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Synthesis, Structure, and Reactivity of Tantalum and Tungsten Homoenolate Complexes

Hayato Tsurugi, Takashi Ohno, Tsuneaki Yamagata, and Kazushi Mashima*

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

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Preparation and characterization of homoenolate complexes of tantalum, $Cp^*Cl_3Ta(CH_2CR^1{}_2C(=O)OR^2)$ (**1a**: $R^1 = H$, $R^2 = Et$; **1b**: $R^1 = R^2 = Me$; **1c**: $R^1 = Me$, $R^2 = C_6H_4CH_3$-4), and tungsten, $(Xyl-N=)Cl_3W(CH_2CH_2C(=O)OEt)$ (**7**), using zinc homoenolate reagents are described. Intramolecular coordination of the carbonyl moiety to the metal center in these complexes was confirmed by their NMR and IR spectroscopy together with X-ray analyses of **1a** and **1b**. The insertion reaction of isocyanide into the metal carbon bond of **1a** and **7**, respectively, resulted in the formation of a diazametallacycle, Cp^*Cl_3Ta-$[N(Xyl)$-$C(=C=N$-$Xyl)$-$C(CH_2CH_2CO_2Et)=N$-$Xyl]$ (**3a**), which possesses a metallacyclic structure with an exocyclic ketene−imine moiety, and an η^2-iminoacyl tungsten complex, $(Xyl$-$N=)W\{C(=N$-$Xyl)$-$CH_2CH_2CO_2Et\}(CNXyl)Cl_3$ (**8**). The β-proton of the homoenolate moiety of **1a** was selectively deprotonated by $KN(SiMe_3)_2$ to afford an η^4-ethyl acrylate complex, $Cp^*Cl_2Ta(\eta^4$-ethyl acrylate) (**4a**). In the case of complex **1b**, in which the β-positions were protected by dimethyl substituents, reaction with the dilithium salt of diazadiene afforded a tantalalactone complex, $Cp^*(\eta^4$-*p*-$MeOC_6H_4$-DAD)$Ta(CH_2$-$CMe_2C(=O)O)$ (**5**). The addition of $Al(C_6F_5)_3$ to **5** afforded a novel zwitterionic complex, Cp^*(*p*-$MeOC_6H_4$-DAD)$Ta(CH_2CMe_2C(=O)O$-$Al(C_6F_5)_3)$ (**6**), in which $Al(C_6F_5)_3$ coordinated to the exocyclic carbonyl oxygen of the tantalalactone.

Introduction

Organometallic compounds with a functionalized alkyl ligand, $[L_nM-(CH_2)_n-FG]$ (FG: functional group), have been the subject of intensive investigation because the introduction of a heteroatom into an alkyl moiety has a profound influence on its stability and reactivity. This class of complexes has important applications as synthetic building blocks in organic chemistry and as catalysts for homogeneous reactions.[1,2] Among functionalized-alkyl organometallic complexes, β-functionalized alkyl complexes have attracted special interest, and titanium homoenolate complexes, which exhibit a unique chelating effect on stabilizing alkyl species, are versatile reagents for carbon−carbon bond formation.[3] Chelating alkyl species have also been used for catalytic reactions by late transition metals: the copolymerization of ethylene and methyl acrylate by palladium catalysts involving β- or γ-functionalized alkylpalladium complexes,[4] and the copolymerization of α-olefins and carbon monoxide providing β-keto alkylpalladium complexes.[5,6] In each polymerization, these species had important roles in incorporating further monomers and in determining the polymer microstructure. Fundamental studies of the β-functionalized alkyl species are thus fascinating and in high demand. Our studies of the chemistry of early transition metal complexes with five-membered aza-[7] and oxametallacycles[8] led to our interest in the β-functionalized alkyl complexes of early transition metals because of the strong interaction between the early transition metal and the functionalized group, forming an intramolecular five-membered chelation. Here we report the preparation of

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* To whom correspondence should be addressed. E-mail: mashima@chem.es.osaka-u.ac.jp. Fax: 81-6-6850-6245.

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homoenolate complexes of tantalum and tungsten, their unique reactions with 2,6-dimethylphenylisocyanide (XylNC), and their transformation of the homoenolate moiety by metal-amido reagents.

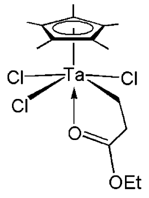
Results and Discussion

Synthesis, Characterization, and Reactivity of Tantalum Homoenolate Complexes. The reaction of Cp^*TaCl_4 with 0.5 equiv of $Zn(CH_2CH_2CO_2Et)_2$[3h] in ether afforded the tantalum homoenolate complex **1a** in 64% yield. Recrystallization from a hot toluene solution gave analytically pure yellow crystals of **1a**. The ^1H NMR spectrum of **1a** showed two triplet resonances at δ 3.55 and 0.65 assignable to α- and β-methylene protons. In the ^{13}C NMR spectrum, the carbonyl carbon signal was shifted downfield (δ_C 193.7) compared to that of the carbonyl carbon (δ_C ca. 170) of organic esters, indicating that the carbonyl group coordinated in an η^1-fashion to the tantalum atom. The coordination of the carbonyl group was further confirmed by IR spectroscopy, in which ν(C=O) appeared at a lower frequency (1625 cm^{-1}) compared to organic esters.

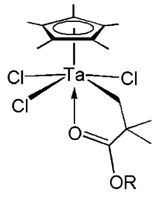
Similarly, β,β'-dimethyl-substituted homoenolate complexes, $Cp^*Cl_3Ta(CH_2CMe_2C(=O)OMe)$ (**1b**) and $Cp^*Cl_3Ta(CH_2CMe_2C(=O)OC_6H_4CH_3\text{-}4)$ (**1c**), were obtained by treating Cp^*TaCl_4 with 1 equiv of $IZn(CH_2CMe_2CO_2R)$ (R = Me, C_6H_4-CH_3-4). The transmetalation from zinc to tantalum proceeded smoothly, and **1b** and **1c** were obtained as yellow crystalline solids. The stretching frequencies of the carbonyl group (1633 cm^{-1}) and the carbonyl carbon resonance (δ 197.2) of **1b** were almost the same as those of **1a**. Thus, the carbonyl group of the homoenolate chain of **1b** also coordinated to the tantalum atom in the same mode. In the case of **1c**, the chemical shift value of the carbonyl carbon (δ 195.3) was assignable to the coordinating carbonyl group of the tantalum atom. The carbonyl stretching frequency of **1c** (1649 cm^{-1}) was slightly increased compared to **1a** and **1b** due to the inductive effect of the aromatic ester.

Table 1. Selected Bond Distances (Å) and Angles (deg) of Complexes 1a and 1b

	1a	1b
Ta−C11	2.2378(16)	2.186(13)
Ta−Cl1	2.4241(4)	2.391(3)
Ta−Cl2	2.4292(4)	2.434(3)
Ta−Cl3	2.3976(4)	2.414(3)
Ta−O1	2.2263(11)	2.234(8)
C11−C12	1.527(2)	1.540(16)
C12−C13	1.480(2)	1.489(17)
C13−O1	1.2372(18)	1.240(14)
C11−Ta−Cl1	83.86(4)	86.8(3)
C11−Ta−Cl2	149.57(4)	150.2(3)
C11−Ta−Cl3	86.62(4)	85.7(4)
C11−Ta−O1	74.30(5)	73.2(4)
Ta−C11−C12	113.28(10)	118.0(9)
Ta−O1−C13	119.09(10)	119.2(8)
C11−C12−C13	110.71(13)	106.8(10)
O1−C13−C12	121.52(13)	122.4(11)
O1−C13−O2	121.98(14)	119.7(12)



1a



R = Me (**1b**)
R = $C_6H_4CH_3$-4 (**1c**)

The chelate structures of **1a** and **1b** were confirmed by X-ray analyses (Figures 1a and 1b). Selected bond distances and angles are summarized in Table 1. The tantalum atom of each complex has a four-legged piano stool geometry with an additional donation from the carbonyl oxygen atom at the opposite side toward the Cp* ligand. Thus, the homoenolate moiety coordinates to the tantalum atom via C(11) and O(1) atoms to form a five-membered chelating structure. The molecular orbital of the d^0 piano stool CpTa fragment had two low-lying empty orbitals, $d_{x^2-y^2}$ and d_{z^2},[9] the latter being situated at the opposite side of the CpTa moiety. The bond angles of Ta−O(1)−C(13) (119.09° and 119.2°) and $Cp_{centroid}$−Ta−O(1) (177.8° and 175.8°) indicate that the lone pair of carbonyl oxygens overlapped with the empty d_{z^2} orbital. A similar interaction between the electron donor molecules, such as phosphine, isocyanide, carbonyl oxygen, and ylide, and the empty d_{z^2} orbital of the tantalum(V) complexes with the four-legged piano stool geometry has been reported.[10]

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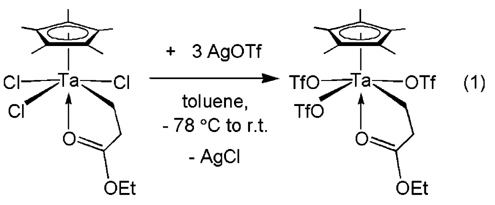
The bond distance of Ta−O(1) [2.2263(11) Å for **1a** and 2.234(8) Å for **1b**] is in the range typically observed for tantalum complexes with a coordinating carbonyl oxygen atom.[11] The Lewis acidic nature of the tantalum atom resulted in the intramolecular chelating structure, which was also observed for tin(IV)[12] and Ti(IV)[3a−e] complexes, whereas homoenolate complexes of Pt(II)[13] and Au(I)[14] have a nonchelating structure due to the soft nature of their metal centers. The coordination mode of the homoenolate depends on the Lewis acidity of the metal. Notable differences between **1a** and **1b** are the distance of the Ta−C(11) bond (2.2378 Å for **1a** and 2.186 Å for **1b**) and the angles of Ta−C(11)−C(12) (113.28° for **1a** and 118.0° for **1b**) and C(11)−C(12)−C(13) (110.71° for **1a** and 106.8° for **1b**), which are presumably due to the steric effect of the dimethyl group at the β-carbon of **1b**.

The triflate ligand has a stronger electron-withdrawing property than halides,[15] and hence the metal center with triflate ligands generally becomes more electron-deficient than that with chlorine ligands. We conducted a ligand exchange reaction of chlorine atoms with triflate ligands and compared the influence of triflate or chloride on the coordination of carbonyl to the tantalum atom. Metathesis reaction of **1a** with 3 equiv of AgOTf in toluene afforded a tris(triflate) complex, Cp*Ta(CH_2CH_2C(=O)OEt)$(OTf)_3$ (**2a**), in 75% yield (eq 1), in which the three triflates comprised the inner sphere ligands. The observed solubility of **2a** in aromatic hydrocarbons is consistent with the general tendency that neutral early transition metal triflate complexes are dissolved in aromatic and aliphatic solvents[16] and an ionized bis(triflate) tantalum complex is insoluble in aromatic and aliphatic hydrocarbons.[17] In the ^{19}F NMR spectrum, two singlet signals were observed as a 2:1 integral ratio, indicating that the triflate ligands were tightly bound in an η^1-coordination mode to tantalum at two *cis* and one *trans* positions relative to the alkyl moiety, and the ligand exchange process between the inner and outer coordination spheres was accordingly ruled out on the basis of the ^{19}F NMR time scale at 308 K. In the ^{13}C NMR spectrum, a resonance due to the methylene carbon α to the tantalum atom was observed at δ 71.6, a value downfield of that for **1a**. Replacement of chloride atoms by triflate ligands strengthened the bond between the carbonyl oxygen atom and the tantalum atom of **1a**, as evidenced by the downfield shift of the carbonyl carbon (δ_C 198.9) and the decreased C=O stretching frequency (1587 cm^{-1}).



(1)

1a **2a**

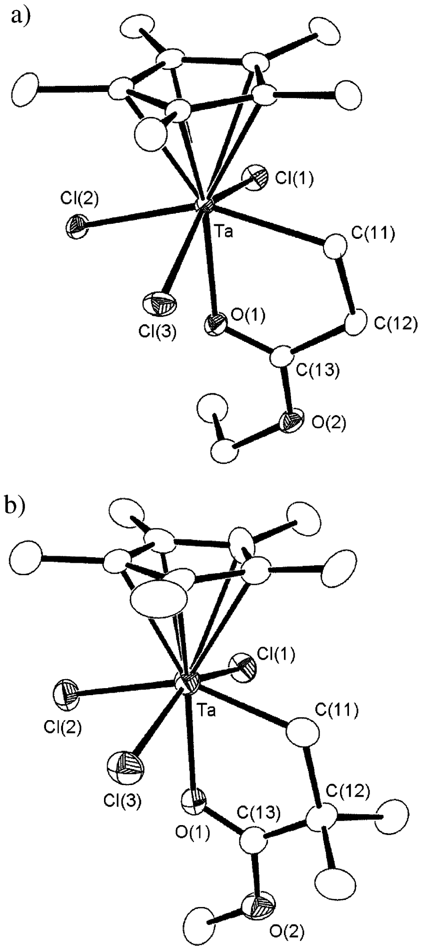


Figure 1. Molecular structure of the complexes **1a** (top) and **1b** (bottom). All hydrogen atoms are omitted for clarity.

The metal−carbon bond of homoenolate is expected to be reactive toward typical unsaturated organic molecules; however, **1a** in $CDCl_3$ did not react with carbon monoxide (1 atm), methyl acrylate, or diphenylacetylene, due to the strong binding between the carbonyl oxygen and the tantalum atom. In contrast, isocyanide reacted with **1a** to give an isocyanide multiple insertion product. The addition of 2,6-dimethylphenylisocyanide to **1a** in toluene afforded Cp*Cl_3Ta[N(Xyl)-C(=C=N-Xyl)-C($CH_2CH_2CO_2$Et)=N-Xyl] (**3a**), in which 3 equiv of isocyanide were consequently inserted into the tantalum carbon bond of **1a** (eq 2). Although the single insertion of isocyanide into metal−alkyl or −iminoacyl bonds of high-valent early transition metal complexes has been extensively studied,[18] there are only a few examples of an isocyanide multiple insertion reaction for tantalum complexes.[18d,i,k] The ^{13}C NMR spectrum of **3a** displayed the carbonyl carbon signal around δ 170, the chemical shift suggesting that the ester group of the homoenolate moiety was released from the tantalum atom. The IR spectrum of **3a** exhibited three strong bands at 2037, 1731, and 1548 cm^{-1}, which are assignable to ketene−imine, carbonyl, and imine groups, respectively. The structural characteristics of **3a** were revealed by the X-ray analysis (Figure 2). Selected bond distances and angles are listed in Table 2. Complex **3a** has a diazametallacycle structure with an exocyclic ketene−imine group. Rothwell et al. reported a similar metallacyclic structure for tantalum complexes supported by bulky aryloxy ligands.[18d,i] The bond distance of Ta−N(1) [2.370(3) Å] is much longer than that of Ta−N(3) [2.063(3) Å], indicating that the former bond is an imine-donating bond to the tantalum atom,[18d,i,h] while

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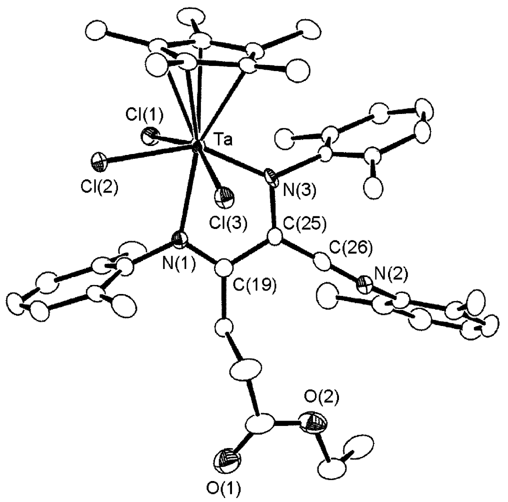
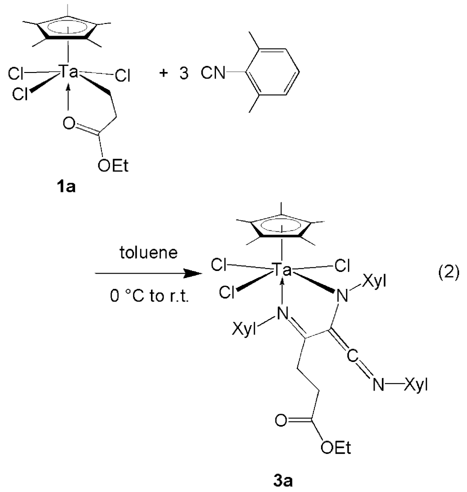


Figure 2. Molecular structure of **3a**. All hydrogen atoms are omitted for clarity.

Table 2. Selected Bond Distances (Å) and Angles (deg) of Complex 3a

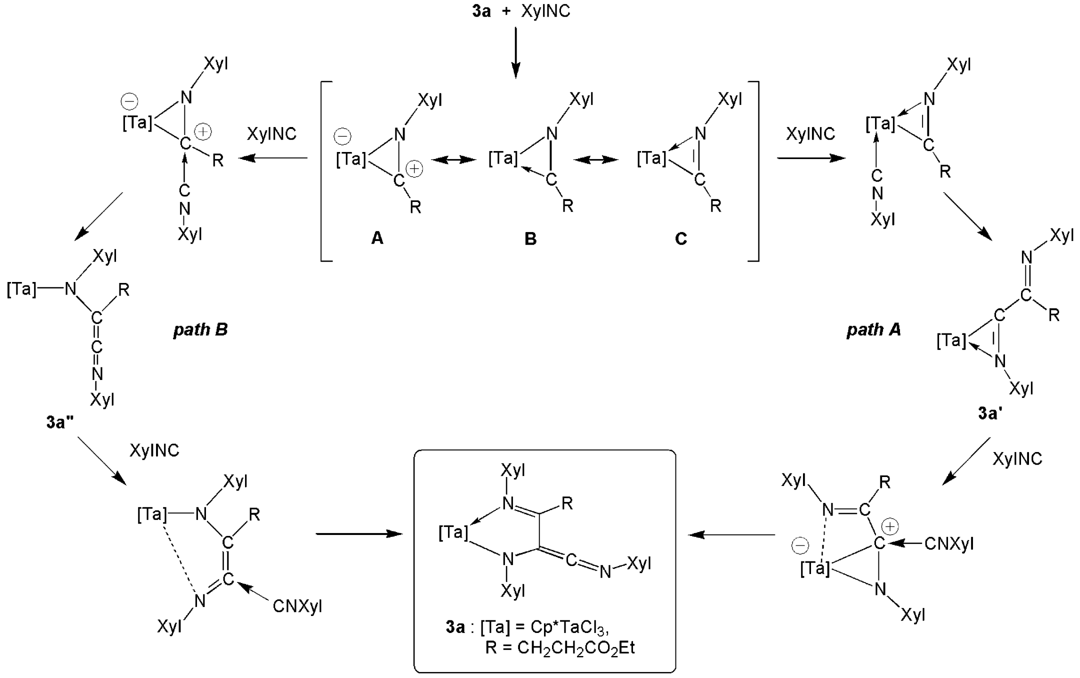
Ta−N1	2.370(3)	Ta−N3	2.063(3)
Ta−Cl1	2.441(1)	Ta−Cl2	2.4544(9)
Ta−Cl3	2.473(1)	N1−C19	1.307(4)
C19−C25	1.442(5)	N3−C25	1.434(4)
C25−C26	1.354(5)	N2−C26	1.200(5)
O1−C22	1.218(5)		
N3−Ta−Cl1	97.05(10)	N3−Ta−Cl2	148.86(8)
N3−Ta−Cl3	85.5(1)	N1−Ta−N3	72.7(1)
N1−C19−C25	114.5(3)	N3−C25−C19	117.1(3)
N2−C26−C25	170.0(5)		

the latter bond has the typical distance of a Ta−N(arylamido) bond.[7f,19] The ketene−imine moiety is revealed by the bond distances of C(25)−C(26) [1.354(5) Å] and N(2)−C(26) [1.200(5) Å] and the bond angle of C(25)−C(26)−N(2) [170.0(5)°].[18i,20] The ester moiety of the homoenolate fragment of **3a** is located at the outer coordination sphere of the tantalum atom, suggesting that the resulting isocyanide insertion is initiated by the replacement of the coordinated carbonyl moiety by the first equivalent of isocyanide.



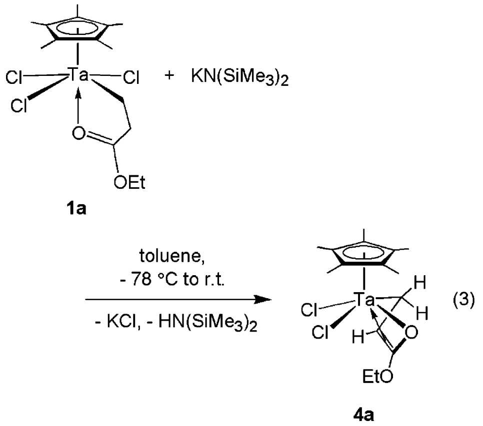
Scheme 1 shows two plausible mechanisms for the formation of **3a**. The first step of the reaction between **1a** and isocyanide, after the release of the carbonyl moiety from the tantalum atom, afforded an η^2-iminoacyl species. Typical η^2-iminoacyl ligands of high-valent early transition metal, lanthanide, and actinide complexes are described as the three resonance structures **A** (zwitterionic resonance form), **B** (amido−carbene resonance form), and **C** (η^2-iminoacyl resonance form), schematically shown in Scheme 1.[18a] The formation of **3a** was rationally illustrated by two pathways (path A and path B). In path A, the migratory insertion of isocyanide into the metal−iminoacyl bond, giving **3a′**, followed by nucleophilic attack of the third isocyanide at the iminoacyl carbon, results in the formation of **3a**. A similar mechanism for the formation of the imine−η^2-iminoacyl species, corresponding to **3a′**, was proposed by Royo et al. for the reaction of Cp*Ta(=NR) derivatives with excess XylNC.[18k] The other pathway (path B) involves a nucleophilic attack of isocyanide at the iminoacyl carbon to form an amido−

Scheme 1

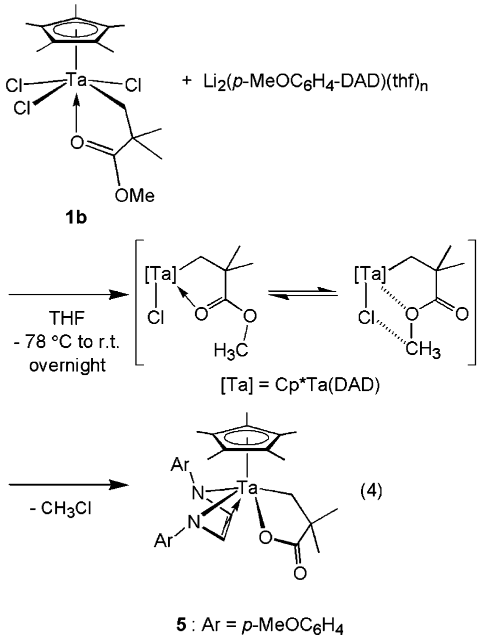


ketene−imine complex **3a″**, which is followed by the nucleophilic attack of CNXyl to the ketene−imine carbon. Tilley and co-workers reported that the reaction of the thorium−silicon bond with 2 equiv of carbon monoxide gave a metaloxy ketene complex, $Cp^{*}_2Th(Cl)[OC({=}C{=}O)Si(SiMe_3)_3]$, an analogue to **3a″**, and the following nucleophilic attack of isocyanide at the ketene carbon afforded a dioxametallacycle bearing a ketene−imine moiety, $Cp^{*}_2(Cl)Th[OC({=}C{=}N{-}Xyl)C\{Si(SiMe_3)_3\}{=}O]$.[21] It is likely that the reaction proceeded through path A because an isoelectronic tungsten−homoenolate complex reacted with 2 equiv of XylNC to give an η^2-iminoacyl complex with an η^1-XylNC ligand (vide infra).

Reaction of Tantalum Homoenolate Complexes with Metal-Amide Reagent. Deprotonation of the methylene proton β to the tantalum atom and α to the carbonyl group was accomplished by treatment of **1a** with 1 equiv of $KN(SiMe_3)_2$, giving an η^4-EA (EA = ethyl acrylate) complex, $Cp^{*}Cl_2Ta(CH_2CH{=}C(O)OEt)$ (**4a**) (eq 3). Similar oxatantalacyclopentene complexes, $Cp^{*}Cl_2Ta(CMe_2CH{=}C(O)CH_3)$,[22] $Cp^{*}Cl_2Ta(CH_2CH{=}C(O)OMe)$,[23] and $Cp^{*}Cl_2Ta(CH_2C(Me){=}C(O)OMe)$,[8] have been reported. The ^1H NMR spectrum of **4a** showed three doublets of doublets (δ 5.11, 1.32, and 0.53), assignable to an olefinic proton and methylene protons bound to the tantalum atom, and the spectral pattern was identical to that of $Cp^{*}Cl_2Ta(CH_2CH{=}C(O)OMe)$.[23] The ^{13}C NMR spectrum of **4a** displayed a new signal at δ 161.8, assignable to an olefinic carbon bound to oxygen atoms, suggesting the formation of oxatantalacyclopentene. In contrast, the reaction of **1a** with the dilithium salt of 1,4-bis(*p*-methoxyphenyl)-1,4-diaza-1,3-butadiene (abbreviated *p*-$MeOC_6H_4$-DAD) provided no isolable species from a complicated reaction mixture.



The reaction of **1b** with $KN(SiMe_3)_2$ did not proceed because the β-methylene protons were protected by two methyl groups. On the other hand, reaction of **1b** with 1 equiv of the dilithium salt of *p*-$MeOC_6H_4$-DAD afforded a tantalalactone complex, $Cp^{*}(\eta^4\text{-}p\text{-}MeOC_6H_4\text{-}DAD)Ta(CH_2CMe_2C({=}O)O)$ (**5**) (eq 4), whose formulation was revealed by spectroscopic methods. The metal−homoenolate fragment was transformed to metallalactone by cleavage of the $O{-}CH_3$ bond from the ester group. The formation of **5** might involve an elimination of CH_3Cl via a four-membered transition state. The same reaction pathway was proposed by Qian et al. for their titanium complexes.[24] Metallalactone complexes of late transition metals are prepared by the oxidative addition of acrylic acid or lactone to electron-rich low-valent metals[25] or a coupling reaction among metal, alkene, and carbon dioxide.[26] Early transition metals, titanalactone,[27] zirconalactone,[28] and tantalalactone[29] are prepared by the reaction of low-valent ethylene or benzyne complexes with CO_2. Complex **5** is a relatively rare example of metallalactone complexes of early transition metals.



The ^1H and ^{13}C NMR spectra of **5** displayed only two methoxy groups of the *p*-$MeOC_6H_4$-DAD, indicating the elimination of the methyl group of the ester. In the ^{13}C NMR spectrum, the carbonyl carbon was observed at δ 190.6, a higher field shift than that of **1b**. The IR spectrum of **5** exhibited ν-

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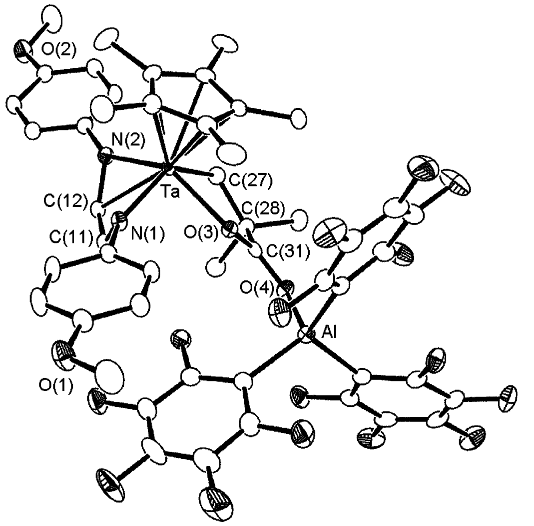
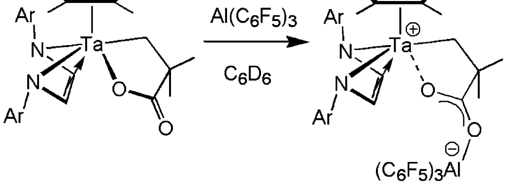


Figure 3. Molecular structure of **6**. All hydrogen atoms are omitted for clarity.

(CO) at 1668 cm^{-1}, consistent with those of metallalactone complexes of early transition metals, $Cp^*{}_2Ti(CH_2CH_2C(=O)O)$ (1653 cm^{-1}),[27] $Cp_2Zr(CH_2CH_2C(=O)O)$ (1687 cm^{-1}),[28] and $Cp^*(\eta^4\text{-}C_4H_6)Ta(C_6H_4C(=O)O)$ (1670 cm^{-1}).[29]

Because the reaction of carbonyl compounds with strong organo Lewis acids such as $B(C_6F_5)_3$ and $Al(C_6F_5)_3$ form stable adducts,[30,31] the addition of 1 equiv of organo Lewis acid, $Al(C_6F_5)_3$, to tantalalactone **5** yielded a zwitterionic metallalactone$-Al(C_6F_5)_3$ adduct **6** (eq 5). In the ^{1}H NMR spectrum, the resonances of methylene protons and Cp* protons were shifted upfield compared to those of **5**. A downfield shifted carbonyl carbon was observed by ^{13}C NMR spectroscopy.



(5)

5

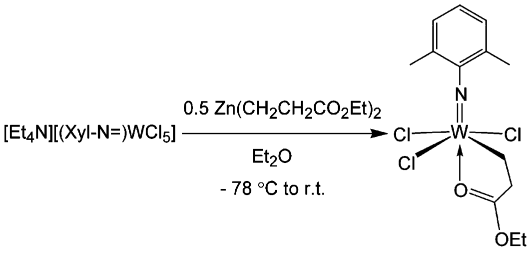
6 : Ar = 4-MeOC$_6$H$_4$

Recrystallization by slow evaporation of the solvent gave single crystals suitable for X-ray diffraction study, and the molecular structure of **6** was finally confirmed by X-ray analysis. Figure 3 shows the molecular structure. Selected bond distances and angles are summarized in Table 3. The single-crystal X-ray diffraction study clearly demonstrated that tris(pentafluorophenyl)alane is bound to the exocyclic oxygen atom of tantalalactone and the carboxylate moiety bridges the tantalum and aluminum atoms. A similar structure was reported by Chen et al. for the zwitterionic zirconocene complex [*rac*-(EBI)ZrMe][μ-$OC(CHMe_2)OAl(C_6F_5)_3$] (EBI = $C_2H_4(Ind)_2$).[32] The bond distance of Ta−O(3) [2.182(2) Å] is significantly elongated from the tantalum−oxygen covalent bond distance (1.888−2.043 Å) observed in oxatantallacycle complexes.[8,18h,22,23] The same bond distances of C(31)−O(3) [1.268(2) Å] and C(31)−O(4) [1.269(3) Å] and the sp^2-hybridized C(31) [360.0° for the sum of the angles around C(31)] represent a resonance structure of the carboxyl group. The aluminum−oxygen bond distance [1.810(2) Å] is comparable to that of $(C_6F_5)_3Al(MMA)$ [1.811(2) Å],[33] but shorter than that of $(C_6F_5)_3Al(THF)$ [1.860(2) Å],[34] $(C_6F_5)_3Al(OH_2)$ [1.857(3) Å],[35] and $(C_6F_5)_3Al(OHCH_3)$ [1.858(2) Å].[35] The diazadiene ligand coordinated in an η^4-*supine* fashion to the tantalum atom, and the bond distances of Ta−C(11) [2.489(2) Å] and Ta−C(12) [2.478(2) Å] are short enough for the tantalum atom to interact with the inner olefin carbons of the diazadiene ligand.[7b,36] Although a long−short−long sequence of the diazadiene moiety was not clearly observed, the bond distance of C(11)−C(12) [1.381(3) Å] was shorter than that of the free ligand, *s-trans*-cyclohexyl-DAD [1.457(2) Å],[37] and the bond distances of N(1)−C(11) [1.378(3) Å] and N(2)−C(12) [1.391(3) Å] were longer than those found for the *s-trans*-cyclohexyl-DAD [1.258(2) Å].

Table 3. Selected Bond Distances (Å) and Angles (deg) of Complex 6

Ta−N1	2.038(2)	Ta−N2	2.026(2)
Ta−C11	2.489(2)	Ta−C12	2.478(2)
Ta−C27	2.256(2)	Ta−O3	2.182(2)
N1−C11	1.378(3)	N2−C12	1.391(3)
C11−C12	1.381(3)	C31−O3	1.268(2)
C31−O4	1.269(3)	C27−C28	1.544(3)
C28−C31	1.520(3)	Al−O4	1.810(2)
Al−C32	2.001(2)	Al−C38	2.003(2)
Al−C44	1.996(3)		
N1−Ta−C11	33.61(7)	N2−Ta−C12	34.13(8)
N1−Ta−N2	84.69(8)	O3−Ta−C27	85.09(8)
Ta−O3−C31	121.4(1)	O3−C31−O4	122.5(2)
O3−C31−C28	119.2(2)	O4−C31−C28	118.3(2)
Al−O4−C31	135.5(1)		

Preparation of Tungsten Homoenolate Complex and Reactivity to 2,6-Dimethylphenylisocyanide. The zinc homoenolates were versatile alkylation reagents and applicable to prepare other transition metals.[3e,h] Treatment of $[Et_4N][(Xyl\text{-}N=)WCl_5]$ with 0.5 equiv of $Zn(CH_2CH_2CO_2Et)_2$ in ether gave a tungsten homoenolate complex, $(Xyl\text{-}N=)Cl_3W(CH_2CH_2C(=O)OEt)$ (**7**), as dark red crystalline solids (eq 6). The chelating structure of the homoenolate moiety was confirmed by NMR and IR spectroscopy. The ^{1}H NMR spectrum of **7** displayed two triplet resonances (δ 4.08 and 2.27), assignable to the methylene protons at the α- and β-positions of the homoenolate moiety. The downfield shift of the carbonyl carbon resonance (δ 194.9) compared to that of the carbonyl carbon resonance of organic esters and the lower stretching frequency of the carbonyl group (1620 cm^{-1}) clearly indicated that the carbonyl group of the homoenolate moiety coordinated to the tungsten atom. The chemical shift value and the stretching frequency of the carbonyl group were identical to those of **1a**−**c**.



(6)

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We conducted a reaction of tungsten homoenolate **7** with an excess of 2,6-dimethylphenylisocyanide to give **8**, which

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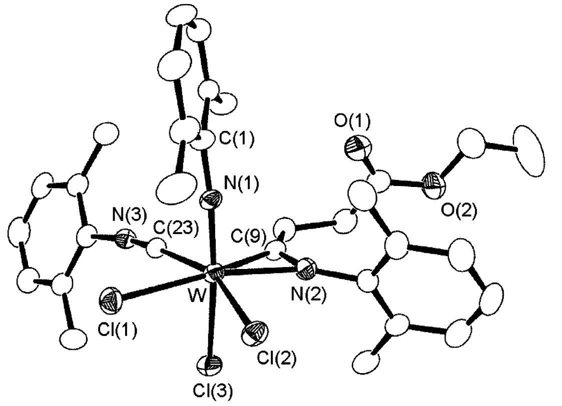
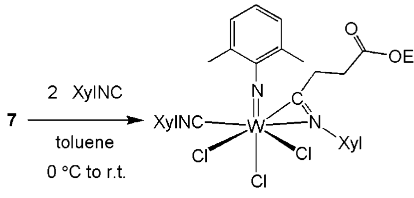


Figure 4. Molecular structure of **8**. All hydrogen atoms and solvent molecule are omitted for clarity.

possesses an η^2-iminoacyl group and an η^1-isocyanide ligand (eq 7). Even in the presence of excess XylNC, further insertion of XylNC did not proceed. The ^{13}C NMR spectrum of **8** exhibited three resonances due to the iminoacyl carbon (δ 198.2), the carbonyl carbon (δ 170.6), and the isocyanide carbon (δ 149.9). The chemical shift value of the iminoacyl carbon was in the range of typical η^2-iminoacyl moieties bound to early transition metals.[18a] The chemical shift value of the carbonyl carbon was consistently assigned to a noncoordinating carbonyl group, and the resonance due to isocyanide indicated that isocyanide coordinated in an η^1-fashion to the tungsten atom.



(7)

8

Complex **8** was isolated as yellow crystals, and the molecular structure was determined by X-ray analysis (Figure 4). The selected bond distances and angles are shown in Table 4.

Table 4. Selected Bond Distances (Å) and Angles (deg) of Complex 8

W−N1	1.748(6)	W−N2	2.119(7)
W−Cl1	2.444(2)	W−Cl2	2.400(2)
W−Cl3	2.480(2)	W−C9	2.131(8)
W−C23	2.171(8)	N2−C9	1.256(9)
N3−C23	1.149(6)		
N1−W−Cl3	170.8(2)	C23−W−Cl2	158.9(2)
N2−W−Cl1	166.5(2)	C9−W−Cl1	154.9(2)
W−N1−C1	174.8(3)	N3−C23−W	175.4(4)

Complex **8** adopts a pseudo-octahedral geometry around the tungsten atom, where the imido nitrogen atom (N1) and the η^2-iminoacyl group occupy *cis* positions. Three chlorine atoms are attached in a facial fashion to the tungsten atom. Complex **8** has a short bond distance of W−N(1) [1.748(6) Å] and a linear angle of W−N(1)−C(1) [174.8(3)°], consistent with the tungsten−nitrogen triple bond character.[38] The bond distances of W−N(2) [2.119(7) Å], W−C(9) [2.131(8) Å], and N(2)−C(9) [1.256(9) Å] are consistent with a typical η^2-iminoacyl bond to early transition metals.[18a,39] XylNC occupies a position *cis* to the imido nitrogen atom N(1) and the η^2-iminoacyl C═N moiety. The bond distance of W−C(23) [2.171(8) Å] is longer than that of the low-valent homoleptic tungsten complex, W(CNXyl)$_6$ (average: 2.05 Å).[40] The elongated bond length of W−C(23) is due to the lack of π-back-bonding from the metal to the π^* orbital of the isocyanide ligand, presumably because of the strong π-bonding interaction between the tungsten atom and the imido nitrogen atom. The oxygen atom (O1) of the ester carbonyl moiety is outside the coordination sphere of the tungsten atom, as predicted by the spectral data.

Conclusion

We demonstrated that zinc homoenolates are versatile reagents for preparing tantalum and tungsten homoenolate complexes. The isolated homoenolate complexes had a five-membered chelating structure through the coordination of the carbonyl oxygen of the homoenolate group to the metal. X-ray analyses of tantalum complexes **1a** and **1b** revealed that the carbonyl group of the homoenolate moiety was positioned at the opposite side toward the Cp* ligand and the lone pair of the carbonyl oxygens overlapped with the empty d$_{z^2}$ orbital of the tantalum atom. As a result, the carbonyl oxygen of the homoenolate moiety was tightly bound to the tantalum atom and the metal−carbon bond of the homoenolate complexes showed less reactivity toward insertion of unsaturated small molecules, except for 2,6-dimethylisocyanide: 3 equiv of isocyanide inserted consecutively into the Ta−C bond of **1a** to give **3a** because the coordinated carbonyl moiety was released by the first coordination of isocyanide. Similarly, tungsten homoenolate complex **6** reacted with XylNC to give **8**, which had an η^2-iminoacyl moiety and an η^1-isocyanide ligand. The reaction of **1a** with KN(SiMe$_3$)$_2$ afforded the ethyl acrylate complex **4a** via the deprotonation reaction, while the reaction of **1b** with Li$_2$(*p*-MeOC$_6$H$_4$-DAD)(thf)$_n$ resulted in the formation of tantalalactone complex **5**. The organo-Lewis acid Al(C$_6$F$_5$)$_3$ reacted with the exocyclic carbonyl oxygen atom of **5** to form the zwitterionic tantalum−aluminum adduct **6**. The molecular structure of **6**, determined by X-ray diffraction study, indicates

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that the carboxylate moiety of **6** interacted with both the tantalum and aluminum atoms.

Experimental Section

General Procedures. All manipulations involving air- and moisture-sensitive organometallic compounds were operated using the standard glovebox and Schlenk techniques under argon. Complexes Cp^*TaCl_4,[41] $[Et_4N][(Xyl\text{-}N{=})WCl_5]$,[42] $Zn(CH_2CH_2CO_2Et)_2$,[3h] $IZn(CH_2CMe_2CO_2Me)$,[3e] $ICH_2CMe_2CO_2H$,[43] $Al(C_6F_5)_3\cdot(C_7H_8)_{0.5}$,[44] and 1,4-bis(*p*-methoxyphenyl)-1,4-diaza-1,3-butadiene[45] were prepared according to the literature. AgOTf, $B(C_6F_5)_3$, $KN(SiMe_3)_2$, and 2,6-dimethylphenylisocyanide were purchased and used as received. Hexane, THF, toluene, and ether were dried and deoxygenated by distillation over sodium benzophenone ketyl under argon. Benzene-d_6 was distilled from P_2O_5 and thoroughly degassed by trap-to-trap distillation before use. Bromobenzene-d_5 and chloroform-d_1 were distilled over CaH_2 and then degassed. The ^1H (300 MHz) and ^{13}C (75 Hz) NMR spectra were measured on a Varian-Mercury-300 spectrometer. The elemental analyses were recorded by using a Perkin-Elmer 2400 at the Faculty of Engineering Science, Osaka University. All melting points were measured in sealed tubes under argon atmosphere and were not corrected.

Preparation of $Cp^*Cl_3Ta(CH_2CH_2C(=O)OEt)$ (1a). To a suspension of Cp^*TaCl_4 (441 mg, 0.96 mmol) in ether (20 mL) was added a solution of $Zn(CH_2CH_2CO_2Et)_2$ in ether (0.42 M, 1.4 mL, 0.59 mmol, 0.6 equiv) at −78 °C. The reaction mixture was allowed to warm to room temperature and further stirred overnight at room temperature. After all volatiles were removed under reduced pressure, the residue was extracted with toluene (30 mL and then 20 mL). The combined toluene extract was concentrated under reduced pressure to give **1a** as yellow powders (320 mg, 64% yield), mp 193−200 °C (dec). ^1H NMR (300 MHz, $CDCl_3$, 308 K): δ 4.66 (q, $^3J_{H-H} = 7.1$ Hz, 2H, OCH_2), 3.55 (t, $^3J_{H-H} = 6.9$ Hz, 2H, $TaCH_2CH_2$), 2.43 (s, 15H, C_5Me_5), 1.47 (t, $^3J_{H-H} = 7.1$ Hz, 3H, OCH_2CH_3), 0.65 (t, $^3J_{H-H} = 6.9$ Hz, 2H, $TaCH_2$). ^{13}C NMR (75 MHz, $CDCl_3$, 308 K): δ 193.7 (s, C=O), 128.9 (s, C_5Me_5), 66.2 (t, $^1J_{C-H} = 150$ Hz, OCH_2CH_3), 62.7 (t, $^1J_{C-H} = 127$ Hz, $TaCH_2$), 37.6 (t, $^1J_{C-H} = 128$ Hz, $TaCH_2CH_2$), 14.3 (q, $^1J_{C-H} = 130$ Hz, OCH_2CH_3), 13.1 (q, $^1J_{C-H} = 128$ Hz, C_5Me_5). IR (Nujol): 1625 cm^{-1} (C=O). FAB-MS: *m*/*z* 487 ($M^+ - Cl$). Anal. Calcd for $C_{15}H_{24}O_2Cl_3Ta$: C, 34.40; H, 4.62. Found: C, 34.72; H, 4.93.

Preparation of $Cp^*Cl_3Ta(CH_2CMe_2C(=O)OMe)$ (1b). A solution of $IZn(CH_2CMe_2CO_2Me)$ (0.98 mmol, 1.2 equiv) in THF (4.3 mL) was added to a suspension of Cp^*TaCl_4 (371 mg, 0.81 mmol) in ether (30 mL) cooled at −78 °C. The reaction mixture was allowed to warm to room temperature and stirred overnight. Solvent was evaporated under reduced pressure, and the resulting yellow oil was extracted with hexane (60 mL). The hexane extract was evaporated to give **1b** as yellow microcrystals (159 mg, 36% yield), mp 172−179 °C (dec). ^1H NMR (300 MHz, $CDCl_3$, 308 K): δ 4.19 (s, 3H, OCH_3), 2.41 (s, 15H, C_5Me_5), 1.23 (s, 6H, CMe_2), 0.57 (s, 2H, $TaCH_2$). ^{13}C NMR (75 MHz, $CDCl_3$, 308 K): δ 197.2 (s, C=O), 128.9 (s, C_5Me_5), 82.6 (t, $^1J_{C-H} = 125.0$ Hz, $TaCH_2$), 56.5 (q, $^1J_{C-H} = 149.7$ Hz, OCH_3), 47.6 (s, $TaCH_2CMe_2$), 29.3 (q, $^1J_{C-H} = 129.0$ Hz, $TaCH_2CMe_2$), 13.1 (q, $^1J_{C-H} = 129.0$ Hz, C_5Me_5). IR (Nujol): 1633 cm^{-1} (C=O). FAB-MS: *m*/*z* 500 ($M^+ - Cl$).

Preparation of $ICH_2CMe_2CO_2C_6H_4CH_3$-4. To a mixture of $ICH_2CMe_2CO_2H$ (29.22 g, 128.1 mmol) and $(CF_3CO)_2O$ (20 mL, 0.14 mol) was added *p*-cresol (15 mL, 0.15 mol). The reaction mixture was stirred overnight at room temperature. $ICH_2CMe_2CO_2C_6H_4CH_3$-4 was vacuum distilled out of the reaction mixture as a colorless oil (18.5 g, 45% yield), bp 99 °C (0.1 mmHg). ^1H NMR (300 MHz, $CDCl_3$, 308 K): δ 7.19 (d, 2H, $^3J_{H-H} = 8.9$ Hz, aromatic protons), 7.02 (d, 2H, $^3J_{H-H} = 8.9$ Hz, aromatic protons), 3.49 (s, 2H, ICH_2), 2.37 (s, 3H, $Ar-CH_3$), 1.51 (s, 6H, $C(CH_3)_2$); ^{13}C NMR (75 MHz, $CDCl_3$, 308 K): δ 173.0 (C=O), 148.4 (aromatic carbon), 135.3 (aromatic carbon), 129.7 (aromatic carbons), 121.0 (aromatic carbons), 43.7 ($C(CH_3)_2$), 25.4 ($C(CH_3)_2$), 20.9 ($Ar-CH_3$), 15.8 (ICH_2). IR (Nujol): 1758 cm^{-1} (C=O). EI-MS: *m*/*z* 318 ($[M^+]$). HRMS: *m*/*z* calcd for $C_{12}H_{15}O_2I$ 318.0117, found 318.0096.

Preparation of $IZn(CH_2CMe_2CO_2C_6H_4CH_3$-4). $ICH_2CMe_2CO_2C_6H_4CH_3$-4 (2.5 mL, 12.4 mmol) was added to a THF (8 mL) suspension of activated zinc (0.976 g, 14.9 mmol, 1.2 equiv). After the reaction mixture was stirred overnight at room temperature, THF (20 mL) was added to the reaction mixture. After insoluble materials were removed by centrifugation, the brown supernatant was concentrated to give brown oil, which was extracted with ether (80 mL). Ether was evaporated, and the resulting pale yellow oil was washed with toluene (10 mL) and hexane (20 mL) to give $IZn(CH_2CMe_2CO_2C_6H_4CH_3$-4) as white powder (1.98 g, 42% yield). ^1H NMR (300 MHz, $CDCl_3$, 308 K): δ 7.17 (d, 2H, $^3J_{H-H} = 8.4$ Hz, aromatic protons), 6.94 (d, 2H, $^3J_{H-H} = 8.4$ Hz, aromatic protons), 2.35 (s, 3H, $Ar-CH_3$), 1.44 (s, 6H, $C(CH_3)_2$), 0.72 (s, 2H, $ZnCH_2$). ^{13}C NMR (75 MHz, $CDCl_3$, 308 K): δ 189.0 (C=O), 148.7 (aromatic carbon), 136.0 (aromatic carbon), 130.0 (aromatic carbons), 120.6 (aromatic carbons), 45.1 ($C(CH_3)_2$), 30.3 ($C(CH_3)_2$), 26.9 ($ZnCH_2$), 21.0 ($Ar-CH_3$). IR (Nujol): 1681 cm^{-1} (C=O).

Preparation of $Cp^*Cl_3Ta(CH_2CMe_2C(=O)OC_6H_4CH_3$-4) (1c). To a suspension of Cp^*TaCl_4 (829 mg, 1.82 mmol) in ether (20 mL) was added a solution of $IZn(CH_2CMe_2CO_2C_6H_4CH_3$-4) (697 mg, 1.82 mmol) in ether (15 mL) at −78 °C. The reaction mixture was allowed to warm to room temperature and further stirred overnight at room temperature. After all volatiles were removed under reduced pressure, the residue was extracted with toluene (160 mL). Toluene was evaporated to give a yellow oil, which was extracted with hexane (160 mL). The hexane extract was concentrated under reduced pressure, and the resulting yellow oil was washed with hexane to give **1c** as yellow powders (231 mg, 21% yield), mp 144−147 °C (dec). ^1H NMR (300 MHz, $CDCl_3$, 308 K): δ 7.33 (d, 2H, $^3J_{H-H} = 8.5$ Hz, aromatic protons), 7.20 (d, 2H, $^3J_{H-H} = 8.5$ Hz, aromatic protons), 2.42 (s, 15H, C_5Me_5), 2.34 (s, 3H, $Ar-CH_3$), 1.41 (s, 6H, CMe_2), 0.66 (s, 2H, $TaCH_2$). ^{13}C NMR (75 MHz, $CDCl_3$, 308 K): δ 195.3 (s, C=O), 148.8 (s, *ipso*-Ar), 136.3 (*para*-Ar), 130.0 (d, $^1J_{C-H} = 161$ Hz, *meta*-Ar), 128.9 (s, C_5Me_5), 120.1 (d, $^1J_{C-H} = 164$ Hz, *ortho*-Ar), 82.0 (t, $^1J_{C-H} = 120$ Hz, $TaCH_2$), 48.2 (s, $TaCH_2CMe_2$), 29.4 (q, $^1J_{C-H} = 129$ Hz, $TaCH_2CMe_2$), 21.0 (q, $^1J_{C-H} = 127$ Hz, $ArCH_3$), 13.2 (q, $^1J_{C-H} = 129$ Hz, C_5Me_5). IR (Nujol): 1649 cm^{-1} (C=O). FAB-MS: *m*/*z* 577 ($M^+ - Cl$). Anal. Calcd for $C_{22}H_{30}O_2Cl_3Ta$: C, 43.05; H, 4.93. Found: C, 43.38; H, 4.94.

Preparation of $Cp^*Ta(CH_2CH_2C(=O)OEt)(OTf)_3$ (2a). To a solution of **1a** (76 mg, 0.15 mmol) in toluene (10 mL) at −78 °C was added a solution of AgOTf (0.52 mmol, 3.6 equiv) in toluene (4 mL). The reaction mixture was allowed to warm to room temperature, and the reaction mixture was stirred overnight. After the insoluble materials were removed by centrifugation, all volatiles were evaporated to leave a yellow waxy solid. The solid was washed with hexane (3 mL), and then solvent was evaporated to give **2a** as light yellow powders (94 mg, 75% yield), mp 115−123 °C (dec). ^1H NMR (300 MHz, $CDCl_3$, 308 K): δ 4.74 (q, $^3J_{H-H} = 7.1$ Hz,

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2H, OCH$_2$), 3.81 (pseudo t, $^3J_{\mathrm{H-H}} = 7.0$ Hz, 2H, TaCH$_2$C*H*$_2$), 2.54 (s, 15H, C$_5$*Me*$_5$), 1.53 (pseudo t, $^3J_{\mathrm{H-H}} = 7.0$ Hz, 2H, TaCH$_2$), 1.42 (t, $^3J_{\mathrm{H-H}} = 7.1$ Hz, 3H, OCH$_2$C*H*$_3$). ^{13}C NMR (75 MHz, CDCl$_3$, 308 K): δ 198.9 (s, C=O), 133.6 (s, *C*$_5$Me$_5$), 119.2 (q, $^1J_{\mathrm{C-F}} = 317$ Hz, CF$_3$), 118.8 (q, $^1J_{\mathrm{C-F}} = 317$ Hz, 2C, CF$_3$), 71.6 (t, $^1J_{\mathrm{C-H}} = 126$ Hz, TaCH$_2$), 70.4 (t, $^1J_{\mathrm{C-H}} = 153$ Hz, O*C*H$_2$CH$_3$), 37.0 (t, $^1J_{\mathrm{C-H}} = 131$ Hz, TaCH$_2$*C*H$_2$), 13.7 (q, $^1J_{\mathrm{C-H}} = 128$ Hz, OCH$_2$*C*H$_3$), 11.7 (q, $^1J_{\mathrm{C-H}} = 130$ Hz, C$_5$*Me*$_5$). ^{19}F NMR (282 MHz, CDCl$_3$, 308 K): δ −76.4 (s, 6F, OSO$_2$CF$_3$ *cis* to TaCH$_2$), −77.8 (s, 3F, OSO$_2$CF$_3$ *trans* to TaCH$_2$). IR (Nujol): 1587 cm^{-1} (C=O). FAB-MS: *m/z* 715 (M$^+$ − OTf). Anal. Calcd for C$_{18}$H$_{24}$S$_3$O$_{11}$F$_9$Ta: C, 25.01; H, 2.80. Found: C, 25.03; H, 2.79.

Preparation of Cp*Cl$_3$Ta[N(Xyl)-C(=C=N-Xyl)-C(CH$_2$CH$_2$CO$_2$Et)=N-Xyl] (3a). 2,6-Dimethyphenylisocyanide (111 mg, 0.85 mmol) was added to a solution of **1a** (143 mg, 0.27 mmol) in toluene (10 mL) at 0 °C. The reaction mixture was stirred overnight at room temperature. The solvent was evaporated under reduced pressure, and the resulting red waxy solid was washed with hexane (5 mL) to give red precipitates, which were dried under reduced pressure to give **3a** as red powders (202 mg, 80% yield), mp 177−185 °C (dec). ^{1}H NMR (300 MHz, CDCl$_3$, 308 K): δ 7.1−6.8 (m, 9H, aromatic protons), 3.84 (q, $^3J_{\mathrm{H-H}} = 7.1$ Hz, 2H, OCH$_2$), 2.52 (s, 6H, CH$_3$), 2.50 (m, 4H, CH$_2$CH$_2$), 2.39 (s, 6H, CH$_3$), 2.12 (s, 6H, CH$_3$), 2.06 (s, 15H, C$_5$Me$_5$), 1.01 (t, $^3J_{\mathrm{H-H}} = 7.1$ Hz, 3H, OCH$_2$C*H*$_3$). ^{13}C NMR (75 MHz, CDCl$_3$, 308 K): δ 172.9 (s), 171.1 (s), and 168.9 (s) (corresponding to C=N, C=O, and C=C=N), 152.4 (s, *ipso*), 147.6 (s, *ipso*), 137.4 (s, *o*-Xyl), 135.9 (s, *o*-Xyl), 134.7 (s, *o*-Xyl), 130.8 (s, *ipso*), 129.6 (d, $^1J_{\mathrm{C-H}} = 161$ Hz, *p*-Xyl), 128.5 (d, $^1J_{\mathrm{C-H}} = 164$ Hz, *m*-Xyl), 128.5 (d, $^1J_{\mathrm{C-H}} = 161$ Hz, *p*-Xyl), 127.8 (d, $^1J_{\mathrm{C-H}} = 158$ Hz, *m*-Xyl), 127.4 (s, *C*$_5$Me$_5$), 126.8 (d, $^1J_{\mathrm{C-H}} = 160$ Hz, *p*-Xyl), 125.8 (d, $^1J_{\mathrm{C-H}} = 158$ Hz, *p*-Xyl), 107.5 (s, C=C=N), 60.7 (t, $^1J_{\mathrm{C-H}} = 147$ Hz, OCH$_2$), 31.4 (t, $^1J_{\mathrm{C-H}} = 135$ Hz, CH$_2$), 27.8 (t, $^1J_{\mathrm{C-H}} = 127$ Hz, CH$_2$), 22.5 (q, $^1J_{\mathrm{C-H}} = 127$ Hz, CH$_3$), 20.1 (q, $^1J_{\mathrm{C-H}} = 127$ Hz, CH$_3$), 18.8 (q, $^1J_{\mathrm{C-H}} = 127$ Hz, CH$_3$), 14.1 (q, $^1J_{\mathrm{C-H}} = 127$ Hz, OCH$_2$*C*H$_3$), 12.0 (q, $^1J_{\mathrm{C-H}} = 128$ Hz, C$_5$*Me*$_5$). IR (Nujol): 2047 cm^{-1} (C=C=N), 1731 cm^{-1} (C=O), 1548 cm^{-1} (C=N). FAB-MS: *m/z* 880 (M$^+$ − Cl). Anal. Calcd for C$_{42}$H$_{51}$N$_3$O$_2$Cl$_3$Ta: C, 55.00; H, 5.60; N, 4.58. Found: C, 55.07; H, 5.92; N, 4.48.

Preparation of Cp*Cl$_2$Ta(CH$_2$CH=C(O)OEt) (4a). To a suspension of **1a** (401 mg, 0.77 mmol) in toluene (15 mL) at −78 °C was added a solution of KN(SiMe$_3$)$_2$ (0.90 mmol, 1.2 equiv) in toluene (1.8 mL). The reaction mixture was allowed to warm to room temperature and stirred further for 2 h. Removal of solvent under reduced pressure afforded a red-brown residue, which was extracted with hexane (30 mL). After insoluble materials were removed by centrifugation, a clear solution was concentrated to give **4a** as purple microcrystals (224 mg, 60% yield), mp 96−103 °C. ^{1}H NMR (300 MHz, CDCl$_3$, 308 K): δ 4.92 (dd, $^3J_{\mathrm{H-H}} = 4.7$ and 7.7 Hz, 1H, TaCH$_2$C*H*), 4.12 (m, 1H, OCH$_2$CH$_3$), 2.26 (s, 15H, C$_5$*Me*$_5$), 1.34 (t, $^3J_{\mathrm{H-H}} = 7.1$ Hz, 3H, OCH$_2$CH$_3$), 1.32 (dd, $^1J_{\mathrm{H-H}} = 8.6$ Hz, $^3J_{\mathrm{H-H}} = 7.7$ Hz, 1H, TaCH*H*), 0.53 (dd, $^1J_{\mathrm{H-H}} = 8.6$ Hz, $^3J_{\mathrm{H-H}} = 4.7$ Hz, 1H, TaC*H*H). ^{13}C NMR (75 MHz, CDCl$_3$, 308 K): δ 161.8 (s, HC=*C*), 125.0 (s, *C*$_5$Me$_5$), 71.3 (d, $^1J_{\mathrm{C-H}} = 174$ Hz, TaCH$_2$CH), 67.0 (t, $^1J_{\mathrm{C-H}} = 147$ Hz, Ta*C*H$_2$), 64.1 (t, $^1J_{\mathrm{C-H}} = 147$ Hz, O*C*H$_2$CH$_3$), 14.8 (q, $^1J_{\mathrm{C-H}} = 127$ Hz, OCH$_2$*C*H$_3$), 11.5 (q, $^1J_{\mathrm{C-H}} = 128$ Hz, C$_5$*Me*$_5$). IR (Nujol): 1531 cm^{-1} (C=C). FAB-MS: *m/z* 451 (M$^+$ − Cl). Anal. Calcd for C$_{15}$H$_{23}$Cl$_2$O$_2$Ta: C, 36.98; H, 4.76. Found: C, 37.12; H, 4.98.

Preparation of Cp*(*p*-MeOC$_6$H$_4$-DAD)Ta(CH$_2$CMe$_2$C(=O)O) (5). A solution of Li$_2$(*p*-MeOC$_6$H$_4$-DAD) in THF (5.0 mL) was added to a solution of **1b** (185 mg, 0.34 mmol) in THF (10 mL) cooled at −78 °C. After the reaction mixture was stirred overnight at room temperature, all volatiles were removed under reduced pressure. The residue was extracted with toluene (20 mL), and then toluene was removed. The resulting oil was treated with hexane (2 mL) to give **5** as yellow-brown powders (203 mg, 83% yield), mp 148−160 °C (dec). ^{1}H NMR (300 MHz, CDCl$_3$, 308 K): δ 7.29 (d, $^3J_{\mathrm{H-H}} = 9.1$ Hz, 2H, aromatic protons), 6.90 (m, 6H, aromatic protons), 6.21 (d, $^2J_{\mathrm{H-H}} = 3.3$ Hz, 1H, N−CH), 5.76 (d, $^2J_{\mathrm{H-H}} = 3.3$ Hz, 1H, N−CH), 3.82 (s, 3H, OMe), 3.80 (s, 3H, OMe), 1.99 (s, 15H, C$_5$*Me*$_5$), 1.14 (s, 3H, C*Me*), 0.77 (s, 3H, C*Me*), 1.12 and 0.68 (AB*q*, $^2J_{\mathrm{H-H}} = 13.5$ Hz, 2H, TaCHH). ^{13}C NMR (75 MHz, CDCl$_3$, 308 K): δ 190.6 (s, C=O), 156.9 (s, *p*-*C*$_6$H$_4$OCH$_3$), 156.7 (s, *p*-*C*$_6$H$_4$OCH$_3$), 143.4 (s, 2C, *ipso*-C$_6$H$_4$OCH$_3$), 125.4 (d, $^1J_{\mathrm{C-H}} = 159.5$ Hz, aromatic carbons), 124.7 (d, $^1J_{\mathrm{C-H}} = 160.1$ Hz, aromatic carbons), 118.5 (s, *C*$_5$Me$_5$), 113.8 (d, $^1J_{\mathrm{C-H}} = 159.5$ Hz, aromatic carbon), 113.7 (d, $^1J_{\mathrm{C-H}} = 159.5$ Hz, aromatic carbon), 109.4 (d, $^1J_{\mathrm{C-H}} = 176.2$ Hz, N−CH)), 104.3 (d, $^1J_{\mathrm{C-H}} = 176.8$ Hz, N−CH), 59.9 (br, TaCH$_2$), 55.6 (q, $^1J_{\mathrm{C-H}} = 143.4$ Hz, OCH$_3$), 55.5 (q, $^1J_{\mathrm{C-H}} = 143.4$ Hz, OCH$_3$), 46.4 (s, *C*Me$_2$), 32.9 (q, $^1J_{\mathrm{C-H}} = 128.4$ Hz, C*Me*), 30.7 (q, $^1J_{\mathrm{C-H}} = 130.7$ Hz, C*Me*), 11.6 (q, $^1J_{\mathrm{C-H}} = 127.8$ Hz, C$_5$*Me*$_5$). IR (Nujol): 1668 cm^{-1} (C=O), 1506 cm^{-1} (C=C). FAB-MS: *m/z* 684 (M$^+$), 669 (M$^+$ − CH$_3$). Anal. Calcd for C$_{31}$H$_{39}$N$_2$O$_4$Ta: C, 54.39; H, 5.74; N, 4.09. Found: C, 54.97; H, 6.02; N, 3.98.

Preparation of Cp*(*p*-MeOC$_6$H$_4$-DAD)Ta(CH$_2$CMe$_2$C(=O)-O-Al(C$_6$F$_5$)$_3$) (6). In a glovebox, toluene (5 mL) was added to a mixture of **5** (115 mg, 0.17 mmol) and Al(C$_6$F$_5$)$_3$(toluene)$_{0.5}$ (99 mg, 0.17 mmol). The reaction mixture was stirred overnight, and then toluene was evaporated. The resulting brown oil was washed with hexane (5 mL) to give **6** as yellow-brown powders (135 mg, 66% yield), mp 226−234 °C (dec). Single crystals were obtained by the slow evaporation of C$_6$D$_6$ from a NMR tube sample in a glovebox. ^{1}H NMR (300 MHz, C$_6$D$_6$, 308 K): δ 6.87 (d, $^3J_{\mathrm{H-H}} = 9.1$ Hz, 2H, Ar), 6.80 (d, $^3J_{\mathrm{H-H}} = 8.5$ Hz, 4H, Ar), 6.68 (d, $^3J_{\mathrm{H-H}} = 8.8$ Hz, 2H, Ar), 6.26 (d, $^1J_{\mathrm{H-H}} = 3.0$ Hz, 1H, N−CH), 5.40 (d, $^1J_{\mathrm{H-H}} = 3.0$ Hz, 1H, N−CH), 3.46 (s, 3H, OMe), 3.41 (s, 3H, OMe), 1.50 (s, 15H, C$_5$*Me*$_5$), 1.38 (s, 3H, C*Me*), 1.11 (s, 3H, C*Me*), 0.93 and 0.03 (AB*q*, $^2J_{\mathrm{H-H}} = 14.7$ Hz, 2H, TaCH$_2$). ^{13}C NMR (75 MHz, C$_6$D$_6$, 298 K): δ 200.4 (s, C=O), 159.2 (s, *p*-*C*$_6$H$_4$OCH$_3$), 158.8 (s, *p*-*C*$_6$H$_4$OCH$_3$), 150.9 (d, $^1J_{\mathrm{C-F}} = 231$ Hz, *o*-C$_6$F$_5$), 143.1 (s, *ipso*-*C*$_6$H$_4$OCH$_3$), 142.3 (s, *ipso*-*C*$_6$H$_4$OCH$_3$), 142.0 (d, $^1J_{\mathrm{C-F}} = 250$ Hz, *p*-C$_6$F$_5$), 137.7 (d, $^1J_{\mathrm{C-F}} = 268$ Hz, *m*-C$_6$F$_5$), 127.0 (d, $^1J_{\mathrm{C-H}} = 158$ Hz, *o*-*C*$_6$H$_4$OCH$_3$), 126.2 (d, $^1J_{\mathrm{C-H}} = 161$ Hz, *o*-*C*$_6$H$_4$OCH$_3$), 120.5 (s, *C*$_5$Me$_5$), 114.6 (d, $^1J_{\mathrm{C-H}} = 160$ Hz, *m*-*C*$_6$H$_4$OCH$_3$), 114.1 (d, $^1J_{\mathrm{C-H}} = 161$ Hz, *m*-*C*$_6$H$_4$OCH$_3$), 108.1 (d, $^1J_{\mathrm{C-H}} = 181$ Hz, N−CH), 107.8 (d, $^1J_{\mathrm{C-H}} = 182$ Hz, N−CH), 55.8 (q, $^1J_{\mathrm{C-H}} = 143$ Hz, OCH$_3$), 55.5 (q, $^1J_{\mathrm{C-H}} = 144$ Hz, OCH$_3$), 55.5 (t, $^1J_{\mathrm{C-H}} = 119$ Hz, TaCH$_2$), 47.8 (s, *C*Me$_2$), 33.8 (q, $^1J_{\mathrm{C-H}} = 130$ Hz, C*Me*), 32.3 (q, $^1J_{\mathrm{C-H}} = 115$ Hz, C*Me*), 11.8 (q, $^1J_{\mathrm{C-H}} = 128$ Hz, C$_5$*Me*$_5$). ^{19}F NMR (282 MHz, C$_6$D$_6$, 308 K): δ −123.7 (m, 6F, *ortho*), −155.7 (t, $^3J_{\mathrm{F-F}} = 15.9$ Hz, 3F, *para*), −163.1 (m, 6F, *meta*). IR (Nujol): 1508 cm^{-1} (C=C). Anal. Calcd for C$_{49}$H$_{39}$N$_2$O$_4$F$_{15}$AlTa: C, 48.53; H, 3.24; N, 2.31. Found: C, 48.93; H, 3.45; N, 2.70.

Preparation of (Xyl-N=)Cl$_3$W(CH$_2$CH$_2$C(=O)OEt) (7). To a suspension of [Et$_4$N][(Xyl-N=)WCl$_5$] (3.109 g, 5.10 mmol) in ether (30 mL) at −78 °C was added a solution of Zn(CH$_2$CH$_2$CO$_2$Et)$_2$ in ether (0.58 M, 5.0 mL, 2.88 mmol). The reaction mixture was allowed to warm to room temperature and then stirred for 2 h. All volatiles were removed, and the resulting residue was extracted by hexane (60 mL × 4). The combined extract was concentrated to give **7** as dark red crystalline solids (1.25 g, 48% yield), mp 85−89 °C (dec). ^{1}H NMR (300 MHz, CDCl$_3$, 308 K): δ 7.26 (d, $^3J_{\mathrm{H-H}} = 7.7$ Hz, 2H, *m*-Ph), 6.68 (t, $^3J_{\mathrm{H-H}} = 7.7$ Hz, 1H, *p*-Ph), 4.73 (q, $^3J_{\mathrm{H-H}} = 7.1$ Hz, 2H, OC*H*$_2$CH$_3$), 4.08 (t, $^3J_{\mathrm{H-H}} = 6.6$ Hz, 2H, WCH$_2$C*H*$_2$), 3.08 (s, 6H, ArC*H*$_3$), 2.27 (t, $^3J_{\mathrm{H-H}} = 6.6$ Hz, 2H, WC*H*$_2$), 1.51 (t, $^3J_{\mathrm{H-H}} = 7.1$ Hz, 3H, OCH$_2$C*H*$_3$). ^{13}C NMR (75 MHz, CDCl$_3$, 308 K): δ 194.9 (s, *C*O$_2$Et), 142.6 (*o*-Xyl), 131.6 (d, $^1J_{\mathrm{C-H}} = 160$ Hz, *p*-Xyl), 126.3 (d, $^1J_{\mathrm{C-H}} = 161$ Hz, *m*-Xyl), 66.7 (t, $^1J_{\mathrm{C-H}} = 148$ Hz, O*C*H$_2$CH$_3$), 65.4 (t, $^1J_{\mathrm{W-C}} = 33.4$ Hz,

Table 5. Crystal Data and Data Collection Parameters of 1a, 1b, 3a, 6, and 8[a,b]

	1a	**1b**
formula	$C_{15}H_{24}Cl_3O_2Ta$	$C_{16}H_{26}Cl_3O_2Ta$
fw	523.64	537.67
cryst syst	monoclinic	orthorhombic
space group	$P2_1/c$ (No. 14)	*Pccn* (No. 56)
a, Å	8.6818(3)	25.7248(20)
b, Å	13.6267(3)	21.1152(17)
c, Å	14.9759(4)	8.6368(8)
α, deg		
β, deg	92.3894(14)	
γ, deg		
V, Å^3	1770.17(8)	4691.4(7)
Z	4	8
D_{calcd}, g/cm^{-3}	1.965	1.522
no. of reflns for cell det	74492	38549
F(000)	1016	2096
μ [Mo Kα], cm^{-1}	66.63	50.30
T, K	120	120
cryst size, mm	0.22 × 0.10 × 0.06	0.21 × 0.15 × 0.05
$2\theta_{max}$, deg	60.08	55.0
no. of reflns measd	49 755	65 872
no. of unique data (R_{int})	5165 (0.0261)	5379 (0.2416)
no. of observns ($I > 2.0\sigma(I)$)	4890	3034
no. of variables	286	199
R1 ($I > 2.0\sigma(I)$)	0.0132	0.0679
wR2 ($I > 2.0\sigma(I)$)	0.0276	0.1602
R1 (all data)	0.0152	0.1383
wR2 (all data)	0.0280	0.1843
GOF on F^2	1.11	1.03
Δρ, e Å^{-3}	0.475, −0.406	1.936, −1.510

	3a	**6**	**8**
formula	$C_{42}H_{51}Cl_3N_3O_2Ta$	$C_{49}H_{39}O_4N_2F_{15}AlTa$	$C_{31}H_{36}Cl_3N_3O_2W(C_7H_8)$
fw	917.19	1212.76	864.99
cryst syst	triclinic	monoclinic	monoclinic
space group	$P\bar{1}$ (No. 2)	$P2_1/c$ (No. 14)	$P2_1/a$ (No. 14)
a, Å	9.436(4)	11.646(1)	15.302(2)
b, Å	11.148(4)	30.716(3)	12.380(2)
c, Å	20.172(8)	14.1092(8)	19.488(3)
α, deg	76.47(3)		
β, deg	76.69(3)	109.847(3)	93.025(6)
γ, deg	80.30(3)		
V, Å^3	1992(1)	4747.4(6)	3686.5(8)
Z	2	4	4
D_{calcd}, g/cm^{-3}	1.528	1.697	1.558
no. of reflns for cell det	39 014	111 001	81 658
F(000)	928	2400	1736
μ [Mo Kα], cm^{-1}	29.94	24.36	33.91
T, K	120	120	120
cryst size, mm	0.20 × 0.15 × 0.05	0.40 × 0.65 × 0.10	0.20 × 0.25 × 0.05
$2\theta_{max}$, deg	55.0	55.0	54.8
no. of reflns measd	34 100	84 125	61 273
no. of unique data (R_{int})	8987 (0.076)	10865 (0.040)	8276 (0.058)
no. of observns ($I > 2.0\sigma(I)$)	7327	9819	6746
no. of variables	664	649	413
R1 ($I > 2.0\sigma(I)$)	0.0360	0.0229	0.0353
wR2 ($I > 2.0\sigma(I)$)	0.0607	0.0792	0.1058
R1 (all data)	0.0523	0.0268	0.0472
wR2 (all data)	0.0634	0.0833	0.1125
GOF on F^2	0.956	0.725	0.848
Δρ, e Å^{-3}	1.27, −1.79	0.90, −0.77	1.58, −1.56

[a] $R1 = (\sum||F_o| - |F_c||)/(\sum|F_o|)$. [b] $wR2 = [\{\sum w(F_o^2 - F_c^2)^2\}/\{\sum w(F_o^4)\}]^{1/2}$.

$^1J_{C-H}$ = 132 Hz, WCH_2), 37.9 (t, $^1J_{C-H}$ = 130 Hz, WCH_2CH_2), 18.3 (q, $^1J_{C-H}$ = 128 Hz, Ar-CH_3), 14.1 (q, $^1J_{C-H}$ = 128 Hz, OCH_2CH_3). IR (Nujol): 1620 cm^{-1} (C=O). Anal. Calcd for $C_{13}H_{18}O_2N_1Cl_3W$: C, 30.59; H, 3.55; N, 2.74. Found: C, 30.53; H, 3.63; N, 2.64.

Preparation of (Xyl-N=)W{C(=N-Xyl)$CH_2CH_2CO_2$Et}-(CNXyl)Cl_3 (8). To a solution of **7** (63 mg, 0.122 mmol) in toluene (1 mL) was layered a solution of 2,6-dimethylphenylisocyanide (40.5 mg, 0.309 mmol) in toluene (3 mL). Yellow crystals of **8** were formed after 3 days. The crystals were separated, washed with hexane, and then dried under reduced pressure to give **8** as yellow crystals (54 mg, 57% yield), mp 207−210 °C (dec). ^{1}H NMR (300 MHz, $CDCl_3$, 298 K): δ 7.33 (t, $^3J_{H-H}$ = 7.7 Hz, 1H, *p*-Xyl), 7.25−7.15 (m, 4H, *m*- and *p*-Xyl), 7.01 (d, $^3J_{H-H}$ = 7.4 Hz, 3H, *m*-Xyl), 6.84 (t, $^3J_{H-H}$ = 7.7 Hz, 1H, *p*-Xyl), 4.11 (ddd, $^2J_{H-H}$ = 18.8 Hz, $^3J_{H-H}$ = 6.8 and 9.1 Hz, 1H, C*H*HCO$_2$Et), 4.0−3.7 (m, 3H, CH*H*CO$_2$Et and CO$_2$C*H*$_2$CH$_3$), 2.90 (ddd, $^2J_{H-H}$ = 17.8 Hz, $^3J_{H-H}$ = 5.1 and 6.8 Hz, 1H, N=CC*H*H), 2.80−2.65 (1H, N=CCH*H* overlapped with ArCH$_3$ resonance), 2.75 (br s, 6H, ArCH$_3$), 2.59 (s, 6H, ArCH$_3$), 2.42 (s, 3H, ArCH$_3$), 1.88 (s, 3H, ArCH$_3$), 1.07 (t, $^3J_{H-H}$ = 7.1 Hz, 3H, OCH$_2$C*H*$_3$). ^{13}C NMR (75 MHz, $CDCl_3$, 298 K): δ 198.2 (W−*C*=N), 170.6 (C=O), 149.9 (W−*C*NXyl), 136.5, 134.2, 134.1, 132.4, 131.0, 129.3, 128.8$_9$, 128.8$_5$, 128.7, 128.5, 128.4, 128.1, 127.4 (br), 127.3 (br), 125.2, 61.4 (OCH_2), 31.3, 29.5, 20.0 ($ArCH_3$), 19.2 ($ArCH_3$), 19.1 ($ArCH_3$), 18.7 ($ArCH_3$), 14.1 ($OCH_2\mathit{C}H_3$). IR (Nujol): 2210 cm^{-1} (C≡N), 1773 cm^{-1} (C═N), 1726 cm^{-1} (C═O). FAB-MS: *m*/*z* 736 ($M^+ - Cl$). Anal. Calcd for $C_{31}H_{36}O_2N_3Cl_3W{\cdot}0.33(C_7H_8)$ (confirmed by integrated ^1H NMR spectrum): C, 49.82; H, 4.85; N, 5.23. Found: C, 49.94; H, 4.85; N, 5.14.

X-ray Crystallography. All crystals were handled similarly. The crystals were fixed on the end of glass fibers with heavy mineral oil or inside a CryoLoop (Hampton Research Corp.) with heavy mineral oil and placed in a nitrogen stream at 120(1) K. All measurements were made on a Rigaku RAXIS-RAPID imaging plate diffractometer with graphite-monochromated Mo Kα radiation ($\lambda = 0.71075$). Indexing was performed from 3 or 4 oscillations, which were exposed for the appropriate time for each crystal. The camera radius was 127.40 mm. Readout was performed in the 0.100 mm pixel mode. For the data collection, reflections were measured at a temperature of 120(1) K. Crystal data and structure refinement parameters are summarized in Table 5.

The structure of **1a** and **1b** were solved by direct methods (SIR97).[46] The structures of **3a** and **6** were solved by direct methods (SIR92).[47] The structure of **8** was solved by direct methods (SHELXS-97).[48] All of the structures were refined on F^2 by a full-matrix least-squares method, using SHELXL-97.[49] Non-hydrogen atoms were anisotropically refined, and all H atoms were isotropically refined for **1a** and **3a**. Non-hydrogen atoms were anisotropically refined, and all H atoms were included in the refinement on calculated positions riding on their carrier atoms for **1b** and **6**. For **8**, most of the non-hydrogen atoms, except for the solvated toluene molecule, were anisotropically refined and the rest were refined isotropically. All H atoms were included in the refinement on calculated positions riding on their carrier atoms. The ORTEP-3 program[50] was used to draw the molecule.

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Supporting Information Available: CIF files giving crystallographic data for **1a**, **1b**, **3a**, **6**, and **8**. This material is available free of charge via the Internet at http://pubs.acs.org.

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