Acid-Catalyzed Isomerization of Rhenium Alkyne Complexes to Rhenium Allene Complexes via 1-Metallacyclopropene Intermediates

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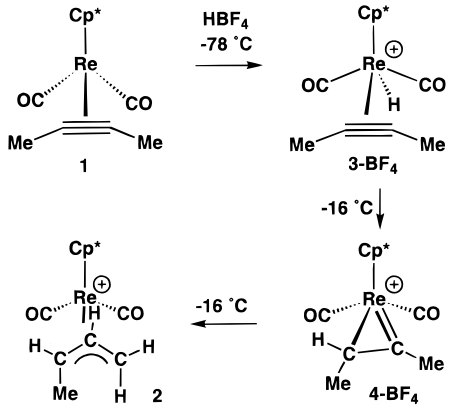
The alkyne complexes $C_5Me_5(CO)_2Re(\eta^2$-MeC≡CMe) (**1**) and $C_5H_5(CO)_2Re(\eta^2$-MeC≡CMe) (**6**) underwent acid-catalyzed isomerization by way of 1-metallacyclopropene intermediates to form the allene complexes $C_5Me_5(CO)_2Re(\eta^2$-2,3-MeHC═C═$CH_2)$ (**5**) and $C_5H_5(CO)_2Re(\eta^2$-2,3-MeHC═C═$CH_2)$ (**7**). Stoichiometric reaction of **1** with CF_3CO_2H initially produced the kinetic addition product $C_5Me_5(CO)_2Re[\eta^2$-(*Z*)-MeHC═CMe$O_2CCF_3]$ (**8-Z**), which slowly isomerized to the thermodynamically more stable *E* isomer **8-E**. The reaction of **6** with CF_3CO_2H at −73 °C produced only $C_5H_5(CO)_2Re[\eta^2$-(*E*)-MeHC═CMe$O_2CCF_3]$ (**9-E**), which isomerized at −60 °C to a 80:20 equilibrium mixture of **9-E** and **9-Z**. Treatment of **9-E** and **9-Z** with base led to formation of allene complex **7**. The rate of this elimination was independent of base concentration. Labeling studies showed that the 1-metallacyclopropene intermediate $C_5H_5(CO)_2Re(\eta^2$-CMeCHMe)$^+CF_3CO_2^-$ (**12-CF_3CO_2**) undergoes a number of important reactions which include, in order of decreasing relative rates: (1) addition of trifluoroacetate to give enol trifluoroacetate complexes, (2) deprotonation to give complexed allenes, (3) degenerate 1,2-hydride migrations, (4) hydride migrations to give η^3-allyl complexes, and (5) deprotonation to give complexed alkynes.

Introduction

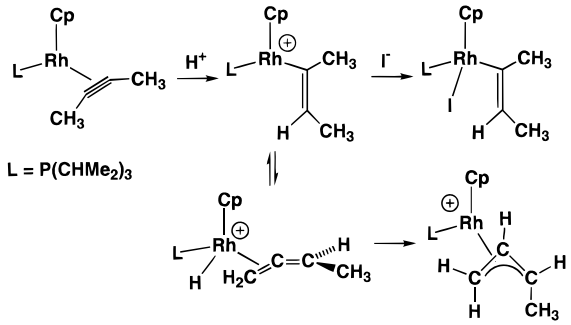
We have recently reported several interesting transformations of rhenium alkyne complexes, including hydride abstraction from the butyne complex $C_5Me_5(CO)_2Re(\eta^2$-MeC≡CMe) (**1**) to give the η^3-propargyl complex $C_5Me_5(CO)_2Re(\eta^3$-MeC≡$CCH_2)^+PF_6^-$,[1] and protonation of **1** to eventually give the η^3-allyl complex $C_5Me_5(CO)_2Re(\eta^3$-*exo,anti*-MeHC$CHCH_2)^+BF_4^-$ (**2**) (Scheme 1).[2] On closer inspection, the protonation of **1** with HBF_4 at −78 °C was found to produce the rhenium alkyne hydride complex $C_5Me_5(CO)_2ReH(\eta^2$-MeC≡CMe)$^+BF_4^-$ (**3-BF_4**), which then rearranged at −16 °C to the 1-metallacyclopropene complex $C_5Me_5(CO)_2Re(\eta^2$-CMeCHMe)$^+BF_4^-$ (**4-BF_4**) by a net proton migration from rhenium to an alkyne carbon. Finally, **4-BF_4** was converted to the η^3-allyl complex **2** by a 1,2-hydride shift. We also found that protonation of the allene complex $C_5Me_5(CO)_2Re(\eta^2$-2,3-MeHC═C═$CH_2)$ (**5**) with HBF_4 produced the same 1-metallacyclopropene intermediate **4-BF_4** and eventually the η^3-allyl complex **2**. This indicates a close relationship between the chemistry of isomeric allene and alkyne complexes.

In pioneering work, Werner reported that protonation of the rhodium−alkyne complex $C_5H_5(P(i\text{-}Pr)_3)Rh(\eta^2$-MeC≡CMe) produced the η^3-allyl complex $C_5H_5(P(i\text{-}Pr)_3)Rh(\eta^3$-MeHC$CHCH_2)$ (Scheme 2).[3] An intermediate suggested to be a cationic η^1-vinyl complex was trapped by iodide to give a neutral rhodium vinyl iodide complex. Werner also discovered that the rhodium alkyne complex isomerized to the rhodium allene complex C_5H_5-

Scheme 1



Scheme 2



(1) Casey, C. P.; Yi, C. S. *J. Am. Chem. Soc.* **1992**, *114*, 6597.
(2) Casey, C. P.; Brady, J. T.; Boller, T. M.; Weinhold, F.; Hayashi, R. K. *J. Am. Chem. Soc.*, in press.
(3) Wolf, J.; Werner, H. *Organometallics* **1987**, *6*, 1164.

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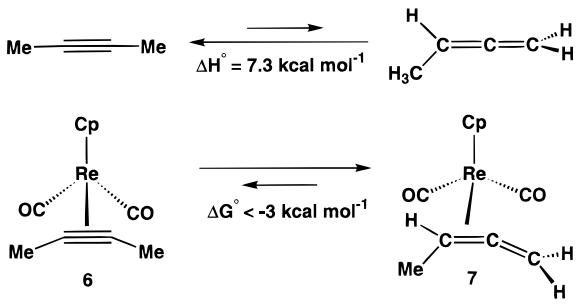
Scheme 3



(P(*i*-Pr)$_3$)Rh(η^2-H$_2$C=C=CHMe) when chromatographed on Al_2O_3. Deuteration experiments indicated that the isomerization involved initial addition of acid to the alkyne carbon followed by subsequent deprotonation of a methyl group.

Our analogous work with rhenium complexes reported here is similar to that of Werner and provides evidence that the reactive intermediate in both the isomerization of alkyne complexes to allene complexes and the conversion of alkyne complexes to cationic η^3-allyl complexes is a 1-metallacyclopropene rather than an η^1-vinyl species. We have also discovered the reversible addition of trifluoroacetic acid across the triple bond of alkyne complexes to produce enol trifluoroacetate complexes.

Results

Isomerization of the Alkyne Complex $C_5H_5(CO)_2Re(\eta^2$-MeC≡CMe) (6) to the Allene Complex $C_5H_5(CO)_2Re(\eta^2$-2,3-MeHC=C=CH$_2$) (7). In the course of investigating the replacement of the alkyne ligand of $C_5H_5(CO)_2Re(\eta^2$-MeC≡CMe) (**6**) by CO, we found that **6** slowly rearranged to allene complex $C_5H_5(CO)_2Re(\eta^2$-2,3-MeHC=C=CH$_2$) (**7**) upon heating at 80 °C for 3 days in C_6D_6 in an acid-washed NMR tube. The conversion of **6** to **7** occurred in 42% NMR yield and was accompanied by extensive decomposition to unidentified products.[4]

This isomerization of an alkyne complex to an allene complex is surprising since the free butyne ligand is 7.3 kcal mol^{-1} more stable then the free methylallene ligand.[5,6] Complexation of the allene ligand to rhenium must be favored over complexation of the alkyne ligand by at least 10 kcal mol^{-1} to explain the reversal of the normal stability order (Scheme 3).

Acid-Catalyzed Isomerization of Alkyne Complexes to Allene Complexes. We began our mechanistic investigations of this intriguing isomerization by closely examining the reaction conditions employed. We conjectured that the isomerization of alkyne complex **6** to the allene complex **7** might be due to adventitious acid from the acid washing of NMR tubes. The possible role of acid catalysis was investigated by studying the conversion of **6** to **7** in the presence of a catalytic amount of trifluoroacetic acid. When 0.1 equiv of trifluoroacetic acid was added to a solution of **6** in C_6D_6 at room temperature, a small new Cp resonance at δ 4.43 (subsequently assigned to the enol trifluoroacetate rhenium complex **9-E**) in the ^{1}H NMR spectrum was noted in addition to the Cp resonance of **6** at δ 4.55. When this solution was heated at 75 °C, rearrangement of alkyne complex **6** to allene complex **7** occurred more rapidly than when no acid was intentionally added. The conversion of **6** to **7** was complete within 90 min, and a 76% NMR yield of **7** was observed. At equilibrium, no alkyne complex **6** was detected and 1% would easily have been observed. This indicates that the equilibrium ratio of **7**:**6** is greater than 100:1. After completion of the reaction, the small Cp resonance at δ 4.43 was still seen in the ^{1}H NMR spectrum in addition to the resonance at δ 4.44 for the Cp of **7**.

In a control experiment, a solution of **6** in C_6D_6 was heated at 80 °C for 21 h in a carefully base washed NMR tube. No isomerization of **6** to **7** was seen by ^{1}H NMR spectroscopy. Clearly, the isomerization of **6** to **7** is acid-catalyzed.

The Cp* alkyne complex **1** underwent an analogous acid-catalyzed rearrangement to the allene complex $C_5Me_5(CO)_2Re(\eta^2$-2,3-MeHC=C=CH$_2$) (**5**). When a C_6D_6 solution of **1** containing 0.1 equiv of trifluoroacetic acid was heated at 75 °C for 3 h, the allene complex **5** was formed in 77% NMR yield. The ^{1}H NMR spectrum of the reaction mixture also showed a small amount (15%) of a second complex with a Cp* resonance at δ 1.57 (subsequently assigned to the enol trifluoroacetate rhenium complex **8-Z**). At equilibrium, no alkyne complex **1** was detected and 1% would easily have been observed. This indicates that the equilibrium ratio of **5**:**1** is greater than 100:1. Allene complex **5** was purified by silica gel chromatography and isolated in 53% yield as a pale yellow solid.

Spectroscopic Characterization of Allene Complexes. Comparison of the ^{1}H NMR spectrum of allene complex **7** with those of known allene complexes[7] indicated that the more substituted double bond of the allene was bonded to the metal. In the ^{1}H NMR spectrum of **7**, two doublets at δ 6.52 (d, ^4J = 2.9 Hz, *H*HC=) and 5.48 (d, ^4J = 3.0 Hz, H*H*C=) were assigned to two geminal hydrogens on the uncomplexed double bond of the allene ligand. These geminal hydrogens have a long-range four-bond coupling to the allene hydrogen on the double bond coordinated to rhenium. The absence of geminal coupling is consistent with the +3 to −3 Hz coupling range reported for geminal allene hydrogens.[8] A low-frequency resonance at δ 2.54 coupled to the geminal allene hydrogens and to the methyl group of the allene ligand was assigned to the vinyl hydrogen on the double bond coordinated to rhenium. In the ^{13}C NMR spectrum of **7**, typical resonances for the allene carbons were seen at δ 154.8 (center carbon), 105.2 (noncoordinated carbon), and 5.6 (metal bound carbon).[7d] Two carbonyls were seen at δ 203.0 and 202.3; note that rapid rotation about the Re−allene bond does not interchange the environments of the CO ligands.

(4) Casey, C. P.; Brady, J. T.; Hayashi, R. K. Unpublished results.
(5) For 2-butyne, ΔH_f° = 34.69 kcal mol^{-1}: Goldstein, E.; Ma, B.; Lii, J.-H.; Allinger, N. L. *J. Phys. Org. Chem.* **1996**, *9*, 191.
(6) For methylallene, ΔH_f° = 42.00 kcal mol^{-1}: Cowperthwaite, M.; Bauer, S. H. *J. Chem. Phys.* **1962**, *36*, 1743.

(7) (a) Zhuang, J.-M.; Sutton, D. *Organometallics* **1991**, *10*, 1516. (b) Franck-Neumann, M.; Brion, F. *Angew. Chem., Int. Ed. Engl.* **1979**, *18*, 688. (c) Foxman, B.; Marten, D.; Rosan, A.; Raghu, S.; Rosenblum, M. *J. Am. Chem. Soc.* **1977**, *99*, 2160. (d) Pu, J.; Peng, T.-S.; Arif, A. M.; Gladysz, J. A. *Organometallics* **1992**, *11*, 3232.
(8) Pretsch, E.; Simon, W.; Seibl, J.; Clerc, T. *Tables of Spectral Data for Structure Determination of Organic Compounds*, 2nd ed.; Biemann, K., Translator; Springer-Verlag: Berlin, 1989.

The ^1H and ^{13}C NMR resonances of the allene ligand of **5** were similar to those of the allene ligand of **7**.

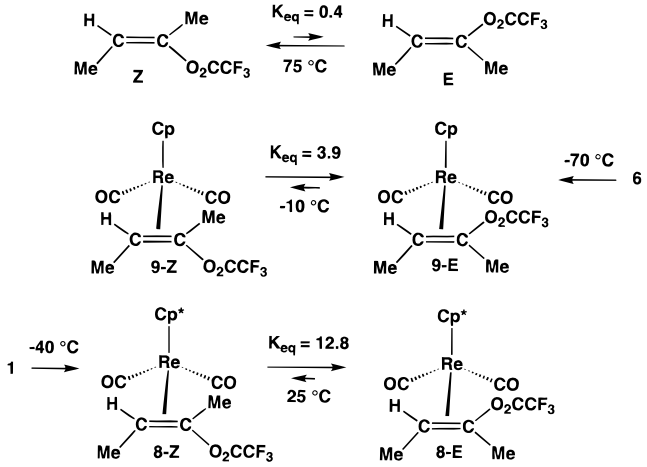
Stoichiometric Reaction of $C_5Me_5(CO)_2Re(\eta^2$-MeC≡CMe) (1) with Trifluoroacetic Acid. In previous work, we found that the stoichiometric reaction of alkyne complex $C_5Me_5(CO)_2Re(\eta^2$-MeC≡CMe) (**1**) with HBF_4 led to the formation of the η^3-allyl complex $C_5Me_5(CO)_2Re(\eta^3$-*exo,anti*-MeHCCHCH$_2)^+BF_4^-$ (**2**) via the rhenium alkyne hydride complex $C_5Me_5(CO)_2ReH(\eta^2$-MeC≡CMe)$^+BF_4^-$ (**3-BF$_4$**) and the 1-metallacyclopropene complex $C_5Me_5(CO)_2Re(\eta^2$-CMeCHMe)$^+BF_4^-$ (**4-BF$_4$**) (Scheme 1).[2] The stoichiometric reaction of **1** with trifluoroacetic acid was investigated in an effort to observe related or additional intermediates in the isomerization of **1** to **5**. As detailed below, we found that trifluoroacetic acid protonates **1** at −78 °C to give the rhenium hydride complex $C_5Me_5(CO)_2ReH(\eta^2$-MeC≡CMe)$^+CF_3CO_2^-$ (**3-CF$_3$CO$_2$**), which then added trifluoroacetate at −40 °C to give the (*Z*) enol trifluoroacetate complex $C_5Me_5(CO)_2Re[\eta^2$-(*Z*)-MeHC═CMeO$_2$CCF$_3$] (**8-Z**).

The addition of 1 equiv of trifluoroacetic acid to a CD_2Cl_2 solution of **1** at −78 °C resulted in protonation at rhenium and formation of the rhenium hydride complex **3-CF$_3$CO$_2$**. The ^1H and ^{13}C NMR spectra of **3-CF$_3$CO$_2$** at −60 °C were similar to those of the previously synthesized tetrafluoroborate salt **3-BF$_4$**. The hydride resonance of **3-CF$_3$CO$_2$** appeared at δ −5.52. The resonance at δ 2.11 for the Cp* ligand is shifted to higher frequency compared with the starting alkyne complex **1** (δ 1.97) as expected for a cationic rhenium complex. Only a single alkyne methyl resonance was seen in both the ^1H and ^{13}C NMR spectra of **3-CF$_3$CO$_2$**, and only a single carbonyl resonance at δ 184.9 was seen in the ^{13}C NMR spectrum, consistent with the presence of a mirror plane and the trans geometry assigned to the rhenium carbonyls.

The reaction of alkyne complex **1** with deuterated trifluoroacetic acid was investigated to determine how easily hydride **3-CF$_3$CO$_2$** exchanged with added trifluoroacetic acid. The rhenium deuteride $C_5Me_5(CO)_2ReD(\eta^2$-MeC≡CMe)$^+CF_3CO_2^-$ (**3-CF$_3$CO$_2$-D**) was formed in CD_2Cl_2 at −78 °C by the treatment of **1** with deuterated trifluoroacetic acid (70 μmol). Protiotrifluoroacetic acid (90 μmol) was added to the CD_2Cl_2 solution of **3-CF$_3$CO$_2$-D** at −78 °C, and the solution was examined by low-temperature ^1H NMR spectroscopy. The first ^1H NMR spectrum at −73 °C showed that some protio trifluoroacetic acid had already been exchanged into **3-CF$_3$CO$_2$-D** during mixing. The ratio of integrals for the ReH resonance at δ −5.52 to the Cp* resonance at δ 2.11 indicated 46% H and 54% D at the hydride site. Exchange of protium into the rhenium hydride site was monitored by ^1H NMR spectroscopy at −73 °C for 7 h. The hydride resonance at δ −5.52 continued to increase and reached 0.64 H after 7 h. The half-life for the H/D exchange was approximately 4 h at −73 °C. It should be noted that the hydrogen exchange into **3** is much faster when the counterion is the more basic trifluoroacetate in **3-CF$_3$CO$_2$-D** than when the counterion is tetrafluoroborate in **3-BF$_4$**.

When the temperature was raised to −40 °C, the metal hydride complex **3-CF$_3$CO$_2$** was rapidly converted to the (*Z*) enol trifluoroacetate complex $C_5Me_5(CO)_2Re[\eta^2$-(*Z*)-MeHC═CMeO$_2$CCF$_3$] (**8-Z**) (Scheme 4). The ^1H NMR chemical shift of the Cp* ligand of alkene complex **8-Z** was the same as that of the minor compound previously observed during the acid-catalyzed isomerization of alkyne complex **1** to allene complex **5**. A solution of **8-Z** slowly isomerized at room temperature over several days to a 93:7 equilibrium mixture of the thermodynamically more stable (*E*) enol trifluoroacetate complex $C_5Me_5(CO)_2Re[\eta^2$-(*E*)-MeHC═CMeO$_2$CCF$_3$] (**8-E**) and **8-Z** (82% yield by ^1H NMR).

Scheme 4



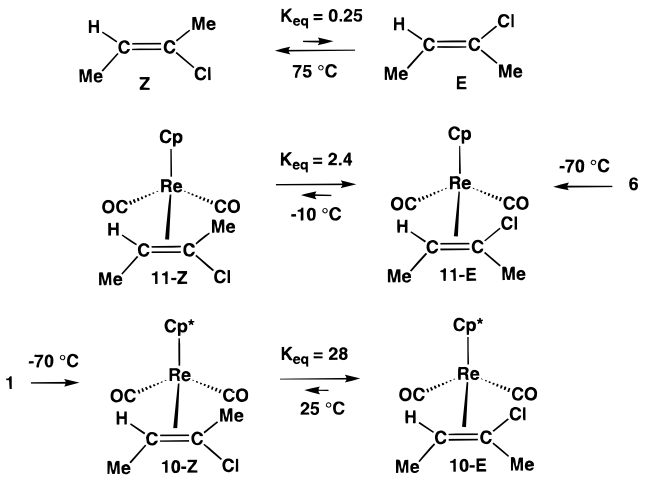
Stoichiometric Reaction of $C_5H_5(CO)_2Re(\eta^2$-MeC≡CMe) (6) with Trifluoroacetic Acid. The stoichiometric reaction of **6** with trifluoroacetic acid at −70 °C in CD_2Cl_2 immediately produced only the enol trifluoroacetate $C_5H_5(CO)_2Re[\eta^2$-(*E*)-MeHC═CMeO$_2$CCF$_3$] (**9-E**). In contrast to the reaction of Cp* complex **1** with trifluoroacetic acid, no metal hydride intermediate was detected. The formation of the enol trifluoroacetate **9-E** from Cp complex **6** occurred at much lower temperature (−70 °C) than formation of enol trifluoroacetate complex **8-Z** from Cp* complex **1** (−40 °C).

When the temperature was raised to −10 °C, **9-E** slowly isomerized over a period of hours to an 79:21 equilibrium mixture of **9-E** and $C_5H_5(CO)_2Re[\eta^2$-(*Z*)-MeHC═CMeO$_2$CCF$_3$] (**9-Z**). In the Cp series, **9-E** is both the kinetically and thermodynamically preferred isomer, while in the Cp* series, **8-Z** is the kinetically formed isomer but **8-E** is the thermodynamically preferred isomer.

When a mixture of the yellow frozen C_6D_6 solution **6** and 1.0 equiv of frozen trifluoroacetic acid was thawed, a colorless solution was formed immediately. The solution contained a 77:23 equilibrium mixture of **9-E** and **9-Z**. The Cp resonance of **9-E** at δ 4.43 was the same as that of the minor component seen earlier in the isomerization of alkyne complex **6** to allene complex **7** catalyzed by 0.1 equiv of trifluoroacetic acid in C_6D_6.

Vinyl Chloride Complexes from Addition of HCl to Alkyne Complexes. The enol trifluoroacetate complexes were readily characterized in solution, but we were unsuccessful in isolating pure samples; attempted recrystallization led to decomposition to brown oils. In an effort to form related stable alkene complexes, the addition of HCl to Cp* alkyne complex **1** was investigated. When excess HCl gas was condensed into a CD_2Cl_2 solution of **1** at −78 °C, the solution im-

Scheme 5



mediately turned colorless and ^{1}H NMR spectroscopy at −60 °C provided evidence for the formation of the *Z* isomer of the chloroalkene complex $C_5Me_5(CO)_2Re[\eta^2$-(*Z*)-MeHC═CMeCl] (**10-Z**) (Scheme 5). No metal hydride intermediate was detected. Rapid evaporation of solvent led to the isolation of pure **10-Z** as a tan powder in 86% yield. The mass spectrum (EI) of **10-Z** showed a parent ion peak at *m/z* 468, confirming the formulation of the rhenium chloroalkene complex.

Slow isomerization of the alkene complex **10-Z** occurred in CD_2Cl_2 over several days at room temperature to a 97:3 equilibrium mixture of *E* isomer $C_5Me_5(CO)_2Re[\eta^2$-(*E*)-MeHC═CMeCl] (**10-E**) and **10-Z** (88% yield by ^{1}H NMR).

Addition of HCl to the analogous Cp alkyne complex **6** in CD_2Cl_2 occurred rapidly at −70 °C to form the (*E*)-vinyl chloride complex $C_5H_5(CO)_2Re[\eta^2$-(*E*)-MeHC═CMeCl] (**11-E**) as the only isomer observed by ^{1}H NMR spectroscopy at −70 °C. Note that the stereochemistry of kinetic addition to Cp complex **6** is opposite to that observed for Cp* complex **1**.

When the temperature was raised to −10 °C, pure **11-E** was converted to a 71:29 equilibrium mixture of **11-E** and $C_5H_5(CO)_2Re[\eta^2$-(*Z*)-MeHC═CMeCl] (**11-Z**). When the reaction of **6** with HCl was carried out in C_6D_6 at room temperature, a 76:24 equilibrium mixture of **11-E** and **11-Z** was observed by ^{1}H NMR spectroscopy. Evaporation of C_6D_6 led to isolation of a mixture of **11-E** and **11-Z**.

Assignment of *E/Z* Stereochemistry of Alkene Complexes. The assignment of the double-bond stereochemistry of alkene complexes was made on the basis of the *E:Z* equilibrium constants (Schemes 4 and 5) and is supported by ^{1}H NMR chemical shift correlations (Table 1). While we are reasonably confident of our assignments, we note that it is more important that the isomers equilibrate rather than which isomer is favored at equilibrium. Of course, the stereochemical assignments are crucial for understanding why one of the isomers is kinetically preferred.

For both the noncoordinated enol trifluoroacetates[9] and chloroalkenes,[10] the *Z* isomers which have the

(9) Summerville, R. H.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1974**, *96*, 1110.

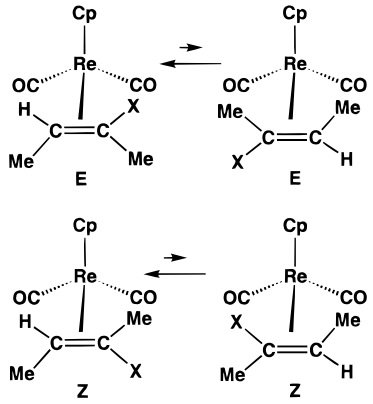
(10) Neureiter, N. P.; Bordwell, F. G. *J. Am. Chem. Soc.* **1960**, *82*, 5354.

Table 1. ^{1}H NMR Chemical Shifts (ppm) of Coordinated Alkene Complexes

compd	*H*MeC═	H*Me*C═	═CX*Me*
(*E*)-MeHC═$CMeO_2CCF_3$[a]	5.43	1.70	1.93
(*Z*)-MeHC═$CMeO_2CCF_3$[a]	5.20	1.55	1.95
8-E[b]	2.42	1.36	2.32
8-Z[b]	2.26	1.62	2.17
9-E[c]	2.87	1.62	2.08
9-Z[c]	2.24	1.72	1.90
(*E*)-MeHC═CMeCl[c]	5.47	1.21	1.73
(*Z*)-MeHC═CMeCl[c]	5.11	1.54	1.80
10-E[b]	4.27	1.50	2.31
10-Z[b]	2.50	1.76	2.28
11-E[c]	3.28	1.70	2.36
11-Z[c]	2.43	1.92	2.21

[a] In CCl_4. [b] In CD_2Cl_2. [c] In C_6D_6.

Scheme 6



sterically large methyl groups[11] trans to one another are the most stable. For $Cp(CO)_2Re$(alkene) complexes, the alkene C═C double bond lies approximately parallel to the Cp ring[12] and one pair of alkene substituents is projected in the direction of the sterically large Cp ring. In X-ray structures of alkene complexes, the sterically large alkene substituents are directed away from the cyclopentadienyl rings.[13] Since rotation about the M−alkene bond is rapid, attention must be focused on the most stable rotamer of the alkene complex to assess how complexation might affect the *E/Z* equilibrium constant (Scheme 6). For both the *E* and *Z* isomers of enol trifluoroacetate and chloroalkene complexes, the rotamer with the sterically small hydrogen directed toward the Cp or Cp* ligand should be preferred. For the *Z* isomers, this requires that the sterically larger methyl group on the alkene carbon bearing the electronegative group be directed toward the more crowded environment of the Cp or Cp* ligand; for the *E* isomers,

(11) The *A* value for Me (1.74 kcal mol^{-1}) is larger than those of either the trifluoroacetate group (0.71 kcal mol^{-1} for acetate) or chlorine (0.52 kcal mol^{-1}). March, J. *Advanced Organic Chemistry*; Wiley: New York, 1992.

(12) To discuss the geometry of $Cp(CO)_2Re(\eta^2$-alkene) complexes, we focus attention on the angle between the plane defined by the Cp centroid, Re, and the alkene centroid and the plane defined by Re and the alkene bond. We will refer to two extreme geometries: a parallel geometry (90° interplanar angle) and a perpendicular geometry (0° interplanar angle). In the case of $Cp(CO)_2Re(\eta^2$-alkene), the alkene ligand is nearly parallel with an interplanar angle close to 90°.

(13) (a) Guerchais, V.; Lapinte, C.; Thépot, J.-Y.; Toupet, L. *Organometallics* **1988**, *7*, 604. (b) Einstein, F. W. B.; Jones, R. H.; Klahn-Oliva, A. H.; Sutton, D. *Organometallics* **1986**, *5*, 2476. (c) Chang, T. C. T.; Foxman, B. M.; Rosenblum, M.; Stockman, C. *J. Am. Chem. Soc.* **1981**, *103*, 7361. (d) Borgne, P. G. L.; Gentric, E.; Grandjean, D. *Acta Crystallogr.* **1975**, *B31*, 2824. (e) Turnbull, M. M.; Foxman, B. M.; Rosenblum, M. *Organometallics* **1988**, *7*, 200.

the sterically smaller trifluoroacetoxy or chloro group is directed toward the Cp or Cp* ligand.

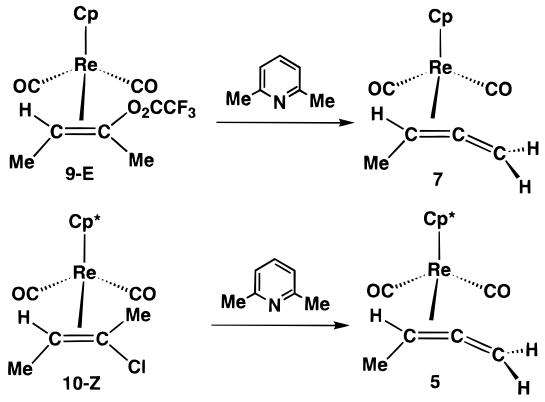
The consequence of this conformational analysis is that complexation is expected to selectively destabilize the *Z* isomers relative to the *E* isomers. The assignment of the major Cp Re enol trifluoroacetate isomer as **9-E** is consistent with the relative destabilization of the *Z* isomer upon complexation: the 29:71 *E:Z* equilibrium ratio of noncoordinated $MeCH{=}CMeO_2CCF_3$ is shifted away from the *Z* isomer to 80:20 **9-E**:**9-Z** for the Cp complexes. For the complexes with the sterically larger Cp* ligands, an even greater shift of the equilibrium constant toward the *E* isomer would be expected; the assignment of the major isomer as **8-E** is consistent with the shift in the equilibrium constant to 93:7 **8-E**:**8-Z**. Similarly, our *E*/*Z* assignments of rhenium chloroalkene complexes explain the progression of *E*:*Z* equilibrium ratios from 20:80 for noncoordinated MeCH=CMeCl to 71:29 for Cp complexes **11-E**:**11-Z** to 97:3 for **10-E**: **10-Z**.

For enol esters[9] and for chloroalkenes,[14] strong ^{1}H NMR chemical shift correlations have been observed that involve chemical shifts for vinyl hydrogens cis to trifluoroacetate or chlorine of frequency higher than for those trans to these electronegative groups (Table 1). Complexation of alkenes to rhenium results in large shifts to lower frequency for all vinyl hydrogens. Nevertheless, the differential effect of trifluoroacetoxy or chlorine substituents on the vinyl hydrogen chemical shifts should remain. In this context, it is important to note that the preferred conformation of both *Z* and *E* isomers of alkene complexes have the sterically small vinyl hydrogen directed toward the Cp or Cp* ligand so that no differential effect from metal complexation is expected. Consistent with our stereochemical assignments, the chemical shift of the vinyl hydrogen cis to trifluoroacetate in **8-E** is shifted 0.16 ppm to higher frequency than the vinyl hydrogen trans to trifluoroacetate in **8-Z**. Similar higher frequency shifts for vinyl hydrogens cis to electronegative groups are seen for **9-E** ($\Delta\delta = 0.63$), **10-E** ($\Delta\delta = 1.77$), and **11-E** ($\Delta\delta = 0.85$).

Formation of Allene Complexes by Base-Promoted Elimination from Enol Trifluoroacetate and Chloroalkene Complexes. The mixture of enol trifluoroacetate complexes **9-E** and **9-Z** was thermally stable in C_6D_6 for over 12 h at 75 °C, and none of allene complex **7** was detected by ^{1}H NMR spectroscopy. However, in the presence of 2,6-dimethylpyridine, a mixture of **9-E** and **9-Z** was converted to allene complex **7** at room temperature over 2 days (Scheme 7). Allene complex **7** was isolated in 54% yield following flash chromatography on silica gel.

The conversion of **9-E** and **9-Z** to allene complex **7** was monitored by ^{1}H NMR spectroscopy at 25 °C at different concentrations of 2,6-dimethylpyridine in C_6D_6 solution. The disappearance of the major isomer **9-E** in the presence of 0.7 M 2,6-dimethylpyridine followed pseudo-first-order kinetics with an observed rate constant of 3.5×10^{-5} s^{-1} ($t_{1/2} = 5.5$ h). The minor isomer **9-Z** reacted more slowly with an observed rate constant of 1.3×10^{-5} s^{-1} ($t_{1/2} = 14.3$ h). When the concentration of 2,6-dimethylpyridine was doubled to 1.4 M, only a slight rate increase was observed.[15] The observed rate constants for the conversion of **9-E** and **9-Z** to **7** in the presence of 1.4 M 2,6-dimethylpyridine were 4.1×10^{-5} s^{-1} ($t_{1/2} = 4.7$ h) and 1.6×10^{-5} s^{-1} ($t_{1/2} = 11.8$ h), respectively.

Scheme 7



The Cp* chloroalkene complex **10-Z** reacted with 2,6-dimethylpyridine in C_6D_6 at 25 °C to produce the allene complex **5**. The disappearance of **10-Z** in the presence of 1.4 M 2,6-dimethylpyridine followed pseudo-first-order kinetics with an observed rate constant of 4.0×10^{-5} s^{-1} ($t_{1/2} = 4.8$ h). The preferred synthetic route from alkyne complex **1** to allene complex **5** involves addition of 1 equiv of HCl in CH_2Cl_2 to **1** at room temperature, followed by addition of excess 2,6-dimethylpyridine.

Addition of Trifluoroacetic Acid to Allene Complexes. The addition of trifluoroacetic acid to Cp* allene complex **5** in CD_2Cl_2 at low temperature gave **8-Z** as the only observed isomer; this is the same kinetically preferred isomer as observed in the addition to alkyne complex **1**. The ^{1}H NMR spectrum at −70 °C showed a 42:58 ratio of allene complex **5** to enol trifluoroacetate complex **8-Z**. After the temperature was raised to −50 °C, complete conversion to **8-Z** was seen. While reaction of **5** with HBF_4 at −70 °C cleanly gave 1-metallacyclopropene complex **4-BF$_4$**, none of the 1-metallacyclopropene complex **4-CF$_3$CO$_2$** was detected in the reaction with CF_3CO_2H. When it was warmed to room temperature, **8-Z** was slowly converted over a week to a 95:5 equilibrium ratio of **8-E** to **8-Z**.

Similarly, the addition of trifluoroacetic acid to Cp allene complex **7** in C_6D_6 at room temperature gave at equilibrium a 77:23 ratio of **9-E** to **9-Z**. Careful investigation of the reaction of CF_3CO_2D with **7** provided insight into the mechanism of enol trifluoracetate formation.

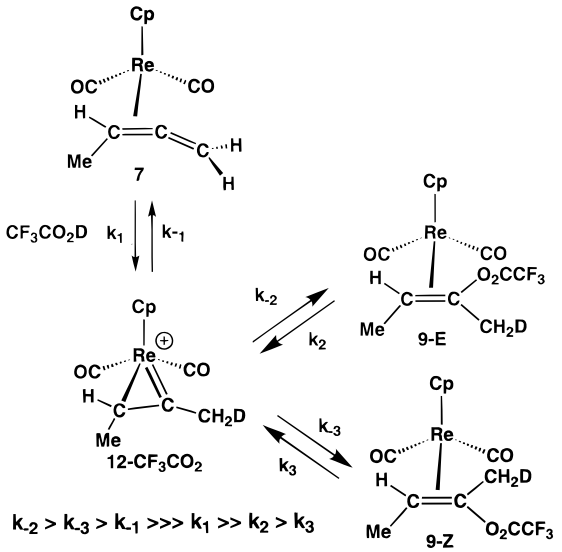
Treatment of a CD_2Cl_2 solution of allene complex **7** with 10 equiv of CF_3CO_2D at −78 °C led to the immediate and exclusive formation of the monodeuterated enol trifluoroacetate complex **9-E** (Scheme 8). The rapid rate of this addition requires $\Delta G^{\ddagger} \leq 14$ kcal mol^{-1}.[16,17] ^{1}H NMR spectroscopy of **9-E** at −73 °C

(14) Abudarham, J. P.; Meyet, J.; Smadja, W.; Levisalles, J. *Org. Magn. Reson.* **1977**, *10*, 192.

(15) The small rate increase seen at higher 2,6-dimethylpyridine concentration is probably within experimental error but may be due to a slight increase in solvent polarity.

(16) Even if the sample was warmed to −60 °C for seconds during the transfer to the precooled NMR spectrometer, a half-life of 30 s would have allowed easy detection of unreacted starting material. This requires a second-order rate constant of greater than 0.38 M^{-1} s^{-1} for the ~0.6 M CF_3CO_2H solution.

Scheme 8



showed one deuterium in the methyl group (δ 2.16, 2.04 H) geminal to trifluoroacetate, consistent with D^+ addition to the unbound allene carbon. The presence of only a single deuterium indicates that **9-E** is not in equilibrium with **7** at −73 °C.

When the temperature was raised to −60 °C, slow isomerization ($t_{1/2}$ = 46 min) of **9-E** occurred to produce a 80:20 equilibrium mixture of **9-E** and **9-Z**. This rate of equilibration in the presence of 0.5 M trifluoroacetic acid corresponds to $\Delta G^{\ddagger} \cong 16$ kcal mol^{-1}.[17] During this equilibration at −60 °C, no further deuterium incorporation into the enol trifluoroacetate complexes was observed by ^{1}H NMR spectroscopy. This indicated that **9-E** and **9-Z** were not isomerizing by way of allene complex **7**, which would have led to incorporation of additional deuterium. This labeling result provides strong evidence that isomerization occurs by ionization of trifluoroacetate to form the 1-metallacyclopropene $C_5H_5(CO)_2Re(\eta^2$-$CMeCHMe)^+CF_3CO_2^-$ (**12-CF_3CO_2**), which then readds trifluoroacetate to either face of the 1-metallacyclopropene.

Exchange of deuterium into the methyl groups geminal to the trifluoroacetate groups of **9-E** and **9-Z** was observed upon warming to −20 °C. ^{1}H NMR spectroscopy showed that the integrals for the methyl resonances of **9-E** (δ 2.16) and **9-Z** (δ 2.17) slowly diminished over a period of hours ($t_{1/2}$ = 80 min for conversion of monodeuterated material) as deuterium was incorporated into the methyl group. This rate of deuterium exchange in the presence of 0.5 M trifluoroacetic acid corresponds to $\Delta G^{\ddagger} \cong 18$ kcal mol^{-1}.[17] This pattern of deuterium incorporation requires reversible formation of allene complex **7** via deprotonation of 1-metallacyclopropene **12-CF_3CO_2**.

After 5 days at −20 °C, the solution of **9-E** and **9-Z** containing CF_3CO_2D was warmed to room temperature, evaporated to dryness, and analyzed by ^{1}H NMR spectroscopy in C_6D_6. No incorporation of deuterium into either the vinyl hydrogen or the methyl group of the MeHC═ unit was seen. Reversible loss of H^+ from 1-metallacyclopropene **12-CF_3CO_2** to form alkyne complex **6** can be excluded, since this would have led to incorporation of vinyl deuterium. Similarly, degenerate 1,2-hydride migration within **12-CF_3CO_2** can be excluded, since this would have led to equal incorporation of deuterium into both methyl groups.

The rate of deuterium incorporation into **9-E** and **9-Z** was much faster than the base-promoted formation of allene complex **7** from **9-E** and **9-Z**, which was independent of the concentration of 2,6-dimethylpyridine. This indicates that trifluoroacetic acid accelerates the reversible formation of **7** from **9-E** and **9-Z**.

Discussion

Complexation Reverses Relative Stabilities of Alkynes and Allenes. Free 2-butyne is substantially more stable than free 1,2-butadiene (difference in heats of formation 7.3 kcal mol^{-1}).[5,6] The isomerization of alkyne complexes **1** and **6** to the allene complexes **5** and **7** indicates a reversal of the relative stabilities of alkynes and allenes upon complexation. The complete (>99%) conversion of alkyne complex **1** to the allene complex **5** indicates that **5** is >3 kcal mol^{-1} more stable than **1**. This represents a net >10 kcal mol^{-1} change in stability favoring the allene upon coordination of the free ligands to rhenium. This destabilization results from interaction of an 18e metal center with the filled second π-orbital of a two-electron-donor alkyne ligand.[18] In the case of an allene complexed to an 18e metal center, the second π-orbital of the allene does not interact with filled orbitals at the 18e rhenium center.

Conversion of an alkyne complex (not directly observed) to an allene complex is probably also involved in the reaction of PhC≡CCH_3 with *trans*-$[ReCl(N_2)(Ph_2PCH_2CH_2PPh_2)_2]$, which led to the formation of the rhenium allene complex $[ReCl(\eta^2$-$PhCH{=}C{=}CH_2)(Ph_2PCH_2CH_2PPh_2)_2]$.[19] As mentioned in the Introduction, Werner observed isomerization of a rhodium alkyne complex to a rhodium allene complex.[3] The isomerization of manganese alkyne complexes to allene complexes has also been reported. Treatment of the alkyne complex $(C_5H_4Me)(CO)_2Mn(\eta^2$-$MeCO_2C{\equiv}CMe)$ with basic aluminum oxide led to the formation of the allene complex $(C_5H_4Me)(CO)_2Mn(\eta^2$-1,2-$MeCO_2C{=}C{=}CH_2)$.[20] The cyclooctyne complex $C_5H_5(CO)_2Mn(\eta^2$-cyclooctyne) isomerized on basic silica or acidic alumina to the cyclic allene complex $C_5H_5(CO)_2Mn(\eta^2$-1,2-cyclooctadiene).[21]

Mechanism of Isomerization of Alkyne Complexes to Allene Complexes. Much of what we know about the chemistry of alkyne complexes in the presence of acids is summarized in Scheme 9. The essential core of the mechanism of isomerization of alkyne complexes to allene complexes involves protonation of an alkyne carbon to give a 1-metallacyclopropene intermediate followed by loss of a proton from the methyl attached to the carbene-like carbon of the 1-metallacyclopropene.

(17) The free energy of activation for reactions run at a single temperature was calculated using the formula: $\Delta G^{\ddagger} = -RT\ln(k) + \ln(\kappa/h) + \ln(T)$, where k is the rate constant, κ is the Boltzmann constant, and h is Planck's constant.

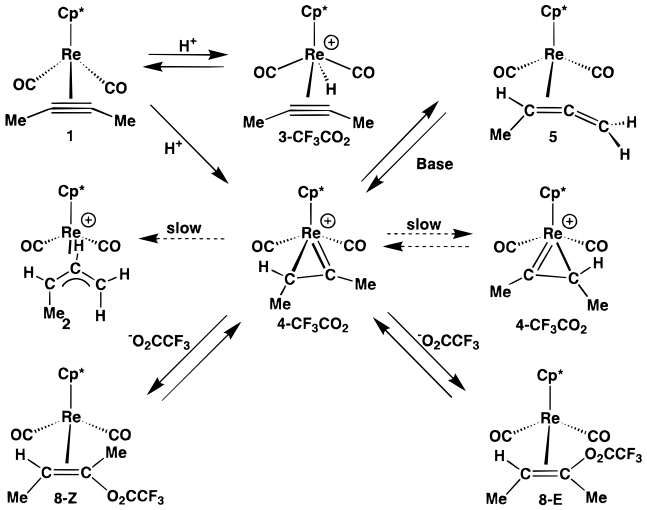
(18) Templeton, J. L. *Adv. Organomet. Chem.* **1989**, *29*, 1.

(19) Hughes, D. L.; Pombeiro, A. J. L.; Pickett, C. J.; Richards, R. L. *J. Chem. Soc., Chem. Commun.* **1984**, 992.

(20) Franck-Neumann, M.; Brion, F. *Angew. Chem., Int. Ed. Engl.* **1979**, *18*, 688.

(21) Coughlan, S. M.; Yang, G. K. *J. Organomet. Chem.* **1993**, *450*, 151.

Scheme 9



Several complex equilibria are also associated with the isomerization.

Trifluoroacetic acid rapidly protonated Cp* alkyne complex **1** at rhenium to give the trans rhenium hydride complex **3-CF_3CO_2**. In the case of protonation of **1** by HBF_4, we found that protonation was reversible and that hydride exchange of **3-BF_4** with added CF_3CO_2D occurred more rapidly than isomerization to the observable 1-metallacyclopropene **4-BF_4**. The exchange of CF_3CO_2H with **3-CF_3CO_2-D** occurred even more rapidly than exchange into tetrafluoroborate salt **3-BF_4**.

It is interesting that the conversion of **3-CF_3CO_2** to the enol trifluoroacetate **8-Z**, presumably via 1-metallacyclopropene **4-CF_3CO_2**, occurred much faster than the conversion of **3-BF_4** to **4-BF_4**. In the absence of added HBF_4, the counterion of hydride complex **3-CF_3CO_2** is the more basic trifluoroacetate ion, which can deprotonate **3-CF_3CO_2** more rapidly and thus afford more opportunity for reprotonation at the alkyne carbon of **1**. In other words, the rate of conversion of **3** to **4** is the product of the rate of deprotonation of hydride complex **3** times the partitioning between protonation of **1** at carbon vs rhenium. The slower conversion of **3-BF_4** to **4-BF_4** compared with the conversion of **3-CF_3CO_2** to **8-Z** is attributed to the slower rate of deprotonation of **4-BF_4**. In agreement with this rationale, H/D exchange occurred more rapidly for **3-CF_3CO_2** than for **3-BF_4**.

The enol trifluoroacetate complex **8-Z** can be considered the resting state in the CF_3CO_2H-catalyzed conversion of alkyne complex **1** to allene complex **5**. When the isomerization of **1** to **5** was carried out in the presence of 0.1 equiv of CF_3CO_2H, **8-Z** was detected in the reaction mixture. In the presence of more than 1 equiv of CF_3CO_2H, **1** was stoichiometrically converted to **8-Z**. The kinetically formed enol trifluoroacetate **8-Z** isomerized to the more stable isomer **8-E** at room temperature. This isomerization is proposed to proceed by dissociation of trifluoroacetate to give 1-metallacyclopropene **4-CF_3CO_2** followed by readdition of trifluoroacetate to the opposite face. It is important to note that 1-metallacyclopropene **4-CF_3CO_2** has never been observed directly, presumably because the trifluoroacetate counterion adds too rapidly to give enol trifluoroacetate **8-Z**. However, 1-metallacyclopropene **4-BF_4** has been seen in the presence of the less nucleophilic trifluoroacetic acid.

Complexation to rhenium greatly accelerates the addition of trifluoroacetic acid to alkynes. The addition of neat CF_3CO_2H to internal alkynes has a half-life of 20 min at 60 °C,[22] while the addition of 0.03 M CF_3CO_2H to Cp complex **5** occurred rapidly at −78 °C and the addition of 0.03 M CF_3CO_2H to Cp* complex **1** occurred within minutes at −40 °C. This rate acceleration is a reflection of the great stabilization of a vinyl cation intermediate upon complexation to a metal center to give a 1-metallacyclopropene complex.

A similar addition of trifluoroacetic acid to the manganese acetylene complex $C_5Me_5(CO)_2Mn(\eta^2\text{-}HC{\equiv}CH)$ to give the enol trifluoroacetate complex $C_5Me_5(CO)_2Mn[\eta^2\text{-}H_2C{=}CHO_2CCF_3]$ was seen by Alt, although no intermediates were detected.[23]

Two isomerizations of the tetrafluoroborate salt of 1-metallacyclopropene **4-BF_4**, a degenerate 1,2-hydride shift and a hydride shift to generate η^3-allyl complex **2**, are not observed for the trifluoroacetate salt **4-CF_3CO_2**. The greater nucleophilicity of the trifluoroacetate counterion leads to addition of trifluoroacetate and formation of enol trifluoroacetate complexes **8-Z** and **8-E**. Effectively, rapid reaction with trifluoracetate prevents these isomerizations.

In the presence of the added base 2,6-dimethylpyridine, the Cp enol trifluoroacetate complexes **9-E** and **9-Z** were converted to allene complex **7**. Since the rate of conversion was independent of base concentration, the rate-determining step is proposed to be ionization of the trifluoroacetate to form a 1-metallacyclopropene intermediate. We cannot determine whether the 1-metallacyclopropene is directly deprotonated by 2,6-dimethylpyridine or whether it is deprotonated by trifluoroacetate to give trifluoracetic acid which then is deprotonated by 2,6-dimethylpyridine.

The reaction of alkene complexes **9-E** and **9-Z** with base to form allene complex **7** was much slower ($\Delta\Delta G^{\ddagger} \cong 8$ kcal mol^{-1}) than equilibration of **9-E** and **9-Z** in the presence of excess trifluoroacetic acid. This was initially surprising, since both processes were envisioned to proceed via the same 1-metallacyclopropene intermediate **12-CF_3CO_2**. Our explanation of the rate difference centers on the different reaction conditions employed. In the elimination reaction, excess base is present, while excess trifluoroacetic acid is present during equilibration of the enol trifluoroacetates. We suggest that trifluoroacetic acid promotes the elimination of trifluoroacetate from the enol trifluoroacetates by hydrogen bonding to provide the better leaving group ($CF_3CO_2H{\cdots}O_2CCF_3^-$).

The interconversion of the Cp enol trifluoroacetates **9-E** and **9-Z** with allene complex **7** was demonstrated by exchange experiments with CF_3CO_2D. Deuterium was incorporated only into the methyl groups geminal to the trifluoroacetate group. This is readily explained by reversible ionization of trifluoroacetate to give 1-metallacyclopropene **4-CF_3CO_2** followed by reversible deprotonation to give allene complex **7**.

Stereochemistry of Nucleophilic Attack on 1-Metallacyclopropenes. Kinetic addition of trifluoroace-

(22) Peterson, P. E.; Duddey, J. E. *J. Am. Chem. Soc.* **1966**, *88*, 4990.
(23) Alt, H. G.; Engelhardt, H. E. *J. Organomet. Chem.* **1988**, *346*, 211.

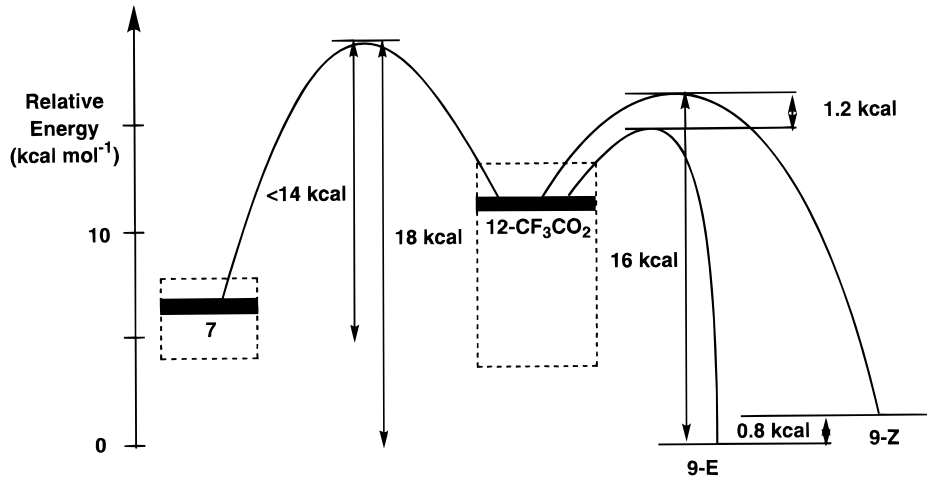
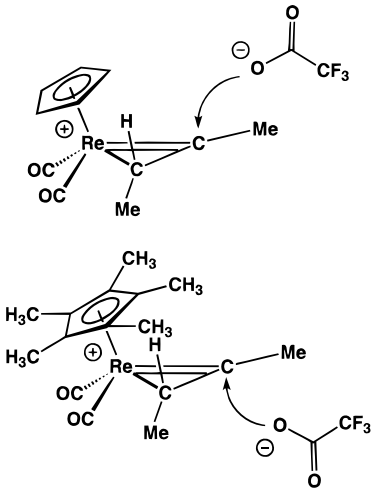


Figure 1. Free energy diagram for the conversion of allene complex **7** to enol trifluoroacetate complexes **9-E** and **9-Z** *via* 1-metallacyclopropene complex **12-CF_3CO_2.**

Scheme 10



tate to the Cp 1-metallacyclopropene **12-CF_3CO_2** occurs preferentially from the face nearest the Cp ligand to give **9-E** as the only detected isomer (Scheme 10). Upon equilibration, a 80:20 ratio of **9-E** to **9-Z** is obtained. In the case of Cp* alkyne complex **1**, kinetic addition of trifluoroacetic acid leads exclusively to **8-Z**, the product of attack on 1-metallacyclopropene intermediate **4-CF_3CO_2** from the face opposite the sterically large Cp* group, even though this forces a methyl group to move toward the Cp* group. Since Me is sterically larger than a trifluoroacetate group, equilibration leads to a 93:7 mixture of **8-E** and **8-Z**.

Relative Rates of Transformations of 1-Metallacyclopropenes. The reaction of Cp allene complex **7** with CF_3CO_2D was followed from −78 °C to room temperature and provided insight into the relative rates of transformations of the 1-metallacylopropene complex **12-CF_3CO_2** (Figure 1). The exclusive formation of enol trifluoracetate **9-E** was too fast to measure at −78 °C; this requires $\Delta G^{\ddagger} \leq 14$ kcal mol^{-1} for conversion of **7** to **12-CF_3CO_2** and $\Delta\Delta G^{\ddagger} \geq 1.2$ kcal mol^{-1} for selective conversion of **12-CF_3CO_2** to **9-E** versus **9-Z**. The equilibration of **9-E** and **9-Z** occurred at higher temperature to give a 80:20 ratio of **9-E** to **9-Z**; this establishes $\Delta G° = 0.8$ kcal mol^{-1} and $\Delta G^{\ddagger} \cong 16$ kcal mol^{-1} for the equilibration. The incorporation of deuterium into the methyl groups of **9-E** and **9-Z**, which requires reversible formation of allene complex **7**, occurred at still higher temperature with $\Delta G^{\ddagger} \cong 18$ kcal mol^{-1}. Two other previously observed transformations of the 1-metallacyclopropenes, degenerate 1,2-hydride migration and rearrangement to an η^3-allyl complex, were too slow to observe under these conditions. The energies of allene complex **7** and the trifluoroacetate salt of the 1-metallacyclopropene complex **12-CF_3CO_2** relative to one another and to **9-E** and **9-Z** are not precisely known.

Summary. We have begun to uncover a growing body of chemistry involving 1-metallacyclopropene intermediates. We have found three ways to generate 1-metallacyclopropenes: (1) addition of electrophiles to alkyne complexes, (2) addition of electrophiles to allene complexes, and (3) ionization of complexed haloalkenes or enol trifluoroacetates. Important reactions of 1-metallacyclopropenes include, in order of decreasing relative rates: (1) addition of anions to give haloalkene or enol trifluoroacetate complexes, (2) deprotonation to give complexed allenes, (3) degenerate 1,2-hydride migrations, (4) hydride migrations to give η^3-allyl complexes,[2,24] and (5) deprotonation to give complexed alkynes. The electron-deficient nature of the carbene-like carbon of 1-metallacyclopropenes explains their propensity to add nucleophiles. The development of new carbon−carbon bond-forming reactions from the addition of carbon nucleophiles to 1-metallacyclopropene complexes is under investigation.

Experimental Section

General Methods. All air-sensitive materials were manipulated under dry nitrogen in a glovebox or by standard high-vacuum and Schlenk techniques. Benzene and benzene-d_6 were distilled from purple solutions of sodium and benzophenone. CH_2Cl_2 and CD_2Cl_2 were distilled from calcium hydride. Trifluoroacetic acid was distilled from P_2O_5. ^{1}H NMR spectra were obtained on a Bruker WP200, WP270, AC250, AC300, or AM500 spectrometer. $^{13}C\{^1H\}$ NMR spectra were obtained on a Bruker AC300 (75 MHz) or AM500 (126 MHz) spectrometer. Infrared spectra were obtained on a ATI Mattson Genesis spectrometer. Mass spectra of solid samples were obtained on a Kratos MS-80 spectrometer.

[*trans*-$C_5Me_5(CO)_2ReH(\eta^2$-MeC≡CMe)][CF_3CO_2] (3-CF_3CO_2). Addition of CF_3CO_2H (4.2 μL, 54 μmol) by syringe to a

(24) Casey, C. P.; Selmeczy, A. D.; Nash, J. R.; Yi, C. S.; Powell, D. R.; Hayashi, R. K. *J. Am. Chem. Soc.* **1996**, *118*, 6698.

yellow solution of $C_5Me_5(CO)_2Re(\eta^2$-MeC≡CMe) (**1**)[25] (7.7 mg, 18 μmol) in 0.3 mL of CD_2Cl_2 at −78 °C produced a dark solution of **3-CF_3CO_2**. ^{1}H NMR (500 MHz, CD_2Cl_2, −60 °C): δ 2.56 (s, MeC≡), 2.11 (s, Cp*), −5.52 (s, ReH). $^{13}C\{^1H\}$ NMR (126 MHz, CD_2Cl_2, −60 °C): δ 184.9 (CO), 159.3 (CF_3CO_2, $^2J_{CF}$ = 42.7 Hz), 114.6 (CF_3CO_2, $^1J_{CF}$ = 283.8 Hz), 105.3 (C_5Me_5), 65.3 (Me*C*≡), 10.4 (C_5Me_5), 9.8 (*Me*C≡).

$C_5Me_5(CO)_2Re(\eta^2$-MeHC=CMeO_2CCF_3) (8-Z and 8-E). Addition of 1 equiv of CF_3CO_2H (1.3 μL, 17 μmol) to a yellow CD_2Cl_2 solution of **1** (7.3 mg, 17 μmol) containing 5 μL of $CHCl_3$ as an internal NMR standard initially produced $C_5Me_5(CO)_2Re[\eta^2$-(*Z*)-MeHC=CMeO_2CCF_3] (**8-Z**). **8-Z** slowly isomerized to the *E* isomer $C_5Me_5(CO)_2Re[\eta^2$-(*E*)-MeHC=CMeO_2CCF_3] (**8-E**) over 5 days at room temperature. The equilibrium ratio of **8-E** to **8-Z** was 93:7, and the NMR yield was 82%.

8-E. ^{1}H NMR (500 MHz, CD_2Cl_2): δ 2.42 (q, ^3J = 6.5 Hz, HC=), 2.32 (s, *Me*CF_3CO_2C=), 1.85 (s, Cp*), 1.36 (d, ^3J = 6.5 Hz, *Me*HC=). $^{13}C\{^1H\}$ NMR (126 MHz, CD_2Cl_2): δ 200.2 (CO), 163.8 (q, $^2J_{CF}$ = 36 Hz, CF_3CO_2), 113.8 (q, $^1J_{CF}$ = 290 Hz, CF_3), 101.1 (C_5Me_5), 73.1 (CF_3CO_2C=), 30.1 (MeH*C*=), 12.1 (Me), 10.1 (Me), 8.9 (C_5Me_5).

8-Z. ^{1}H NMR (500 MHz, CD_2Cl_2): δ 2.26 (q, ^3J = 6.5 Hz, HC=), 2.17 (s, *Me*CF_3CO_2C=), 1.96 (s, Cp*), 1.62 (d, ^3J = 6.5 Hz, *Me*HC=). $^{13}C\{^1H\}$ NMR (126 MHz, CD_2Cl_2): δ 208.2 (CO), 202.6 (CO), 156.7 (q, $^2J_{CF}$ = 41 Hz, CF_3CO_2), 114.0 (q, $^1J_{CF}$ = 277 Hz, CF_3), 99.0 (C_5Me_5), 90.3 (CF_3CO_2C=), 30.1 (MeH*C*=), 23.0 (Me), 19.1 (Me), 9.9 (C_5Me_5).

$C_5H_5(CO)_2Re(\eta^2$-MeHC=CMeO_2CCF_3) (9-E and 9-Z). Addition of 1 equiv of CF_3CO_2H (16 μmol) to a frozen yellow C_6D_6 solution of $C_5H_5(CO)_2Re(\eta^2$-MeC≡CMe) (**6**;[26] 5.7 mg, 16 μmol) containing $CHCl_3$ as an internal NMR standard produced upon thawing a 77:23 mixture of $C_5H_5(CO)_2Re[\eta^2$-(*E*)-MeHC=CMeO_2CCF_3] (**9-E**) and $C_5H_5(CO)_2Re[\eta^2$-(*Z*)-MeHC=CMeO_2CCF_3] (**9-Z**) (85% yield by ^{1}H NMR). IR (C_6H_6): 1983 (s), 1908 (s), 1778 (w) cm^{-1}.

9-E. ^{1}H NMR (500 MHz, C_6D_6): δ 4.43 (s, C_5H_5), 2.87 (q, ^3J = 11.2 Hz, HC=), 2.08 (s, *Me*CF_3CO_2C=), 1.62 (d, ^3J = 11.2 Hz, *Me*HC=). $^{13}C\{^1H\}$ NMR (126 MHz, C_6D_6): δ 203.7 (CO), 199.3 (CO), 159.2 (q, $^2J_{CF}$ = 42 Hz, CF_3CO_2), 115.4 (q, $^1J_{CF}$ = 282 Hz, CF_3), 89.8 (CF_3CO_2C=), 87.6 (Cp), 29.7 (MeH*C*=), 22.7 (Me), 19.9 (Me).

9-Z. ^{1}H NMR (500 MHz, C_6D_6): δ 4.41 (s, C_5H_5), 2.24 (q, ^3J = 11.2 Hz, HC=), 1.90 (s, *Me*CF_3CO_2C=), 1.72 (d, ^3J = 11.2 Hz, *Me*HC=). $^{13}C\{^1H\}$ NMR (126 MHz, C_6D_6): δ 201.2 (CO), 200.9 (CO), 156.2 (q, $^2J_{CF}$ = 42 Hz, CF_3CO_2), 115.6 (q, $^1J_{CF}$ = 282 Hz, CF_3), 87.7 (Cp), 84.3 (CF_3CO_2C=), 30.1 (MeH*C*=), 24.4 (Me), 19.7 (Me).

$C_5H_5(CO)_2Re(\eta^2$-2,3-MeHC=C=CH_2) (7). Addition of 1 equiv of CF_3CO_2H (19 μmol) to a C_6D_6 solution of **6** (7 mg, 19 μmol) produced a mixture of $C_5H_5(CO)_2Re[\eta^2$-(*E*)-MeHC=CMeO_2-CCF_3] (**9-E**) and $C_5H_5(CO)_2Re[\eta^2$-(*Z*)-MeHC=CMeO_2CCF_3] (**9-Z**), to which 10 equiv of 2,6-dimethylpyridine (190 μmol) was added to form $C_5H_5(CO)_2Re(\eta^2$-MeHC=C=CH_2) (**7**) over a period of 2 days. **7** was isolated by flash chromatography on silica gel to yield 3.8 mg (54% yield) of a yellow solid. ^{1}H NMR (500 MHz, C_6D_6): δ 6.52 (d, ^4J = 2.9 Hz, *H*HC=), 5.48 (d, ^4J = 3.0 Hz, H*H*C=), 4.44 (s, Cp), 2.54 (qdd, ^3J = 6.1 Hz, ^4J = 3.0 Hz, ^4J = 2.9 Hz, *H*MeC=), 1.70 (d, ^3J = 6.1 Hz, Me). $^{13}C\{^1H\}$ NMR (126 MHz, C_6D_6): δ 203.0 (CO), 202.3 (CO), 154.8 (C=*C*=C), 105.2 (C=*C*H_2), 87.1 (Cp), 30.2 (Me), 5.6 (MeH*C*=). IR (pentane): 1989 (s), 1923 (s) cm^{-1}. HRMS (EI) calcd (found) for $C_{11}H_{11}O_2Re$: *m*/*z* 362.0318 (362.0287).

$C_5Me_5(CO)_2Re(\eta^2$-MeHC=CMeCl) (10-Z and 10-E). Addition of excess HCl gas (660 μmol) to a yellow CH_2Cl_2 solution of **1** (30.6 mg, 71 μmol) led to immediate formation of $C_5Me_5(CO)_2Re[\eta^2$-(*Z*)-MeHC=CMeCl] (**10-Z**). Evaporation of solvent gave **10-Z** (21.3 mg, 64% yield) as a tan solid. **10-Z** in CD_2Cl_2 solution equilibrated to a 97:3 mixture of $C_5Me_5(CO)_2$-$Re[\eta^2$-(*E*)-MeHC=CMeCl] (**10-E**) and **10-Z** over 4 days (88% NMR yield).

10-E. ^{1}H NMR (300 MHz, CD_2Cl_2): δ 4.27 (qq, ^3J = 7.1 Hz, ^4J = 1.3 Hz, *H*MeC=), 2.31 (d, ^4J = 1.3 Hz, *Me*ClC=), 1.88 (s, C_5Me_5), 1.50 (d, ^3J = 7.1 Hz, *Me*HC=). $^{13}C\{^1H\}$ NMR (126 MHz, CD_2Cl_2): δ 208.2 (CO), 199.7 (CO), 100.4 (C_5Me_5), 75.2 (Cl*C*=), 35.1 (HMe*C*=), 29.9 (Me), 21.6 (Me), 9.3 (C_5Me_5).

10-Z. ^{1}H NMR (300 MHz, CD_2Cl_2): δ 2.50 (q, ^3J = 7.2 Hz, *H*MeC=), 2.28 (s, *Me*ClC=), 2.00 (s, C_5Me_5), 1.76 (d, ^3J = 7.2 Hz, *Me*HC=). $^{13}C\{^1H\}$ NMR (126 MHz, CD_2Cl_2): δ 208.7 (CO), 203.2 (CO), 100.2 (C_5Me_5), 75.3 (Cl*C*=), 38.5 (MeH*C*=), 31.4 (Me), 19.9 (Me), 10.6 (C_5Me_5). IR (pentane): 1964 (s), 1879 (s) cm^{-1}. HRMS (EI) calcd (found) for $C_{16}H_{22}O_2ClRe$: *m*/*z* 468.0858 (468.0854).

$C_5H_5(CO)_2Re(\eta^2$-MeHC=CMeCl) (11-E and 11-Z). Addition of 1 equiv of HCl gas (21 μmol) to a yellow CD_2Cl_2 solution of **6** (7.6 mg, 21 μmol) at −70 °C produced a tan solution of $C_5H_5(CO)_2Re[\eta^2$-(*E*)-MeHC=CMeCl] (**11-E**). ^{1}H NMR spectroscopy at −70 °C indicated that **11-E** was the only Cp compound in solution. When the mixture was warmed to room temperature, a 71:29 equilibrium ratio of **11-E** to **11-Z** (93% yield) was observed by NMR spectroscopy.

11-E. ^{1}H NMR (300 MHz, C_6D_6): δ 4.55 (s, Cp), 3.28 (q, ^3J = 6.1 Hz, HC=), 2.36 (s, *Me*ClC=), 1.70 (d, ^3J = 6.1 Hz, *Me*HC=). $^{13}C\{^1H\}$ NMR (126 MHz, C_6D_6): δ 205.3 (CO), 200.4 (CO), 88.9 (Cp), 86.8 (Cl*C*=), 38.5 (MeH*C*=), 30.5 (Me), 20.7 (Me).

11-Z. ^{1}H NMR (300 MHz, C_6D_6): δ 4.43 (s, Cp), 2.43 (q, ^3J = 6.1 Hz, HC=), 2.21 (s, *Me*ClC=), 1.92 (d, ^3J = 6.1 Hz, *Me*HC=). $^{13}C\{^1H\}$ NMR (126 MHz, C_6D_6): δ 203.3 (CO), 201.2 (CO), 88.1 (Cp), 84.2 (Cl*C*=), 35.0 (MeH*C*=), 31.2 (Me), 23.1 (Me). IR (pentane): 1988 (s), 1915 (s) cm^{-1}. HRMS (EI) calcd (found) for $C_{11}H_{12}O_2ClRe$: *m*/*z* 398.0056 (398.0085).

$C_5Me_5(CO)_2Re(\eta^2$-2,3-MeHC=C=CH_2) (5). HCl gas (7 equiv) was added to a yellow CH_2Cl_2 solution of **1** (57.8 mg, 130 μmol) at 25 °C to give a light tan solution of $C_5Me_5(CO)_2$-$Re[\eta^2$-(*Z*)-MeHC=CMeCl] (**10-Z**). Excess HCl and solvent were evaporated under high vacuum. The residue was dissolved in CH_2Cl_2, and excess 2,6-dimethylpyridine (10 equiv) was added to give a yellow solution of $C_5Me_5(CO)_2Re(\eta^2$-2,3-MeHC=C=CH_2) (**5**). The yellow solution was filtered through silica gel, and solvent was evaporated to give **5** (58.4 mg, 100%) as a yellow powder. ^{1}H NMR (300 MHz, CD_2Cl_2): δ 6.25 (d, ^4J = 3.0 Hz, H*H*C=), 5.16 (d, ^4J = 3.0 Hz, *H*HC=), 1.95 (s, Cp*), 1.71 (qt, ^3J = 5.9 Hz, ^4J = 3.0 Hz, Me*H*C=), 1.62 (d, ^3J = 5.9 Hz, *Me*HC=). $^{13}C\{^1H\}$ NMR (126 MHz, CD_2Cl_2): δ 207.6 (CO), 206.0 (CO), 164.4 (C=*C*=C), 101.6 (C_5Me_5), 99.3 (H_2C=), 30.1 (*Me*HC=), 10.4 (MeH*C*=), 10.1 (C_5Me_5). IR (CH_2Cl_2): 1962 (s), 1886 (vs) cm^{-1}. HRMS (EI) calcd (found) for $C_{16}H_{21}O_2Re$: *m*/*z* 432.1101 (432.1097).

NMR Kinetics of Allene Complex Formation. The rate of conversion of **9-E** and **9-Z** to **7** was determined by monitoring the methyl doublet resonances of **9-E** and **9-Z** (δ 1.62 and δ 1.72) and **7** (δ 1.70) in the ^{1}H NMR spectra. The disappearance of **9-E** and **9-Z** (19 μmol) in a C_6D_6 solution (0.3 mL) with 1.4 M 2,6-dimethylpyridine was measured versus an internal standard of *p*-$(Me_3Si)_2C_6H_4$ (15 μmol) at 25 °C over a period of 30 h. The reaction tube was immersed in a 25 °C oil bath and periodically removed to obtain ^{1}H NMR spectra. A plot of ln [**9-E**] vs time was linear (k_{obs} = 4.1 × 10^{-5} s^{-1}, $t_{1/2}$ = 4.7 h). A plot of ln [**9-Z**] vs time was also linear (k_{obs} = 1.6 × 10^{-5} s^{-1}, $t_{1/2}$ = 11.8 h). At a lower concentration of 2,6-dimethylpyridine (0.7 M), the rates were only slightly decreased: **9-E**, k_{obs}

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$= 3.5 \times 10^{-5}$ s^{-1} and $t_{1/2} = 5.5$ h; **9-Z**, $k_{obs} = 1.3 \times 10^{-5}$ s^{-1} and $t_{1/2} = 14.3$ h.

The rate of conversion of **10-Z** to **5** was determined by monitoring the Cp* resonances of **10-Z** (δ 1.66) and **5** (δ 1.59) in the ^{1}H NMR spectra. The disappearance of **10-Z** (3 μmol) in a C_6D_6 solution (0.3 mL) containing 1.4 M 2,6-dimethylpyridine was measured versus an internal standard of *p*-$(Me_3Si)_2C_6H_4$ at 25 °C over a period of 12 h in a ^{1}H NMR spectrometer. A plot of ln [**10-Z**] vs time was linear ($k_{obs} = 4.0 \times 10^{-5}$ s^{-1}, $t_{1/2} = 4.8$ h).

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