New Carbonylation Reaction of Tungsten−Propargyl Compounds via Protonation at a Prolonged Period

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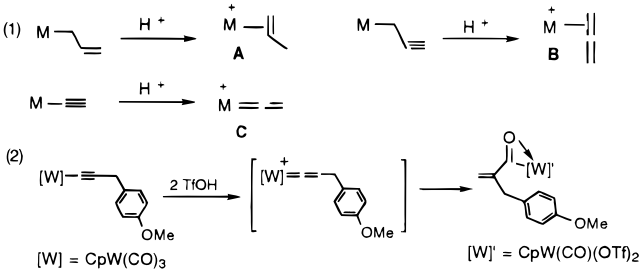
The CpW(CO)$_3$(η^1-CH$_2$C≡CR) (R = Me **1**, Ph **2**) complexes were treated with triflic acid (2.0 equiv) in cold dichloromethane (−78 °C), and after a long period to the mixture was added water or RNH$_2$ to give good yields of carbonylation products CpW(CO)$_2$(η^1,η^2-CH$_2$-CHCHR−Y−CO−) (R = Me, Ph; Y = RN, O). These products were fully characterized by appropriate physical methods including single-crystal X-ray diffraction. If a chiral amine such as (*R*)-methylbenzylamine was used in the reaction, two optically active isomers in equal proportions were obtained and further separated on a silica column. In the case of (C$_5$Me$_5$)W(CO)$_3$(η^1-CH$_2$C≡CPh) (**9**), its reactions with triflic acid and water in the same reaction sequence produce (C$_5$Me$_5$)W(CO)$_2$(η^1,η^2-CH$_2$CHCHPh−O−CO−) as two diastereomers which undergo mutual exchange according to variable-temperature ^{1}H NMR spectroscopy.

Introduction

The action of a metal−η^1-unsaturated hydrocarbyl compound with a strong acid is a general method for generation of metal−η^2-carbocations.[1,2] Scheme 1 (eq 1) shows three representative examples of formation of metal−η^2-alkene[3] (**A**), −η^2-allene[4] (**B**), and −η^1-vinylidene[5] (**C**) carbocations via protonation of their corresponding allyl, propargyl, and alkynyl compounds. Recently, we discovered[6] that protonation of tungsten−η^1-alkynyl complexes *in a prolonged reaction period* ultimately led to an oxidative carbonylation reaction to give tungsten(IV) acyl complexes via a tungsten(II)−η^1-vinylidene intermediate, as shown in Scheme 1 (eq 2). This observation raises an interesting question regarding the kinetic stabilities of the other two carbocations (**A** and **B**) in a prolonged reaction period; this issue has not been studied thoroughly. In this article, we study the reaction chemistry of tungsten−η^1-propargyl complexes CpW(CO)$_3$(η^1-CH$_2$C≡CR) (R = Me **1**, Ph **2**) after protonation over different periods, and the effect of reaction time on the chemical reactivity of the resulting tungsten−η^2-allene cation (**B**) will be reported in detail.

Scheme 1



Results and Discussion

It was previously reported[7,8] that treatment of tungsten−propargyl compounds such as **1** and **2** with triflic

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[1] Review papers: (a) Norton, J. R. In *Inorganic Reactions and Methods*; Verlag Chemie: Weinheim, 1987. (b) Pearson, R. G. *Chem. Rev.* **1985**, *85*, 41.

[2] (a) Collman, J. P.; Hegedus, L. S.; Norton, J. R.; Finke, R. G. *Principles and Application of Organotransition Metal Chemistry*; University Science Books: Mill Valley, CA, 1987; Chapter 8, p 433. (b) Hegedus, L. S. *Transition Metals in the Synthesis of Complex Organic Molecules*; University Science Books: Mill Valley, 1994; Chapter 2, p 43.

[3] Organic Syntheses via metal−η^2-alkene cations, see representative papers: (a) Welker, M. E. *Chem. Rev.* **1992**, *92*, 97. (b) Jiang, S.; Turos, E. *Organometallics* **1993**, *12*, 4280. (c) Jiang, S.; Turos, E. *Tetrahedron Lett.* **1991**, 4639. (d) Rosenblum, M.; Watkins, J. C. *J. Am. Chem. Soc.* **1990**, *112*, 6316. (e) Bell, P. B.; Wojcicki, A. *Inorg. Chem.* **1981**, *20*, 1585.

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[8] (a) Lin, S. H.; Vong, W. J.: Liu, R. S. *Organometallics* **1995**, *14*, 1619. (b) Chen, C.-H. Fan, J.-S.; Lee, G.-H.; Shieh, S.-J.; Wang, S.-L.; Peng S.-M.; Liu, R.-S. *J. Am. Chem. Soc.* **1996**, *118*, 9279. (c) Shiu, L. H.; Wang S.-L.; Wu M.-J.; Liu R. S. *J. Chem. Soc., Chem. Commun.* **1997**, 2005. (d) Cheng, M.-H.; Ho, Y.-H.; Lee, G.-H.; Peng, S.-M.; Chu, S.-Y.; Liu, R.-S. *Organometallics* **1994**, *13*, 4082.

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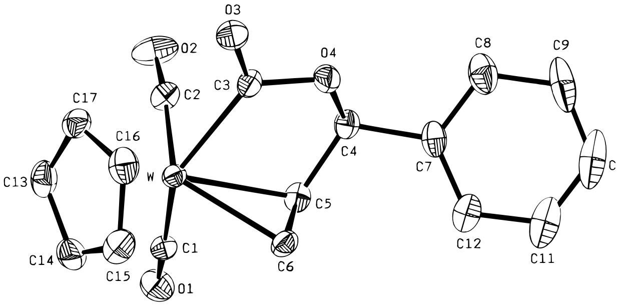

Figure 1. Molecular structure of compound **5** with selected bond distances (Å) and angles (deg): W−C(3) = 2.211(6), W−C(5) = 2.288(6), W−C(6) = 2.250(6), C(3)−O(3) = 1.204(7), C(4)−O(4) = 1.427(7), C(4)−C(5) = 1.514(9), C(5)−C(6) = 1.402(8).

acid (CF_3SO_3H) in cold CH_2Cl_2 (−78 °C) followed by immediate addition of water, alcohol, and amine led to alkoxycarbonylation reaction to yield syn-π-2-carboxylated allyl complexes **3**. According to the chemistry of related $CpFe(CO)_2(\eta^1\text{-}CH_2C{\equiv}CR)$ complexes,[7] formation of **3** can be envisaged to originate from the cis-η^2-allene intermediate (**D**), of which the CO group is initially attacked by YXH (YX = HO, RO, R_2N) to form species **E**; further insertion of the W−COXY bond of **E** into its central allene carbon generates the syn-isomer of **3**. To study the effect of reaction time on the chemical reactivity of tungsten−η^2-allene cation **D**, the solution was warmed to 23 °C in a period of 10 h before treatment of water or $R'NH_2$ ($R' = Bu^i$, $PhCH_2$). After workup of the solution, the new organometallic products **4**−**7** show NMR spectral data distinct from those expected for tungsten−syn-π-allyl complexes **3**, although compounds of these two types have the same formula according to mass and elemental analyses. In addition to an ν(CO) absorption band in the 1650−1600 cm^{-1} region, there are two terminal W−CO stretching frequencies (ν(CO) ca. 2000 and 1930 cm^{-1}) for compounds **4**−**7**, and these values are much larger than those (ν(CO) 1940 and 1870 cm^{-1}) of compound **3**.[7,8] This information suggests that a new carbonylation reaction occurs in the reaction of water or amine with the aged solution of **D′**. In contrast, the reaction of MeOH with the same aged solution **D′** did not produce any neutral organometallic product. It is very difficult to deduce the structures of **4**−**7** based on their spectral data alone. Characterization of the structures relies on an X-ray diffraction study of compound **5**.[9] Figure 1 shows the ORTEP drawing for its molecular structure, which reveals that $CpW(CO)_2$ fragment is bound to an α-hydroxycarbonyl alkene moiety in a η^1,η^2 fashion. The C(4) carbon of **5** becomes an sp^3-hydridized carbon, whereas the C(5)−C(6) carbon resembles a coordinated olefin, as shown by the C(4)−C(5) (1.514 Å) and C(5)−C(6) (1.402 Å) bond lengths. The arrangement of the C(4)−C(5)−C(6)−N atoms of **5** is close to a U-shaped conformation, with the W−C(5) bond trans to the C(6)−Ph bond to minimize its steric hindrance. Only one single diastereomer was observed for compounds **4**−**7**, and the lack of the other diastereomer is probably due to its sterically congested structure because it is shown later that analogous diastereomers can undergo mutual exchange at room temperature (vide infra). We also investigated this reaction with chiral (*R*)-methylbenzylamine with an aged acidification solution of compound **2**, and two optically pure diastereomers **8a** and **8b** were produced and further separated on a silica column to give 28% and 29% yields, respectively. Both **8a** and **8b** presumably have the same configuration (2S*, 3S*) at the two C^2H−C^3HPh carbons because the magnitudes of the coupling constant (J_{23} = 2.9−3.0 Hz) are very close to those (J_{23} = 2.8−3.3 Hz) of compounds **4**−**7**. The X-ray structure[10] of chiral compound **8b** is shown in Figure 2, which confirms the proposed configurations at the C(5) and C(6) carbons as that of compound **5**. Similarly, the W−C(5) bond of **8b** is trans to the C(6)−Ph group to minimize steric interactions.

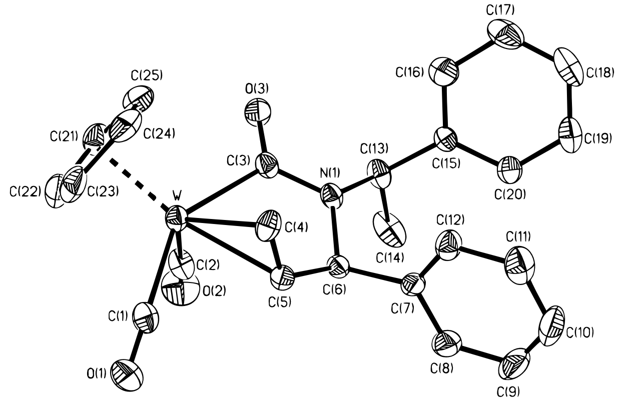

Figure 2. Molecular structure of compound **8b** with selected bond distances (Å) and angles (deg): W−C(3) = 2.240(5), W−C(5) = 2.299(5), W−C(4) = 2.240(4), C(3)−O(3) = 1.235(6), C(3)−N(1) = 1.376(6), C(6)−N(1) = 1.458(6), C(5)−C(6) = 1.518(6), C(4)−C(5) = 1.400(7).

We attempted to characterize the proposed tungsten−η^2-cis-allene cation (**D**) generated from **2** as well as the species in its aged solution **D′**. Protonation of $CpM(CO)_3(\eta^1\text{-}CH_2C{\equiv}CR)$ (M = Mo, W)[7,8] with strong acid is believed to yield η^2-cis-allene species initially, but its NMR characterization is not yet reported. Addition of excess anhydrous diethyl ether to the two solution gave two dark black solids **D** and **D′**, respectively, which were virtually insoluble in polar solvents such as CH_2Cl_2, $CHCl_3$, and CH_3CN. We therefore prepared $Cp^*W(CO)_3(\eta^1\text{-}CH_2C{\equiv}CPh)$[11] ($Cp^* = C_5Me_5$) (**9**) because pentamethylcyclopentadienylmetal complexes are usually more soluble[12] than their cyclopentadienylmetal analogues. Scheme 3 shows the outcome for the same reaction sequence.

Similar to its cyclopentadienyl analogue **1** and **2**, compounds **10** and **11a**,**b** are obtained in 85% and 56% yields, respectively, via water treatment of the fresh (**D**) and the aged (**D′**) solution of **9** after acidification with triflic acid. The diastereoisomeric ratio of **11a** and **11b** was ca. 3:1; these two isomers could undergo mutual exchange (vide infra) at elevated temperatures. Addition of benzylamine to the aged solution **D′** of **9** also gave the new carbonylation product **12** as a single diastereomer in 49% yield. The stereochemistry of **12** is assigned

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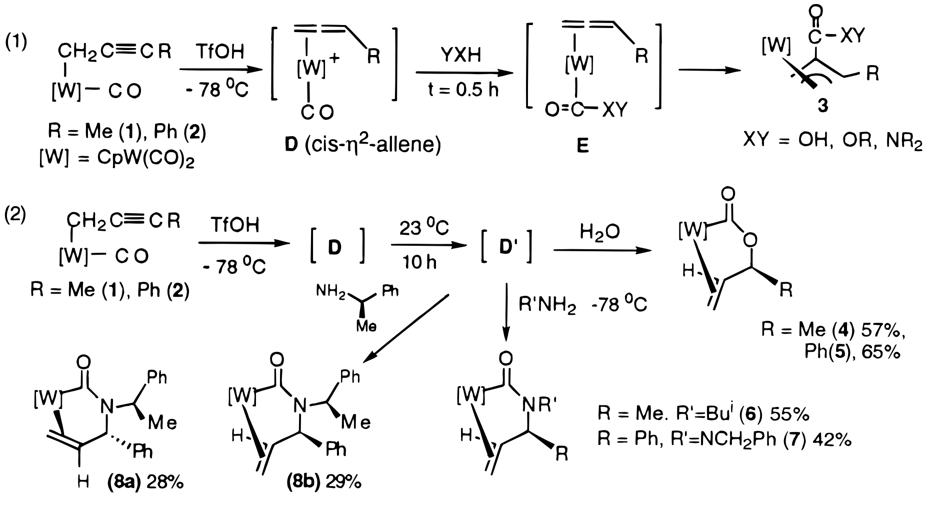
[9] Crystal data for **5**: monoclinic space group, *P*21/n, $a = 6.4197(20)$ Å, $b = 11.2660(14)$ Å, $c = 20.658(3)$ Å, $\beta = 95.27(3)°$, $V = 1487.7(5)$ Å^3, $Z = 4$. Of the 2621 unique reflections, 2181 were considered observed having $I > 2\sigma(I)$. Final $R = 0.020$, $R_w = 0.020$.

[10] Crystal data for **8b**: monoclinic space group, $P2_12_12_1$, $a = 12.1514(2)$ Å, $b = 13.2603(2)$ Å, $c = 13.5770(3)$ Å, $V = 2187.68(7)$ Å^3, $Z = 4$. Of the 13 374 unique reflections, 5021 were considered observed having $I > 2\sigma(I)$. Final R = 0.028, $R_w = 0.048$.

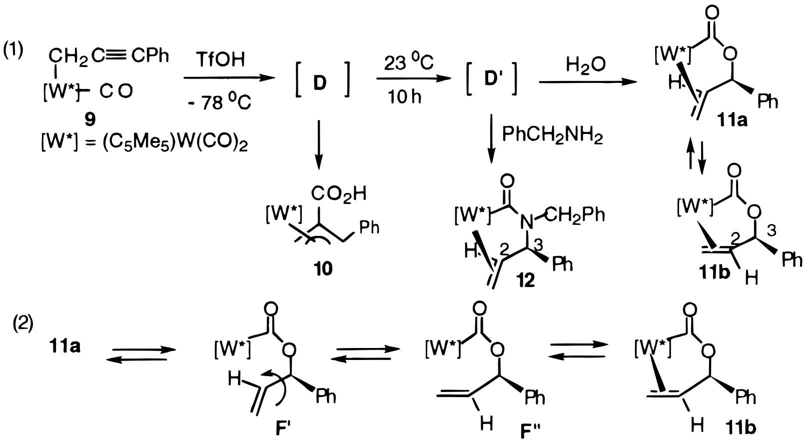
[11] Bell, P. B.; Wojcicki, A. *Inorg. Chem.* **1981**, *20*, 1585.

[12] Collman, J. P.; Hegedus, L. S.; Norton, J. R.; Finke, R. G. *Principles and Application of Organotransition Metal Chemistry;* University Science Books: Mill Valley, CA, 1987; Chapter 3, p 165.

Scheme 2



Scheme 3

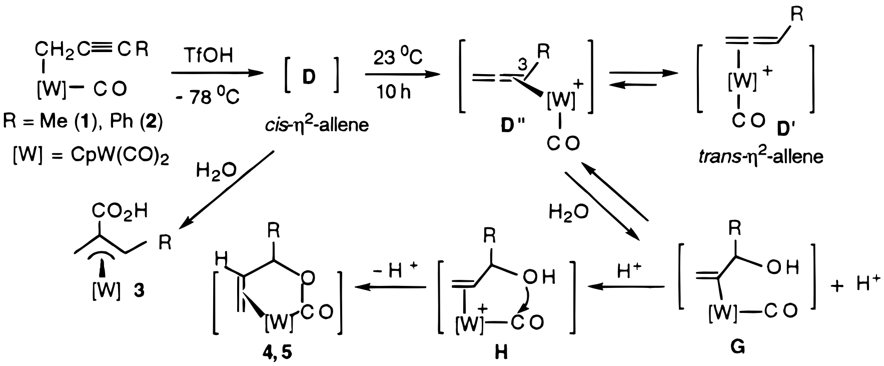


to have the (2R*, 3R*) configuration as inferred from the coupling constant $J_{23} = 3.4$ Hz. Attempts to obtain the NMR spectral data of the solid forms precipitated from the solutions **D** and **D′** were still unsuccessful due to their poor solubility in common solvents. We are aware that solid samples **D** and **D′** have different chemical properties compared to the solution species in mother CH_2Cl_2. For instance, treatment of the two solid samples with water gave compounds **10** and **11a** in 38% and 12% yields, respectively; the yield was very low, particularly for **D′**. It is likely that the species in these two phases are not the same.

Figure 3 shows variable-temperature ^{1}H NMR spectra for the two diastereomers **11a** and **11b** in $CDCl_3$. The major diastereomer **11a** is assigned to have the (2R*, 3R*) configuration based on the proton coupling constant $J_{23} = 2.9$ Hz and the chemical shift of C^2H (δ 4.12 ppm), which are close to those ($J_{23} = 3.0$ Hz and C^2H δ 4.00 ppm) of compound **5**. The minor isomer **11b** is assigned to have the (2R*, 3S*) configuration, and its proton parameters ($J_{23} = 0$. Hz and C^2H δ 3.12 ppm) are quite distinct from compounds **11a** and **5**. As the temperatures were raised from −10 °C, the resonances become broad in the 40−50 °C range. Recooling the temperatures to −10 °C regenerates the well-defined spectra of the two species. Attempts to raise the temperatures above 60 °C led to rapid decomposition of the compound. A proton spin transfer experiment also supported the exchange process. Irradiation of the C^2H proton signal (δ 3.12 ppm) of **11b** showed a complete disappearance of the C^2H proton signal (δ 4.12 ppm) of **11a**. Scheme 3 (eq 2) shows the mechanism for mutual exchange of these two species. We propose the mechanism in Scheme 3, which involves dissociation of the C=C double bond of **11a** from the tungsten center to form the 16e species **F′**. Subsequent rotation of the C^2-C^3 single bond of **F′** gives another conformer **F″**, and finally compound **11b**.

One unanswered issue is the alternation of chemoselectivity for the fresh and aged solution of tungsten−η^1-propargyl complexes after acidification with triflic acid. We did not have experimental data to elucidate the formation mechanism of the new carbonylation products **4**−**7**, **8a**,**b**, and **11a**,**b** because NMR characterization of the two solution species was unsuccessful. Neverthelss, a speculative mechanism is helpful to understand the nature of whole reaction sequence. It is reported earlier that protonation of $CpFe(CO)_2(\eta^1\text{-}CH_2C{\equiv}CPh)$ with HPF_6[7a] in acetic anhydride gave cis-η^2-allene as the kinetic product, which was then isomerized to the more stable trans-η^2-allene species such as **D′** in Scheme 4 as the temperatures was raised. In Scheme 4, the fresh acidification solution of compounds **1** and **2** consisted exclusively of cis-η^2-allene species **D**, which reacted with water to give syn-π-allyl complexes **3**. In a prolonged reaction period, species **D** undergoes isomerization to give trans-η^2-allene **D′** species via intermediate **D″**.[13] The C^2-C^3 bond of **D″** can be

Scheme 4



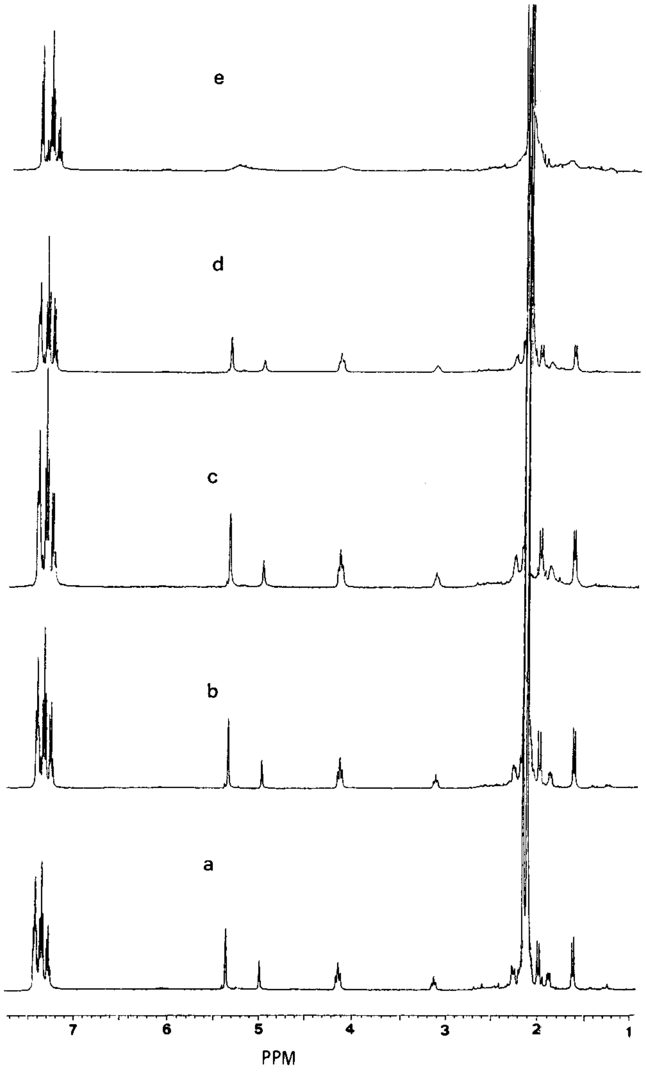


Figure 3. NMR spectra of compounds **11a** and **11b** in $CDCl_3$ at various temperatures: (a) −10 °C, (b) 10 °C, (c) 25 °C, (d) 35 °C, (e) 45 °C.

attacked by water because it is coordinated to a tungsten fragment. We envisage that formation of new carbonylation products such as **4** and **5** likely arises from addition of water at the C^3 carbon of **D**″ to yield the species **G**, and this process is proposed to be reversible. Further cleavage of the W-vinyl bond of **G** yields species **H**, which undergoes subsequent intramolecular alkoxycarbonylation to give the observed products **4** and **5**.

In summary, we demonstrate two types of carbonylation reactions in the acidification solution of tungsten−propargyl compounds **1** and **2** via treatment with water and amines. The alternation of chemoselectivities is probably due to the presence of different tungsten−η^2-allene cations, which respectively yield syn-π-allyl and η^1,η^2-carboxylated olefin species such as **4**−**7**, **8a**, **b**, and **11a**,**b**. We have characterized new carbonylation products **4**−**7**, **8a**,**b**, and **11a**,**b** with appropriate physical methods including X-ray diffraction studies of the representative compounds **5** and **8b**. Variable-temperature ^{1}H NMR spectra show that the two diastereomers **11a** and **11b** can undergo mutual exchange at elevated temperatures; the mechanism of exchange is proposed to precede via dissociation of the coordinated olefin to form a 16e species.

Experimental Section

Unless otherwise noted, all reactions were carried out under nitrogen atmosphere in oven-dried glassware using standard syringe, cannula, and septa apparatus. Benzene, diethyl ether, tetrahydrofuran, and hexane were dried with sodium benzophenone and distilled before use. Dichloromethane was dried over CaH_2 and distilled before use. $W(CO)_6$, dicyclopentadiene, propargyl alcohol, and sodium were obtained commercially and used without purification. Tungsten propargyl compounds **1**, **2**, and **9** were prepared according to the procedures in the literature.[7a,11]

Synthesis of Compound 4. To a CH_2Cl_2 solution (15 mL) of compound **1** (200 mg, 0.52 mmol) was added CF_3SO_3H (160 mg, 1.05 mmol) at − 78 °C, and the mixture was stirred for 1 h before the reaction mixture was slowly warmed to room temperature over 12 h. The solution was recooled to − 78 °C and treated with saturated $NaHCO_3$ (5.0 mL) solution. The mixture was warmed to 23 °C and the organic layer was extracted with diethyl ether twice (15 mL). The combined organic extract was dried in vacuo and chromatographed on a silica column to yield compound **4** as a yellow solid (120 mg, 0.29 mmol, 57%). IR (CH_2Cl_2, cm^{-1}): ν(W−CO) 2003(s); 1930(s); 1639(br s). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 5.45 (5H, s, Cp), 4.54 (1H, m, C^3H), 3.82 (1H, m, C^2H), 2.32 (1H, d, $J = 6.3$ Hz, C^1H), 2.18 (1H, d, $J = 7.2$ Hz, C^1H), 1.46 (3H, d, $J = 6.1$ Hz, Me). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 220.4, 214.0, 209.1, 90.9, 73.4, 73.2, 22.5, 16.0. MS (EI; 75 eV/m): 404 (M^+). Anal. Calcd for $C_{12}H_{12}WO_4$: C, 35.67; H, 2.99. Found: C, 35.34; H, 3.13.

Sythesis of Compound 5. To a CH_2Cl_2 (15 mL) solution of compound **2** (200 mg, 0.45 mmol) at − 78 °C was added CF_3SO_3H (134 mg, 0.89 mmol), and the mixture was stirred for 1 h before it was slowly warmed to 23 °C over 12 h. The reaction mixture was recooled to − 78 °C and treated with $NaHCO_3$ (3.0 mL), and the mixture was warmed to 23 °C over 6 h. The organic layer was extracted with diethyl ether (15 mL) and evaporated under reduced pressure. The crude product was chromatographed on a silica column to yield compound **5** as a

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(13) Ben-Shoshan, R.; Petit, R. *J. Am. Chem. Soc.* **1967**, *89*, 2231.

yellow solid (130 mg, 0.27 mmol, 65%). IR (CH_2Cl_2, cm^{-1}): ν(W−CO) 2012(s), 1946(s), 1648. ^1H NMR ($CDCl_3$, 400 MHz): δ 7.43−7.23 (5H, m, Ph), 5.51 (5H, s, Cp), 5.45 (1H, d, J = 2.8 Hz, C^3H), 4.00 (1H, m, C^2H), 2.32 (1H, d, J = 7.8 Hz, C^1HH'), 2.30 (1H, d, J = 7.8 Hz, C^1HH'). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 219.9, 214.0, 207.8, 141.7, 128.4, 127.8, 126.2, 91.1, 79.0, 72.2, 15.9; MS (EI; 75 eV/m): 466 (M^+). Anal. Calcd for $C_{17}H_{14}WO_4$: C, 43.80; H, 3.03. Found: C, 43.70; H, 3.02

Synthesis of Compound 6. To a CH_2Cl_2 solution (15 mL) of compound **1** (200 mg, 0.52 mmol) at − 78 °C was added CF_3SO_3H (160 mg, 1.05 mmol), and the mixture was stirred for 1 h and then slowly warmed to 23 °C over 12 h. The reaction mixture was recooled to − 78 °C and treated with isobutylamine (73.6 mg, 1 mmol). The solution was warmed to 23 °C with rapid stirring for 6 h. The organic material was extracted with diethyl ether (15 mL) and evaporated to dryness under reduced pressure. The crude product was then purified on a silica column to yield compound **6** as a yellow solid (130 mg, 0.28 mmol, 55%). IR (CH_2Cl_2, cm^{-1}): ν(CO) 1992(s), 1925(s), 1620(br s). ^1H NMR ($CDCl_3$, 400 MHz): δ 5.38 (5H, s, Cp), 3.76 (1H, m, C^3H), 3.66 (1H, m, C^2H), 3.46 (1H, m), 2.37 (1H, m), 2.32 (1H, d, J = 8.0 Hz, CHH'), 2.02 (1H, d, J = 7.1 Hz, CHH'), 1.70 (1H, m, $CHMe_2$), 1.37 (3H, d, J = 6.3 Hz, Me), 0.80 (3H, d, J = 3.2 Hz, Me), 0.74 (3H, d, J = 3.2 Hz, Me). ^{13}C NMR ($CDCl_3$, 300 MHz: δ 225.2, 217.1, 205.7, 91.5, 68.7, 58.2, 48.8, 26.5, 24.2, 19.9, 18.1. MS (EI, 75 eV/m): 458(M^+). Anal. Calcd for $C_{16}H_{21}WO_3N$: C, 41.85; H, 4.61; N, 3.05. Found: C, 41.88; H, 4.82; N, 3.01.

Synthesis of Compound 7. To a CH_2Cl_2 solution (15 mL) of compound **2** (200 mg, 0.45 mmol) at − 78 °C was added CF_3SO_3H (134 mg, 0.89 mmol), and the mixture was stirred for 1 h before it was slowly warmed to 23 °C over 12 h. The reaction mixture was recooled to − 78 °C and treated with benzylamine (982 mg, 9.16 mmol). The mixture was kept stirring for 8 h. The solution was then quenched with water and washed with saturated NH_4Cl solution. The organic material was extracted with diethyl ether (15 mL). The combined organic extract was dried and evaporated under reduced pressure.The crude product was then purified using preparative TLC (diethyl ether/hexane, 1:1) to yield compound **7** as a yellow solid (100 mg, 0.18 mmol, 42%), IR (CH_2Cl_2, cm^{-1}): 1992(s), 1925(s), 1638(br). ^1H NMR ($CDCl_3$, 300 MHz): δ 7.32−7.26 (2H, m, Ph), 7.12−7.08 (6H, m, Ph), 6.78 (2H, m, Ph), 5.47 (5H, s, Cp), 5.23 (1H, d, J = 13.0 Hz, $NCHH$,), 4.39 (1H, d, J = 3.2 Hz, C^3H), 3.71 (1H, m, C^2H), 3.10 (1H, d, J = 13.0 Hz, $NCHH'$), 2.45 (1H, d, J = 6.9 Hz, C^1HH'), 2.27 (1H, d, J = 6.6 Hz, C^1HH'). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 223.4, 216.0, 207.0, 143.2, 132.6, 128.7, 128.4, 128.2, 127.2, 127.8, 127.7, 127.6, 126.6, 91.4, 68.1, 64.8, 45.2, 17.7. MS (EI, 75 eV/m): 550 (M^+). Anal. Calcd for $C_{24}H_{21}WNO_3$: C, 51.91; H, 3.81; N, 2.52. Found: C, 52.49; H, 3.97; N, 2.50.

Synthesis of Compounds 8a and 8b. To a CH_2Cl_2 solution (15.0 mL) of compound **2** (200 mg, 0.45 mmol) at − 78 °C was added CF_3SO_3H (134 mg, 0.89 mmol), and the mixture was stirred for 1 h before it was warmed to room temperature over 12 h. The reaction mixture was recooled to −78 °C and treated with (*R*-(+)-α-methylbenzylamine (752 mg, 6.2 mmol). The solution was warmed to 23 °C over 24 h before treatment with saturated NH_4Cl solution (3.0 mL). The organic layer was separated, concentrated, and purified on a silica column to yield compounds **8a** (71 mg, 0.12 mmol, 27%) and **8b** (71 mg, 0.25 mmol, 28%), respectively.

Spectral Data for 8a: IR (CH_2Cl_2, cm^{-1}): 1995(s), 1928(s), 1641(br). ^1H NMR ($CDCl_3$, 400 MHz): δ 7.14−7.04 (8H, m, Ph), 6.81 (2H, d, J = 5.8 Hz, Ph), 5.45 (5H, s, Cp), 5.12 (1H, m, NCH), 4.37 (1H, d, J = 3.0 Hz, C^3H), 3.73 (1H, m, C^2H), 2.55 (1H, d, J = 8.0 Hz, C^1HH'), 2.29 (1H, d, J = 8.4 Hz, C^1HH), 1.05 (3H, d, J = 7.2 Hz, Me). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 224.1, 216.7, 206.0 144.1, 140.6, 128.6, 127.8, 127.7, 126.2, 91.6 (Cp), 68.1, 65.6, 51.0, 17.9, 17.3. MS (EI^+, 75 eV/m): 569 (M^+). $[\alpha]_D^{25}$ = −6.3 (c = 1.0, CH_2Cl_2). Anal. Calcd for $C_{25}H_{23}WNO_3$: C, 52.74; H, 4.07; N, 2.46. Found: C, 52.63; H, 4.28; N, 2.53.

Spectral Data for 8b: IR (CH_2Cl_2, cm^{-1}): 1995(s), 1926(s), 1642(br). ^1H NMR ($CDCl_3$, 400 MHz): δ 7.44−7.27 (m, 9H, Ph), 7.12 (1H, d, J = 2.8 Hz, Ph), 5.66 (5H, s, Cp), 5.09 (1H, m, NCH), 5.02 (1H, d, J = 2.9 Hz, C^3H), 3.87 (1H, m, C^2H), 2.71 (1H, d, J = 10.0 Hz), 2.49 (1H, d, J = 8.4 Hz, CHH'), 1.64 (3H, d, J = 7.2 Hz, CHH'). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 224.0, 216.3, 206.5, 143.6, 143.2, 128.7, 127.6, 127.5, 127.4, 91.7, 67.5, 66.4, 51.4, 17.3, 16.6. MS (EI^+, 75 eV/m): 569 (M^+). $[\alpha]_D^{25}$ = 98.6 (c = 1.0, CH_2Cl_2). Anal. Calcd for $C_{25}H_{23}WNO_3$: C, 52.74; H, 4.07; N, 2.46. Found: C, 52.55; H, 4.18; N, 2.51.

Synthesis of Compounds 11a and 11b. To a CH_2Cl_2 solution (15.0 mL) of compound **9** (200 mg, 0.38 mmol) at − 78 °C was added CF_3SO_3H (115.8 mg, 0.77 mmol), and the mixture was stirred for 1 h before it was warmed to room temperature over 12 h. The reaction mixture was recooled to −78 °C and treated with saturated $NaHCO_3$ solution. This cold solution was warmed to 23 °C over 24 h with rapid stirring. The organic layer was separated, concentrated, and purified on a silica column to yield compounds **11a** and **11b** as yellow solids (116 mg, 0.21 mmol, 56%, **11a**/**11b** = 3:1). IR (CH_2Cl_2, cm^{-1}): 1995(s), 1928(s), 1637 (br). ^1H NMR ($CDCl_3$, 400 MHz): for **11a**, δ 7.45−7.30 (10H, m), 5.36 (1H, d, J = 2.9 Hz, C^3H), 4.12 (1H, m, C^2H), 2.10 (15H, Me), 2.00 (1H, d, J = 6.0 Hz, C^1HH'), 1.60 (1H, 1H, d, J = 6.0 Hz, C^1HH'), for **11b**, δ 7.45−7.30 (10H, m), 4.95 (1H, s, C^3H), 3.12 (1H, m, C^2H), 2.14 (15H, Me), the two C^1H_2 proton resonances were masked by those of pentamethyl groups. ^{13}C NMR (CDCl3, 100 MHz): **11a**, 227.2, 218.0, 211.5, 142.0, 128.2, 127.6, 126.2, 103.1, 78.4, 75.7, 25.5, 10.6; **11b**, 222.0, 211.5, 208.8, 142,5, 128.5, 127,4, 125.7, 101.5, 79.8, 50.7, 33.4, 10.6. Anal. Calcd for $C_{22}H_{24}WO_4$: C, 49.27; H, 4.51. Found: C, 49.68; H, 4.56.

Synthesis of Compound 12. To a CH_2Cl_2 solution (15.0 mL) of compound **9** (200 mg, 0.38 mmol) at − 78 °C was added CF_3SO_3H (116 mg, 0.77 mmol), and the mixture was stirred for 1 h before it was warmed to room temperature over 12 h. The reaction mixture was recooled to − 78 °C and treated with benzylamine (2.0 mL). This cold solution was stirred and warmed to 23 °C over 24 h. The organic layer was separated, concentrated, and purified on a silica column to yield compound **12** as yellow solid (118 mg, 0.18 mmol, 49%). IR (CH_2Cl_2, cm^{-1}): 1993(s), 1927(s), 1608 (br). ^1H NMR ($CDCl_3$, 400 MHz): δ 7.35−7.10 (8H, m), 6.75−6.80 (2H, br s, Ph), 5.28 (1H, d, J = 13.2 Hz, $NCHH'$), 4.20 (1H, d, J = 3.4 Hz C^1HH'), 3.88 (1H, m, C^2H), 3.13 (1H, d, J = 13.2 Hz, $NCHH'$), 2.10 (1H, s, Me), 1.56 (1H, d, J = 5.2 Hz, C^1HH'). ^{13}C NMR ($CDCl_3$, 100 Hz): 231.0, 220.3, 210.5, 143.6, 138.1, 128.8, 128.3, 127.8, 127.4, 126.4, 102.8, 71.7, 64.8, 45.0, 28.1, 10.5. MS (EI, 75 eV/m): 625 (M^+). Anal. Calcd for $C_{29}H_{31}WNO_3$: C, 55.69; H, 4.02. Found: C, 55.76; H, 4.14.

X-ray Diffraction Studies of 5 and 8b. Single crystals of **5** and **8b** were sealed in glass capillaries under an inert atmosphere. Data for **5** and **8b** were collected on a Nonius CAD 4 using graphite-monochromated Mo Kα radiation. The structures of **5** and **8b** were solved by the heavy-atom method, respectively; all data reduction and structural refinements were performed with the NRCCSDP package. Crystal data, details of data collection, and structural analysis of these three compounds are presented in the Supporting Information. For all structures, all nonhydrogen atoms were refined with anisotropic parameters, and all hydrogen atoms included in the structure factors were placed in idealized positions.

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Supporting Information Available: Tables of crystal data, atomic coordinates, and bond distances and angles of **5** and **8b**. This material is available free of charge via the Internet at http://pubs.acs.org.

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