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Oxidative Carbonylation of Alkynyltungsten Compounds via Protonation with Triflic Acid

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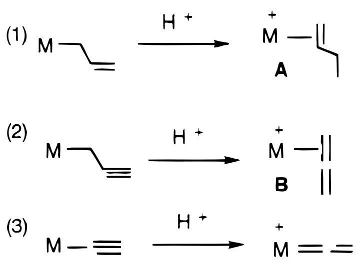
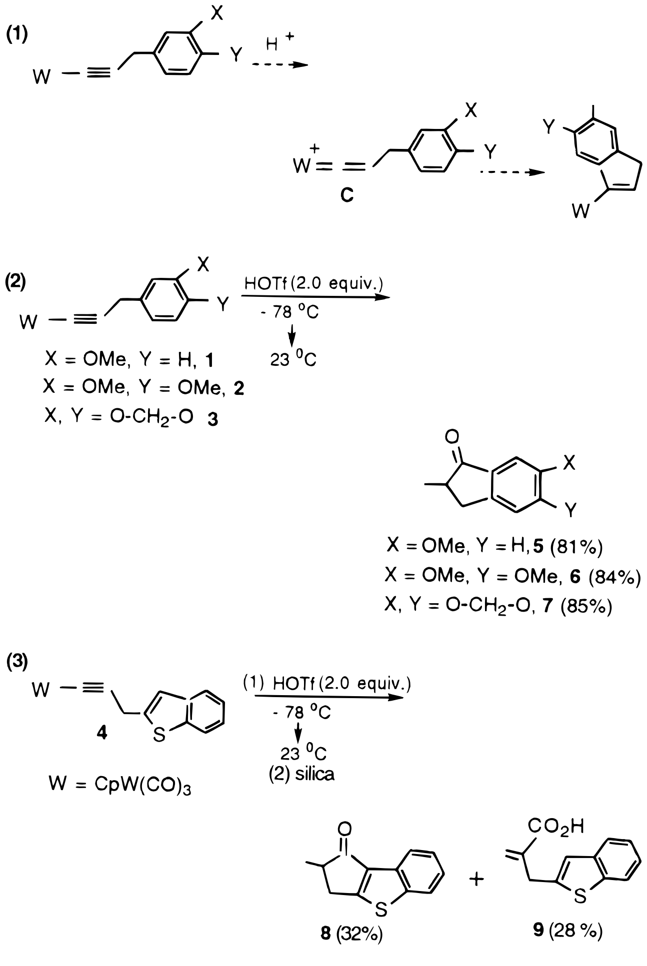
Summary: Treatment of several alkynyltungsten(II) compounds with 4.0 mol equiv of CF_3SO_3H led to oxidative carbonylation to yield acyltungsten(IV) compounds; this reaction can be applied to syntheses of indanones and unsaturated carbonyl compounds.

The actions of organic molecules with superacids such as triflic acid, CF_3SO_3H, often give rise to organic reactions of unusual types.[1−3] CF_3SO_3H can easily ionize organic olefins, alkynes, alcohols, epoxides, acetals, aryls, acyl halides and organic carbonyls to form reactive carbocations, further leading to formation or scission of carbon−carbon bonds.[1−4] This principle is widely applicable to cycloaddition reaction, intramolecular cyclization, electrophilic substitution of olefins and aromatic compounds, addition of organic carbonyls to enol ethers, Beckman rearrangement, and rearrangement of phenols.[1−4] Although CF_3SO_3H is also often used in organometallic reactions, its scope is limited to two major uses: generations of (1) metal hydrides[5] and (2) metal-bound carbocations.[6] Scheme 1 (parts 1−3) lists three important representatives for generation of metal carbocations such as η^2-alkene (**A**), η^2-allene (**B**), and η^1-vinylidene species (**C**) via protonation of their corresponding allyl, propargyl, and alkynyl complexes.[6] The significance of these three carbocations is well-known because of their roles in many metal-mediated or -catalyzed organic syntheses.[7−9] Although numerous studies have focused on the reactivity of these metal carbocations, there has been no report that a Brønsted acid can oxidize a metal center via protonation of these unsaturated metal hydrocarbonyl complexes. In this communication, we report the new discovery that CF_3SO_3H can induce oxidative carbonylation of tungsten−

Scheme 1



Scheme 2



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(7) For organic syntheses via metal−η^2-alkene cations, see the following 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.

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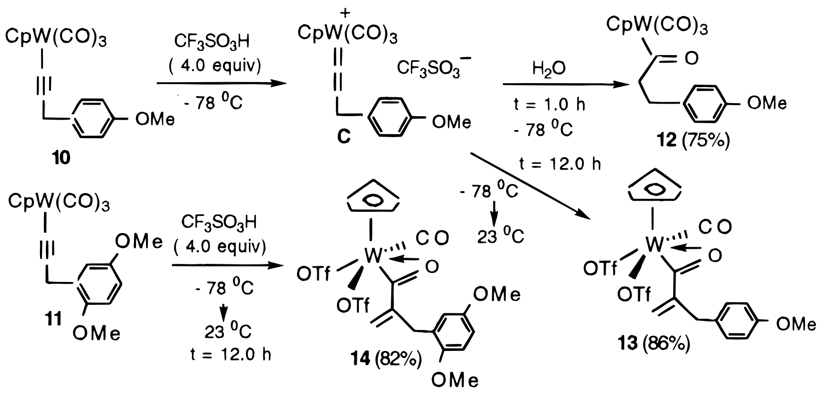
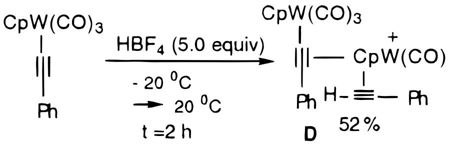
Scheme 3



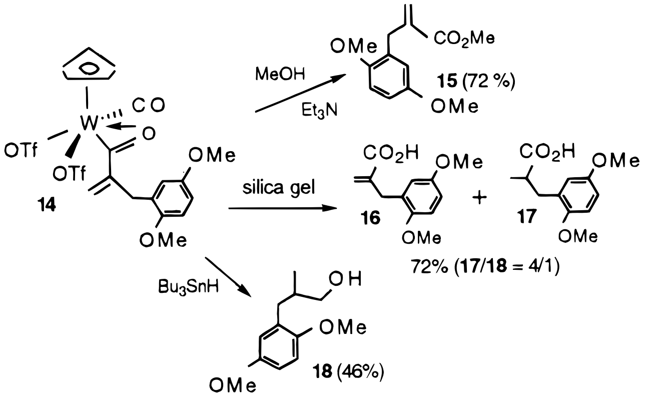
alkynyl compounds over *a prolonged reaction period*; application of this reaction to organic syntheses is also reported.

As a continuation of our interest in alkynyltungsten compounds,[10] we have studied the protonation of alkynyltungsten complexes **1**−**4** tethered with an electron-rich phenyl or thiophene group. We envision that the resulting metal−η^1-vinylidene cations (**C**) may form a vinyltungsten species via arylation at its W=C carbon[9a] as shown in Scheme 2 (part 1). In a typical reaction, compounds **1**−**3** were treated with CF_3SO_3H (2.0 equiv) in cold CH_2Cl_2 (−78 °C) and stirred for 2 h before the temperature was slowly brought to 23 °C over a period of 12 h. For compound **1**, monitoring its CH_2Cl_2 solution by proton NMR spectra reveals that indanone **5** is the only detectable species together with a single cyclopentadienyl signal at δ 6.10 ppm due to an unidentified tungsten complex. Workup of this solution delivered **5**−**7** in good yields (81−86%). Similarly, the reaction of alkynyltungsten complex **4** with CF_3SO_3H (2.0 equiv) under the same experimental conditions gave cyclopentanone **8** and several unknown tungsten species. Filtration of this CH_2Cl_2 solution through a short silica bed at 23 °C afforded **8** and **9** in 32% and 28% yields, respectively. In this transformation, we are aware that 2.0 mol equiv of CF_3SO_3H is insufficient to furnish the hydrogen content of indanones **5-8**; additional hydrogen sources may be available from the small water content in CF_3SO_3H.

Formation of synthetically useful indanones **5**−**9** from **1**−**4** represents an unusual carbonylation reaction. It is difficult to deduce the formation mechanism of **5**−**9** without isolation of organometallic reaction intermediates. The alkynyl compounds **1**−**4** are not suitable for this study because the observed tungsten intermediates are kinetically unstable, easily forming indanones according to in situ NMR studies. We therefore prepared[11] alkynyltungsten compounds **10** and **11** in order to obtain kinetically stable intermediates with the use of a suitable amount of CF_3SO_3H; the best result is the use of 4.0 mol equiv of CF_3SO_3H. Notably, the protonation reaction of alkynyltungsten compounds was previously reported.[12] Treatment of CpW(CO)$_3$(η^1-phenylethynyl) with excess HBF_4 (5.0 equiv) in CH_2Cl_2 gave the binuclear species cation **D**[12] in 52% yield:



Scheme 4



CF_3SO_3H acidification of **10** and **11**, however, proceeded in a distinct reaction pathway outlined in Scheme 3. Treatment of compound **10** with CF_3SO_3H (4.0 equiv) in cold CH_2Cl_2 (−78 °C) led to its disappearance after a short reaction period (ca. 1.0 h). Subsequent treatment of this solution with water at −78 °C led to formation of **12** in 75% yield, indicating that the vinylidenetungsten cation **C** was first formed[9a] in the CF_3SO_3H acidification of **10**. As shown in Scheme 3, slow warming of this acidic solution to 23 °C (ca. 12 h) produced the stable acyltungsten(IV) complex **13** in 86% yield. If 2.0 equiv of CF_3SO_3H was used in the same reaction sequence, five unknown species were formed without

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(8) For organic syntheses via metal−η^2-allene cations, see the representative papers: (a) Bell, P. B.; Wojcicki, A. *Inorg. Chem.* **1981,** *20*, 1585. (b) Raghu, S.; Rosenblum, M. *J. Am. Chem. Soc.* **1973**, *95*, 3060. (c) Blosser, P. W.; Shimpff, D. G.; Gallucci, J. C.; Wojcicki, A. *Organometallics* **1993**, *12*, 1393. (d) Chen, C.-C.; Fan, J.-S.; Shieh, S.-J.; Lee, G.-H.; Peng, S.-M.; Wang, S.-L.; Liu, R.-S. *J. Am. Chem. Soc.* **1996**, *118*, 9279.

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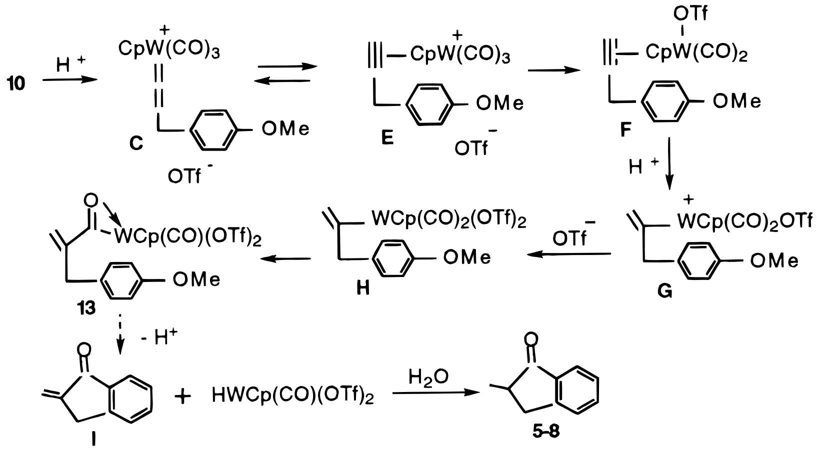
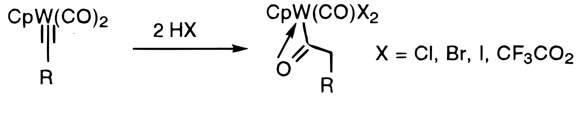
Scheme 5



formation of acyltungsten species **13**. Acidification of **11** with CF_3SO_3H (4.0 equiv) afforded the acyl compound **14** (82%) after a prolonged reaction period. Compounds **13** and **14** were present as oils and were thus not suitable for X-ray diffraction studies. It is difficult to deduce the structure on the basis of spectral data alone. Fortunately, compounds of this type have been previously prepared[13] from the reaction of HX (X = CF_3CO_2, Cl, Br, I) with carbynyltungsten compounds $Cp(CO)_2W{\equiv}R$:



A good match has been found to compare the IR and NMR spectral data of **13** and **14** to these of the known compounds. For compound **13**, the single W−CO group is characterized by the IR absorption band at 2060 cm^{-1} and also by the ^{13}C NMR signal at 197.9 ppm in CD_2Cl_2. The η^2-acyl group is indicated by both the IR band at 1580 cm^{-1} and the ^{13}C NMR signal at 263.2 ppm. The two coordinated CF_3SO_3 ligands are nonequivalent, as shown by their ^{13}C NMR signals in CD_2Cl_2 as two quartets at δ 119.0 ppm (J_{CF} = 315.6 Hz) and δ 118.5 ppm (J_{CF} = 315.4 Hz), respectively. The free vinyl group of **13** has the ^1H NMR signals at δ 6.37 and 6.35 ppm, respectively, and the corresponding carbons have the signals at 145.8 and 143.1 ppm, respectively.

The acyltungsten compounds **13** and **14** are useful for production of unsaturated acids and esters. Treatment of a CH_2Cl_2 solution of **14** with a mixture of MeOH and Et_3N afforded the unsaturated ester **15** in 72% yield (Scheme 4). Filtration of a CH_2Cl_2 solution of **14** through a silica bed afforded a mixture of acids **16** and **17** in a combined yield of 72% (**16**/**17** = 4/1). Reduction of this acyl species with Bu_3SnH (5.0 equiv) in CH_2Cl_2 delivered the alcohol **18** in 46% yield.

Scheme 5 shows a plausible mechanism to account for formation of **13** from alkynyltungsten species **10**. We propose that the initial vinylidene intermediate **C** undergoes a tungsten η^1-vinylidene$\rightleftharpoons\eta^2$-alkyne rearrangement[14] to yield species **E**. In the presence of free OTf^- anion, species **E** is envisaged to undergo ligand substitution to yield the neutral intermediate W(II) intermediate **F**. Further protonation at the η^2-alkyne ligand of **F** leads to oxidation, yielding the vinyltungsten(IV) cation **G**. This high-valent 16-electron species **G** is readily captured by an OTf anion to yield the 16-electron species **H**, which subsequently undergoes CO insertion to yield the η^2-acyl species **13**. If a highly nucleophilic phenyl or thione group is present, orthoarylation will occur to yield the unsaturated indanone **I**, the precursor for **5**−**8**, accompanied by release of a hydridotungsten(IV) species. Unsaturated indanone is further reduced with this hydridotungsten(IV) species to yield compounds **5**−**8**; in this case, 2 mol equiv of CF_3SO_3H suffices this intramolecular arylation reaction.

In summary, we report that alkynyltungsten compounds can be oxidized by CF_3SO_3H over a prolonged reaction period, leading to a rearrangement and carbonylation reaction. We elucidate the reaction mechanism with isolation and characterization of the two acyltungsten(IV) species **13** and **14**. This oxidation is useful for syntheses of different classes of indanones or unsaturated esters and acids; in most cases, the yields are reasonable. Further expansion of this reaction scope is under investigation.

Acknowledgment. We gratefully acknowledge financial support from the National Science Council for financial support of this work.

Supporting Information Available: Text giving additional information on synthetic procedures and spectral data for compounds **1**−**18** (11 pages). Ordering information is given on any current masthead page.

OM980093H

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