Ionic Hydrogenation of Alkynes by HOTf and $Cp(CO)_3WH$

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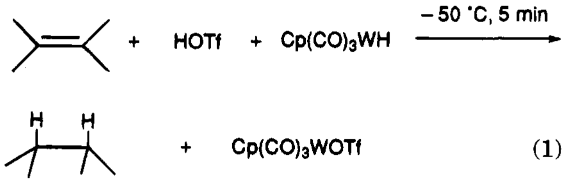
Alkynes can be hydrogenated at room temperature by an ionic hydrogenation method using triflic acid (CF_3SO_3H) as the proton donor and a transition metal hydride ($Cp(CO)_3WH$) as the hydride donor. Reaction of PhC≡CH with HOTf and $Cp(CO)_3WH$ gives ethylbenzene as the final product in high yield. Intermediates observed in this reaction are the vinyl triflate $CH_2{=}C(Ph)(OTf)$ and the geminal ditriflate $Ph(CH_3)C(OTf)_2$, which result from the addition of 1 or 2 equiv of HOTf to the C≡C triple bond of the alkyne. Hydrogenation of PhC≡CMe by HOTf and $Cp(CO)_3WH$ similarly produces propylbenzene as the ultimate product. Along with vinyl triflates, additional intermediates observed in this reaction were the cis and trans isomers of the *β*-methylstyrene complex $[Cp(CO)_3W(\eta^2\text{-}PhHC{=}CHCH_3)]^+[OTf]^-$. Hydrogenation of *n*-butylacetylene to *n*-hexane does occur upon reaction with $HOTf/Cp(CO)_3WH$, but is very slow. In the absence of metal hydrides, 2-methyl-1-buten-3-yne reacts with HOTf to give the vinyl triflate $CH_2{=}CMeC(OTf){=}CH_2$, but reaction with HOTf and $Cp(CO)_3WH$ gives $Me_2C{=}C(OTf)Me$. The key characteristics required for the metal hydride used in these hydrogenations are the ability to donate hydride in the presence of strong acid, and the absence of rapid decomposition of the hydride through reaction with the strong acid. $Cp(CO)_3WH$ meets these requirements, but $HSiEt_3$, while an effective hydride donor, is decomposed by HOTf on the time scale of these alkyne hydrogenation reactions.

Hydrogenations of C=C, C=O, and other functional groups have been accomplished by ionic hydrogenations, which involve addition of H^+ from an acid and H^- from a hydride source.[1] An inherent problem with the use of an acid and a hydride together is their potential to react with each other and produce H_2. The most commonly used acid/hydride pair was developed by Kursanov and co-workers over two decades ago and utilizes CF_3CO_2H as the acid and $HSiEt_3$ as the hydride donor.[1] This reagent pair is relatively stable under typical alkene hydrogenation conditions (several hours at 50 °C). We recently reported[2] that ionic hydrogenations of hindered olefins can be accomplished within a few minutes at a much lower temperature (−50 °C) using triflic acid (CF_3SO_3H, abbreviated as HOTf) and either transition metal hydrides or $HSiEt_3$ as the hydride donor (eq 1). Even though $HSiEt_3$ reacts with HOTf to give H_2 and Et_3SiOTf, the overall hydrogenation reaction is sufficiently fast that the consumption of $HSiEt_3$ by reaction with acid is not a significant problem in alkene hydrogenations. For hydrogenations that occur more slowly, however, the decomposition of $HSiEt_3$ induced by HOTf could become the predominant reaction. A requirement for a hydride source to be effective under these conditions would be stability toward acid on a longer time scale, while still maintaining the ability to function efficiently as a source of H^-. The transition metal hydride $Cp(CO)_3WH$ offers precisely these crucial advantages over $HSiEt_3$ in its ability to function as a hydride donor in the presence of a strong acid, and these characteristics are utilized in the first efficient application of ionic hydrogenation methods for alkyne hydrogenations.



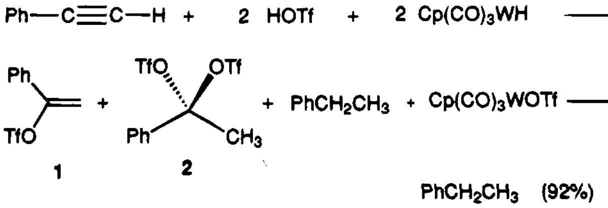
(1)

In contrast to the well-developed use of ionic hydrogenation methods for hydrogenation of alkenes, little is known about the potential use of such methods for hydrogenation of alkynes. A recent review noted the paucity of reports "on the success, or failure, of the attempted reduction of C≡C bonds by the ionic hydrogenation type of reaction".[3] Kursanov and co-workers reported that low yields were obtained from attempted ionic hydrogenation of aryl alkynes using $CF_3CO_2H/HSiEt_3$.[4] Hydrogenation of PhC≡CH using $H_3PO_4{\cdot}BF_3$ as the acid and *p*-diethylbenzene as the hydride donor was reported to provide only 30−35% yields of ethylbenzene.[4] In this paper we report that alkynes can be successfully hydrogenated in good yields using HOTf as the acid and $Cp(CO)_3WH$ as the hydride donor.

Results

A summary of the reaction conditions and product yields from the ionic hydrogenation of alkynes by HOTf and $Cp(CO)_3WH$ is provided in Table 1.

Addition of HOTf to a solution of PhC≡CH and $Cp(CO)_3WH$ (eq 2) results in an immediate color change to



(2)

[⊗] Abstract published in *Advance ACS Abstracts,* October 15, 1995.

[1] (a) Kursanov, D. N.; Parnes, Z. N.; Loim, N. M. *Synthesis* **1974**, 633−651. (b) Kursanov, D. N.; Parnes, Z. N.; Kalinkin, M. I.; Loim, N. M. *Ionic Hydrogenation and Related Reactions*; Harwood Academic Publishers: New York, 1985.

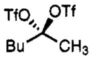
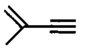
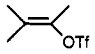
[2] Bullock, R. M.; Song, J.-S. *J. Am. Chem. Soc.* **1994**, *116*, 8602−8612.

[3] Pasto, D. J. In *Comprehensive Organic Synthesis*; Trost, B. M., Ed.; Pergamon Press: New York, 1991; Vol. 8; Chapter 3.3, p 487.

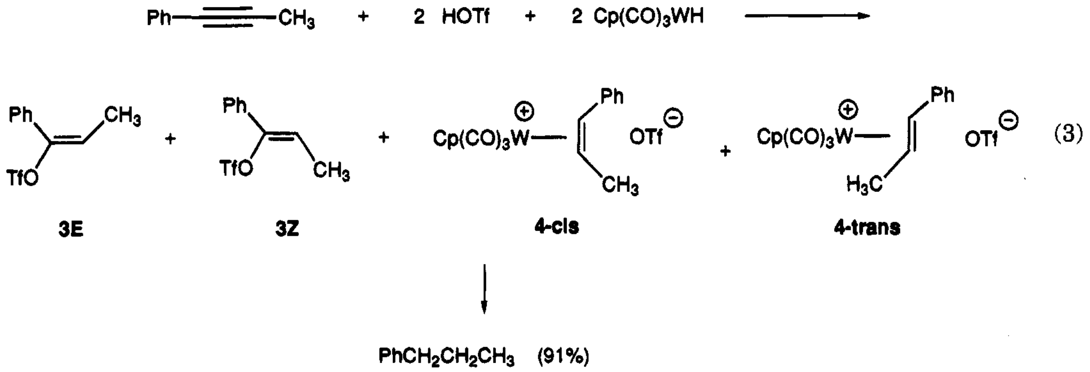
[4] See page 16 of ref 1b.

0022-3263/95/1960-7170$09.00/0

Table 1. Ionic Hydrogenations of Alkynes Using $HW(CO)_3Cp$ and HOTf

alkyne	alkyne conc (M)	HOTf (equiv)	$Cp(CO)_3WH$ (equiv)	product	% yield	conditions
$PhC\equiv CH$	0.079	2.7	2.0	$PhCH_2CH_3$	92	22 °C, 28 h
$PhC\equiv CSiMe_3$	0.044	4.4	2.4	$PhCH_2CH_3$	97	22 °C, 2 d
$PhC\equiv CMe$	0.066	2.9	3.5	$Ph(CH_2)_2CH_3$	91	22 °C, 5 d
$n\text{-}BuC\equiv CH$	0.086	5.1	2.6	$CH_3(CH_2)_4CH_3$	57	22 °C, 11 d
$n\text{-}BuC\equiv CH$	0.080	3.4	–		95	22 °C, 2 h
	0.33	2.0	1.4		86	22 °C, 3 d

Scheme 1



wine-red due to the formation of the tungsten triflate complex $Cp(CO)_3WOTf$. An NMR spectrum taken after 5 min showed the vinyl triflate **1** (25%), the geminal ditriflate **2** (5%), and ethylbenzene (64%), which results from double ionic hydrogenation of the $C\equiv C$ triple bond. After 30 min, the yield of **1** dropped to 8% and the yield of ethylbenzene increased to 82%. Conversion of **1** to ethylbenzene was faster than that of **2**; the yield of ethylbenzene slowly rose to 92% (t = 28 h) as **2** was consumed. The geminal ditriflate **2** was independently prepared from reaction of $PhC\equiv CH$ with 2 equiv of HOTf, but attempts to isolate it were not successful.

No reaction was observed between **1** and $Cp(CO)_3WH$ in the absence of HOTf, indicating that direct hydride displacement of triflate does not occur, but addition of HOTf to a solution of **1** and $Cp(CO)_3WH$ led to ethylbenzene. Use of an excess of $PhC\equiv CH$ (1.3 equiv) over the HOTf concentration did not lead to the observation of styrene, even with $Cp(CO)_3WH$ being present in excess. The vinyl triflate **1** was formed, along with unreacted $PhC\equiv CH$; no styrene or ethylbenzene was observed. These experiments demonstrate that HOTf functions not only as a source of protons (as required by the stoichiometry) but also assists in the reversion of the vinyl triflate to the vinyl cation, which can then abstract hydride from $Cp(CO)_3WH$.

A comparison was made of the utility of $Cp(CO)_3WH$ vs $HSiEt_3$ as hydride donors in the hydrogenation of $PhC\equiv CH$. Addition of HOTf to a solution of $PhC\equiv CH$ and $HSiEt_3$ resulted in bubbles of H_2 being formed from reaction of $HSiEt_3$ with HOTf. An NMR spectrum showed a low yield (16%) of ethylbenzene; the major product was **1** (76%). The presence of H_2 (δ 4.61) and Et_3SiOTf were also verified by NMR.

In the course of carrying out ^1H NMR experiments using $PhC\equiv CH$, we found that the integration of the acetylenic proton was frequently low compared to the five aromatic protons. We suspected that this might be due to a long T_1 for this proton. A T_1 measurement carried out on $PhC\equiv CH$ in rigorously degassed CD_2Cl_2 solution at 26 °C revealed that the T_1 for $PhC\equiv C\mathit{H}$ was indeed unusually long, 289 s (4.8 min!). The nearest proton to the acetylenic one is five bonds away, making intramolecular dipole–dipole relaxation inefficient. Levy and coworkers measured the ^{13}C NMR T_1 values of $PhC\equiv CH$ and related compounds;[5] the T_1 for $Ph\mathit{C}\equiv CH$ is also long (132 s measured at 25 MHz).

Addition of HOTf to a solution of $PhC\equiv CSiMe_3$ resulted in cleavage of the C–Si bond and formation of Me_3SiOTf and $PhC\equiv CH$, which was converted as above to the vinyl triflate **1** and the geminal ditriflate **2**. In the presence of $Cp(CO)_3WH$, addition of HOTf to a solution of $PhC\equiv CSiMe_3$ led to the formation of the hydrogenation product ethylbenzene (97% yield after 2 days). Bis(trimethylsilyl)acetylene reacts with HOTf to give $HC\equiv CH$ and 2 equiv of Me_3SiOTf; no hydrogenation of the resultant $HC\equiv CH$ was observed when $Me_3SiC\equiv CSiMe_3$ was reacted with HOTf and $Cp(CO)_3WH$. Protiodesilylation of Si–C bonds of trimethylsilyl-substituted alkynes is well-known, and the kinetics of protiodemetalation of a series of $Me_3SiC\equiv CMR_3$ (M = Si, Ge, Sn) was recently reported.[6]

Addition of HOTf to a solution of $PhC\equiv CMe$ and $Cp(CO)_3WH$ leads to the vinyl triflates **3*E*** and **3*Z*** (eq 3, Scheme 1). Organometallic intermediates were also observed in the ionic hydrogenation of $PhC\equiv CMe$ by $HOTf/Cp(CO)_3WH$: the cis and trans isomers of the β-methylstyrene complex $[Cp(CO)_3W(\eta^2\text{-}PhHC{=}CHCH_3)]^+[OTf]^-$ (**4**) were observed by NMR. Figure 1 shows the time-dependent concentrations resulting from addition of HOTf to a solution of $PhC\equiv CMe$ and $Cp(CO)_3WH$ at 22 °C. The intermediate tungsten complex **4** built up to a maximum yield of 40% in this experiment and then decreased in concentration as the propylbenzene formed. The ^1H NMR resonances of the coordinated β-methylstyrene vinyl protons appear 0.7–1.5 ppm upfield of the

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(5) Levy, G. C.; Cargioli, J. D.; Anet, F. A. L. *J. Am. Chem. Soc.* **1973**, *95*, 1527–1535.

(6) Dallaire, C.; Brook, M. A. *Organometallics* **1993**, *12*, 2332–2338.

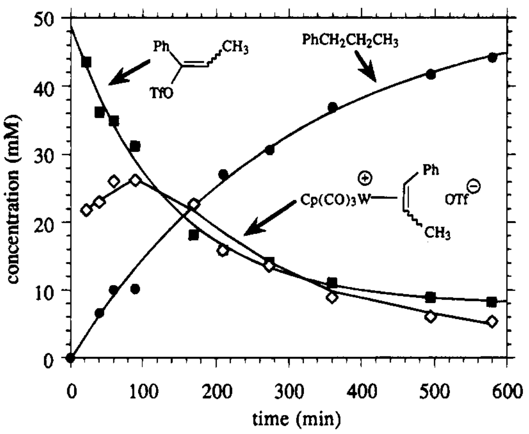
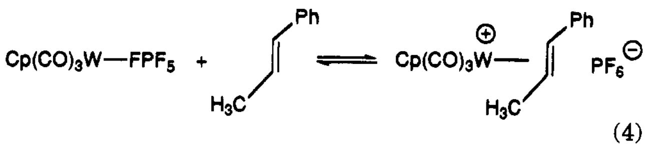


Figure 1. Time dependence of vinyl triflates (**3*E***+**3*Z***; squares), β-methylstyrene complexes (**4-*cis*** + **4-*trans***; open diamonds), and propylbenzene (circles) from reaction of PhC≡CMe (66 mM) and $Cp(CO)_3WH$ (3.5 equiv) and HOTf (2.9 equiv) in CD_2Cl_2 at 22 °C.

corresponding resonances for free β-methylstyrene. Figure 1 shows only the first ~70% of this hydrogenation; the final yield of propylbenzene was 91%. The **4-*cis***/**4-*trans*** ratio decreased from 2:1 at $t = 22$ min to 0.3:1 at $t = 6$ h; the figure shows the sum of these isomers. Similarly the **3*E***/**3*Z*** ratio changed as the reaction proceeded, from 3.5:1 at $t = 22$ min to 2.4:1 at $t = 6$ h; the figure plots the sum of the isomers. The β-methylstyrene complexes **4-*cis*** and **4-*trans*** are kinetically stabilized intermediates; dissociation of β-methylstyrene irreversibly forms the tungsten triflate complex $Cp(CO)_3WOTf$. Under these conditions free β-methylstyrene is rapidly hydrogenated to propylbenzene.[2] When hydride abstraction from $Cp(CO)_3WH$ by Ph_3COTf[7] was carried out in the presence of *trans*-β-methylstyrene, $Cp(CO)_3WOTf$ was the only observable organometallic product; no **4-*trans*** was observed. While triflate is too strongly bound to tungsten to be displaced by β-methylstyrene, the PF_6^- ligand is more weakly bound to tungsten compared to OTf^-.[8] Hydride abstraction from $Cp(CO)_3WH$ by $Ph_3C^+PF_6^-$ gives $Cp(CO)_3WFPF_5$.[9] An NMR spectrum at −40 °C of a solution of *trans*-β-methylstyrene and $Cp(CO)_3WFPF_5$ gave evidence (eq 4) for the formation of

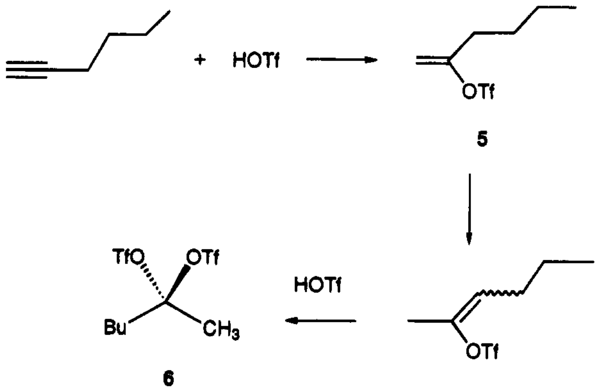


(4)

$[Cp(CO)_3W(\eta^2\text{-}trans\text{-}PhHC{=}CHCH_3)]^+[PF_6]^-$; the resonances assigned to the β-methylstyrene ligand in this complex were similar in chemical shift and coupling constants to those observed for the analogous complex **4-*trans***, with a triflate counterion. Beck and co-workers reported a similar equilibrium, in which formation of $[Cp(CO)_3Mo(\eta^2\text{-}CH_3CH{=}CHCH_3)]^+[BF_4]^-$ was observed at low temperature, upon addition of 2-butene to $Cp(CO)_3MoFBF_3$.[10] In contrast to the formation of geminal ditriflate **2** from the reaction of PhC≡CH with 2 equiv of HOTf, the yield of $PhC(OTf)_2CH_2CH_3$ formed from reaction of PhC≡CMe with HOTf was low (<20%).

Since no analogous η^2-styrene complex of tungsten was observed in the hydrogenation of PhC≡CH, it is surprising that the β-methylstyrene complex **4** forms to such a large extent. Precedent for the formation of a tungsten complex as a kinetic product in an ionic hydrogenation comes from our previous characterization of an isopropyl alcohol complex, $[Cp(CO)_3W(HO^iPr)]^+[OTf]^-$, which results from ionic hydrogenation of acetone by $HOTf/Cp(CO)_3WH$.[11]

Addition of excess HOTf to a solution of *n*-BuC≡CH resulted in the initial formation of 1-hexen-2-yl triflate (**5**). This vinyl triflate isomerized to a mixture of internal double bond isomers ((*E*)- and (*Z*)-2-hexen-2-yl triflate) before conversion to the geminal ditriflate **6** (eq 5). When



(5)

HOTf (2.6 equiv) was added to a solution of *n*-BuC≡CH containing $Cp(CO)_3WH$, vinyl triflates were again observed as intermediates, and *n*-hexane was very slowly formed as the product of ionic hydrogenation (eq 6). After

$$^{n}Bu{-}C{\equiv}C{-}H \;+\; 2\;HOTf \;+\; 2\;Cp(CO)_3WH \longrightarrow CH_3(CH_2)_4CH_3 \qquad (6)$$

4 days, the yield of *n*-hexane was 34%; the yield increased slightly to 36% after 3 more days. An additional 2.6 equiv of HOTf was added, and the yield of *n*-hexane after 4 days increased to 57%.

The reaction of *tert*-butylacetylene with $HOTf/Cp(CO)_3WH$ produces the vinyl triflate **7** (34%) along with 2,3-dimethylbutane (56%). A proposed mechanism that accounts for these products is shown in Scheme 2. Protonation of the alkyne gives an unobserved vinyl cation; trapping by OTf^- gives the vinyl triflate **7**, while competitive hydride transfer from $Cp(CO)_3WH$ to this vinyl cation intermediate gives *tert*-butylethylene. Hydrogenation of *tert*-butylethylene to 2,3-dimethylbutane was shown earlier[2] to involve protonation, methyl group migration to convert the secondary carbenium ion into a tertiary carbenium ion, and hydride abstraction to give the product.

The hydrogenation of isopropenylacetylene (**8**) by $HOTf/Cp(CO)_3WH$ was investigated to observe the behavior of a compound containing both C=C and C≡C functional-

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(7) Straus, D. A.; Zhang, C.; Tilley, T. D. *J. Organomet. Chem.* **1989**, *369*, C13-C17.

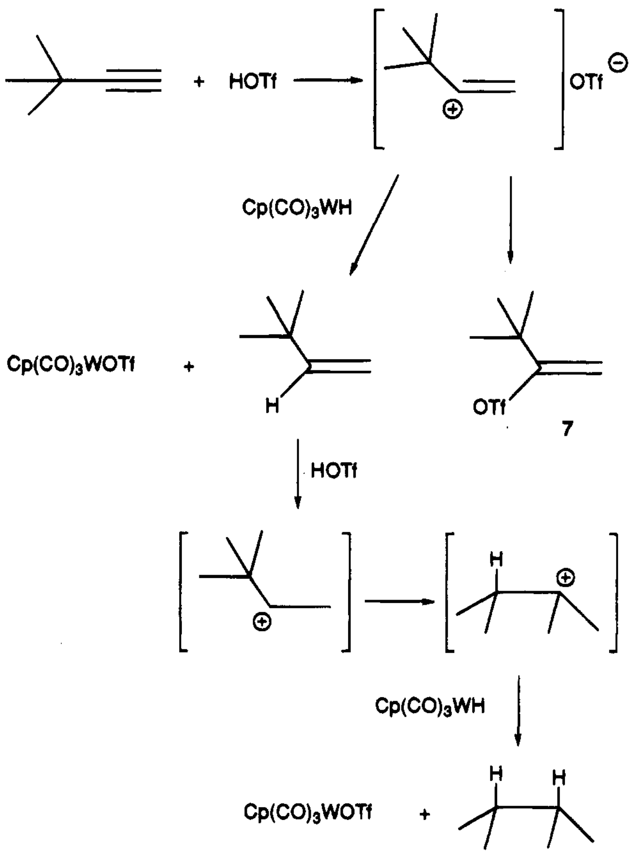
(8) For a review of complexes with coordinated triflate ligands, see: Lawrance, G. A. *Chem. Rev.* **1986**, *86*, 17−33. For a review of metal complexes with weakly coordinating anions, see: Beck, W.; Sünkel, K. *Chem. Rev.* **1988**, *88*, 1405−1421.

(9) Beck, W.; Schloter, K. *Z. Naturforsch.* **1978**, *33b*, 1214−1222.

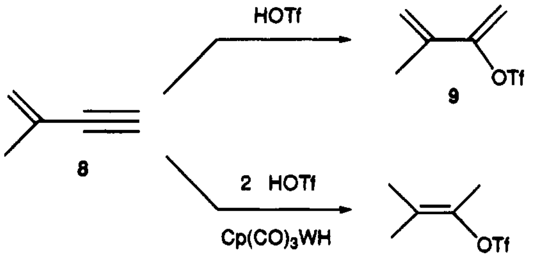
(10) Sünkel, K.; Ernst, H.; Beck, W. *Z. Naturforsch.* **1981**, *36b*, 474−481.

(11) Song, J.-S.; Szalda, D. J.; Bullock, R. M.; Lawrie, C. J. C.; Rodkin, M. A.; Norton, J. R. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 1233−1235.

Scheme 2



ities.[12] Addition of HOTf to **8** (in the absence of metal hydride) produced **9** (eq 7). Vinyl triflate **9** was isolated as a colorless oil following distillation, but it is thermally unstable, decomposing to a dark viscous oil even when stored at +3 °C under Ar. Ionic hydrogenation of **8** by HOTf/Cp(CO)$_3$WH produces (CH$_3$)$_2$C=C(CH$_3$)OTf. The mechanism of this reaction involves conversion of **8** to **9** and then ionic hydrogenation of the C=C bond of **9** to give (CH$_3$)$_2$CHC(OTf)=CH$_2$, followed by acid-catalyzed isomerization to give (CH$_3$)$_2$C=C(CH$_3$)OTf (eq 8).



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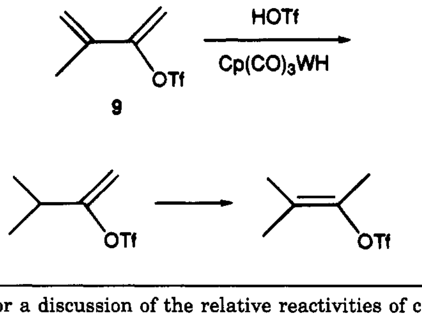

(8)

Discussion

Comparison of Ionic Hydrogenations of Alkenes and Alkynes. Significant differences are found in these ionic hydrogenations of alkynes compared with the previously reported[2] ionic hydrogenation of alkenes under similar conditions. The alkyne hydrogenations are much slower, occurring over a period of hours or days at room temperature, compared to a few minutes at low temperature for alkene hydrogenations. In the ionic hydrogenations of alkenes, alkyl triflates were generally not observed as intermediates, the one exception being an alkyl triflate observed in the ionic hydrogenation of allylbenzene. In contrast, vinyl triflates were observed in these alkyne hydrogenations, and conversion of the vinyl triflates to the final hydrogenated product is slow. In the hydrogenation of PhC≡CH, over half of the ethylbenzene is formed in the first 5 min of the reaction; the remaining ethylbenzene eventually to be produced goes through the vinyl triflate and geminal ditriflate intermediates, which are more slowly converted to ethylbenzene. Styrene was not observed as an intermediate in the hydrogenation of PhC≡CH, but this is not surprising since it was already shown to be very rapidly hydrogenated to ethylbenzene under these conditions. The overall 92% yield of ethylbenzene from ionic hydrogenation of PhC≡CH is significantly higher than the 57% yield of ethylbenzene resulting from ionic hydrogenation of styrene by HOTf/Cp(CO)$_3$WH. In the ionic hydrogenation of styrene, the carbenium ion formed in the initial protonation is generated in the presence of a high concentration of styrene, and polymerization competes with hydrogenation, thereby lowering the yield of ethylbenzene. In contrast, the vinyl triflates observed as intermediates in the ionic hydrogenation of alkynes are slowly converted to the hydrogenation product; competing polymerization does not occur to an observable extent.

Vinyl Triflates and Geminal Ditriflates. Vinyl triflates are observed from addition of 1 equiv of HOTf to the C≡C bond; addition of a second equivalent of HOTf produces geminal ditriflates. Both vinyl triflates and geminal ditriflates are available from other routes. Formation of vinyl triflates by addition of HOTf to an alkyne was first reported in 1969 by Stang and Summerville.[13] Since that time the synthesis and reactions of vinyl triflates have been studied in detail.[14] A more general and widely used synthetic method for vinyl triflates involves the reaction of Tf$_2$O with enolizable ketones in the presence of a base. Geminal ditriflates have been shown to form from the same reagents[15] when the reaction is carried out at 0 °C. Wright and Pulley[16] have investigated the intermediacy of geminal ditriflates in the formation of vinyl triflates from Tf$_2$O and ketones and have examined the influence of reaction temperature and solvent on these reactions. A different synthetic method for geminal ditriflates involves reaction of gemi-

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[12] For a discussion of the relative reactivities of carbon–carbon double and triple bonds toward electrophiles, see: Melloni, G.; Modena, G.; Tonellato, U. *Acc. Chem. Res.* **1981**, *14*, 227–233.

[13] Stang, P. J.; Summerville, R. H. *J. Am. Chem. Soc.* **1969**, *91*, 4600–4601.

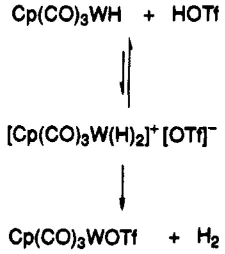
[14] For reviews covering aspects of the synthesis and reactivity of vinyl triflates, see: (a) Stang, P. J. *Acc. Chem. Res.* **1978**, *11*, 107–114. (b) Stang, P. J.; Hanack, M.; Subramanian, L. R. *Synthesis* **1982**, 85–126. (c) Ritter, K. *Synthesis* **1993**, 735–762.

[15] (a) García Martínez, A.; Espada Ríos, I.; Teso Vilar, E. *Synthesis* **1979**, 382–383. (b) García Martínez, A.; Martinez Alvarez, R.; García Fraile, A.; Subramanian, L. R.; Hanack, M. *Synthesis* **1987**, 49–51.

[16] Wright, M. E.; Pulley, S. R. *J. Org. Chem.* **1989**, *54*, 2886–2889.

nal diiodides with AgOTf.[17] The geminal ditriflates reported in this paper result from addition of a second equivalent of HOTf to the vinyl triflates. Olah and Spear reported the analogous formation of geminal difluorosulfates from addition of 2 equiv of FSO_3H to alkynes.[18]

Metal Hydrides as Hydride Donors under Acidic Conditions. Since the ionic hydrogenation of alkynes is much slower than that of alkenes, the requirements for potentially suitable hydride donors for the alkyne hydrogenations are more stringent. Ionic hydrogenation of hindered alkenes can be accomplished at room temperature or below, using either $HSiEt_3$ or any of the following transition metal hydrides:[2] $CpW(CO)_3H$, $Cp^*W(CO)_3H$, $CpMo(CO)_3H$, $HMn(CO)_5$, $HRe(CO)_5$, $Cp^*Os(CO)_2H$ ($Cp = \eta^5\text{-}C_5H_5$, $Cp^* = \eta^5\text{-}C_5Me_5$). Even though $HSiEt_3$ reacts quickly at room temperature with HOTf to give Et_3SiOTf and H_2, the hydrogenation proceeds so quickly that the consumption of $HSiEt_3$ by reaction with acid is not a significant problem in alkene hydrogenations. This is not the case for ionic hydrogenation of alkynes, however. Attempted use of HOTf and $HSiEt_3$ for hydrogenation of PhC≡CH gave only a low yield of ethylbenzene, with most of the $HSiEt_3$ decomposing upon reaction with the acid. This might make it appear that a requirement for the successful use of metal hydrides in these hydrogenations be that they not react with acid, or at least that their reaction with acid be slow on the time scale of the hydrogenation. In fact, the rapid reaction of a metal hydride with acid does not necessarily preclude it from being useful in these ionic hydrogenations. The reaction of $CpW(CO)_3H$ with HOTf (eq 9) is rapid, giving protonation at the metal to produce the cationic dihydride $[CpW(CO)_3(H)_2]^+OTf^-$.[19] Since $CpW(CO)_3H$ is only partially protonated (~16% by 1.2 equiv of HOTf), there remains an ample concentration of $CpW(CO)_3H$ to function effectively as the hydride donor under the reaction conditions. Formation of H_2 from reaction of $CpW(CO)_3H$ with HOTf is slow, being only partially complete after weeks at room temperature. A requirement for successful utilization of a hydride source in the ionic hydrogenation of alkynes is, therefore, the absence of a fast pathway for decomposition of the hydride upon reaction with acid. This is a key characteristic that distinguishes the transition metal hydride[20] $CpW(CO)_3H$ from the main group compound $HSiEt_3$. The formation of H_2 and the organometallic triflate complex $CpW(CO)_3OTf$ occurs slowly due to the relative thermal stability of $[CpW(CO)_3(H)_2]^+OTf^-$, while $HSiEt_3$ is not very useful in these hydrogenations due to its rapid formation of H_2 upon reaction with HOTf.



(9)

Experimental Section

General. All reactions were carried out under an atmosphere of argon using Schlenk or vacuum-line techniques, or in a Vacuum Atmospheres drybox. CH_2Cl_2, CD_2Cl_2, and 1,2-dichloroethane were distilled from CaH_2. $CpW(CO)_3H$ was prepared using a minor modification of a previously reported method,[21] by reaction of excess cyclopentadiene with $(CO)_3W(EtCN)_3$.[22] Alkynes were purchased from Aldrich, Wiley Organics, Farchan, or ICN. All reactions were performed at 22 °C unless otherwise indicated. HOTf was purified by distillation and stored under Ar. Screw-capped NMR tubes with septa were used for NMR tube reactions requiring addition of reagents by syringe while maintaining an inert atmosphere in the tubes.

Ionic Hydrogenation of PhC≡CH by $Cp(CO)_3WH$ and HOTf. $Cp(CO)_3WH$ (27.7 mg, 0.083 mmol) was added to an NMR tube, and CD_2Cl_2 was added to give a volume of 0.52 mL. PhC≡CH (4.5 μL, 0.041 mmol) and 1,2-dichloroethane (2 μL, internal integration standard) were added, and an NMR spectrum was recorded. HOTf (10 μL, 0.11 mmol) was added, the tube was shaken, and the color changed to wine-red. An NMR spectrum recorded at $t = 5$ min showed the formation of **1** (25%), **2** (5%), and ethylbenzene (64%). At $t = 30$ min, the yields were **1** (8%), **2** (6%), and ethylbenzene (82%). After 28 h, the yield of ethylbenzene was 92%. The NMR also indicated the formation of 2 equiv of $Cp(CO)_3WOTf$ for each equivalent of ethylbenzene produced.

Preparation of 1-Phenylethenyl Triflate (1) and Its Reaction with $Cp(CO)_3WH$ and HOTf. HOTf (3.5 μL, 0.039 mmol) was added to a solution of PhC≡CH (4 μL, 0.036 mmol) and 1,2-dichloroethane (2 μL) in CD_2Cl_2 (0.56 mL). The tube was shaken, and an NMR spectrum recorded at $t = 10$ min indicated **1** (80%) had formed. $Cp(CO)_3WH$ (32 mg, 0.098 mmol) was added to the tube and the solution was shaken for 5 min at 22 °C. The ^1H NMR spectrum indicated no reaction. HOTf (5 μL, 0.056 mmol) was added to the tube and an immediate color change to wine-red was observed due to the formation of $Cp(CO)_3WOTf$. At $t = 10$ min, the ^1H NMR spectrum revealed the formation of ethylbenzene (22%) and **2** (5%). After 20 h, ethylbenzene (74%) and **2** (23%) were observed by NMR.

Reaction of $Cp(CO)_3WH$ and HOTf with an Excess of PhC≡CH. $Cp(CO)_3WH$ (27.0 mg, 0.081 mmol) was added to an NMR tube, and CD_2Cl_2 was added to give a volume of 0.51 mL. PhC≡CH (5 μL, 0.046 mmol) and 1,2-dichloroethane (4 μL, internal integration standard) were added, and an NMR spectrum was recorded. HOTf (3 μL, 0.034 mmol) was added, the tube was shaken, and the color changed to yellow. An NMR spectrum recorded at $t = 5$ min showed the formation of **1** along with unreacted PhC≡CH. No styrene or ethylbenzene were observed (estimated detection limit 1%). Only a trace of $Cp(CO)_3WOTf$ (~0.1%) was detected.

NMR of 1-phenylethenyl triflate (1): ^1H NMR (CD_2Cl_2) δ 7.59–7.44 (m, 5H), 5.67 (d, $^2J_{HH} = 4.1$ Hz, 1H), 5.39 (d, $^2J_{HH} = 4.1$ Hz, 1H) [lit.[23] NMR in CCl_4 δ 5.50 (d), 5.41 (d)].

NMR of 1,1-bis(triflyloxy)ethylbenzene (2): ^1H NMR (CD_2Cl_2) δ 8.40 (dd, $J = 8.6$ Hz, $J = 1.2$ Hz, 2H), 8.13 (tm, $J = 7.6$ Hz, 1H), 7.76 (tm, $J = 7.6$ Hz, 2H) 3.12 (s, 3H); ^{13}C NMR (CD_2Cl_2, gated decoupled) δ 218.1 (s), 143.0 (dt, $^1J_{HC} = 163$ Hz, $J = 9$ Hz), 134.1 (dt, $^1J_{HC} = 165$ Hz, $^2J_{HC} = 7$ Hz), 130.9 (t, $^2J_{HC} = 8$ Hz), 130.8 (ddd, $^1J_{HC} = 167$ Hz, $^2J_{HC} = 7$ Hz, $^3J_{HC} = 1.4$ Hz), 119.3 (q, $^1J_{FC} = 317.3$ Hz), 24.7 (q, $^1J_{HC} = 131.7$ Hz).

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Ionic Hydrogenation of $PhC\equiv CH$ by $HSiEt_3$ and HOTf. HOTf (9 μL, 0.10 mmol) was added to a solution containing $PhC\equiv CH$ (5 μL, 0.045 mmol), $HSiEt_3$ (15 μL, 0.094 mmol), and 1,2-dichloroethane (2 μL) in CD_2Cl_2 (0.56 mL). Bubbles formed immediately, and an NMR spectrum at $t = 15$ min showed the formation of **1** (76%) and ethylbenzene (16%) along with H_2 (δ 4.61) and Et_3SiOTf.

T_1 experiment for $PhC\equiv CH$. A solution of $PhC\equiv CH$ (10 μL, 0.091 mmol) in CD_2Cl_2 (0.66 mL) was freeze–pump–thawed 6 times, and the NMR tube was flame-sealed under high vacuum. The T_1 measurement was carried out on a Bruker AM-300 NMR using the standard inversion-recovery pulse sequence, 180°–τ–90°. The NMR probe temperature was determined[24] using the measured difference in chemical shifts of the methyl and OH protons in MeOH. The T_1 measured at 26 °C was 289 s for PhCC*H* (δ 3.13); the T_1 was 42 s for the aromatic resonance at δ 7.36.

Ionic Hydrogenation of $PhC\equiv CSiMe_3$ by $Cp(CO)_3WH$ and HOTf. HOTf (10 μL, 0.11 mmol) was added to a solution containing $Cp(CO)_3WH$ (20 mg, 0.060 mmol), $PhC\equiv CSiMe_3$ (5 μL, 0.025 mmol), and 1,2-dichloroethane (1 μL) in CD_2Cl_2 (0.57 mL). After 50 min, the ^1H NMR spectrum of the resulting wine-red solution showed the formation of **2** (13%), ethylbenzene (85%), and Me_3SiOTf (91%). At $t = 2$ days, the yield of ethylbenzene had increased to 97%.

Reaction of $PhC\equiv CSiMe_3$ with HOTf. HOTf (3.5 μL, 0.039 mmol) was added to a solution of $PhC\equiv CSiMe_3$ (5 μL, 0.045 mmol) and 1,2-dichloroethane (1 μL) in CD_2Cl_2 (0.57 mL). At $t = 30$ min, the ^1H NMR spectrum showed $PhC\equiv CSiMe_3$ (3%), $PhC\equiv CH$ (45%), and **1** (51%). Additional HOTf (3.5 μL, 0.039 mmol) was added, and an NMR spectrum recorded 10 min later indicated the formation of and **1** (61%) and **2** (39%).

Attempted Ionic Hydrogenation of $Me_3SiC\equiv CSiMe_3$ by $Cp(CO)_3WH$ and HOTf. HOTf (5 μL, 0.056 mmol) was added to a solution containing $Cp(CO)_3WH$ (20 mg, 0.06 mmol), $Me_3SiC\equiv CSiMe_3$ (3 μL, 0.013 mmol), and 1,2-dichloroethane (1 μL) in CD_2Cl_2 (0.71 mL). An NMR spectrum recorded at $t = 30$ min showed the formation of $HC\equiv CH$ (δ 1.96, 48%) and Me_3SiOTf (δ 0.45, 100%, 2 equiv based on $Me_3SiC\equiv CSiMe_3$).

Ionic Hydrogenation of $PhC\equiv CMe$ by $Cp(CO)_3WH$ and HOTf. HOTf (10 μL, 0.113 mmol) was added to a solution containing $Cp(CO)_3WH$ (45 mg, 0.135 mmol), $PhC\equiv CMe$ (5 μL, 0.039 mmol), and 1,2-dichloroethane (2 μL) in CD_2Cl_2 (0.59 mL.) The progress of the reaction was monitored periodically vs the internal standard; results are shown in Figure 1. The reaction reached completion over 5 days to yield $Cp(CO)_3WOTf$ (1.91 equiv based on initial $PhC\equiv CMe$) and propylbenzene (91%).

(*E*)-1-Phenylpropen-1yl triflate (3*E*): ^1H NMR (CD_2Cl_2) δ 7.45–7.38 (m, 5H), 5.98 (q, $^3J_{HH} = 7.2$ Hz, 1H), 1.93 (d, $^3J_{HH} = 7.2$ Hz).

(*Z*)-1-Phenylpropen-1yl triflate (3*Z*): ^1H NMR (CD_2Cl_2) δ 7.45–7.38 (m, 5H), 5.97 (q, $^3J_{HH} = 7.5$ Hz, 1H), 1.84 (d, $^3J_{HH} = 7.5$ Hz).

$[Cp(CO)_3W(\eta^2$-*trans*-$PhHC{=}CHCH_3)]^+[OTf]^-$(4-*trans*): ^1H NMR (CD_2Cl_2) δ 7.30–7.15 (m, 5H), 5.82 (s, 5H), 5.19 (d, $^3J_{HH} = 13.6$ Hz, 1H), 4.76 (dq, $^3J_{HH} = 13.6$ Hz, $^3J_{HH} = 6.0$ Hz, 1H), 2.38 (d, $^3J_{HH} = 6.0$ Hz, 3H).

$[Cp(CO)_3W(\eta^2$-*cis*-$PhHC{=}CHCH_3)]^+[OTf]^-$ (4-*cis*): ^1H NMR (CD_2Cl_2) δ 7.30–7.15 (m, 5H), 5.79 (s, 5H), 5.78 (d, $^3J_{HH} = 10$ Hz, 1H), 4.84 (dq, $^3J_{HH} = 10$ Hz, $^3J_{HH} = 6.5$ Hz, 1H), 2.60 (dd, $^3J_{HH} = 6.5$ Hz, $^3J_{HH} = 0.7$ Hz, 3H). Assignment of some of the ^1H NMR resonances of **4-*cis*** were complicated by overlap of the Cp resonance at δ 5.79 with the vinyl resonance at δ 5.78; clarification of these overlapping resonances was made by preparing an analog of **4-*cis*** with a deuterated cyclopentadienyl ring using $(C_5D_5)W(CO)_3H$.

$[Cp(CO)_3W(\eta^2$-*trans*-$PhHC{=}CHCH_3)]^+[PF_6]^-$ observed by NMR at −40 °C from addition of excess *trans*-β-methylstyrene to $Cp(CO)_3WFPF_5$:[9] ^1H NMR (CD_2Cl_2) δ 7.30–7.15 (m, 5H), 5.82 (s, 5H), 5.26 (d, $^3J_{HH} = 13.6$ Hz, 1H), 4.83 (dq, $^3J_{HH} = 13.6$ Hz, $^3J_{HH} = 6.0$ Hz, 1H), 2.36 (d, $^3J_{HH} = 6.0$ Hz, 3H). Spectra of *trans*-β-methylstyrene and *cis*-β-methylstyrene in CD_2Cl_2 are provided for comparison. ***trans*-*β*-Methylstyrene**: ^1H NMR (CD_2Cl_2) δ 7.40–7.10 (m, 5H), 6.43 (dq, $^3J_{HH} = 15.7$ Hz, $^3J_{HH} = 1.4$ Hz, 1H), 6.28 (dq, $^3J_{HH} = 15.7$ Hz, $^3J_{HH} = 6.4$ Hz, 1H), 1.90 (dd, $^3J_{HH} = 6.40$ Hz, $^3J_{HH} = 1.4$ Hz, 3H, ($PhHC{=}CHCH_3$)). ***cis*-*β*-Methylstyrene**: ^1H NMR (CD_2Cl_2) δ 7.40–7.15 (m, 5H), 6.49 (dq, $^3J_{HH} = 11.6$ Hz, $^3J_{HH} = 1.8$ Hz), 5.83 (dq, $^3J_{HH} = 11.6$ Hz, $^3J_{HH} = 7.2$ Hz), 1.93 (dd, $^3J_{HH} = 7.2$ Hz, $^3J_{HH} = 1.8$ Hz, 3H).

Ionic Hydrogenation of *n*-$BuC\equiv CH$ by $Cp(CO)_3WH$ and HOTf. HOTf (10 μL, 0.11 mmol) was added to a solution of *n*-$BuC\equiv CH$ (5 μL, 0.043 mmol), $Cp(CO)_3WH$ (38.4 mg, 0.11 mmol) and 1,2-dichloroethane (2 μL) in CD_2Cl_2 (0.50 mL). An NMR spectrum recorded after 5 min showed **5** (61%) along with the internal double bond isomers (*E*)- and (*Z*)-2-hexen-2-yl triflate. Subsequent spectra showed complete conversion of **5** to this mixture of isomers. The yield of *n*-hexane was 34% after 4 days, but increased only to 36% after a total of 7 days. Additional HOTf (10 μL) was added, and the yield of *n*-hexane increased to 57% after an additional 4 days. The formation of *n*-hexane was confirmed by NMR and by GC–MS.

1-Hexen-2-yl triflate (5): ^1H NMR (CD_2Cl_2) δ 5.08 (d, $J = 3.6$ Hz, 1H), 4.97 (dt, $J = 3.6$ Hz, 1.1 Hz, 1H), 2.35 (t, $J = 7.6$ Hz, 2H), 1.5–1.3 (m, 4H), 0.93 (t, $J = 7.3$ Hz, 3H) [lit.[25] NMR in CCl_4 δ 5.06 (d, J = 4 Hz, 1H), 4.92 (d, J = 4 Hz, 1H), 2.37 (m, 2H), 1.50 (m, 4H), 0.98 (m, 3H)].

Reaction of *n*-$BuC\equiv CH$ with HOTf To Give 2,2-Bis(triflyloxy)hexane (6). HOTf (13 μL, 0.15 mmol) was added to a solution of *n*-$BuC\equiv CH$ (5 μL, 0.044 mmol) and 1,2-dichloroethane (4 μL) in CD_2Cl_2 (0.55 mL). Vinyl triflate intermediates were observed, and after 2 h at 22 °C, the ^1H NMR spectrum showed the formation of **6** (95%): ^1H NMR (CD_2Cl_2) δ 3.15 (tq, $^3J_{HH} = 7.4$ Hz, $^4J_{HH} = 1.4$ Hz, 2H), 2.96 (t, $^4J_{HH} = 1.4$ Hz, 3H), 1.80 (quintet, $^3J_{HH} = 7.4$ Hz, 2H), 1.45 (sextet, $^3J_{HH} = 7.4$ Hz, 2H), 0.97 (t, $^3J_{HH} = 7.4$ Hz, 3H); ^{13}C NMR (gated decoupled, CD_2Cl_2) δ 144.1 (*C*(OTf)), 118.8 (q, $^1J_{FC} = 317$ Hz, *C*F_3), 44.4 (tt, $^1J_{HC} = 154$ Hz, $^2J_{HC} = 4$ Hz, $(TfO)_2CCH_2$), 30.1 (q, $^1J_{HC} = 132$ Hz, $C(OTf)_2CH_3$), 26.8 (tm, $^1J_{HC} = 130$ Hz, $CH_3CH_2CH_2$), 22.2 (tm $^1J_{HC} = 126$ Hz, CH_3CH_2), 13.1 (qt, $^1J_{HC} = 126$ Hz, $^3J_{HC} = 4$ Hz, CH_2CH_3).

Ionic Hydrogenation of *tert*-Butylacetylene by $Cp(CO)_3WH$ and HOTf. HOTf (7.5 μL, 0.085 mmol) was added to a solution containing $Cp(CO)_3WH$ (25 mg, 0.075 mmol), *tert*-butylacetylene (5 μL, 0.041 mmol), and 1,2-dichloroethane (1.5 μL) in CD_2Cl_2 (0.60 mL.) An NMR spectrum recorded after 30 min showed 2,3-dimethylbutane (56%) and 3,3-dimethyl-1-buten-2-yl triflate (34%).

3,3-Dimethyl-1-buten-2-yl triflate: ^1H NMR (CD_2Cl_2) δ 5.05 (d, $^2J_{HH} = 4.3$ Hz, 1H), 4.99 (d, $^2J_{HH} = 4.3$ Hz, 1H), 1.17 (s, 9H) [lit.[25] NMR in CCl_4 δ 5.03 (d, $J = 4.0$ Hz, 1H), 4.91 (d, $J = 4.0$ Hz, 1H), 1.20 (s, 9H)].

Ionic Hydrogenation of Isopropenylacetylene (2-Methyl-1-buten-3-yne, 8) by $Cp(CO)_3WH$ and HOTf. HOTf (19 μL, 0.21 mmol) was added to a solution containing $Cp(CO)_3WH$ (100 mg, 0.30 mmol), **8** (20 μL, 0.21 mmol), and 1,2-dichloroethane (1 μL) in CD_2Cl_2 (0.64 mL). At $t = 10$ min, an NMR indicated the formation of $CH_2{\equiv}CHMeC(OTf){=}CH_2$ (**9**, 86%). Additional HOTf (19 μL, 0.21 mmol) was added, and 15 min later, $Me_2C{=}C(OTf)Me$ (50%) was observed. After 3 days the yield of $Me_2C{=}C(OTf)Me$ had increased to 86%.

$Me_2C{=}C(OTf)Me$, 3-methyl-2-buten-2-yl triflate: ^1H NMR (CD_2Cl_2) δ 2.03, 1.78, 1.75 (m, 3H each) [lit.[25] NMR in CCl_4 δ 2.05 (m, 3H), 1.78 (br s, 6H)]; ^{13}C NMR (gated decoupled, CD_2Cl_2) δ 140.9, 125.3 (m), 19.2 (qq, $^1J_{HC} = 128$ Hz, $^3J_{HC} = 4.4$ Hz), 18.3 (qq, $^1J_{HC} = 128$, $^3J_{HC} = 4.5$ Hz), 16.4 (q, $^1J_{HC} = 129$ Hz).

Reaction of 8 with HOTf. HOTf (6 μL, 0.063 mmol) was added to a solution of **8** (6 μL, 0.063 mmol) and 1,2-dichloroethane (5 μL) in CD_2Cl_2 (0.57 mL). The solution immediately turned to yellow, and an ^1H NMR spectrum taken at $t = 5$ min indicated the formation of $CH_2{=}CMeC(OTf){=}CH_2$ (**9**, 90%). Addition of more HOTf (6 μL) resulted in the consump-

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tion of **9** and the formation of unidentified products (presumably polymers).

Preparation of CH_2=CMeC(OTf)=CH_2 (9). HOTf (2.67 mL, 0.030 mol) was added slowly to a solution of **8** (3.0 mL, 0.032 mol) in CH_2Cl_2 (300 mL) at −40 °C. The resulting brown solution was stirred for 30 min at −40 °C and was then allowed to warm up to room temperature over 3 h. The reaction mixture was washed with saturated aqueous $NaHCO_3$ (3 × 150 mL), and the organic layer was dried (K_2CO_3). The solvent was evaporated, and the product was distilled (24 °C, 0.4 mm Hg) to give CH_2=CMeC(OTf)=CH_2 (2.3 g, 34%) as a clear, colorless oil. The compound decomposed to a black viscous oil after being stored for 3 months under Ar in a refrigerator: ^{1}H NMR (CD_2Cl_2) δ 5.44 (s, 1H), 5.26 (s, 3H), 1.95 (s, 3H); ^{13}C NMR (gated decoupled; CD_2Cl_2) δ 154.4, 136.0 (m), 119.0 (q, $^1J_{FC}$ = 320 Hz), 117.1 (tq, $^1J_{HC}$ = 160 Hz, $^3J_{HC}$ = 6 Hz), 105.4 (t, $^1J_{HC}$ = 164 Hz), 19.6 (qdd, $^1J_{HC}$ = 128 Hz, $^3J_{HC}$ = 10 Hz, $^3J_{HC}$ = 7 Hz); IR (KBr, cm^{-1}) ν_s = 1649 (m), ν_{as} = 1608 (s) C=C−C=C stretch; MS 216.2 (M^+). Anal. Calcd for $C_6H_7O_3F_3S$: C, 33.34; H, 3.26. Found: C, 32.48; H, 3.33.

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