence, the reactivity of the diene moiety is assumed to likely be higher than that of the benzyl group. Zirconocene−imido complexes have been prepared by reductive elimination of methane from Zr(Me)(NHAr)Cp_2.[49] The complexes **8** and **9** were further characterized by X-ray analyses.



8 9 (1)

X-ray structures of **8** and **9** are shown in Figures 3 and 4, respectively, and selected bond distances and angles are listed in Table 3. Notable structural features are that the complex **8** has an amido ligand and a DMBD ligand, while the complex **9** has η^1-2,3-dimethyl-2-butenyl ligand and an imido ligand. The DMBD ligand of **8** is coordinated in an η^4-supine-s-cis fashion to the tantalum center with a fold angle of 99.5(2)° between the plane of the diene carbons and the plane of C11, Ta, and C14. The bond distance (2.016(3) Å) of Ta−N and the angle (142.5(3)°) of Ta−N−C24 of **8** are normal for an amido moiety. Complex **9** adopts a three-legged piano-stool geometry surrounded by two carbon atoms and one nitrogen atom. The bond distance (1.788(3) Å) of Ta−N is much shorter than that of the amido complex **8**, and the angle (165.3(3)°) of Ta−N−C24 is much larger than that of **8**. The Ta−N bond distance of the imido complex **9** is longer than that of half-metallocene imido complexes[28,43−48] but is shorter than that of **6**.

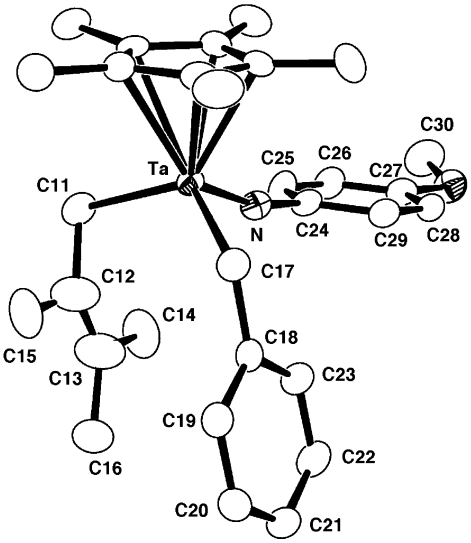


Figure 4. ORTEP view of **9** showing 50% probability displacement ellipsoids. Hydrogen atoms are omitted for clarity.

Table 3. Selected Bond Distances (Å) and Angles (deg) of 8 and 9

	8	9
Ta−N	2.016(3)	1.788(3)
Ta−C17	2.329(5)	2.240(4)
Ta−C11	2.247(4)	2.187(4)
Ta−C12	2.517(4)	
Ta−C13	2.515(4)	
Ta−C14	2.233(4)	
N−C24	1.415(5)	1.387(5)
C11−C12	1.464(6)	1.522(7)
C12−C13	1.390(7)	1.174(9)
C13−C14	1.452(6)	1.636(10)
C12−C15	1.494(7)	1.657(10)
C13−C16	1.506(6)	1.489(7)
C17−C18	1.499(6)	1.497(5)
Ta−N−C24	142.5(3)	165.3(3)
Ta−C17−C18	120.7(3)	122.7(2)
Ta−C11−C12	82.5(3)	94.2(3)
Ta−C12−C11	62.3(2)	
Ta−C12−C13	73.9(3)	
Ta−C12−C15	133.8(3)	
Ta−C13−C12	74.0(2)	
Ta−C13−C14	61.8(2)	
Ta−C13−C16	136.6(3)	
Ta−C14−C13	83.2(3)	
C11−C12−C13	114.7(4)	132.6(9)
C13−C12−C15	123.2(4)	111.5(7)
C11−C12−C15	122.1(4)	115.9(6)
C12−C13−C14	115.0(4)	112.6(7)
C12−C13−C16	124.9(4)	131.6(9)
C14−C13−C16	120.0(4)	115.5(6)

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[49] Walsh, P. J.; Hollander, F. J.; Bergman, R. G. *Organometallics* **1993**, *12*, 3705.

Conclusions

In this contribution, we have described the synthesis of the stable benzylidene tantalum complex **1**, bearing Cp* and 2,3-dimethyl-1,3-butadiene ligands, as a single syn rotamer, fully characterized by spectral data and X-ray analysis. The complex **1** is coordinatively unsaturated and reacts with unsaturated organic compounds and protic compounds. Of particular interest is the formation of four-membered metallacycles upon reaction with ethylene and cyclopentene. In the reaction of **1** with *tert*-butyl cyanide the selective rupture of the azametallacyclobutene led to the imido complex **6**. *p*-Methoxyaniline reacted with **1** to afford another imido complex, **9**, by stepwise reactions: the first product was the amido complex **8**, which then converted to the amido complex **9** after the proton migration from the nitrogen atom of the amido group to the diene unit at elevated temperature. The addition of methanol to **1** resulted in the selective formation of the benzyl methoxy complex **7**. Thus, the phosphine-free benzylidene complex **1** showed unique reactivity.

Experimental Section

General Procedures. All manipulations involving air- and moisture-sensitive tantalum complexes were carried out using the standard Schlenk techniques under argon. Hexane, THF, toluene, and ether were dried and deoxygenated by distillation over sodium benzophenone ketyl under argon. Benzene-d_6 was distilled from Na/K alloy and thoroughly degassed by trap-to-trap distillation before use. The complexes $\mathrm{TaCl_4Cp}$ and $\mathrm{TaCl_2Cp^*}$(η^4-*supine*-DMBD) (**2**) were prepared according to the literature.[39] The ^{1}H (400, 300, and 270 MHz) and ^{13}C (100 and 75 MHz) NMR spectra were measured on a JEOL JNM-AL400, a Varian UNITY-INOVA-300, or a JEOL GSX-270 spectrometer. All melting points were measured in sealed tubes under an argon atmosphere and were not corrected.

Preparation of $\mathrm{Ta(CHPh)Cp^*}$(η^4-DMBD) (1). To a solution of **2** (4.64 g, 9.9 mmol) in toluene (20 mL) cooled to −78 °C was added a suspension of $\mathrm{Mg(PhCH_2)_2}$ (1.5 equiv, 14.8 mmol) in toluene via syringe, and then the reaction mixture was stirred for 24 h at 25 °C. The solution turned reddish brown. All volatiles were removed under reduced pressure to give a residue, from which the product was extracted with hexane (400 mL). Recrystallization from a mixture of toluene (10 mL) and hexane (10 mL) at −20 °C afforded **1** as reddish brown crystals in 49% yield, mp 116−117 °C dec. ^{1}H NMR (400 MHz, $\mathrm{C_6D_6}$, 35 °C): δ −0.89 (d, $^2J_{\mathrm{HH}} = 10.3$ Hz, 2H, $\mathrm{H^{1,4}}$(anti) of DMBD), 1.92 (s, 15H, $\mathrm{C_5}\mathit{Me}_5$), 2.60 (s, 6H, $\mathrm{CH_3}$ of DMBD), 3.05 (d, $^2J_{\mathrm{HH}} = 10.3$ Hz, 2H, $\mathrm{H^{1,4}}$(syn) of DMBD), 5.88 (s, 1H, Ta═CH), 6.85−7.22 (m, 5H, $\mathrm{C_6H_5}$). ^{13}C NMR (100 MHz, $\mathrm{C_6D_6}$, 35 °C): δ 11.9 (q, $^1J_{\mathrm{C-H}} = 127$ Hz, $C_5\mathrm{Me_5}$), 24.1 (q, $^1J_{\mathrm{C-H}} = 126$ Hz, $\mathrm{CH_3}$ of DMBD), 59.4 (t, $^1J_{\mathrm{C-H}} = 143$ Hz, $\mathrm{C^{1,4}}$ of DMBD), 111.5 (s, $C_5\mathrm{Me_5}$), 121.7 (s, $\mathrm{C^{2,3}}$ of DMBD), 122.6 (d, $^1J_{\mathrm{C-H}} = 159$ Hz, *p*-$\mathrm{C_6H_5}$), 126.4 (d, $^1J_{\mathrm{C-H}} = 159$ Hz, *o*-$\mathrm{C_6H_5}$), 126.6 (d, $^1J_{\mathrm{C-H}} = 157$ Hz, *m*-$\mathrm{C_6H_5}$), 153.5 (s, *ipso*-$\mathrm{C_6H_5}$), 242.8 (d, $J_{\mathrm{C-H}} = 90$ Hz, *C*H═Ta). Anal. Calcd for $\mathrm{C_{23}H_{31}Ta}$: C, 56.56; H, 6.40. Found: C, 55.98; H, 6.53.

Preparation of $\mathrm{Ta(CH_2Ph)_2Cp}$(η^4-DMBD) (3). To a solution of $\mathrm{TaCl_4Cp}$ (2.14 g, 5.52 mmol) in THF (50 mL) and HMPA (2 mL) cooled to −78 °C was added a solution of (2,3,3-trimethylallyl)magnesium bromide (2 equiv, 11.0 mmol). The reaction mixture was stirred for 24 h at 25 °C and refluxed for 1 h at 60 °C. To the reaction mixture cooled to −78 °C was added a suspension of $\mathrm{Mg(PhCH_2)_2}$ (1.3 equiv, 7.2 mmol) in ether via syringe, and this mixture was stirred for 2 h at 25 °C. All volatiles were removed under reduced pressure to give a reddish purple residue. The product was extracted with hexane (150 mL), and then recrystallization from hexane (2 mL) at −20 °C afforded **3** as deep purple crystals in 23% yield, mp 85−87 °C dec. ^{1}H NMR (270 MHz, $\mathrm{C_6D_6}$, 35 °C): δ −0.41 (d, $^2J_{\mathrm{HH}} = 5.9$ Hz, 2H, $\mathrm{H^{1,4}}$(anti) of DMBD), −0.12 (d, $^2J_{\mathrm{HH}} = 5.8$ Hz, 2H, $\mathrm{H^{1,4}}$(syn) of DMBD), 1.14 (d, $^2J_{\mathrm{HH}} = 11.1$ Hz, 2H, $\mathrm{TaC}H\mathrm{HPh}$), 1.76 (d, $^2J_{\mathrm{HH}} = 11.4$ Hz, 2H, $\mathrm{TaCH}H\mathrm{Ph}$), 2.44 (s, 6H, Me of DMBD), 5.61 (s, 5H, $\mathrm{C_5H_5}$), 6.73 (d, 4H, *o*-Ph), 6.89 (t, 2H, *p*-Ph), 7.22 (t, 4H, *m*-Ph); ^{13}C NMR (75 MHz, $\mathrm{C_6D_6}$, 10 °C): δ 20.1 (q, $^1J_{\mathrm{CH}} = 125$ Hz, $\mathrm{CH_3}$ of DMBD), 60.4 (t, $^1J_{\mathrm{CH}} = 148$ Hz, $\mathrm{C^{1,4}}$ of DMBD), 71.3 (t, $^1J_{\mathrm{CH}} = 117$ Hz, Ta−$C\mathrm{H_2Ph}$), 111.6 (d, $^1J_{\mathrm{CH}} = 174$ Hz, $\mathrm{C_5H_5}$), 120.6 (s, $\mathrm{C^{2,3}}$ of DMBD), 122.4 (d, $^1J_{\mathrm{CH}} = 158$ Hz, *p*-Ph), 126.9 (d, $^1J_{\mathrm{CH}} = 153$ Hz, *o*-Ph), 127.9 (d, $^1J_{\mathrm{CH}} = 155$ Hz, *m*-Ph), 152.8 (s, *ipso*-$\mathrm{C_6H_5}$).

Preparation of $\overline{\mathrm{Ta(CH_2CH_2C}}\mathrm{HPh)Cp^*}$($\eta^4$-DMBD) (4). In a solution of **1** (0.26 g, 0.53 mmol) in hexane (15 mL) cooled to −78 °C, ethylene (atmospheric pressure) was introduced. After it was stirred for 12 h at 25 °C, the solution gradually turned red, and then the reaction mixture was evaporated under reduced pressure to give **4** as microcrystals, which were rinsed with two portions of hexane: 66% yield, mp 92−96 °C dec. ^{1}H NMR (300 MHz, $\mathrm{C_6D_6}$, 35 °C): δ −0.54 (d, $^2J_{\mathrm{HH}} = 4.6$ Hz, 1H, $\mathrm{H^1}$(anti) of DMBD), −0.53 (d, $^2J_{\mathrm{HH}} = 5.6$ Hz, 1H, $\mathrm{H^4}$(anti) of DMBD), 0.37 (d, 1H, $\mathrm{H^1}$(syn) of DMBD), 0.47 (d, 1H, $\mathrm{H^4}$(syn) of DMBD), 1.24 (s, 3H, Me of DMBD), 1.45 (m, 2H, −$\mathrm{C}H_2$-CHPh, 1,77 (s, 15H, $\mathrm{C_5}\mathit{Me}_5$), 1.98 (s, 3H, Me of DMBD), 2.18 (m, 2H, $\mathrm{TaC}H_2$-), 3.07 (t, $^2J_{\mathrm{HH}} = 8.0$ Hz, 1H, $\mathrm{TaC}H\mathrm{Ph}$), 6.83 (d, 2H, *o*-Ph), 6.91 (t, $^2J_{\mathrm{HH}} = 7.4$ Hz, 1H, *p*-Ph), 7.25 (t, $^2J_{\mathrm{HH}} = 7.4$ Hz, 2H, *m*-Ph). Anal. Calcd for $\mathrm{C_{25}H_{35}Ta}$: C, 58.14; H, 6.83. Found: C, 57.81; H, 6.77.

Preparation of $\overline{\mathrm{Ta(CH(C_3H_6)CHC}}\mathrm{HPh)Cp^*}$($\eta^4$-DMBD) (5). To a solution of **1** (0.12 g, 0.24 mmol) in toluene (10 mL) at −78 °C was added cyclopentene (1.0 equiv, 0.24 mmol) via syringe. The reaction mixture was warmed to room temperature and then stirred for 24 h at room temperature. The resulting red solution was evaporated to dryness, and then the product was extracted with hexane (25 mL). Recrystallization from hexane (0.3 mL) at −20 °C afforded **5** as deep red crystals in 26% yield, mp 106−108 °C dec. ^{1}H NMR (300 MHz, $\mathrm{C_6D_6}$, 10 °C): δ −0.56 (m, 2H, $\mathrm{H^{1,4}}$(anti) of DMBD), 0.20 (m, 1H, $\mathrm{C}H\mathrm{CHPh}$), 0.51 (d, $^2J_{\mathrm{HH}} = 6.7$ Hz, 1H, $\mathrm{H^1}$(syn) of DMBD), 0.88 (d, $^2J_{\mathrm{HH}} = 5.8$ Hz, 1H, $\mathrm{H^4}$(syn) of DMBD), 1.57 (s, 15H, $\mathrm{C_5}\mathit{Me}_5$), 1.69 (m, 1H, $\mathrm{CH_2C}H\mathrm{HCH_2}$), 2.09 (m, 1H, $\mathrm{CH_2CH}H\mathrm{CH_2}$), 2.22 (s, 3H, Me of DMBD), 2.27 (s, 3H, Me of DMBD), 2.43 (m, 4H, $\mathrm{C}H_2\mathrm{CH_2C}H_2$), 3.10 (m, 1H, $\mathrm{TaC}H$−), 3.10 (d, $^2J_{\mathrm{HH}} = 9.1$ Hz, 1H, $\mathrm{TaC}H\mathrm{Ph}$−), 6.98−7.30 (m, 5H, Ph). ^{13}C NMR (75 MHz, $\mathrm{C_6D_6}$, 10 °C): δ 11.0 (q, $^1J_{\mathrm{CH}} = 127$ Hz, $\mathrm{C_5}\mathit{Me}_5$), 20.3 (q, $^1J_{\mathrm{CH}} = 126$ Hz, Me of DMBD), 22.1 (q, $^1J_{\mathrm{CH}} = 130$ Hz, Me of DMBD), 32.7 (t, $^1J_{\mathrm{CH}} = 129$ Hz, $\mathrm{CH_2}$), 33.1 (t, $^1J_{\mathrm{CH}} = 120$ Hz, $\mathrm{CH_2}$), 36.3 (t, $^1J_{\mathrm{CH}} = 131$ Hz, $\mathrm{CH_2}$), 59.1 (t, $^1J_{\mathrm{CH}} = 139$ Hz) and 59.9 (t, $^1J_{\mathrm{CH}} = 140$ Hz) for $\mathrm{C^1}$ and $\mathrm{C^4}$ of DMBD, 78.0 (d, $^1J_{\mathrm{CH}} = 137$ Hz, TaCHPh), 92.7 (d, $^1J_{\mathrm{CH}} = 128$ Hz, TaCH), 116.0 (s, $C_5\mathrm{Me_5}$), 118.5 (s) and 120.9 (s) for $\mathrm{C^2}$ and $\mathrm{C^3}$ of DMBD, 122.2 (d, $^1J_{\mathrm{CH}} = 158$ Hz, $C\mathrm{HCHPh}$), 126.0 (d, $^1J_{\mathrm{CH}} = 157$ Hz, *p*-Ph), 127.5 (d, $^1J_{\mathrm{CH}} = 154$ Hz, *o*-Ph), 128.3 (d, $^1J_{\mathrm{CH}} = 157$ Hz, *m*-Ph), 150.9 (s, *ipso*-Ph). Anal. Calcd for $\mathrm{C_{28}H_{39}Ta}$: C, 60.43; H, 7.06. Found: C, 60.55; H, 6.60.

Preparation of $\mathrm{Ta(NC(^tBu){=}CHPh)Cp^*}$($\eta^4$-DMBD) (6). To a solution of **1** (0.22 g, 0.44 mmol) in toluene (20 mL) cooled to −78 °C was added *tert*-butyl cyanide (1.0 equiv, 0.44 mmol) via syringe and stirred for 3 h at 25 °C. The solution turned reddish orange. After all volatiles were removed under reduced pressure, the product was extracted with hexane (20 mL). Recrystallization from hexane (0.4 mL) at −20 °C afforded **6** as red crystals in 48% yield, mp 73−75 °C dec. ^{1}H NMR (300 MHz, $\mathrm{C_6D_6}$, 35 °C): δ −1.16 (d, $^2J_{\mathrm{HH}} = 10.8$ Hz, 1H, $\mathrm{H^1}$(anti) of DMBD), −0.75 (d, $^2J_{\mathrm{HH}} = 10.5$ Hz, 1H, $\mathrm{H^1}$(anti) of DMBD), 1.24 (s, 9H, $\mathrm{(CH_3)_3}$), 1.87 (s, 15H, $\mathrm{C_5Me_5}$), 2.18 (s, 3H, Me of DMBD), 2.35 (s, 3H, Me of DMBD), 3.18 (d, 1H, $\mathrm{H^1}$(syn) of DMBD), 3.24 (d, 1H, $\mathrm{H^4}$(syn) of DMBD), 5.44 (s, 1H, ═$\mathrm{C}H\mathrm{Ph}$), 7.10 (t, 1H, *p*-Ph), 7.27 (t, 2H, *m*-Ph), 7.75 (d, 2H, *o*-Ph). ^{13}C

Table 4. Crystal Data and Data Collection Parameters of 1, 6, 8, and 9

complex	**1**	**6**	**8**	**9**
formula	$C_{23}H_{31}Ta$	$C_{28}H_{40}NTa$	$C_{30}H_{40}NOTa$	$C_{30}H_{40}NOTa$
fw	488.42	571.56	611.58	611.58
cryst syst	monoclinic	triclinic	triclinic	orthorhombic
space group	$P2_1/m$ (No. 11)	$P\bar{1}$ (No. 2)	$P\bar{1}$ (No. 2)	$Pna2_1$ (No. 33)
a, Å	8.8250(13)	9.516(4)	12.9814(6)	18.6968(4)
b, Å	12.556(2)	9.718(3)	11.5472(5)	13.5132(3)
c, Å	8.9251(11)	14.636(5)	10.1734(5)	10.4565(2)
α, deg	90.0	76.40(3)	72.6661(13)	90.0
β, deg	93.092(9)	79.06(3)	74.8582(13)	90.0
γ, deg	90.0	87.99(3)	66.1851(14)	90.0
V, Å^3	987.6(3)	1291.5(8)	1314.33(11)	2641.90(10)
Z	2	2	2	4
no. of rflns for cell determn (θ range, deg)	11 158 (2.84−27.47)	14 067 (3.05−27.54)	61 049 (1.74−31.55)	67 152 (1.86−32.56)
D_{calcd}, g cm^{-3}	1.643	1.470	1.545	1.538
F(000)	484	576	616	1232
μ(Mo Kα), mm^{-1}	5.566	4.269	4.203	4.182
diffractometer	R-AXIS RAPID	R-AXIS RAPID	R-AXIS RAPID	R-AXIS RAPID
T, K	213(1)	213(1)	153(1)	153(1)
cryst size, mm	0.36 × 0.32 × 0.08	0.23 × 0.20 × 0.16	0.31 × 0.29 × 0.22	0.35 × 0.34 × 0.27
no. of images	54	44	180	94
total oscillation angles, deg	270.0	220.0	540.0	282.0
exposure time, min deg^{-1}	1.00	1.00	1.00	3.00
$2\theta_{max}$, deg	55.0	55.0	55.0	55.0
no. of rflns measd	10 706	12 599	25 466	28 460
no. of unique data (R_{int})	2361 (0.0472)	5897 (0.0255)	6003 (0.0610)	5898 (0.0297)
completeness to $\theta = 27.50$, %	99.6	99.4	99.6	99.9
no. of observns	2261	5491	5646	5527
max and min transmissn	0.0950, 0.3246[a]	0.2145, 0.5056	0.2145, 0.5056[b]	0.0950, 0.3246[a]
no. of variables, restraints	180, 0	311, 0	455, 0	297, 5
R1, wR2 (all data)	0.0209, 0.0543	0.0287, 0.0640	0.0339, 0.0830	0.0204, 0.0486
R1, wR2 ($I > 2.0\sigma(I)$)	0.0227, 0.0557	0.0256, 0.0627	0.0315, 0.0816	0.0204, 0.0474
Flack param (χ)				0.023(8)
GOF on F^2	1.050	1.039	1.105	1.023
$\Delta\rho$, e Å^{-3}	0.797, −0.929	1.152, −1.236	2.565, −1.967	1.066, −0.698
Δ/σ(max)	0.001	0.002	0.001	0.003

[a] Multiscan absorption correction. [b] Numerical absorption correction.

NMR (75 MHz, C_6D_6, 35 °C): δ 11.3 (q, $^1J_{CH} = 127$ Hz, C_5Me_5), 24.2 (q, $^1J_{CH} = 127$ Hz, Me of DMBD), 24.9 (q, $^1J_{CH} = 128$ Hz, Me of DMBD), 31.5 (q, $^1J_{CH} = 125$ Hz, Me_3C), 37.1 (s, Me_3C), 59.5 (t, $^1J_{CH} = 146$ Hz) and 60.6 (t, $^1J_{CH} = 143$ Hz) for C^1 and C^4 of DMBD, 106.8 (d, $^1J_{CH} = 149$ Hz, $=CHPh$), 113.1 (s, C_5Me_5), 121.6 (s) and 122.2 (s) for C^2 and C^3 of DMBD, 124.2 (d, $^1J_{CH} = 159$ Hz, *p*-Ph), 127.6 (d, $^1J_{CH} = 156$ Hz, *o*-Ph), 128.3 (d, $^1J_{CH} = 158$ Hz, *m*-Ph), 140.1 (s, *ipso*-C_6H_5), 164.6 (s, N−C=). Anal. Calcd for $C_{28}H_{40}NTa$: C, 58.84; H, 7.05; N, 2.45. Found: C, 58.26; H, 6.90; N, 2.59.

Preparation of Ta(CH_2Ph)(OCH_3)Cp*(η^4-DMBD) (7). To a solution of **1** (0.53 g, 1.09 mmol) in toluene (10 mL) cooled to −78 °C was added methanol (1.0 equiv, 1.09 mmol) via syringe. The reaction mixture was gradually warmed to room temperature and then stirred for 2 h at 25 °C. The solution turned red-orange. All volatiles were slowly evaporated to give complex **7** as deep red microcrystals in 98% yield, mp 113−117 °C dec. ^{1}H NMR (400 MHz, C_6D_6, 35 °C): δ −0.36 (d, $^2J_{HH} = 6.8$ Hz, 1H, H^1(anti) of DMBD), −0.24 (d, 1H, H^1(syn) of DMBD), 0.27 (d, $^2J_{HH} = 6.0$ Hz, 1H, H^4(anti) of DMBD), 0.99 (d, 1H, H^4(syn) of DMBD), 1.83 (s, 15H, C_5Me_5), 1.84 (d, $^2J_{HH} = 12.2$ Hz, 1H, TaC*H*HPh), 2.10 (s, 3H, Me of DMBD), 2.17 (d, 1H, TaCH*H*Ph), 2.29 (s, 3H, Me of DMBD), 3.42 (s, 3H, OMe), 6.94 (1H, *p*-Ph), 7.18 (2H, *o*-Ph), 7.25 (2H, *m*-Ph). ^{13}C NMR (75 MHz, C_6D_6, 35 °C): δ 11.8 (q, $^1J_{CH} = 127$ Hz, C_5Me_5), 21.1 (q, $^1J_{CH} = 125$ Hz, Me of DMBD), 22.0 (q, $^1J_{CH} = 122$ Hz, Me of DMBD), 47.8 (t, $^1J_{CH} = 119$ Hz, TaCH_2Ph), 58.1 (q, $^1J_{CH} = 141$ Hz, OMe), 59.9 (t, $^1J_{CH} = 145$ Hz) and 54.2 (t, $^1J_{CH} = 142$ Hz) for C^1 and C^4 of DMBD, 118.1 (s, C_5Me_5), 120.7 (s) and 130.4 (s) for C^2 and C^3 of DMBD, 122.2 (d, $^1J_{CH} = 156$ Hz, *p*-Ph), 127.7 (d, $^1J_{CH} = 155$ Hz, *o*-Ph), 129.1 (d, $^1J_{CH} = 153$ Hz, *m*-Ph), 154.3 (s, *ipso*-Ph). Anal. Calcd for $C_{24}H_{35}OTa$: C, 55.38; H, 6.78. Found: C, 55.3; H, 6.60.

Preparation of Ta(CH_2Ph)($NHC_6H_4OCH_3$)Cp*(η^4-DMBD) (8). To a solution of **1** (0.61 g, 1.24 mmol) in toluene (10 mL) cooled to −78 °C was added a toluene solution of *p*-methoxyaniline (1.1 equiv, 1.37 mmol) via syringe, and then the solution was stirred, resulting in a red-orange solution. With the temperature of the solution kept below −10 °C, the mixture was evaporated to dryness to give **8** as red-orange microcrystals in 98% yield, mp 104−107 °C dec. ^{1}H NMR (300 MHz, C_6D_6, 10 °C): δ 0.42 (d, $^2J_{HH} = 6.0$ Hz, 1H, H^1(anti) of DMBD), −0.26 (d, $^2J_{HH} = 4.8$ Hz, 1H, H^4(anti) of DMBD), 0.29 (d, 1H, H^4(syn) of DMBD), 0.68 (d, $^2J_{HH} = 13.2$ Hz, 1H, TaC*H*H), 0.77 (d, 1H, H^1(syn) of DMBD), 1.71 (s, 3H, Me of DMBD), 1.72 (s, 15H, C_5Me_5), 1.73 (s, 1H, NH), 2.31 (s, 3H, Me of DMBD), 3.38 (s, 3H, OMe), 3.51 (d, 1H, TaCH*H*), 6.76−7.19 (m, 9H, *m*-Ph). ^{13}C NMR (75 MHz, C_6D_6, 10 °C): δ 11.8 (q, $^1J_{CH} = 127$ Hz, C_5Me_5), 19.9 (q, $^1J_{CH} = 126$ Hz, Me of DMBD), 21.5 (q, $^1J_{CH} = 125$ Hz, Me of DMBD), 48.8 (t, $^1J_{CH} = 120$ Hz, CH_2−Ph), 55.4 (q, $^1J_{CH} = 143$ Hz, OMe), 57.4 (t, $^1J_{CH} = 143$ Hz) and 65.6 (t, $^1J_{CH} = 141$ Hz) for C^1 and C^4 of DMBD, 114.2 (d, $^1J_{CH} = 158$ Hz, *o*-C_6H_4-OMe), 116.0 (s, C_5Me_5), 122.6 (d, $^1J_{CH} = 159$ Hz, *m*-C_6H_4-OMe), 123.1 (s) and 123.5 (s) for C^2 and C^3 of DMBD, 123.1 (d, $^1J_{CH} = 157$ Hz, *p*-Ph), 127.8 (d, $^1J_{CH} = 156$ Hz, *o*-Ph), 130.8 (d, $^1J_{CH} = 154$ Hz, *m*-Ph), 147.3 (s, *p*-C_6H_4-OMe), 153.2 (s, *ipso*-C_6H_4−OMe), 155.8 (s, *ipso*-Ph). Anal. Calcd for $C_{30}H_{40}NOTa$: C, 58.92; H, 6.59; N, 2.29. Found: C, 58.7; H, 6.46; N, 2.31.

Preparation of Ta(CH_2Ph)($NC_6H_4OCH_3$)Cp*(η^1-2,3-dimethyl-2-butene) (9). To a solution of **1** (0.40 g, 0.81 mmol) in toluene (10 mL) cooled to −78 °C was added a toluene solution of *p*-methoxyaniline (1.1 equiv, 0.90 mmol) via syringe, and the mixture was stirred for 2 h at 25 °C and for 12 h at 60 °C, leading to an orange solution, from which **9** was obtained as orange microcrystals in 94% yield, mp 130−132 °C dec. ^{1}H NMR (300 MHz, C_6D_6, 35 °C): δ 1.52 (s, 3H, Me of 2,3-dimethyl-2-butene), 1.54 (s, 3H, Me of 2,3-dimethyl-2-butene), 1.78 (d, $^2J_{HH} = 13$ Hz, 1H, TaC*H*HPh), 1.79 (s, 15H, C_5Me_5), 1.91 (d, 1H, TaCH*H*Ph), 2.02 (s, 3H, Me of 2,3-

dimethyl-2-butene), 2.02 (s, 2H, TaC*H*$_2$), 3.40 (s, 3H, OMe), 6.77−6.83 (m, 4H, C$_6$*H*$_4$OMe), 6.96 (t, $^2J_{HH} = 7.3$ Hz, 1H, *p*-Ph), 7.30 (dd, 2H, *m*-Ph), 7.50 (d, $^2J_{HH} = 7.3$ Hz, 2H, *o*-Ph). ^{13}C NMR (75 MHz, C$_6$D$_6$, 35 °C): δ 11.3 (q, $^1J_{CH} = 127$ Hz, C$_5$*Me*$_5$), 22.1 (q, $^1J_{CH} = 125$ Hz, Me of 2,3-dimethyl-2-butene), 22.6 (q, $^1J_{CH} = 125$ Hz, Me of 2,3-dimethyl-2-butene), 23.0 (q, $^1J_{CH} = 126$ Hz, Me of 2,3-dimethyl-2-butene), 55.5 (q, $^1J_{CH} = 143$ Hz, OMe), 66.1 (t, $^1J_{CH} = 115$ Hz, C^1 of 2,3-dimethyl-2-butene), 68.3 (t, $^1J_{CH} = 131$ Hz, *C*H$_2$−Ph), 114.2 (s) and 115.4 (s) for C^2 and C^3 of 2,3-dimethyl-2-butene, 123.1 (d, $^1J_{CH} = 157$ Hz, *o*-*C*$_6$H$_4$OMe), 125.4 (s, *C*$_5$Me$_5$), 127.2 (d, $^1J_{CH} = 159$ Hz, *m*-*C*$_6$H$_4$-OMe), 128.1 (d, $^1J_{CH} = 157$ Hz, *p*-Ph), 129.8 (d, $^1J_{CH} = 163$ Hz, *o*-Ph), 130.0 (d, $^1J_{CH} = 153$ Hz, *m*-Ph), 151.3 (s, *p*-*C*$_6$H$_4$-OMe), 152.3 (s, *ipso*-*C*$_6$H$_4$OMe), 156.0 (s, *ipso*-Ph). Anal. Calcd for C$_{30}$H$_{40}$NOTa: C, 58.92; H, 6.59; N, 2.29. Found: C, 58.4; H, 6.45; N, 2.50.

Crystallographic Data Collection and Structure Determination of 1, 6, 8, and 9. The crystal evaluation and data collection were performed on a Rigaku R-AXIS RAPID diffractometer with Mo Kα radiation ($\lambda = 0.710\ 69$ Å, 50 kV−40 mA) and a imaging plate detector to crystal distance of 127 mm. The purple crystals of **1** and **6** were coated with silicone grease and sealed in glass capillaries under an argon atmosphere. The orange crystals of **8** and **9** were fixed on the end of glass fibers with cyanoacrylate adhesive. All crystals were placed in a nitrogen stream at 213(1) K (**1** and **6**) and 153(1) K (**8** and **9**). Data sets were corrected for Lorentz and polarization effects. The multiscan absorption correction, using the program ABSCOR, was applied to the raw data (**1**, **6**, and **8**), and the numerical absorption correction using the NUMABS software was applied to the raw data of **9**.

The atomic parameters of most of the atoms for all crystals were solved by the direct methods of SIR-97.[50] The non-hydrogen atoms were refined anisotropically on F^2 by the full-matrix least-squares method, using SHELXL-97.[51] All hydrogen atoms of all crystals were located on the difference Fourier maps. The function minimized was $[\sum w(F_o^2 - F_c^2)^2]$ ($w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$), where $P = (\mathrm{Max}(F_o^2,0) + 2F_c^2)/3$ with $\sigma^2(F_o^2)$ from counting statistics. The functions R1 and wR2 were defined as $(\sum||F_o| - |F_c||)/\sum|F_o|$ and $[\sum w(F_o^2 - F_c^2)^2/\sum(wF_o^4)]^{1/2}$, respectively. All calculations of least-squares refinements were performed with SHELXL-97 programs on an Origin 3400 computer of Silicon Graphics Inc. at the Research Center for Structural Biology Institute for Protein Research, Osaka University. The geometric parameters and X-ray structure analysis data for **1**, **6**, **8**, and **9** are summarized in Table 4.

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Supporting Information Available: Figures giving the numbering schemes and tables giving crystallographic data for complexes **1**, **6**, **8**, and **9**. This material is available free of charge via the Internet at http://pubs.acs.org.

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