Protonation of Rhenium Alkyne Complexes Produces η^3-Allyl Rhenium Complexes via Observable 1-Metallacyclopropene Intermediates

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Abstract: Protonation of the rhenium η^2-alkyne complex $C_5Me_5(CO)_2Re(\eta^2$-MeC≡CMe) (**4**) with HBF_4 at room temperature produced the η^3-allyl complex $C_5Me_5(CO)_2Re(\eta^3$-*exo,anti*-MeHC−CH−$CH_2)^+BF_4^-$ (**5**). The protonation of **4** at −78 °C occurred at rhenium to give the rhenium alkyne hydride complex $C_5Me_5(CO)_2$-$ReH(\eta^2$-MeC≡CMe)$^+BF_4^-$ (**6**). At −16 °C, net proton migration from rhenium to the alkyne ligand of **6** occurred to produce the 1-metallacyclopropene complex $C_5Me_5(CO)_2Re(\eta^2$-CMeCHMe)$^+BF_4^-$ (**7**), which then rearranged to form the η^3-allyl complex **5**. The degenerate rearrangement of **7** by hydride migration between the two metallacyclopropene carbons was demonstrated by deuterium labeling. Protonation of the rhenium η^2-alkyne complex $C_5Me_5(CO)_2Re(\eta^2$-PhC≡CPh) (**10**) with HBF_4 at −78 °C initially produced the rhenium alkyne hydride complex $C_5Me_5(CO)_2ReH(\eta^2$-PhC≡CPh)$^+BF_4^-$ (**11**), which was observed spectroscopically. Upon warming to room temperature, **11** was converted to the stable 1-metallacyclopropene complex $C_5Me_5(CO)_2$-$Re(\eta^2$-CPhCHPh)$^+BF_4^-$ (**12**), which was characterized by X-ray crystallography. Hybrid density functional theory calculations and natural bond orbital analysis were performed on the 1-metallacyclopropene cation $[C_5H_5(CO)_2Re(\eta^2$-MeCCHMe)]$^+$ to compare η^2-vinyl vs 1-metallacyclopropene formulations.

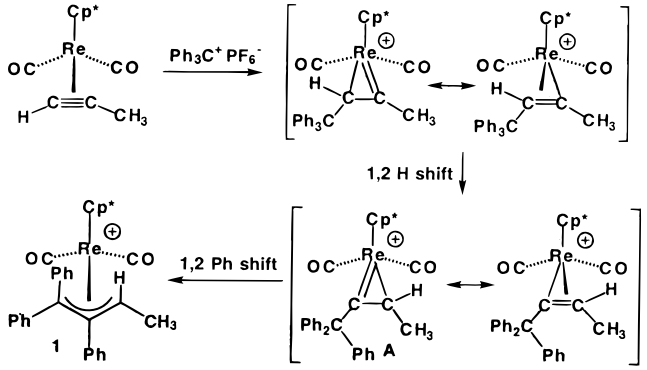
Introduction

We recently discovered two unusual reactions of rhenium alkyne complexes that led to the formation of cationic η^3-allyl rhenium complexes. In both cases, we proposed 1-metallacyclopropene intermediates (also known as η^2-vinyl complexes) to explain these complex transformations. Attempted hydride abstraction from $C_5Me_5(CO)_2Re(\eta^2$-HC≡CCH_3) with $Ph_3C^+PF_6^-$ led instead to formation of the η^3-allyl complex $C_5Me_5(CO)_2$-$Re(\eta^3$-*endo,syn*-CH_3CH−CPh−$CPh_2)^+PF_6^-$ (**1**).[1] A mechanism involving formation of 1-metallacyclopropene intermediate **A** followed by a 1,2-phenyl migration was proposed to explain the formation of **1** (Scheme 1).

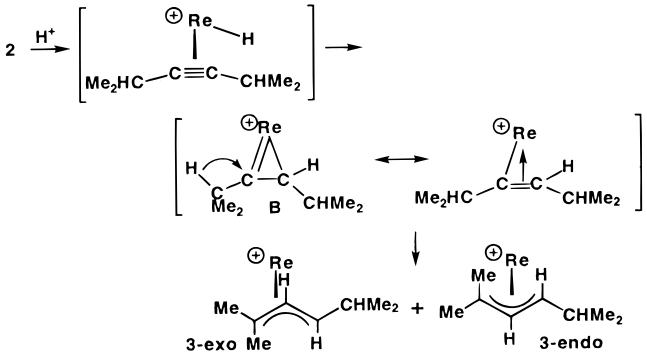
In a second case, protonation of $C_5Me_5(CO)_2Re(\eta^2$-Me_2-CHC≡$CCHMe_2$) (**2**) led to the formation of a 1:1 mixture of the η^3-allyl complexes $C_5Me_5(CO)_2Re(\eta^3$-*exo,syn*-Me_2C−CH−$CHCHMe_2)^+$ PF_6^- (**3-exo**) and $C_5Me_5(CO)_2Re(\eta^3$-*endo,syn*-Me_2C−CH−$CHCHMe_2)^+PF_6^-$ (**3-endo**).[2] A mechanism involving formation of 1-metallacyclopropene intermediate **B** followed by hydride migration was suggested to explain the formation of the η^3-allyl complexes **3-exo** and **3-endo** (Scheme 2).

In related 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-$CHCH_2)$.[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-$(P(i\text{-}Pr)_3)Rh(\eta^2$-$H_2$C═C═CHMe) when chromatographed on Al_2O_3.

Scheme 1



Scheme 2



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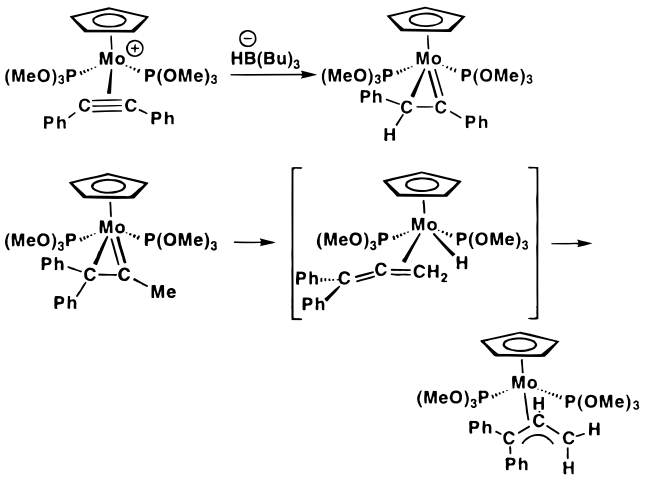
Scheme 3

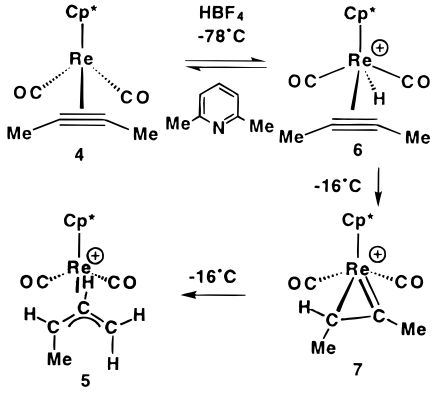


1-Metallacyclopropenes are often stable and isolable compounds. Many examples of molybdenum[4] and tungsten[5] 1-metallacyclopropenes have been reported. For example, hydride addition to the cationic 4-electron donor alkyne complex $C_5H_5[P(OMe)_3]_2Mo(\eta^2\text{-PhC}{\equiv}\text{CPh})^+$ led to the formation of the 1-metallacyclopropene $C_5H_5[P(OMe)_3]_2Mo(\eta^2\text{-CPhCHPh})$.[4b] The rearrangement of 1-metallacyclopropenes to η^3-allyl complexes has also been demonstrated. Green reported that the 1-metallacyclopropene $C_5H_5[P(OMe)_3]_2Mo(\eta^2\text{-CMeCPh}_2)$ slowly rearranged to the η^3-allyl complex $C_5H_5[P(OMe)_3]_2Mo(\eta^3\text{-H}_2\text{C}{-}\text{CH}{-}\text{CPh}_2)$ via a proposed molybdenum allene hydride intermediate (Scheme 3).[4b] Harman found that treatment of the vinyl ether complex $[(NH_3)_5Os(\eta^2\text{-(MeO)(Me)C}{=}\text{CH}_2)][OTf]_2$ with HOTf led to the acid promoted elimination of methanol and formation of the 1-metallacyclopropene complex $[(NH_3)_5Os(\eta^2\text{-MeCCH}_2)][OTf]_3$.[6]

Several examples of 1-rhenacyclopropenes have been reported. Pombeiro isolated *trans*-$(Ph_2PCH_2CH_2PPh_2)_2ClRe[\eta^2\text{-C(CH}_2\text{Ph)CH}_2]^+BF_4^-$ from the protonation of the allene complex *trans*-$(Ph_2PCH_2CH_2PPh_2)_2ClRe(\eta^2\text{-CHPh}{=}\text{C}{=}\text{CH}_2)$ with HBF_4.[7] Green prepared the neutral 1-metallacyclopropene $C_5H_5(PPh_3)BrRe(\eta^2\text{-CPhCHPh})$ by hydride addition to the 4-electron donor alkyne complex $C_5H_5(PPh_3)BrRe(\eta^2\text{-PhC}{\equiv}\text{CPh})^+PF_6^-$.[8]

Here we report that the conversion of rhenium alkyne complexes to η^3-allyl complexes upon treatment with strong acid proceeds through the intervention of two spectrally characterized intermediates: a rhenium alkyne hydride cation and a cationic 1-rhenacyclopropene. Deuterium labeling evidence for degenerate rearrangement of 1-rhenacyclopropenes by hydride migration between the two metallacyclopropene carbons was found. We also report the X-ray crystal structure of a stable 1-rhenacyclopropene isolated from the protonation of a rhenium diphenylacetylene complex. Hybrid density functional theory and natural bond orbital analysis were used to examine the bonding nature of 1-metallacyclopropenes.

Scheme 4



Results

***η^3*-Allyl Rhenium Cation Formation from Protonation of a Neutral Rhenium Alkyne Complex.** Addition of HBF_4 in Et_2O to a yellow CH_2Cl_2 solution of the neutral rhenium alkyne complex $C_5Me_5(CO)_2Re(\eta^2\text{-MeC}{\equiv}\text{CMe})$ (**4**) led to the formation of the cationic η^3-allyl rhenium complex $C_5Me_5(CO)_2Re(\eta^3\text{-}$*exo,anti*$\text{-MeHC}{-}\text{CH}{-}\text{CH}_2)^+BF_4^-$ (**5**). Recrystallization from methylene chloride−diethyl ether gave pure **5** as a white crystalline powder in 89% yield (Scheme 4).

The anti configuration of the allyl methyl group was assigned on the basis of the magnitude of the ^{1}H NMR coupling constants of the central allyl proton, and the exo stereochemistry of the allyl ligand was established by NOE measurements. In the ^{1}H NMR spectrum of **5**, the central allyl proton resonance at δ 3.76 (dt, $^3J = 11.0$ Hz, $^3J = 7.4$ Hz, CH) has one large coupling to an anti allylic proton and two smaller couplings to syn allylic protons. Additional support for the anti configuration of the allyl methyl group comes from its low-frequency chemical shift at δ 1.66 (d, $^3J = 6.6$ Hz); syn allylic methyl groups normally appear at higher frequency near δ 2.0.[9] A W-coupling of 1.5 Hz between the syn protons of the allyl group also supports the

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presence of an anti methyl group. In the ^{13}C NMR spectrum of **5**, three η^3-allyl resonances appear at δ 74.9, 66.7, and 39.1 and two carbonyls appear at δ 197.2 and 193.1. The Cp* resonance of **5** at δ 2.14 is shifted to higher frequency relative to the neutral precursor **4** at δ 1.96 as expected for a cationic Cp* rhenium complex.[10] The infrared spectrum has two high-energy carbonyl bands at 2032 and 1977 cm^{-1}, indicative of a cationic dicarbonyl complex.

^1H NMR NOE difference spectroscopy established an exo orientation of the allyl unit of **5**. Upon irradiation of the Cp* methyl resonance at δ 2.14, a 5.6% NOE enhancement was observed for the central allylic proton at δ 3.76. The syn and anti protons of the η^3-allyl fragment showed only small 1.0% NOE enhancements when the Cp* methyl was irradiated. No NOE enhancement was observed for the anti methyl resonance. The large NOE enhancement observed for the central allylic proton indicates that it is close to the Cp* ring and supports an exo configuration of the allyl fragment. The observed exo structure of **5** is less sterically crowded than the alternative endo structure, which would place an anti methyl group near the Cp* ring.

Low-Temperature Observation of a Rhenium Hydride Intermediate. In an effort to detect intermediates in the conversion of rhenium−alkyne complex **4** into cationic η^3-allyl complex **5**, the protonation of **4** with HBF_4 in Et_2O was carried out at −78 °C and the reaction mixture was examined by low-temperature spectroscopy. Addition of HBF_4 in Et_2O to a yellow CD_2Cl_2 solution of **4** at −78 °C produced a deep red solution of the metal alkyne hydride *trans*-$C_5Me_5(CO)_2ReH(\eta^2\text{-MeC}{\equiv}\text{CMe})^+BF_4^-$ (**6**), which was characterized spectroscopically at −70 °C (Scheme 4). Red solutions of **6** were indefinitely stable at −30 °C but were converted to nearly colorless solutions of **5** upon warming to room temperature. In the ^1H NMR spectrum of **6** at −70 °C, a singlet at δ −5.51 provided compelling evidence for a metal hydride and a single Cp* resonance at δ 2.13 indicated the clean formation of **6**. In the ^{13}C NMR spectrum, the observation of only a single CO resonance at δ 185.1 for equivalent carbonyl ligands established the trans coordination geometry of **6**. As expected for a trans dicarbonyl complex, only one sp alkyne carbon resonance was seen at δ 65.0 and the alkyne methyl groups were equivalent in both the ^1H (δ 2.59) and ^{13}C (δ 9.8) NMR spectra. In the infrared spectrum of **6** in CH_2Cl_2 at −78 °C, two carbonyl bands were observed at 2059 (ν_{sym}, relative integrated absorbance 1.0) and 1999 (ν_{asym}, relative integrated absorbance 1.6) cm^{-1}. These bands appear at higher frequency than those of the neutral alkyne complex **4** (1955 and 1890 cm^{-1}) consistent with the cationic nature of **6**. By using the formula $\cot^2\theta = I_{sym}/I_{asym}$ for calculating the angle (2θ) between symmetry related carbonyl groups,[11] an intercarbonyl angle of 103° was determined; this is consistent with the assigned trans geometry of **6**.

The protonation of **4** is reversible as demonstrated by the reaction of **6** with base. Addition of 2,6-dimethylpyridine to a red solution of **6** at −78 °C resulted in deprotonation of the metal hydride and reformation of a yellow solution of starting material **4** in nearly quantitative yield (96% by NMR).

Observation of a 1-Metallacyclopropene Intermediate. When the conversion of cationic metal hydride **6** to the η^3-allyl complex **5** was monitored by ^1H NMR spectroscopy at −16 °C, the formation of another intermediate was detected. This additional intermediate was spectroscopically characterized (see below) as the 1-metallacyclopropene complex (also known as an η^2-vinyl complex) $C_5Me_5(CO)_2Re(\eta^2\text{-CMeCHMe})^+BF_4^+$ (**7**). The formation of intermediate **7** and its conversion on to η^3-allyl complex **5** over 10 h was followed by ^1H NMR spectroscopy at −16 °C (Figure 1). The disappearance of **6** followed first-order kinetics with a rate constant of 4.5×10^{-5} s^{-1} ($t_{1/2}$ = 4.3 h), corresponding to $\Delta G^{\ddagger}$ = 20.1 kcal mol^{-1}.[12] The maximum amount of intermediate **7** formed was 40% of the rhenium species. The relative rates of formation and conversion of intermediate **7** are readily estimated from the equation $\beta_{max} = \kappa[\exp \kappa/(1-\kappa)]$, where β_{max} is the maximum mole fraction of the intermediate and κ is the ratio of rate constants for formation and consumption of the intermediate.[13] With use of this equation, the rate of formation of intermediate **7** from protonated alkyne complex **6** was estimated to be 1.2 times faster than its rate of conversion to η^3-allyl complex **5** (3.8×10^{-5} s^{-1}).

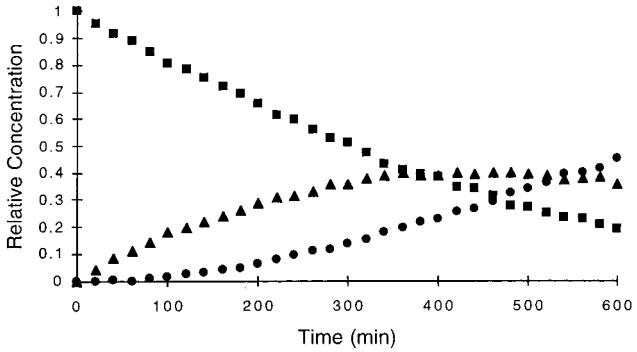

Figure 1. Plot of the relative concentrations of the rhenium species in a CD_2Cl_2 solution at −16 °C: ■, **6**; ▲, **7**; ●, **5**.

Independent Generation of the 1-Metallacyclopropene Intermediate 7 by Protonation of an Allene Complex. In concurrent work, we have shown rhenium alkyne complexes can be isomerized to rhenium allene complexes in the presence of a catalytic amount of acid.[14] Alternatively, the isomerization can be accomplished by addition of HX (HCl or CF_3CO_2H) to a coordinated alkyne to form a RHC═CXR rhenium complex followed by base-promoted elimination of HX to give an allene complex. For example, addition of HCl to $C_5Me_5(CO)_2Re(\eta^2\text{-MeC}{\equiv}\text{CMe})$ (**4**) at 25 °C gave a light tan solution of $C_5Me_5(CO)_2Re[\eta^2\text{-}(E)\text{-MeHC}{=}\text{CClMe}]$ (**8**), which eliminated HCl upon treatment with excess 2,6-dimethylpyridine to give the allene complex $C_5Me_5(CO)_2Re[\eta^2\text{-2,3-MeHC}{=}\text{C}{=}\text{CH}_2]$ (**9**) (Scheme 5).[14]

Protonation of allene complex **9** was explored as an alternative route to the 1-metallacyclopropene complex **7**. When HBF_4 in Et_2O was added to a yellow CD_2Cl_2 solution of allene complex **9** at −78 °C, a red solution formed immediately and then faded over 5 min to give a yellow-red solution. The red species may be a metal hydride allene complex analogous to the red metal hydride alkyne complex **6**. When HBF_4 in Et_2O was added to a frozen CD_2Cl_2 solution of **9** and the solution was melted in a ^1H NMR spectrometer probe at −94 °C, no metal hydride was detected. The first observable compound was the same 1-metallacyclopropene complex **7** as formed from metal hydride alkyne complex **6**. From −94 to −30 °C, **7** was the only species observed (Scheme 5).

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(12) The free energy of activation for reactions run at a single temperature was calculated with 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.

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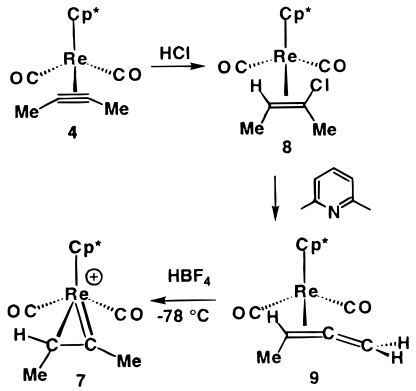
Scheme 5



The structure of 1-metallacyclopropene complex **7** was established by ^{13}C and ^{1}H NMR spectroscopy. In the ^{13}C NMR spectrum of **7**, a very high-frequency resonance at δ 302.6 was assigned to the carbene-like carbon of the 1-metallacyclopropene and resonances at δ 194.8 and 191.1 were seen for the inequivalent carbonyls. In the ^{1}H NMR spectrum of **7**, a δ 2.89 doublet ($^{4}J = 1.8$ Hz) was assigned to the methyl group bound to the carbene-like carbon. This methyl group has a small long-range coupling to a single proton at δ 3.41, which is also strongly coupled (6.1 Hz) to a methyl doublet at δ 1.76. The high-frequency Cp* resonance at δ 2.20 is consistent with a cationic Cp* rhenium complex.

Upon warming to −16 °C, **7** was converted to the η^3-allyl complex **5**. The disappearance of **7** followed first-order kinetics with a rate constant of 3.1×10^{-5} s^{-1} ($t_{1/2} = 6.3$ h), corresponding to $\Delta G^{\ddagger} = 20.3$ kcal mol^{-1}.[12] This rate constant is very similar to that of 3.8×10^{-5} s^{-1} estimated by the β_{max} procedure above.

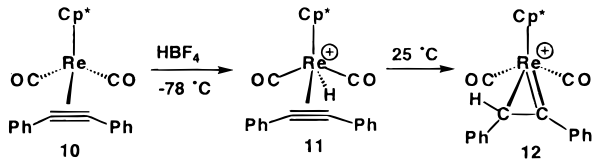
Reinvestigation of the Reaction of Diisopropyl Acetylene Complex 2 with Acid. Previously we had shown that protonation of $C_5Me_5(CO)_2Re(\eta^2$-$Me_2CHC{\equiv}CCHMe_2)$ (**2**) with HBF_4 led to the formation of a 1:1 mixture of η^3-allyl complexes **3-exo** and **3-endo** and had suggested the possibility of rhenium−alkyne hydride and 1-metallacyclopropene intermediates (Scheme 2).[2] Our success in observing related intermediates in the reactions of butyne complex **4** led us to investigate the low-temperature protonation of **2**.

Addition of HBF_4 in Et_2O to **2** at −78 °C resulted in the immediate formation of a red solution of the metal hydride complex *trans*-$C_5Me_5(CO)_2ReH(\eta^2$-$Me_2CHC{\equiv}CCHMe_2)^+BF_4^-$ (**13**). The ^{1}H NMR spectrum of **13** at −60 °C showed a low-frequency metal hydride resonance at δ −5.61. The trans geometry of the complex is supported by the observation of two diastereotopic methyl doublets at δ 1.43 and 1.31 (4 expected for cis) and by the observation of only a single CO resonance at δ 185.3 in the ^{13}C NMR spectrum.

When **13** was monitored by ^{1}H NMR spectroscopy at −20 °C, three new Cp* resonances were seen. Two of these resonances were due to the η^3-allyl complexes **3-exo** and **3-endo**, which were the only two products seen after warming to room temperature. The third Cp* resonance at δ 2.03 was tentatively assigned to the intermediate 1-metallacyclopropene complex $C_5Me_5(CO)_2Re(\eta^2$-*i*-PrCCH-*i*-Pr$)^+BF_4^-$ (**14**).

Isolation of a Stable 2,3-Diphenyl-1-metallacyclopropene Complex. Attempts to isolate **7** were unsuccessful due to its rapid rearrangement to η^3-allyl complex **5** by a 1,2 hydrogen migration. Since replacement of the alkyne methyl groups with phenyl groups precludes the possibility of a 1,2 hydrogen shift to give an η^3-allyl complex, we studied the protonation of the

Scheme 6



diphenylacetylene complex $C_5Me_5(CO)_2Re(\eta^2$-PhC≡CPh) (**10**) in an effort to isolate a stable 1-metallacyclopropene complex.

Addition of HBF_4 in Et_2O to a solution of $C_5Me_5(CO)_2Re(\eta^2$-PhC≡CPh) (**10**) in CH_2Cl_2 at −78 °C gave a red solution of the anticipated rhenium alkyne hydride complex *trans*-$C_5Me_5(CO)_2ReH(\eta^2$-PhC≡CPh$)^+BF_4^-$ (**11**), which was characterized spectroscopically at low temperature (Scheme 6). Both the ^{1}H NMR (ReH, δ −4.04) and ^{13}C NMR spectra were similar to the spectra of the butyne analog **6**.

Upon warming to room temperature, the red solution of **11** turned brown and the 1-metallacyclopropene complex $C_5Me_5(CO)_2Re(\eta^2$-CPhCHPh$)^+BF_4^-$ (**12**) was isolated as a black crystalline solid in 85% yield. **12** was indefinitely stable at room temperature under nitrogen.

In the ^{13}C NMR spectrum of **12**, a high-frequency resonance at δ 280.3 was assigned to the carbene-like carbon of the 1-metallacyclopropene. The lower frequency of this resonance ($\Delta\delta$ 22) compared with the comparable resonance of **7** is attributed to electron donation from the phenyl substituent. The IR spectrum for **12** shows two high-frequency carbonyl bands at 2045 and 1992 cm^{-1} as expected for a cationic complex.

The X-ray crystal structure of **12** confirmed its formulation as a 1-metallacyclopropene (Figure 2, Table 1). The Re−C(1) formal double bond length of 1.984(8) Å is substantially shorter than the Re−C(2) formal single bond length of 2.257(8) Å. The C(1)−C(2) bond length of 1.427(11) Å is shorter than normal C−C single bonds and longer than normal C═C double bonds; it is similar to C−C bond lengths reported for other 1-metallacyclopropenes (1.408 ± 0.013 Å).[15] The stereochemistry at the rhenium center is intermediate between that expected for a 3-legged and a 4-legged piano stool geometry. For a 3-legged piano stool geometry, the ideal angle between the Cp* centroid and the other ligands is 126° and for a 4-legged piano stool geometry this angle is normally 112°. For **12**, the angles between the Cp* centroid and the two carbonyl ligands are 118.6° and 119.7° and the angle between the Cp* centroid and the centroid of the two carbons of the 1-metallacyclopropene is 123.7°. The angle between the two carbonyls is 88.9°, close to the normal angle of a 3-legged piano stool complex; 4-legged piano stool complexes normally have intercarbonyl angles near 79°. The phenyl ring attached to the carbene-like carbon is nearly coplanar (tilted 1.7°) with the 1-metallacyclopropene ring; this allows electron donation from the phenyl π-system to the electron deficient p-orbital of the carbene-like carbon. The 1-metallacyclopropene C−C bond is roughly parallel to the plane of the Cp* ligand but tilted by 14.0° so that the proton of the CHPh group is closer to the Cp* ring and the larger CPh group is away from the Cp* ring.[16] Tilting is seen in other 1-metallacyclopropene complexes and the direction of tilting

(15) Orpen, A. G.; Brammer, L.; Allen, F. H.; Kennard, O.; Watson, D. G.; Taylor, R. *J. Chem. Soc., Dalton Trans.* **1989**, s1.

(16) To more quantitatively discuss the geometry of $Cp(CO)_2Re(\eta^2$-CRCHR) complexes, we focus attention on the angle between the plane defined by the Cp centroid, Re, and the center of the 1-metallacyclopropene C−C bond and the plane defined by Re and this C−C bond. We will refer to two extreme geometries: a parallel geometry (90° interplanar angle) and a perpendicular geometry (0° interplanar angle). In this case the interplanar angle is 76° which is 14° away from a parallel geometry.

Table 1. Selected Bond Lengths (Å) and Angles (deg) for $C_5Me_5(CO)_2Re(\eta^2\text{-CPhCHPh})^+BF_4^-$ (12)

bond lengths (Å)		bond angles (deg)			
Re−C(1)	1.984(8)	C(15)−Re−C(16)	88.9(3)	C(3)−C(2)−Re	123.8(5)
Re−C(2)	2.257(8)	C(1)−Re−C(16)	86.0(4)	C(1)−C(2)−C(3)	121.8(7)
Re−C(15)	1.994(11)	C(2)−Re−C(15)	84.9(4)	Cp*−Re−C(1)	126.2(3)
Re−C(16)	1.922(11)	C(1)−Re−C(2)	38.7(3)	Cp*−Re−C(2)	117.8(3)
C(1)−C(2)	1.427(11)	C(1)−C(2)−Re	60.3(4)	Cp*−Re−C(15)	118.6(4)
C(1)−C(9)	1.413(10)	C(2)−C(1)−Re	81.0(5)	Cp*−Re−C(16)	119.7(4)
C(2)−C(3)	1.505(10)	C(9)−C(1)−Re	146.0(6)		

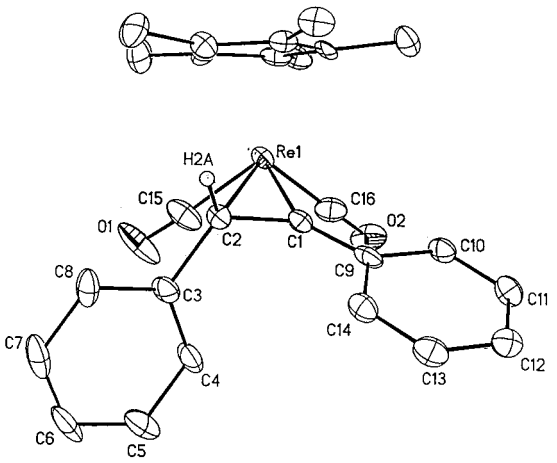


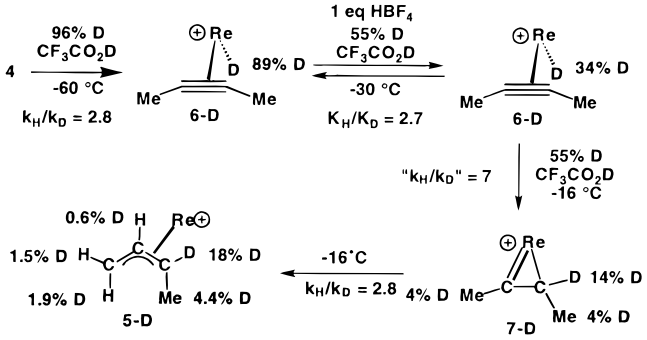
Figure 2. X-ray crystal structure of $C_5Me_5(CO)_2Re(\eta^2\text{-CPhCHPh})^+BF_4^-$ (**12**).

seems to be dominated by steric effects.[4b,e,5c,j,l,8,9] For example, in $Cp(Ph_2MeP)(Br)Re(\eta^2\text{-CPhCHPh})$, the 1-metallacyclopropene is tilted 34° in the direction that places the carbene-like carbon away from the Cp ring, but in $Cp(Ph_2PCH_2CH_2PPh_2)Re(\eta^2\text{-CPhCHPh})^+$, the 1-metallacyclopropene is tilted 38° in the opposite direction, which places the carbene-like carbon closer to the Cp ring.[8]

Deuterium Labeling Studies. In an effort to better understand the mechanism of conversion of alkyne complex **4** to η^3-allyl complex **5**, the reaction of **4** with deuterated trifluoroacetic acid was investigated. A 1:1 mixture of $CDCl_3$ and $CHCl_3$ was added to the reaction mixtures to allow direct comparison of the ^1H and ^2H NMR spectra. This made it possible to accurately determine the ratio of CF_3CO_2H:CF_3CO_2D.

Trifluoroacetic acid protonated alkyne complex **4** at −78 °C to give the metal hydride complex *trans*-$C_5Me_5(CO)_2ReH(\eta^2\text{-MeC}{\equiv}\text{CMe})^+CF_3CO_2^-$ (**6-CF_3CO_2**), whose ^1H NMR spectrum was very similar to that of the related BF_4 salt **6**.[17] Similarly, treatment of **4** with CF_3CO_2D (5 equiv) at −78 °C gave the metal deuteride **6-CF_3CO_2-D**. The ^1H NMR spectrum of **6-CF_3CO_2-D** at −60 °C showed a hydride resonance at δ −5.52 whose integral was 0.10 relative to 15.0 for the Cp* resonance, indicating the sample was ∼90% deuterated (Scheme 7). In the ^1H NMR spectrum, the integration ratios for $CHCl_3$:ReH^+:CF_3CO_2H were 1.00:0.06:0.09. In the ^2H NMR spectrum, the integration ratios for $CDCl_3$:ReD^+:CF_3CO_2D were 1.00:0.49:2.3. Since the ratio of $CHCl_3$:$CDCl_3$ was set to 1.00, these spectra establish the relative amounts of all species: **6-CF_3CO_2-D** = 0.89:**6-CF_3CO_2** = 0.11:CF_3CO_2D = 4.18:CF_3CO_2H = 0.16.[18] Since H/D exchange is slow at low temperature (see below), these data are consistent with a kinetic isotope effect for protonation at Re of $k_H/k_D = 2.8 \pm 0.4$.

Scheme 7



When 4 equiv of CF_3CO_2H and 1 equiv of HBF_4 in Et_2O were added to the above solution of **6-CF_3CO_2-D**, no loss of deuterium was observed at −60 °C. However, when the solution of **6-D** was monitored by ^1H NMR spectroscopy at −30 °C, slow proton exchange occurred (Scheme 7). After 2 days at −30 °C, equilibrium was reached. This indicates that while H−D exchange is slow, it occurs more rapidly than conversion of **6** to 1-metallacyclopropene **7**. The ratio of $CHCl_3$:ReH^+:CF_3CO_2H was 1.00:0.23:2.45 (^1H NMR) and the ratio of $CDCl_3$:ReD^+:CF_3CO_2D was 1.00:0.09:3.04 (^2H NMR).[19] Independent estimation of the ReH^+:ReD^+ ratio of 0.66:0.34 was made by comparing the ReH^+:Cp* resonances in the ^1H NMR spectrum. The equilibrium deuterium isotope effect for protonation at Re, K_{HD} = [**6**][CF_3CO_2D]/[**6-D**][CF_3CO_2H], is 2.7 ± 0.3.

When the above solution was warmed to −16 °C, the slow formation of 1-metallacyclopropene complex **7-D** and its conversion to η^3-allyl complex **5-D** was followed by ^1H NMR spectroscopy over 10 h. The rate of disappearance of **6-D** (k_{obs} = (3.6 ± 0.2) × 10^{-5} s^{-1}, $t_{1/2}$ = 5.3 h) and the maximum build-up of **7-D** (47%) were similar to those seen in the reaction of **4** with HBF_4 in the absence of CF_3CO_2H. The major difference between the two reactions was the observation of the enol trifluoroacetate complex (η^5-C_5Me_5)$Re(CO)_2[\eta^2\text{-}(E)\text{-MeHC}{=}C(O_2CCF_3)Me]$ (**15**) in the reaction carried out in the presence of CF_3CO_2H. **15** formed slowly, but then like the 1-metallacyclopropene complex **7** was converted to the η^3-allyl complex **5-D**. We had previously synthesized **15** independently by the treatment of the alkyne complex **4** with trifluoroacetic acid at room temperature.[14] Reversible addition of trifluoroacetate to the 1-metallacyclopropene complex **7-D** accounts for the formation and eventual conversion of **15**.

After 10 h at −16 °C, the reaction mixture contained 14% starting rhenium hydride **6-D**, 47% 1-metallacyclopropene **7-D**,

(17) The metal hydride was visible as a singlet at δ −5.52. The methyl groups of the Cp* and butyne were seen as singlets at δ 2.11 and δ 2.56, respectively. The ^{13}C NMR spectrum of **6-CF_3CO_2** showed only a single CO resonance at δ 184.9, indicating that the metal hydride complex had a trans geometry. The CF_3 group of the counterion appeared as a quartet at δ 114.6 with a C−F coupling constant of 284 Hz.

(18) Therefore at t = 0, **4** = 1.00, CF_3CO_2D = 5.07, and CF_3CO_2H = 0.27. Using the program Chemical Kinetics Simulator (Version 1.01, IBM, 1996), the conversion of this initial mixture to the observed final ratios of products was simulated with k_H/k_D = 2.8.

(19) Additional CF_3CO_2H reduced the total integration for ReH plus ReD due to lower solubility in this mixed solvent system.

23% **15**, and 17% η^3-allyl complex **5-D**. It was not possible to directly measure the amount of deuterium incorporation into the CH group of the 1-metallacyclopropene since the CH resonance at δ 3.41 was partially obscured by ether resonances. However, analysis of CHMe methyl resonance at δ 1.76 allowed estimation of the extent of incorporation of deuterium into the CDMe group. In undeuterated **7**, the δ 1.76 resonance is a symmetric doublet, but in this sample of **7-D**, it appeared as a 1.00:1.33 doublet. This was assigned to the superposition of a 1:1 doublet for the CHMe group of undeuterated material and a broad singlet for the CDMe group of **7-D** isotopically shifted on top of the low-frequency resonance of the doublet. This superimposed singlet represents 14% of the total signal and indicates that the ring proton of 1-metallacyclopropene **7-D** was 14% deuterated. This corresponds to an approximately (7 ± 2)-fold protium enrichment of the CDMe group relative to the 2.5:3.0 mixture of CF_3CO_2H:CF_3CO_2D (Scheme 7).

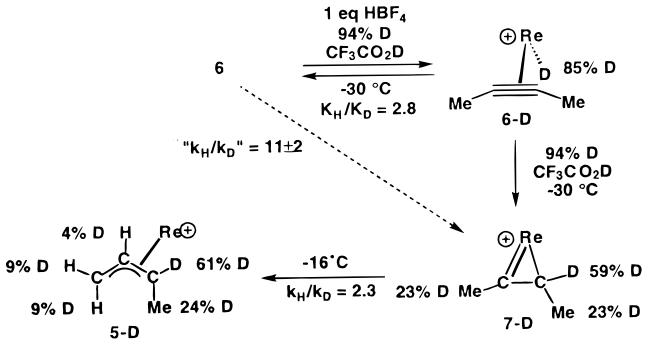
After 4 days at −20 °C, the above reaction mixture was completely converted to η^3-allyl complex **5-D**,[20] which was purified by recrystallization to simplify NMR analysis of deuterium content.[21] Careful integration of the δ 4.53 ^{1}H NMR resonance assigned to the syn allylic hydrogen of the CHMe unit relative to the Cp* resonance showed the presence of 0.82 H. This indicates 18% deuteration at this position, which is a significant decrease from the 34% deuteration of the ReD^+ unit of **6-D**. ^{1}H NMR spectroscopy was too insensitive to accurately assess the small amounts of deuterium incorporated into other sites of **5-D.** ^{2}H NMR spectroscopy of isolated **5-D** showed small amounts of deuterium incorporation at all of the allyl positions. By comparison with the δ 4.5 resonance of the CHMe group (0.18 D by ^{1}H NMR), the amounts of deuterium found at the other allylic positions were 0.006 D at the center allylic position (δ 3.8), 0.015 D at the syn allylic position (δ 3.1), 0.019 D at the anti allylic position (δ 2.9), and 0.044 D in the methyl group (δ 1.7). Significantly, the total amount of deuterium in these three allyl resonances (0.040 D) was about the same as that found in the methyl group (0.044 D) (Scheme 7).

Exchange of deuterium into the metal alkyne hydride complex **6** was also investigated. A solution of the metal hydride complex **6** was generated at −78 °C by the addition of 1 equiv of HBF_4 in Et_2O to a CD_2Cl_2 solution of alkyne complex **4** at −78 °C; the solution also contained 1:1 $CHCl_3$:$CDCl_3$ as an internal standard. When excess CF_3CO_2D (20 equiv) was added at −78 °C, no deuterium exchange into **6** was seen at −60 °C. The solution was warmed to −30 °C and examined periodically by ^{1}H NMR spectroscopy. After 4 h at −30 °C, 38% deuterium incorporation into the MH group was observed by comparison of the integrals for the metal hydride resonance and the Cp* resonance in the ^{1}H NMR spectrum.

Deuterium incorporation increased over 2 days at −30 °C until equilibrium was reached. At this point, 21% conversion to the 1-metallacyclopropene had occurred. The equilibrium deuterium isotope effect for protonation at Re, K_{HD} = [**6**][CF_3CO_2D]/[**6-D**][CF_3CO_2H], was estimated to be 2.8 ± 0.7,[22] which is similar to the value of 2.7 ± 0.3 measured when deuterium was washed out of **6-D** (Scheme 8).

After a total of 3 days at −30 °C, a 56:22:22 mixture of **6-D**:**7-D**:**15-D** was observed. The amount of deuterium in the CHMe group of 1-metallacyclopropene complex **7-D** was determined as before by examination of the resonance center at δ 1.78. The 1.00:3.84 ratio of two peaks was assigned to the superposition of a 1.00:1.00 doublet for the CHMe group of undeuterated material and a broad singlet for the CDMe group of **7-D** isotopically shifted on top of the low-frequency resonance of the doublet. This superimposed singlet represents 59% of the total signal and indicates that the ring proton of 1-metallacyclopropene **7-D** was 59% deuterated. It should be noted that this level of deuteration is *significantly less* than the 85% deuteration of the metal hydride precursor **6-D**. This corresponds to an approximately (11 ± 2)-fold protium enrichment of the CDMe group relative to the 94% deuterated CF_3CO_2D (Scheme 8).

Scheme 8



When this solution of **6-D**, **7-D**, and **15-D** was warmed to −20 °C for 4 days, complete conversion to η^3-allyl complex **5-D** was observed. **5-D** was isolated and purified by recrystallization. Careful integration of the δ 4.53 ^{1}H NMR resonance assigned to the syn allylic hydrogen of the CHMe unit relative to the Cp* resonance showed the presence of 0.39 H. This indicates 61% deuteration at this position, which is a significant decrease from the 85% deuteration of the ReD^+ unit of **6-D** and is similar to the 59% deuteration of the CDMe group of **7-D**. The ^{1}H NMR spectrum also indicated some incorporation into all the allyl positions of **5-D**, but ^{2}H NMR spectroscopy was used to quantitatively measure the deuterium content at the allylic sites. Deuterium levels were set relative to the syn allylic hydrogen of the CHMe which was set to 0.61 D based on the ^{1}H NMR spectrum. The three allyl resonances at δ 3.7, 3.1, and 2.9 integrated to 0.04, 0.09, and 0.09 D, respectively. The methyl resonance integrated to 0.24 D. It is significant that the total deuterium content at these three allylic sites (0.22 D) is similar to the deuterium content of the allylic methyl group (0.24 D). The greater amount of deuterium found in the syn and anti positions of the CH_2 unit compared with the central allylic position can be explained in terms of a kinetic deuterium isotope effect for hydrogen migration from methyl to the central allylic position of k_H/k_D = 2.3 ± 0.5

Proton Migration within the 1-Metallacyclopropene Ring. The observation of deuterium in both the anti methyl group and the other allyl positions of the allyl ligand indicated that the two methyl groups of the 1-metallacyclopropene complex **7** must have equilibrated over the course of the reaction and that deuterium was able to exchange into at least one of the methyl positions. A degenerate rearrangement involving a 1,2-hydride

(20) The ratio of the $CDCl_3$: CF_3CO_2D resonances in the ^{2}H NMR spectrum changed from 1.00:3.00 to 1.00:2.49 and the ratio of the $CHCl_3$: CF_3CO_2H resonances in the ^{1}H NMR spectrum changed from 1.00:2.50 to 1.00:3.28, consistent with exchange of deuterium into **7-D** and of protium into the acid pool.

(21) A control experiment demonstrated that **5** is not deuterated by treatment with CF_3CO_2D.

(22) In the ^{1}H NMR spectrum, the integration ratios for $CHCl_3$: ReH^+: CF_3CO_2H was 1.00:0.04:0.65. In the ^{2}H NMR spectrum, the integration ratios for $CDCl_3$:ReD^+:CF_3CO_2D was 1.00: 0.23: 10.1. Since the ratio of $CHCl_3$:$CDCl_3$ was set to 1.00, these spectra establish the relative amounts of all species: **6-D** = 0.85:**6** = 0.15:CF3CO2D = 39.1:CF3CO2H = 2.50. Independent estimation of the ReD+:ReH+ ratio of 0.85:0.15 was made by comparing the ReH+:Cp* resonances in the 1H NMR spectrum.

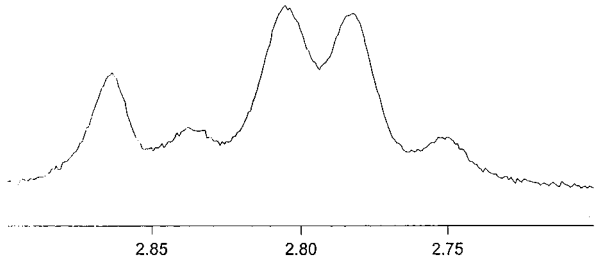
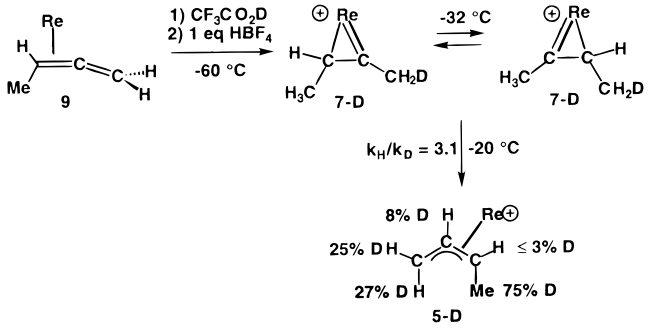
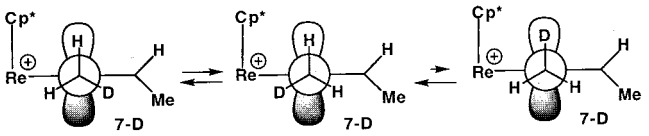


Figure 3. 500 MHz ^{1}H NMR spectrum of the diastereotopic CH_2D group of **7-D** at −60 °C. The singlet at δ 2.87 is due to the corresponding CH_3 group.

Scheme 9



Scheme 10



shift between the two carbons of the 1-metallacyclopropene ring would lead to equal deuterium incorporation into the two methyl sites. Deuterium incorporation into the methyl groups could occur by reversible deprotonation of **7** to form the allene complex **9**.

To determine whether degenerate hydride migration was occurring in 1-metallacyclopropene complex **7**, CF_3CO_2D and then HBF_4 in Et_2O were added to allene complex **9** at −78 °C to generate **7-D**. ^{1}H and ^{2}H NMR spectroscopy indicated that deuterium was initially located predominantly on the methyl group attached to the carbene-like carbon of **7** as expected (Scheme 9). When the solution was warmed to −32 °C, slow equilibration ($t_{1/2}$ = 2.3 h) led to equal incorporation of deuterium into both methyl groups of the 1-metallacyclopropene.

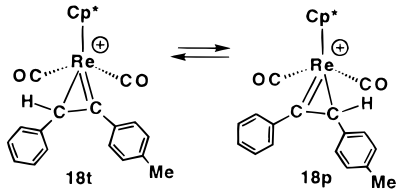
Surprisingly, a large chemical shift difference ($\Delta\delta$ = 11 ppb, J_{gem} = 16 Hz) was seen for the diastereotopic CH_2D protons of the methyl group bound to the carbene-like carbon of **7** (Figure 3).[23] Hyperconjugation is expected to weaken the CH bond in the plane of the p-orbital at the electron-deficient carbene-like carbon of the 1-metallacyclopropene. This should lead to preference for conformations in which the weaker CH bonds occupy this position and to large chemical shift differences between the diastereotopic hydrogens of the CH_2D group (Scheme 10). Similar preferences are seen for carbocations.[24]

Upon warming to room temperature, complete conversion to η^3-allyl complex **5** occurred. ^{2}H NMR analysis showed only a small amount of deuterium (≤0.03 D) in the syn allylic position of the CHMe unit of **5**. This observation excludes conversion

(23) Several examples of diastereotopic CH_2D groups have been reported. (a) Anet, F. A. L.; Kopelevich, M. *J. Am. Chem. Soc.* **1989**, *111*, 3429. (b) Restelli, A.; Siegel, J. S. *J. Am. Chem. Soc.* **1992**, *114*, 1091.

(24) Saunders, M.; Vogel, P. *J. Am. Chem. Soc.* **1971**, *93*, 2558.

Scheme 11



of the 1-metallacyclopropene back to alkyne complex **4**. The deuterium content of **5** (1.35 D total) showed an increase over deuterium content in initially formed **7-D** (1.0 D). This is consistent with a small amount of interconversion of 1-metallacyclopropene and allene complex **9**. The deuterium content of the allylic methyl group of **5** (0.75 D) was similar to that of the remaining three allylic hydrogens (0.60 D), consistent with rapid hydride migration in **7**. The amount of deuterium found in the central allylic position (0.08 D) was somewhat less than in the two terminal allylic positions (0.25 and 0.27 D), consistent with a deuterium isotope effect of $k_H/k_D = 3.1 \pm 0.3$ for the hydride migration involved in conversion of **7** to **5**. This isotope effect is similar to the value of 2.3 ± 0.6 as shown in Scheme 8.

In an effort to determine whether degenerate hydride migration was also occurring in the isolated phenyl-substituted 1-metallacyclopropene complex **12**, an attempt was made to observe coalescence of the phenyl resonances of **12** in the ^{1}H NMR spectrum. However, thermal decomposition of **12** occurred at 60 °C before any exchange broadening was seen.

The unsymmetric alkyne complex $C_5Me_5(CO)_2Re(\eta^2$-PhC≡CTol) (**16**) was synthesized so that isomeric 1-metallacyclopropene complexes could be made and their interconversion monitored. Protonation of **16** with HBF_4 in Et_2O at −78 °C resulted in the formation of the expected metal hydride complex *trans*-$C_5Me_5(CO)_2ReH(\eta^2$-PhC≡CTol)$^+BF_4^-$ (**17**) (^{1}H NMR, δ −4.06, ReH). At −40 °C, **17** rearranged to form a 2.3:1 ratio of the two isomeric 1-metallacyclopropene complexes $C_5Me_5(CO)_2Re(\eta^2$-CTolCHPh)$^+BF_4^-$ (**18t**):$C_5Me_5(CO)_2Re(\eta^2$-CPhCHTol)$^+BF_4^-$ (**18p**). The ratio of **18t**:**18p** was readily measured by monitoring the ratio of the CH resonances of the 1-metallacyclopropene at δ 3.73 and 3.78. As the mixture of isomers was warmed to room temperature, the ratio of **18t**:**18p** changed until it reached an equilibrium value of 4.5:1 (Scheme 11). The equilibration of **18t** and **18p** can be explained by a 1,2-hydrogen shift across the 1-metallacyclopropene ring.

Ab Initio Hybrid Density Functional Calculations and Analysis. To investigate the nature of the bonding interactions in the 1-metallacyclopropene complexes **7** and **12**, we performed electronic structure calculations on a simplified model Cp-$(CO)_2Re(\eta^2$-C′MeC″HMe)$^+$ complex (**12-M**) (C′ and C″ are used to denote the mono- and disubstituted carbons respectively), differing from **12** by replacing Cp* by Cp and Ph by Me. Green has investigated 1-metallacyclopropene complexes utilizing extended-Hückel molecular orbital calculations.[4b,l,8] We employed the B3LYP/LANL2DZ level of hybrid density functional theory[25] (as implemented in the Gaussian 94[26] program system),

(25) For an overview of theoretical methods and basis sets implemented in Gaussian 94, see: Foresman, J. B.; Frisch, A. *Exploring Chemistry with Electronic Structure Methods*, 2nd ed.; Gaussian, Inc.: Pittsburgh, PA, 1996.

(26) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Gill, P. M. W.; Johnson, B. G.; Robb, M. A.; Cheeseman, J. R.; Keith, T.; Petersson, G. A.; Montgomery, J. A.; Raghavachari, K.; Al-Laham, M. A.; Zakrzewski, V. G.; Ortiz, J. V.; Foresman, J. B.; Cioslowski, J.; Stefanov, B. B.; Nanayakkara, A.; Challacombe, M.; Peng, C. Y.; Ayala, P. Y.; Chen, W.; Wong, M. W.; Andres, J. L.; Replogle, E. S.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Binkley, J. S.; Defrees, D. J.; Baker, J.; Stewart, J. P.; Head-Gordon, M.; Gonzalez, C.; Pople, J. A. *Gaussian 94, Revision E.2*; Gaussian, Inc.: Pittsburgh, PA, 1995.

Table 2. Spectroscopic Data of 1-Metallacyclopropenes

compd	M=C	M−C	C−C	torsion angle,[31] deg	^{13}C NMR $\eta^2-{}^{13}CRCR_2$	^{13}C NMR $\eta^2-CR^{13}CR_2$
$[C_5Me_5(CO)_2Re(\eta^2-CPhCHPh)][BF_4]$ (**12**)	1.984	2.257	1.427	70.0	280.3	23.6
[*trans*-$(Ph_2P(CH_2)_2PPh_2)_2ClRe(\eta^2C(CH_2Ph)CH_2)][BF_4]$[7]	1.947	2.193	1.412	84.8	258.2	
$C_5H_5(PMePh_2)BrRe(\eta^2-CPhCHPh)$[8]	1.91	2.13	1.39	40.9	253.6	16.7
$[C_5H_5(Ph_2P(CH_2)_2PPh_2)Re(\eta^2-CPhCHPh)][BF_4]$[8]	1.93	2.26	1.43	81.8	260.9	25.2
$C_9H_7(P(OMe)_3)_2Mo(\eta^2-CSiMe_3CH_2)$[4e]	1.957	2.260	1.436	89.6	276.5	23.9
$C_5H_5(P(OMe)_3)_2Mo(\eta^2-CMeCPh_2)$[4b]	1.963	2.249	1.463	71.5	237.4	35.7
$C_5H_5(P(OMe)_3)_2Mo(\eta^2-CPhCHPh)$[4b]	1.951	2.301	1.433	93.2	255.5	26.8

which uses a relativistically corrected, valence-only (effective core potential) double-ζ treatment of Re (including two full sets of d orbitals) and a full double-ζ basis set for other atoms.

From starting coordinates modeled after the X-ray structure of **12**, we carried out a complete B3LYP/LANL2DZ geometry optimization of the model **12-M** complex. The theoretical structure is in excellent agreement with the experimental X-ray structure of **12**, as displayed for key geometrical parameters in Table 2. In particular, good agreement between calculated bond lengths (Å) for **12-M** and *observed bond lengths* for **12** was seen for Re=C′ [1.995, *1.984(8)*], Re−C″ [2.229, *2.257(8)*], and C′−C″ [1.423, *1.427(11)*]. The tilt of the MC′RC″HR ring relative to the Cp ring is more pronounced in **12-M** (31°) than observed in **12** (14°). Thus, we conclude that B3LYP/LANL2DZ provides a quantitatively satisfactory description of the Re metallacycle that can be employed to analyze the nature of the bonding interactions.

To interpret the B3LYP/LANL2DZ electron density, we employed *natural bond orbital* (NBO) analysis,[27] as implemented in the NBO 4.0 program[28] interfaced to Gaussian 94. NBO analysis leads to an optimal "chemist's basis set" of localized bond-like orbitals that are in close correspondence with the Lewis structure concept, allowing the input density matrix to be expressed as closely as possible in terms of the "best" localized Lewis structure representation (with mathematically optimized bonding pattern, hybrids, polarization coefficients, etc.). This allows arbitrary levels of *ab intio* theory to be expressed compactly and accurately in the language of orbital shapes and interaction energies familiar to experimental chemists.

We also employed the newly developed *natural resonance theory* (NRT) analysis[29] (as implemented in NBO 4.0) to determine quantitative resonance weights and bond orders for the B3LYP/LANL2DZ-optimized species. The NRT method provides an optimal *multi*-structural representation of the ab initio density, allowing electron delocalization effects (departures from a single ideal Lewis structure) to be quantitatively described in the convenient and familiar language of resonance theory. Specific results of the B3LYP/LANL2DZ calculations and associated NBO/NRT analyses will be presented in the Discussion section below.

Discussion

Mechanism of Conversion of Alkyne Complex 4 to η^3-Allyl Complex 5. During the conversion of alkyne complex **4** to η^3-allyl complex **5**, two intermediates were spectroscopically detected: the trans alkyne hydride complex **6** and the 1-metallacyclopropene complex **7** (Scheme 4). Deuterium labeling studies revealed detailed information about the intermediates and their interconversions.

We learned that hydride complex **6** is formed rapidly at −78 °C and that no exchange of the metal hydride with CF_3CO_2D takes place at −60 °C. However, H/D exchange occurred at −30 °C more rapidly than conversion to 1-metallacyclopropene complex **7**. A kinetic isotope of $k_H/k_D = 2.8 \pm 0.4$ and an equilibrium isotope effect of $K_{HD} = [\mathbf{6}][CF_3CO_2D]/[\mathbf{6\text{-}D}][CF_3CO_2H] = 2.7 \pm 0.3$ were found for protonation of **4**. Norton has observed a similar kinetic deuterium isotope effect of 3.7 for self-exchange of $HW(CO)_3Cp$ with the corresponding metal anion.[30]

We learned that the 1-metallacyclopropene **7** can be generated either from alkyne complex **4** via hydride intermediate **6** at −16 °C or from protonation of allene complex **9** at −78 °C without observation of a hydride intermediate. By analogy with the X-ray crystal structure of the diphenyl-substituted 1-metallacyclopropene complex **12**, we believe that the single observed isomer of **7** has hydrogen syn to the Cp* ligand.

Hydride migration within the 1-metallacyclopropene ring of **7** occurred much more rapidly ($t_{1/2} = 2.3$ h at −32 °C) than conversion of **7** to η^3-allyl complex **5** ($t_{1/2} = 6.3$ h at −16 °C). While interconversion of 1-metallacyclopropene **7** and allene complex **9** (leading to deuterium incorporation) occurred at about half the rate at which **7** rearranged to η^3-allyl complex **5**, no interconversion of **7** and alkyne complex **4** was detected.

The conversion of 1-metallacyclopropene complex **7** to η^3-allyl complex **5** involves a 1,2 hydride shift from a methyl group to the carbene-like carbon of **7**. There is a kinetic deuterium isotope effect of about $k_H/k_D \approx 3$ favoring hydrogen migration to the central allylic position of **5**. The formation of the exo-allyl geometry of **5** requires migration of hydrogen to the face of the carbene-like carbon of the 1-metallacyclopropene syn to the Cp* group. Once formed, the η^3-allyl complex **5** is configurationally stable and does not exchange deuterium with CF_3CO_2D.

Since rhenium alkyne deuteride complex **6-D** underwent exchange with CF_3CO_2H more rapidly than it irreversibly rearranged to 1-metallacyclopropene **7-D**, the precise mechanism of this conversion is uncertain. Three possibilities for the conversion of **6** to **7** can be envisioned (Scheme 12). (1) Intramolecular equilibration of trans hydride **6** with a cis hydride isomer **C** followed by hydride addition to the alkyne might produce **7**. Since **C** has never been directly observed, it would have to be present in undetectable amounts. In this mechanism, the isotope effect of 7−11 for hydrogen enrichment of **7** is the product of an equilibrium isotope effect of 2.7 for formation of **6-D** and a kinetic isotope effect of 2.6−4.0 for migration of hydride from the cis hydride to the alkyne carbon of **C**. (2) A second possibility involves reversible deprotonation of trans

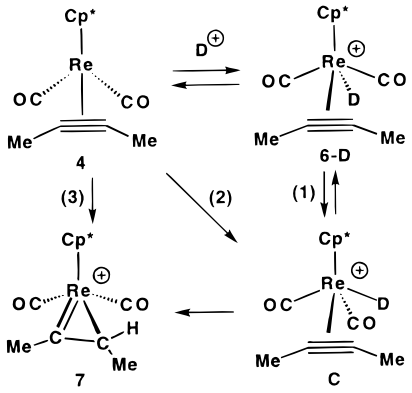
(27) (a) Reed, A. E.; Curtiss, L. A.; Weinhold, F. *Chem. Rev.* **1988**, *88*, 899. (b) Weinhold, F., in, Schleyer, P. v. R. Encyclopedia of Computational Chemistry; Wiley: New York, 1998, and references therein.

(28) Glendening, E. D.; Badenhoop, J. K.; Reed, A. E.; Carpenter, J. E.; Weinhold, F. *NBO 4.0*, Theoretical Chemical Institute, University of Wisconsin: Madison WI, 1996.

(29) Glendening, E. D.; Weinhold, F. *J. Comput. Chem.* **1998**, *19*, 593.

(30) Edidin, R. T.; Sullivan, J. M.; Norton, J. R. *J. Am. Chem. Soc.* **1987**, *109*, 3945.

Scheme 12



alkyne hydride **6**, followed by rate-limiting reprotonation to give a cis alkyne hydride **C** that promptly undergoes hydride migration to give 1-metallacyclopropene **7**. In this case, the isotope effect of 7−11 for hydrogen enrichment of **7** would be ascribed to a kinetic isotope effect of 7−11 for protonation of Re cis to the alkyne ligand. This is larger than the kinetic isotope effect of $k_H/k_D = 3.2 \pm 0.6$ measured for protonation of **4** trans to the alkyne carbon and thus seems less likely. (3) The mechanism we favor involves reversible deprotonation of trans alkyne hydride **6**, followed by reprotonation at an alkyne carbon of **4**. Here, an isotope effect of 7−11 for hydrogen enrichment of **7** would be ascribed to a kinetic isotope effect of 7−11 for protonation at an alkyne carbon.

Mechanism (3) is consistent with the much more rapid hydride exchange with CF_3CO_2D and the much more rapid formation of products derived from a 1-metallacyclopropene intermediate for the trifluoroacetate salt $C_5Me_5(CO)_2ReH(\eta^2$-$MeC{\equiv}CMe)^+CF_3CO_2^-$ (**6-CF_3CO_2**) than for the BF_4 salt of **6**.[14] The more rapid hydride exchange of **6-CF_3CO_2** is readily explained since trifluoroacetate is a stronger base than Et_2O. If the partitioning of protonation at Re or an alkyne carbon of **4** is approximately the same for protonation by either HBF_4 or CF_3CO_2H, then the more often that **4** is cycled through protonation steps, the more often irreversible protonation will occur at carbon to generate a 1-metallacyclopropene. The slower deprotonation of the BF_4 salt of **6** decreases opportunities for protonation at carbon and slows the formation of **7**.

1-Metallacyclopropene vs η^2-Vinyl Descriptions. Currently, M(η^2-$CRCR_2$) complexes are referred to as either η^2-vinyl complexes or 1-metallacyclopropenes. While both names adequately describe the η^2-$CRCR_2$ ligand, the η^2-vinyl seems less helpful to understanding the structure and bonding of the complexes. The structure of these complexes can best be thought of as resulting from a merger of an alkyne complex with an alkene complex: the geometry about the CR carbon is similar to that seen in alkyne complexes, while the geometry about the CR_2 carbon is similar to that seen in alkene complexes (Figure 4).

The term "vinyl group" normally implies a geometry in which the two vinyl carbons and their four attached groups lie in the same plane. In fact, X-ray crystal structures of M(η^2-$CRCR_2$) complexes have large angles between the MCRC and CCR_2 planes (Table 2). In $C_5Me_5(CO)_2Re(\eta^2$-$CPhCHPh)^+BF_4^-$ (**12**), this interplanar angle is 70°.[31] The nearly perpendicular angle between these planes is better understood in terms of the 1-metallacyclopropene formulation. The term η^2-vinyl leads

(31) The torsion angle is the dihedral angle between the substituent on the carbene-like carbon, the 1-metallacyclopropene carbons, and the carbon substituent anti to the C_5 ring.

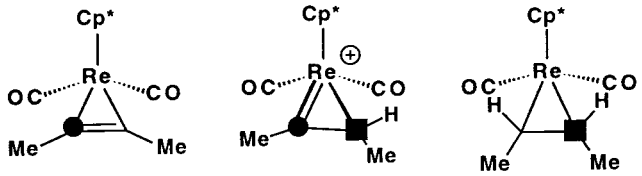
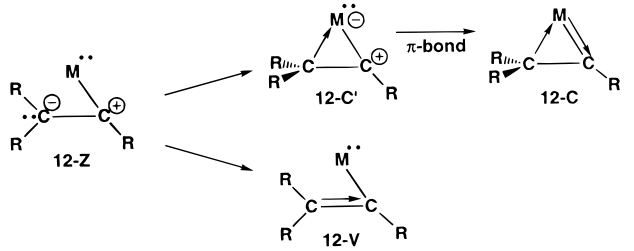


Figure 4.

Scheme 13



to the expectation of a short C═C distance similar to that in alkenes. However, the C−C distance in M(η^2-$CRCR_2$) complexes is between that of single and double bonds; in **12**, this C−C distance is 1.427(11) Å. Thinking about the bonding in an "η^2-vinyl" complex can be perplexing since both the M−C σ-bond and the C═C π-bond which are normally perpendicular need to be directed at the metal.

We believe that the term "1-metallacyclopropene" gives a more accurate description of the η^2-$RCCR_2$ ligand. This term implies a metal−carbon double bond to the monosubstituted carbon and a metal−carbon single bond to the disubstituted carbon. In X-ray crystal structures of M(η^2-$CRCR_2$) complexes, the M−C bond to the monosubstituted carbon is substantially shorter than the M−C bond to the disubstituted carbon; in **12**, the Re═CPh bond distance is 1.984(8) Å while the Re−CHPh bond distance is 2.257(8) Å. The 1-metallacyclopropene formulation implies a carbene-like M═CR unit and a metal alkyl like M−CR_2 unit. This analogy helps to explain the high frequency ^{13}C NMR chemical shifts of the M═^{13}CR carbon of 1-metallacyclopropenes which appear in the range of δ 250−320 (Table 2); this resonance appears at δ 302.6 for **7** and at δ 280.3 for **12**. It also explains the low-frequency ^{13}C NMR chemical shifts of the M−$^{13}CR_2$ carbon of 1-metallacyclopropenes which appear in the range of δ 15−45; this resonance appears at δ 18.4 for **7** and at δ 23.6 for **12**.

1-Metallacyclopropenes vs η^2-Vinyl Descriptions: Hybrid Density Functional Calculations and NBO Analysis. The 1-metallacyclopropene complexes **7** and **12** present certain difficulties with respect to proper nomenclature and Lewis structure representation. As depicted in Schemes 1 and 2, two alternative Lewis structures may be considered, an "η^2-vinyl complex" and a "1-metallacyclopropene". Both diagrams share common M−C′ and C′−C″ σ bonds (C′, and C″ denoting the mono- and disubstituted carbons, respectively), so we may consider them to originate from a common "zwitterionic" precursor (**12-Z**), as pictured in Scheme 13. In the idealization **12-Z**, the formal lone pair hybrid $n_{C''}$ of the anionic CR_2 can form a dative $\sigma_{C''M}$ bond to give metallacycle **12-C′**. Alternatively, the formal lone pair hybrid $n_{C''}$ can form a dative $\pi_{C'C''}$ bond to form the "η^2-vinyl complex" **12-V**; but, because the plane of the C″HR group is severely twisted relative to the ReC′R plane, there is poor overlap for this π-bond. Thus Lewis structures **12-V** and **12-C′** have *mutually exclusive* geometrical demands and can never be in "resonance".

In **12-C′**, the adjacent formal charges on M and C′ can lead to an additional dative $\pi_{MC'}$ bond (with a filled d-type metal

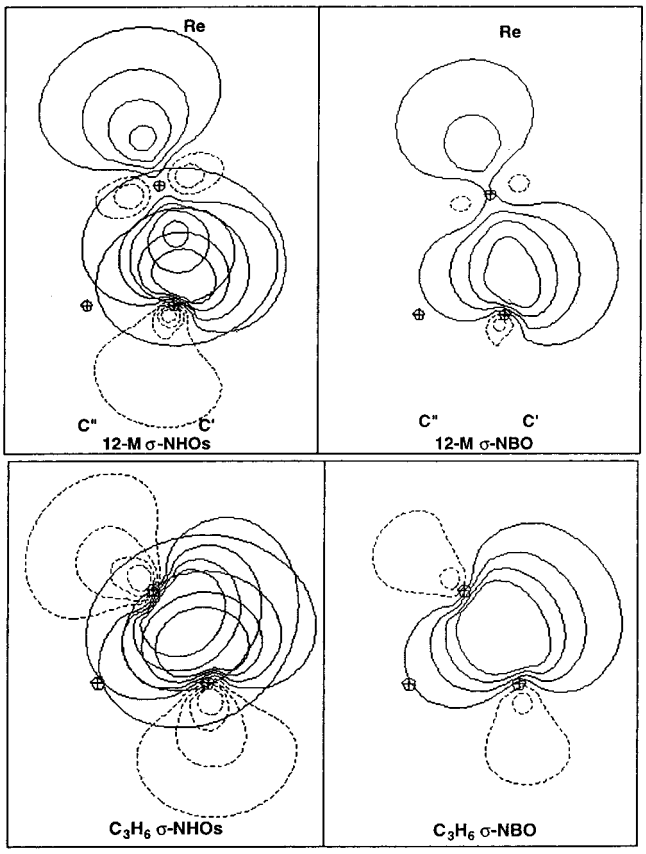


Figure 5. σ bond NHOs (left) and NBO (right) orbital plots of **12-M** (upper) and C_3H_6 (lower).

orbital donating to the formally vacant p-type orbital on C′) to give the final Lewis structure representation **12-C**. However, in **12-V** no such secondary donor−acceptor stabilization is possible, since M lies practically at the intersection of *both* nodal planes of the $\pi^*_{C'C''}$ acceptor orbital. This confers a strong energetic advantage to the final 1-metallacyclopropene structure **12-C**, as confirmed by both the X-ray and ab initio results. Thus, there seem to be *no* good geometrical or electronic reasons for preferring the "η^2-vinyl" depiction over the "1-metallacyclopropene" structure **12-C**.

The foregoing qualitative considerations are strongly supported by NBO analysis of the B3LYP/LANL2DZ model intermediate species $Cp(CO)_2Re(\eta^2\text{-}CMeCHMe)^+$ **12-M**. The NBOs of the σ-bonding framework strongly resemble those of cyclopropane and other small cyclic systems, with highly strained "bent bonds" formed from hybrids $sp^{2.79}$ (on C) and $sd^{3.03}$ (on M), directed 15−20° outside the line of centers (closely similar to the bonding picture originally envisioned by Coulson[32]), as depicted in Figure 5.[33] This figure compares the overlapping natural hybrid orbitals (NHOs) and final NBOs for the $\sigma_{M-C''}$ bond of **12-M** with a corresponding σ_{CC} bond of cyclopropane (optimized B3LYP/6-31G* level), showing the close analogies in bonding character of the metallacycle and parent carbocycle.

The interacting NHOs of the M−C′ "π bond" are similarly depicted in Figure 6, showing the canted d_{z^2}-type metal orbital strongly overlapping the underside lobe (distal to Cp) of the vacant p-type carbon orbital ("LP*" on carbon in NBO output).

(32) Coulson, C. A.; Moffitt, W. E. *Philos. Mag.* **1949**, *40*, 1.

(33) The orbitals depicted in Figures 5 and 6 are actually the "pre-NHOs" and "pre-NBOs" (lacking only the interatomic orthogonality of final NHOs and NBOs) whose overlaps convey an accurate visual impression of interaction strength; see ref 24.

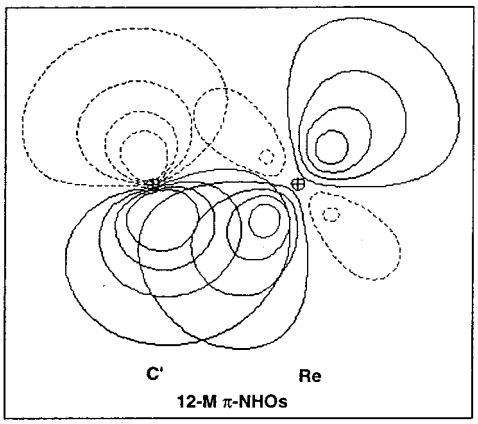
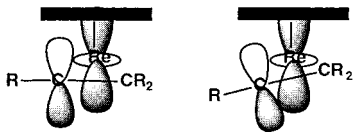


Figure 6. π bond NHOs orbital plot of **12-M**.

Scheme 14



This strong interaction (although not counted as a "bond" in the formal NBO Lewis structure) is estimated to be 53 kcal mol^{-1} by second-order NBO perturbative analysis, and may be interpreted as a highly polarized π-bond with electron density centered on rhenium.

That the overlap of these orbitals cannot be of classical "π" type is related to the fact that the MC_2 ring is not parallel to the Cp ring. The strong bending of the C′ p orbital to achieve favorable overlap with the canted metal *d* orbital in turn necessitates strong tilting of the MC′C″ ring with respect to the Cp ring (Scheme 14). Conjugative or hyperconjugative interactions with surrounding unsaturated or saturated substituents will further weaken this putative "π-bond." Similarly, hyperconjugative interactions between highly strained σ bonds in the ring (particularly, $\sigma_{C'M} \rightarrow \sigma^*_{C''M}$, which weakens each MC and strengthens the connecting CC interaction) will further modify the bond strengths, relative to an idealized **12-Z** ↔ **12-C** hybrid. This simple Lewis structure picture allows one to expect bond orders for MC′ (less than one), MC″ (between one and two), and C′C″ (between one and two) that are generally consistent with the actual structure.

The formal bond orders were further quantified with *natural resonance theory* (NRT) analysis to obtain resonance-weighted "natural bond orders" b_{AB} for all AB atom pairs. NRT analysis of the B3LYP/LANL2DZ density for optimized **12-M** leads to the calculated bond orders $b_{MC'} = 1.39$ and $b_{MC''} = 0.33$. The higher bond order of M═C′R compared with M−C″HR supports the 1-metallacyclopropene formulation. Significant π-bonding character between the two carbons ($b_{C'C''} = 1.43$) is seen. The large C═C partial double-bond character is consistent with the Dewar−Chat−Duncanson model for M(alkene) complexes,[34] which suggests strongly mixed metal alkene and metallacyclopropane character. For comparison, NRT bond orders for the comparable B3LYP/LANL2DZ $Cp(CO)_2Re$(*cis*-2-butene) complex are 0.75 for Re−C and 1.02 for the C−C bond. The bond orders for the alkyne complex $Cp(CO)_2Re$(2-butyne) are 0.74 for Re−C and 2.08 for the C−C bond.

Other NBO atomic and bond indices are also consistent with observed properties of **12**. In particular, the calculated natural

(34) (a) Dewar, M. J. S. *Bull. Soc. Chim. Fr.* **1951**, *18*, C71. (b) Chatt, J.; Duncanson, L. A. *J. Chem. Soc.* **1953**, 2939.

atomic charge of C′ (+0.158) is significantly more positive than that of C″ (−0.250), which is consistent with the pronounced high-frequency ^{13}C NMR chemical shifts of C′ in 1-metallacyclopropenes. Nucleophilic additions[14] and preferential hydride migrations to C′ are also in agreement with the NBO description of a low-occupancy valence orbital and positive charge at this center. In all respects, the NBO orbital description is quite different from the η^2-vinyl formulation and quite supportive of the 1-metallacyclopropene-like picture, but with strong resonance delocalization effects modifying the idealized Lewis structure of **12-C**.

Experimental Section

General Methods. All air-sensitive materials were manipulated under dry nitrogen in a glovebox or by standard high-vacuum and Schlenk techniques. CH_2Cl_2 and CD_2Cl_2 were distilled from calcium hydride. Trifluoroacetic acid was distilled from P_2O_5. ^1H 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 or a Micromass AutoSpec Spectrometer (LSIMS, NSF Award No. 9304546). Elemental analyses were performed by Desert Analytics (Tucson, AZ). HBF_4 was purchased from Aldrich as a 54 wt % solution in Et_2O. $C_5Me_5(CO)_2Re(\eta^2$-MeC≡CMe) (**4**), $C_5Me_5(CO)_2Re(\eta^2$-PhC≡CPh) (**10**), and $C_5Me_5(CO)_2Re(\eta^2$-TolC≡CPh) (**16**) were prepared according to literature procedures.[1]

[$C_5Me_5(CO)_2Re(\eta^3$-MeHCCHCH$_2$)][BF_4] (5). Addition of HBF_4 (22.4 μL, 54 wt % in Et_2O, 160 μmol) by syringe to a yellow solution of $C_5Me_5(CO)_2Re(\eta^2$-MeC≡CMe) (**4**) (69.1 mg, 160 μmol) in 5 mL of CH_2Cl_2 at −78 °C produced a red solution. Upon warming to room temperature, the red solution turned colorless. Evaporation of solvent under vacuum gave a white powder, which was crystallized from $CH_2Cl_2-Et_2O$ to give **5** (73.5 mg, 89%) as a white crystalline powder. ^1H NMR (300 MHz, CD_2Cl_2) δ 4.52 (dqdd, ^3J = 7.4 Hz, ^3J = 6.6 Hz, ^4J = 1.5 Hz, ^4J = 0.7 Hz, C*H*Me), 3.76 (dt, ^3J = 11.0 Hz, ^3J = 7.4 Hz, CH), 3.10 (ddd, ^3J = 7.4 Hz, ^2J = 3.3 Hz, ^4J = 1.5 Hz, CH_{syn}H), 2.86 (ddd, ^3J = 11.0 Hz, ^2J = 3.3 Hz, ^4J = 0.7 Hz, CHH_{anti}), 2.14 (s, Cp*), 1.66 (d, ^3J = 6.6 Hz, CHCH_3). $^{13}C\{^1H\}$ NMR (126 MHz, CD_2Cl_2) 197.2 (CO), 193.1 (CO), 104.0 (C_5Me_5), 74.9 (π-allyl), 66.7 (π-allyl), 39.1 (π-allyl), 15.5 (CHCH_3), 9.7 (C_5Me_5). IR (CH_2Cl_2) 2032 (s), 1977 (vs) cm^{-1}. FABMS calcd (found) for $C_{16}H_{22}O_2Re$: M^+ 433.1 (433.1). Anal. Calcd for $C_{16}H_{22}O_2ReBF_4$: C, 37.00; H, 4.27. Found: C, 36.24; H, 3.80.

[*trans*-$C_5Me_5(CO)_2ReH(\eta^2$-MeC≡CMe)][BF_4] (6). Addition of HBF_4 (3.4 μL, 54 wt % in Et_2O, 24 μmol) by syringe to a yellow solution of $C_5Me_5(CO)_2Re(\eta^2$-MeC≡CMe) (**4**) (10.2 mg, 24 μmol) in 0.3 mL of CD_2Cl_2 at −78 °C produced a red solution of **6**. A quantitative yield of **6** was determined by using 1,4-$(Me_3Si)_2C_6H_4$ as an internal ^1H NMR standard. ^1H NMR (500 MHz, CD_2Cl_2, −70 °C) δ 2.59 (s, MeC≡), 2.13 (s, Cp*), −5.51 (s, ReH). $^{13}C\{^1H\}$ NMR (126 MHz, CD_2Cl_2, −70 °C) δ 185.1 (CO), 105.3 (C_5Me_5), 65.0 (Me*C*≡), 10.4 (C_5Me_5), 9.8 (*Me*C≡). IR (CH_2Cl_2, −78 °C) 2059 (s), 1999 (vs) cm^{-1}.

[$C_5Me_5(CO)_2Re(\eta^2$-CMeCHMe)][BF_4] (7) from Allene Complex 9. Addition of 1 equiv of HBF_4 (4.9 μL, 54 wt % in Et_2O, 35 μmol) to a light yellow solution of **9** (14.9 mg, 35 μmol) in CD_2Cl_2 at −78 °C gave a yellow-orange solution of **7**, as the only species seen by ^1H NMR spectroscopy. ^1H NMR (500 MHz, CD_2Cl_2, −70 °C) δ 3.41 (qq, ^3J = 6.1 Hz, ^4J = 1.8 Hz, ReC*H*Me), 2.89 (d, ^4J = 1.8 Hz, ReCMe), 2.20 (s, Cp*), 1.76 (d, ^3J = 6.1 Hz, ReCH*Me*). $^{13}C\{^1H\}$ NMR (126 MHz, CD_2Cl_2, −70 °C) δ 302.6 (Re=C), 194.8 (CO), 191.1 (CO), 105.4 (C_5Me_5), 36.4 (Re*C*Me), 28.4 (Re*C*HMe), 18.4 (ReCH*Me*), 9.6 (C_5Me_5).

[$C_5Me_5(CO)_2Re(\eta^2$-CMeCHMe)][BF_4] (7) from Alkyne Complex 4. A red CD_2Cl_2 solution of **6** prepared by addition of 1 equiv of HBF_4 (3.4 μL, 54 wt % in Et_2O, 24 μmol) to a solution of **4** (10.2 mg, 24 μmol) at −78 °C was warmed to −16 °C. Conversion of the hydride **6** to η^2-vinyl complex **7** occurred over several hours and **7** was converted to η^3-allyl complex **5** at a similar rate. The maximum formation of **7** occurred after 7 h, where a 1.4:1.6:1.0 mixture of **6**:**7**:**5** was seen.

$C_5Me_5(CO)_2Re[\eta^2$(2,3)-H_2C=C=CHMe] (9). HCl gas (7 equiv) was added to a yellow CH_2Cl_2 solution of **4** (57.8 mg, 130 μmol) at 25 °C to give a light tan solution of $C_5Me_5(CO)_2Re(\eta^2$-(*E*)-MeHC=CClMe) (**8**).[14] 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 containing **9**. The yellow solution was filtered through silica gel and solvent was evaporated to give **9** (58.4 mg, 100%) as a yellow powder. ^1H 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=), 101.6 (C_5Me_5), 99.3 (H_2C=), 30.1 (*Me*HC=), 10.4 (HMe*C*=), 10.1 (C_5Me_5). IR (CH_2Cl_2) 1962 (s), 1886 (vs) cm^{-1}. Mass spec (EI) calcd (found) for $C_{16}H_{21}O_2Re$: *m*/*z* 432.1101 (432.1097).

[*trans*-$C_5Me_5(CO)_2ReH(\eta^2$-PhC≡CPh)][BF_4] (11). Addition of HBF_4 (2.3 μL, 54 wt % in Et_2O, 16 μmol) by syringe to a yellow solution of $C_5Me_5(CO)_2Re(\eta^2$-PhC≡CPh) (**10**) (8.8 mg, 16 μmol) in 0.3 mL of CD_2Cl_2 at −78 °C produced a red solution of **11** as the only species observed. ^1H NMR (500 MHz, CD_2Cl_2, −70 °C) δ 7.76 (d, ^3J = 8.0 Hz, ortho), 7.61 (t, ^3J = 8.0 Hz, ^3J = 7.5 Hz, meta), 7.54 (t, ^3J = 7.5 Hz, para), 2.21 (s, Cp*), −4.04 (s, ReH). $^{13}C\{^1H\}$ NMR (126 MHz, CD_2Cl_2, −70 °C) δ 181.1 (CO), 131.4, 130.6, 129.5, 122.5 (Ph), 106.8 (C_5Me_5), 80.7 (Me*C*≡), 11.0 (C_5Me_5). IR (CH_2Cl_2, −78 °C) 2071 (s), 2015 (s) cm^{-1}.

[$C_5Me_5(CO)_2Re(\eta^2$-CPhCHPh)][BF_4] (12). Addition of HBF_4 (33.1 μL, 54 wt % in Et_2O, 239 μmol) by syringe to a yellow solution of **10** (69.1 mg, 160 μmol) in 5 mL of CH_2Cl_2 at −78 °C produced a red solution. Upon warming to room temperature, the red solution turned brown. Evaporation of solvent under vacuum gave a brown powder, which was crystallized from $CH_2Cl_2-Et_2O$ to give **12** (131 mg, 85%) as a brown crystalline powder. ^1H NMR (500 MHz, CD_2Cl_2) δ 8.06 (t, 1 H, Ph), 8.04 (d, 2 H, Ph), 7.72 (t, 2 H, Ph), 7.31 (t, 1 H, Ph), 7.22 (t, 2 H, Ph), 7.02 (d, 2 H, Ph), 3.77 (s, ReC*H*Ph), 2.21 (s, Cp*). $^{13}C\{^1H\}$ NMR (126 MHz, CD_2Cl_2) δ 280.3 (Re=C), 195.3, 191.1 (CO), 142.2, 140.5, 140.4, 136.8, 131.3, 129.1, 128.4, 127.9 (Ph), 104.8 (C_5Me_5), 23.6 (Re*C*HPh), 10.0 (C_5Me_5). IR (CH_2Cl_2) 2045(s), 1992 (s) cm^{-1}. FABMS calcd (found) for $C_{26}H_{26}O_2Re$: M^+ 557.1 (557.1). Anal. Calcd for $C_{26}H_{26}O_2ReBF_4$: C, 48.53; H, 4.07. Found C, 48.32; H, 3.94.

NMR Kinetics for the Conversion of 6 to 5. The rate of conversion of **6** to **7** then to **5** was determined by monitoring the Cp* resonances of **6** (δ 2.14), **7** (δ 2.20), and **5** (δ 2.09) utilizing ^1H NMR spectroscopy. The disappearance of **6** (31 μmol) in a CD_2Cl_2 solution (0.3 mL) was measured versus an internal standard of *p*-$(TMS)_2(C_6H_4)$ (15 μmol) at −16 °C over a period of 10 h. The temperature was calibrated versus a methanol standard. A plot of ln [**6**] vs time was linear to over 3 half-lives (correlation coefficient >0.98) and gave $k_1 = 4.5 \times 10^{-5}$ s^{-1}, $t_{1/2}$ = 4.3 h, and $\Delta G^{\ddagger}$ = 20.1 kcal mol^{-1}.[12] The relative amounts of **6**, **7**, and **5** versus time showed that the maximum amount of **7** over the course of the reaction was 40%. Utilizing the equation $\beta_{max} = \kappa[\exp \kappa/(1 - \kappa)]$, where β_{max} is the maximum mole fraction of the intermediate and κ is the ratio of rate constants for formation and consumption of the intermediate, the rate of **6** to **7** is 1.2 times faster than the rate of **7** to **5** (3.7×10^{-5} s^{-1}). The rate for **7** to **5** was independently determined by generating **7** by treatment of **9** with HBF_4 in ether at −78 °C and following the conversion of **7** to **5** at −16 °C. A plot of ln[**7**] vs time was linear to over 3 half-lives (correlation coefficient >0.98) and gave $k_2 = 3.1 \times 10^{-5}$ s^{-1}, $t_{1/2}$ = 6.3 h and $\Delta G^{\ddagger}$ = 20.3 kcal mol^{-1}.[12]

Formation of 7-D from 9. Addition of 20 equiv of CF_3CO_2D (13.9 μL, 180 μmol) to a light yellow solution of **9** (3.9 mg, 9 μmol) in CD_2Cl_2 at −78 °C gave a cloudy orange solution to which was added 1 equiv of HBF_4 (1.3 μL, 54 wt % in Et_2O, 9 μmol), which gave a clear yellow orange solution of **7-D** as the only species seen by ^1H NMR spectroscopy. The ^1H NMR of **7-D** was identical to that of **7** except for the methyl group resonance at δ 2.85, which had been

substituted with a deuterium forming a diastereotopic CH_2D group. The ^1H NMR spectrum collected at 500 MHz showed an AB quartet centered at δ 2.80 ($\Delta\delta$ = 11 ppb, J_{gem} = 16 Hz). The AB quartet collapsed to a broad singlet as simulations predicted when the ^1H NMR field was lowered to 250 MHz.[35] Warming of the solution of **7-D** to −32 °C resulted in the equilibration of the amount of deuterium in the two methyl resonances at δ 2.85 and 1.75 via a 1,2 hydrogen shift within the 1-metallacyclopropene ring. The rate to reach equilibration was measured by observing the decrease in integration versus the Cp* of the methyl resonance at δ 2.85 until both methyl groups had equal amounts of deuterium. The rate for the 1,2 hydrogen shift was 8.3×10^{-5} s^{-1}, $t_{1/2}$ = 2.3 h, and $\Delta G^{\ddagger}$ = 18.5 kcal mol^{-1}.[12] Warming of the solution of **7-D** to room temperature resulted in the formation of **5-D**.

X-ray Crystallographic Determination and Refinement. Slow diffusion of Et_2O into a saturated CH_2Cl_2 solution of **12** gave black crystals suitable for X-ray analysis. Crystallographic data for compound **12** were collected on a Siemens P4/CCD diffractometer equipped with graphite monochromated Mo Kα radiation, λ = 0.71073 Å. The sample was cooled to −135 °C with a locally modified nitrogen-streaming device. The intensity data nominally covered a hemisphere of reciprocal space using φ rotation frames collected at 0.3° increments for 30 s/frame. The crystal-to-detector distance was 5.26 cm. Coverage of the unique data was over 92% complete to at least 25° in θ. Crystal decay was estimated by comparing common intensities at the start and end of data collection and found to be negligible. Crystallographic computations were carried out with SHELXTL.[36] A semiempirical absorption correction was applied. The initial position of the Re atom was obtained by direct methods. Other non-hydrogen atoms were obtained from successive Fourier difference maps coupled with isotropic least-squares refinement. All non-hydrogen atoms were refined anisotropically. Idealized positions were used for the hydrogen atoms. An abridged version of the crystal data is given in Table 3. Complete tables of crystal data, data collection parameters, least-squares refinement parameters, positional and thermal parameters, interatomic distances, bond angles, and idealized hydrogen atom positional parameters are available as Supporting Information. Selected bond lengths and angles are listed in Table 1.

(35) The AB pattern was modeled using the program WinDNMR, (v. 1.4: Reich, H. J. *J. Chem. Educ. Software* **1996**).

(36) Sheldrick; G. M. SHELXTL, Version 5 Reference Manual. Siemens Analytical X-ray Instruments, 6300 Enterprise Dr., Madison, WI 53719-1173, 1994.

Table 3. Crystal Data and Structure Refinement for 12

empirical formula	$C_{26}H_{26}BF_4O_2Re$
crystal color, habit	grayish prism
crystal size	0.20 × 0.10 × 0.10 mm
crystal system	monoclinic
space group	*Cc*
unit cell dimens	a = 15.1677(3) Å; α = 90°
	b = 11.5677(3) Å; β = 101.0550(10)°
	c = 14.4477(3) Å; γ = 90°
vol	2487.89(10) $Å^3$
no. of peaks to determine cell	5050
θ range of cell peaks	3−25°
Z	4
formula wt	643.48
density (calcd)	1.718 Mg/m^3
abs coeff	4.935 mm^{-1}
F(000)	1256
final R indices [$I > 2\sigma(I)$]	$R1$ = 0.0286, $wR2$ = 0.0705
R indices (all data)	$R1$ = 0.0307, $wR2$ = 0.0712

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Supporting Information Available: Experimental details and characterization for **13**, **14**, **17**, **18t**, and **18p**, X-ray crystallographic data for **12**, and data for the hybrid density functional calculations of **12-M**, including Z-matrix, natural charges, natural bond orbitals, natural bond orders, interorbital angles, and a comparison of calculated and experimental bond lengths and angles for **12-M** and **12** (15 pages, print/PDF). See any current masthead page for ordering information and Web access instructions.

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