Reaction of $Cp^*(CO)_2Re{=}Re(CO)_2Cp^*$ with Alkynes Produces Dimetallacyclopentenones $Cp^*(CO)_2Re(\mu\text{-}\eta^1,\eta^3\text{-}CR{=}CR'CO)Re(CO)Cp^*$ Which React with Acid To Form Cationic Bridging Vinyl Complexes

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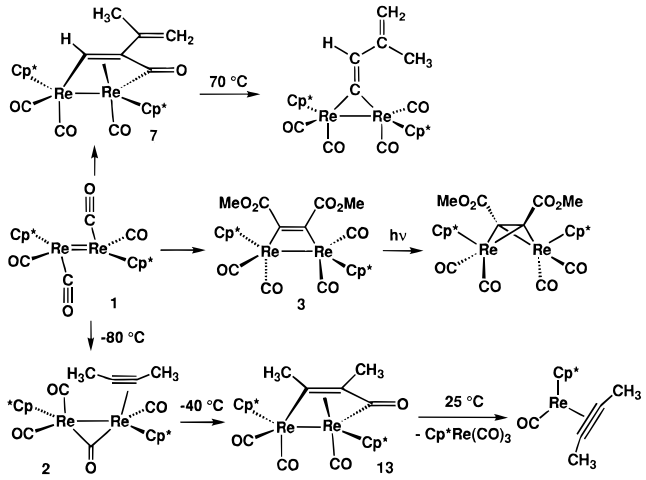
$Cp^*(CO)_2Re{=}Re(CO)_2Cp^*$ (**1**) reacted with terminal alkynes HC≡CR (R = H, CH_3, C_6H_5, $C(CH_3){=}CH_2$, OCH_2CH_3) to produce dimetallacyclopentenones $Cp^*(CO)_2Re(\mu\text{-}\eta^1,\eta^3\text{-}CH{=}CRCO)Re(CO)Cp^*$ (**4**−**8**). The reaction of **1** with alkynes having one ester substituent also gave dimetallacyclopentenones. Reaction of **1** with $HC{\equiv}CCO_2Me$ gave $Cp^*(CO)_2Re[\mu\text{-}\eta^1,\eta^3\text{-}CH{=}C(CO_2CH_3)CO]Re(CO)Cp^*$ (**9**) and with $CH_3C{\equiv}CCO_2Me$ gave $Cp^*(CO)_2Re[\mu\text{-}\eta^1,\eta^3\text{-}(CO_2CH_3)C{=}C(CH_3)CO]Re(CO)Cp^*$ (**10**). At low temperature, the η^2-propyne complex $Cp^*(CO)_2Re(\mu\text{-}CO)Re(CO)(HC{\equiv}CCH_3)Cp^*$ (**12**) and $Cp^*(CO)_2Re[\mu\text{-}\eta^1,\eta^3\text{-}C(CH_3){=}CHCO]Re(CO)Cp^*$ (**11**) were observed as intermediates in the formation of $Cp^*(CO)_2Re[\mu\text{-}\eta^1,\eta^3\text{-}CH{=}C(CH_3)CO]Re(CO)Cp^*$ (**5**). Protonation of dimetallacyclopentenone **2** with CF_3CO_2H produced $[Cp^*(CO)_2Re(\mu\text{-}\eta^1,\eta^2\text{-}CH{=}CH_2)Re(CO)_2Cp^*]^+CF_3CO_2^-$ (**14**), a species with a bridging vinyl group. Protonation of the thermodynamically favored regioisomeric dimetallacyclopentenone **5** gave $[Cp^*(CO)_2Re(\mu\text{-}\eta^1,\eta^2\text{-}(E)\text{-}CH{=}CHCH_3)Re(CO)_2Cp^*]^+CF_3CO_2^-$ (**15**). Protonation of kinetically formed regioisomeric dimetallacyclopentenone **11** at low temperature gave $[Cp^*(CO)_2Re(\mu\text{-}\eta^1,\eta^2\text{-}CCH_3{=}CH_2)Re(CO)_2Cp^*]^+CF_3CO_2^-$ (**16**).

Introduction

$Cp^*(CO)_2Re{=}Re(CO)_2Cp^*$ (**1**) is a rare example of a dimer of a d^6, 16 electron fragment.[1] **1** is thermally stable but is extremely reactive toward H_2 and nucleophiles. **1** forms the bridging dihydride $Cp^*(CO)_2Re(\mu\text{-}H)_2Re(CO)_2Cp^*$ upon exposure to H_2 at −78 °C and adds ligands such as CO, PMe_3, $CH_2{=}CH_2$, and CH_3CN to form the binuclear adducts $Cp^*(CO)_2Re(\mu\text{-}CO)Re(CO)(L)Cp^*$.[2] The reactions of **1** with alkynes are particularly intriguing because of the wide variety of products observed (Scheme 1). Acetylene[2] and $HC{\equiv}CC(CH_3){=}CH_2$[3] react with **1** to form dimetallacyclopentenones which are stable at room temperature but rearrange to bridging vinylidene complexes upon heating. 2-Butyne reacts with **1** to form the observable 1:1 adduct $Cp^*(CO)_2Re(\mu\text{-}CO)Re(CO)(\eta^2\text{-}CH_3C{\equiv}CCH_3)Cp^*$ (**2**) which rearranges to a dimetallacyclopentenone at −40 °C, which in turn fragments at room temperature to give $Cp^*Re(CO)_3$ and the 4-electron donor alkyne complex $Cp^*Re(CO)(CH_3C{\equiv}CCH_3)$.[2] Dimethyl acetylenedicarboxylate (DMAD), an alkyne with strong electron-withdrawing substituents, reacts with **1** to give the dimetallacyclobutene $Cp^*(CO)_2Re(\mu\text{-}\eta^1,\eta^1\text{-}CH_3O_2CC{=}CCO_2CH_3)Re(CO)_2Cp^*$ (**3**), which upon photolysis rearranges to the dimetallabicylobutane complex $Cp^*(CO)_2Re(\mu\text{-}\eta^2,\eta^2\text{-}CH_3O_2CC{\equiv}CCO_2CH_3)Re(CO)_2Cp^*$.[4]

Here we report the reactions of **1** with terminal and internal alkynes bearing a variety of substituents in an effort to probe the steric and electronic effects of substituents on the stability of the dirhenium products. We also report that protonation of dimetallacyclopentenones leads to bridging vinyl dirhenium cations.

Scheme 1



Results

Dimetallacyclopentenones from Terminal Alkynes. Reaction of a dark green C_6D_6 solution of $Cp^*(CO)_2Re{=}Re(CO)_2Cp^*$ (**1**) with a variety of terminal alkynes gave the dimetallacyclopentenone complexes $Cp^*(CO)_2Re(\mu\text{-}\eta^1,\eta^3\text{-}CH{=}CRCO)Re(CO)Cp^*$ [alkyne = $HC{\equiv}CH$ (**4**),[2] $HC{\equiv}CCH_3$ (**5**), $HC{\equiv}CC_6H_5$ (**6**), $HC{\equiv}CC(CH_3){=}CH_2$ (**7**),[3] and $HC{\equiv}COCH_2CH_3$ (**8**)]. All reactions took place very rapidly at room temperature as indicated by an immediate color change from green to orange (**4**−**7**) or red (**8**). In each reaction, only a single regioisomer with hydrogen β to the ketone carbonyl was

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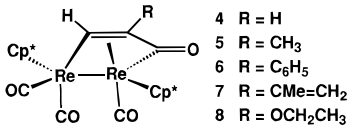


observed. The dimetallacyclopentenones were formed in >95% NMR yield (except for **6** which was formed in 70% NMR yield) and were isolated in moderate to good yields (48−73%) as colored powders. The solid dimetallacyclopentenones are slightly air sensitive but were stable in solution in sealed tubes.

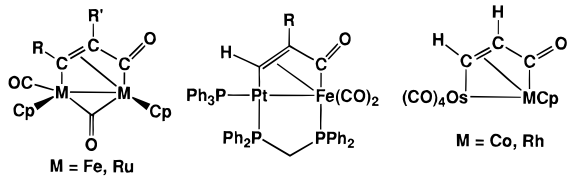
In the ^{1}H NMR spectra of dimetallacyclopentenones **4**−**8**, the inequivalent Cp* ligands gave rise to two intense singlets between δ 1.6 and 1.9. A characteristic high-frequency resonance (δ 7.99−9.29 in C_6D_6) was observed for the proton β to the ketone carbonyl and bound to the carbon bridging the rhenium centers. This assignment was based on a comparison to the chemical shift of the corresponding proton in Cp*$(CO)_2$Re{μ-η^1,η^3-CH=C[C(CH_3)=CH_2]CO}Re(CO)Cp* (**7**) (δ 8.27), a compound for which an X-ray crystal structure has been reported.[3] In the acetylene adduct **4**, the resonance for the proton on the carbon α to the ketone appeared at δ 3.57.[2]

In the ^{1}H NMR spectrum at 100 °C, the Cp* resonances of the dimetallacyclopentenone **5** derived from propyne remained sharp. The significance of this important observation in relation to the mechanism of interconversion of dimetallacyclopentenones and dimetallabicyclobutenes will be dealt with in the Discussion section.

The ^{13}C NMR spectra for **4**−**8** showed two sets of resonances for the Cp* ring and methyl carbons. Each compound exhibited four resonances between δ 214 and 206 which were assigned to the terminal CO and ketone carbonyls. The resonance for the CH carbon β to the ketone appeared between δ 112 and 136, which is in the region expected for a methine carbon bridging two metal centers.[5] The resonances assigned to the carbon α to the ketone appeared between δ 21 and 53, except in the case of the ethyl ethynyl ether adduct **8** which was observed at δ 91.5.

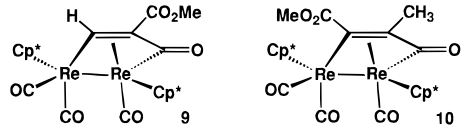
The carbonyl region of the infrared spectra of dimetallacyclopentenones **4**−**8** displayed three bands for terminal CO's (1951−1848 cm^{-1}) and one lower energy band (1712−1676 cm^{-1}) for the ketone carbonyl. The stretching frequencies of the ketones were in the range for μ-η^1,η^3-dimetallacyclopentenones in which the alkene was coordinated to the metal bearing the acyl group.[6,7]

All spectral data for dimetallacyclopentenones **4**−**8** were similar to those of related Fe_2 and Ru_2 and mixed Fe−Pt, Os−Rh, and Os−Co dimetallacyclopentenones such as the following structures:[6,7]



Dimetallacyclopentenones from Alkynes with One Ester Substituent. In contrast to the formation of dimetallacyclopentenones from the reactions of **1** with terminal alkynes, the reaction of **1** with dimethyl acetylenedicarboxylate produced the 3,4-dimetallacyclobutene **3**. The formation of dimetallacyclobutenes from reactions of alkynes bearing two electron-withdrawing groups such as CO_2R or CF_3 with bimetallic compounds is common.[8] Calculations performed by Hoffmann[8a] showed that electron-withdrawing substituents stabilize the dimetallacyclobutene. The reactions of **1** with alkynes bearing a single ester substituent were studied to see whether a dimetallacyclopentenone or a dimetallacyclobutene would be formed. Dimetallacyclobutenes with a single electron withdrawing substituent are rare.[9]

The reaction of methyl propynoate with a green solution of **1** gave a red-orange solution from which Cp*$(CO)_2$Re[μ-η^1,η^3-CH=C(CO_2CH_3)CO]Re(CO)Cp* (**9**) was isolated as an orange powder in 70% yield. Spectral data established the dimetallacyclopentenone structure of **9**. The infrared spectrum of **9** had terminal CO absorbances at 1953 (s), 1906 (vs), and 1869 (s) cm^{-1} with an intensity pattern similar to that of dimetallacyclopentenones **4**−**8** and lower energy bands at 1729 (m) and 1704 (m) cm^{-1} assigned to the ester and ketone carbonyls. In the ^{1}H NMR spectrum of **9** in CD_2Cl_2 at −10 °C, resonances were observed at δ 1.88 and 1.84 for inequivalent Cp* ligands and at δ 8.92[10] for the CH β to the ketone carbonyl and bound to the carbon bridging the rhenium centers. In the ^{13}C NMR spectrum of **9**, characteristic resonances at δ 34.7 and 124.8 were assigned to the α- and β-carbons of the dimetallacyclopentenone unit.



Reaction of a green solution of **1** with methyl 2-butynoate gave an instantaneous color change to a purple solution from which the dimetallacyclopentenone Cp*$(CO)_2$Re[μ-η^1,η^3-(CO_2CH_3)C=C(CH_3)CO]Re(CO)Cp* (**10**) was isolated as a purple solid in 62% yield. The IR spectrum of **10** displayed the "fingerprint" for a dimetallacyclopentenone with absorbances for the terminal CO ligands at 1944 (s), 1909 (vs), and 1867 (s) cm^{-1} and lower energy bands at 1712 (m), 1702 (m), and 1689 (m)

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(7) The absorbance for the ketone in the μ-η^1,η^1-dimetallacyclopentenone $(CO)_2$Ru(μ-η^1,η^1-CH=CHCO)(μ-DPPM)$_2$Ru$(CO)_2$ appears at 1534 cm^{-1}: Mirza, H. A.; Vittal, J. J.; Puddephatt, R. J. *Organometallics* **1994**, *13*, 3063. See also: Johnson, K. A.; Gladfelter, W. L. *Organometallics* **1992**, *11*, 2534.

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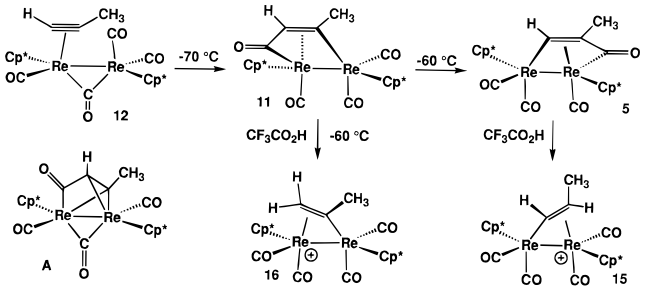
(10) The resonance at δ 8.92 was sharp at −10 °C ($\omega_{1/2}$ = 0.63 Hz) but selectively broadened at higher temperature ($\omega_{1/2}$ = 7.4 Hz, 25 °C). We do not understand this broadening.

cm^{-1} assigned to the ester and ketone carbonyls. In the ^{13}C NMR spectrum of **10**, resonances at δ 41.4 and 135.9 were assigned to the α- and β-carbons of the dimetallacyclopentenone.

Without a proton substituent on the dimetallacyclopentenone, the regiochemistry of **10** was more difficult to assign. The regiochemistry of **10** was assigned on the basis of the comparison of the chemical shift of the methyl group in **10** (δ 1.93) to the chemical shifts of the methyl groups in the two regioisomeric propyne adducts $Cp^*(CO)_2Re[\mu\text{-}\eta^1,\eta^3\text{-}CH{=}C(CH_3)CO]Re(CO)Cp^*$ (**5**, δ 1.83) and $Cp^*(CO)_2Re[\mu\text{-}\eta^1,\eta^3\text{-}(CH_3)C{=}CHCO]Re(CO)Cp^*$ (**11**, δ 2.95, see below). From this we conclude that the ester substituent is bound to the bridging carbon and the methyl group is bound to the carbon α to the ketone.

Scheme 2



Low-Temperature Observation of Two Intermediates in the Reaction of Propyne with 1. To probe the mechanism of alkyne addition to **1**, the reactions were monitored at low temperature by ^1H NMR spectroscopy. The reaction of **1** with acetylene was too fast to observe an intermediate even at −78 °C.[2] However, when the course of the reaction of propyne with **1** was followed by ^1H NMR spectroscopy at low temperature, two intermediates were observed prior to the formation of dimetallacyclopentenone **5** (Scheme 2). A ^1H NMR spectrum taken after 21 min at −80 °C revealed an 80:20 mixture of two compounds. The ^1H NMR spectrum of the major component is consistent with formulation as the η^2-alkyne complex $Cp^*(CO)_2Re(\mu\text{-}CO)Re(CO)(\eta^2\text{-}HC{\equiv}CCH_3)Cp^*$ (**12**). Resonances for inequivalent Cp* ligands were observed at δ 1.73 and 1.51. The resonance for the alkyne proton appeared at δ 6.84 (q, J = 2.2 Hz) and a methyl resonance appeared at δ 2.30 (d, J = 2.2 Hz). Due to the short lifetime of **12**, ^{13}C NMR and IR spectra were not obtained.

The structure of **12** is similar to that previously assigned to the 1:1 adduct $Cp^*(CO)_2Re(\mu\text{-}CO)Re(CO)(\eta^2\text{-}CH_3C{\equiv}CCH_3)Cp^*$ (**2**) which was formed in the reaction of **1** with 2-butyne at −60 °C and which rearranged to the dimetallacyclopentenone $Cp^*(CO)_2Re[\mu\text{-}\eta^1,\eta^3\text{-}C(CH_3){=}C(CH_3)CO]Re(CO)Cp^*$ (**13**) at −40 °C. The structure of **2** was supported by low-temperature IR and ^1H NMR spectroscopy. The infrared spectrum of **2** at −78 °C showed bands for three terminal carbonyls (1925, 1892, 1855 cm^{-1}) and a bridging carbonyl (1662 cm^{-1}). The ^1H NMR spectrum of **2** at −60 °C showed inequivalent Cp*'s (δ 1.73, 1.56) and a single broad resonance for the methyl groups (δ 2.41, $\omega_{1/2}$ = 8 Hz).

The δ 6.84 chemical shift for the CH resonance assigned to **12** falls in the range previously reported for η^2-terminal alkyne complexes [δ 4.02 for $CpRu(PMe_3)_2(\eta^2\text{-}HC{\equiv}CCH_3)$,[11] δ 4.8 for $Cp^*Re(CO)_2(\eta^2\text{-}HC{\equiv}CCH_3)$,[12] δ ~7 for $(\eta^2\text{-}HC{\equiv}CC_6H_5)_2Mo(Ph_2PCH_2CH_2PPh_2)$,[13] and δ 7.68 for $Cp_2Mo(\eta^2\text{-}HC{\equiv}CH)$[14]]. However, this low-frequency chemical shift is also consistent with formulation of the first intermediate as the dimetallatricyclopentanone $Cp^*(CO)Re(\mu\text{-}CO)[\mu\text{-}\eta^2,\eta^2\text{-}C(CH_3)CHCO]Re(CO)Cp^*$ (**A**). The only reported dimetallatricyclopentanone with a hydrogen substituent is Chetcuti's $CpNi[\mu\text{-}\eta^2,\eta^2\text{-}C(Ph)CHCO]Mo(CO)_2Cp$, which has a ^1H NMR chemical shift of δ 7.45 for the key hydrogen.[15]

When the temperature of the reaction mixture of **1** and propyne was raised to −70 °C, the amount of **12** decreased and the amount of the minor component **11** increased. After 14 min at −70 °C, the ratio of **12**:**11** was 67:33. When the temperature was raised to −60 °C, a third compound **5** slowly began to appear. After 13 min at −60 °C, the ratio of **12**:**11**:**5** was 16:69:15. After 23 min at −60 °C, **12** had completely disappeared and **11** and **5** were observed in a ratio of 58:42. After 63 min at −60 °C, the dimetallacyclopentenone $Cp^*(CO)_2Re[\mu\text{-}\eta^1,\eta^3\text{-}CH{=}C(CH_3)CO]Re(CO)Cp^*$ (**5**) (the isolated product of the room-temperature reaction) was the major product and only a trace of **11** remained (**11**:**5** = 5:95).

The spectra of the second intermediate **11** are consistent with its formulation as the regioisomeric dimetallacyclopentenone $Cp^*(CO)_2Re[\mu\text{-}\eta^1,\eta^3\text{-}C(CH_3){=}CHCO]Re(CO)Cp^*$ (**11**) in which the methyl-substituted carbon bridges the two Re centers. In the ^1H NMR spectrum of **11**, inequivalent Cp* resonances were observed at δ 1.75 and 1.52. The chemical shift of the methine proton of **11** at δ 3.06 (br s) was quite similar to that of the proton α to the ketone in the dimetallacyclopentenone **4** formed from acetylene (δ 3.57) and greatly different from that of the proton β to the ketone in **4** (δ 8.14). The chemical shift of the methyl resonance of **11** at δ 2.95 (br s) appeared near that of one of the two methyl resonances (δ 2.92, 1.68) of the dimetallacyclopentenone **13** formed from 2-butyne.[2]

***μ*-Vinyl Complexes from Protonation of Dimetallacyclopentenones.** Knox[6f] has shown that diferra- and diruthenacyclopentenones undergo selective protonolysis of the $C_\alpha{-}C{=}O$ bond to give cationic bridging vinyl complexes. We began a study of the protonation of dirhenacyclopentenones in an effort to provide more evidence concerning the regiochemistry of **11**, the kinetic regioisomer obtained in the reaction of **1** with propyne.

The reaction of dimetallacyclopentenone **4** (from HC≡CH and **1**) with CF_3CO_2H in toluene led to cleavage of the $C_\alpha{-}C{=}O$ bond and formation of the yellow μ-vinyl complex $[Cp^*(CO)_2Re(\mu\text{-}\eta^1,\eta^2\text{-}CH{=}CH_2)Re(CO)_2Cp^*]^+CF_3CO_2^-$ (**14**) in 52% isolated yield. In the ^1H NMR spectrum (CD_2Cl_2), inequivalent Cp* resonances were seen at δ 2.06 and 2.05. The vinyl hydrogen on the

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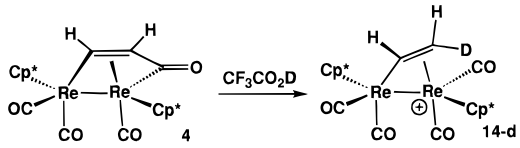


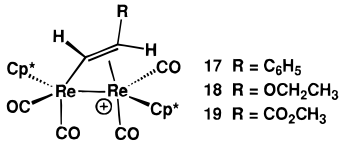
carbon bridging the rheniums appeared at δ 7.92 (dd, J_{trans} = 12 Hz, J_{cis} = 9 Hz) and the =CH_2 protons were observed at δ 4.07 (dd, J_{cis} = 9 Hz, J_{gem} = 1.4 Hz) and 2.63 (dd, J_{trans} = 12 Hz, J_{gem} =1.4 Hz). The reaction of **4** with CF_3CO_2D was stereospecific. The δ 2.63 resonance due to the vinyl hydrogen cis to Re was absent in deuterated vinyl complex [Cp*(CO)$_2$Re(μ-η^1,η^2-(*Z*)-CH=CHD)Re(CO)$_2$Cp*]$^+$$CF_3CO_2^-$ (**14-*d***).

Reaction of the thermodynamic regioisomer **5** (from **1** and propyne) with CF_3CO_2H gave a single μ-vinyl complex, [Cp*(CO)$_2$Re(μ-η^1,η^2-(*E*)-CH=CHCH$_3$)Re(CO)$_2$Cp*]$^+$$CF_3CO_2^-$ (**15**), in 62% isolated yield (Scheme 2). The ^{1}H NMR spectrum of **15** consisted of resonances for inequivalent Cp* ligands at δ 2.11 and 2.05, a methyl doublet at δ 1.90 (d, J = 6.2 Hz), and vinyl resonances at δ 7.50 (d, J_{trans} = 11.4 Hz) and 3.06 (dq, J_{trans} = 11.6, J = 6.2 Hz). The magnitude of the coupling between the vinyl protons is consistent with an *E* configuration of the vinyl group.

The protonation of the kinetic regioisomer **11** formed in the reaction of **1** with propyne at −60 °C gave a different μ-vinyl complex. In an NMR tube reaction of **1** with propyne at −60 °C, a color change to orange over 5 min indicated the formation of the initial dimetallacyclopentenone **11** (Scheme 2). Treatment of this solution of **11** with excess CF_3CO_2H at −60 °C gave a fast color change to yellow. The ^{1}H NMR spectrum of the yellow solution indicated the clean formation of the cationic bridging vinyl complex [Cp*(CO)$_2$Re(μ-η^1,η^2-CCH$_3$=CH$_2$)Re(CO)$_2$Cp*]$^+$$CF_3CO_2^-$ (**16**); no resonances for the μ-vinyl complex **15** derived from the thermodynamic regioisomer **5** were observed. Evaporation of solvent and crystallization from Et_2O gave pure **16** in 52% isolated yield.

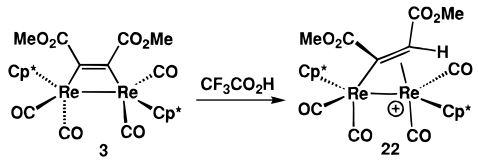
The ^{1}H NMR spectrum of **16** (CD_2Cl_2) showed inequivalent Cp* resonances (δ 2.07, 2.03), a broad methyl resonance at δ 3.13, and vinyl resonances at δ 4.09 (d, J = 0.8 Hz) and 1.95 (d, J = 0.8 Hz). The absence of a far downfield resonance for a proton on a bridging carbon confirmed that the methyl occupied the α position. The chemical shifts and the small geminal coupling constant for the vinyl protons were similar to those seen for the =CH_2 group of the unsubstituted bridging vinyl complex **14**.

When CF_3CO_2H was added to the solution of **1** and propyne after 15 min reaction time at −60 °C, a 1:1 mixture of μ-vinyl complexes **15** and **16** was observed. Dimetallacyclopentenones **6**, **8**, and **9** also reacted with CF_3CO_2H in toluene to produce cationic bridging vinyl complexes **17**, **18**, and **19** which were isolated as yellow-orange powders in low to moderate yields (37−65%).



Surprisingly, protonation of the dimetallacyclopentenone **10** derived from methyl 2-butynoate was not regiospecific. Treatment of **10** with CF_3CO_2H in toluene gave a 60:40 mixture of the two regioisomeric μ-vinyl cation complexes {Cp*(CO)$_2$Re[μ-η^1,η^2-(*E*)-CC(CO$_2$CH$_3$)=CH(CH$_3$)]Re(CO)$_2$Cp*}$^+$$CF_3CO_2^-$ (**20**) and {Cp*(CO)$_2$Re[μ-η^1,η^2-(*E*)-C(CH$_3$)=CH(CO$_2$CH$_3$)]Re(CO)$_2$Cp*}$^+$$CF_3CO_2^-$ (**21**).

Treatment of dimetallacyclobutene **3**[16] with CF_3CO_2H produced the μ-vinyl complex {Cp*(CO)$_2$Re[μ-η^1,η^2-(*E*)-(CH$_3$CO$_2$)C=CH(CO$_2$CH$_3$)]Re(CO)$_2$Cp*}$^+$$CF_3CO_2^-$ (**22**).

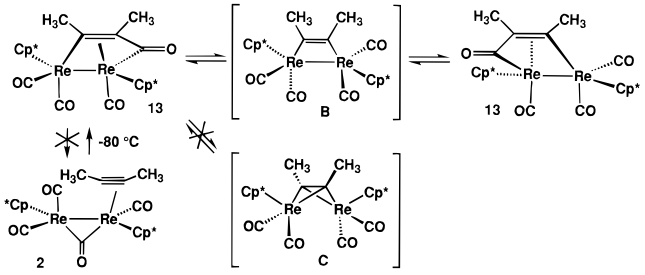


The ^{1}H NMR spectrum of **22** had resonances for inequivalent Cp* ligands (δ 2.13, 2.06), inequivalent methoxy groups (δ 3.78, 3.75), and a vinyl proton (δ 2.37). Previously, Stone reported that protonation of the diplatinacyclobutene (cod)Pt(μ-η^1,η^1-CF_3C=CCF_3)-Pt(cod) (cod = cyclooctadiene) with HBF_4·Et_2O gave the μ-vinyl cation [(cod)Pt(μ-η^1,η^2-CF_3C=$CHCF_3$)Pt(cod)]$^+$-BF_4^- and that protonation of (cod)Pt(μ-η^1,η^1-*p*-MeOC$_6$F$_4$C=CC$_6$F$_4$-*p*-OMe)Pt(cod) gave the bridging hydride [(cod)Pt(μ-H)(μ-η^1,η^1-*p*-MeOC$_6$F$_4$C=CC$_6$F$_4$-*p*-OMe)Pt(cod)]$^+$$BF_4^-$.[17]

Discussion

Mechanism of Interconversion of Regioisomeric Dimetallacyclopentenones. The dimetallacyclopentenones Cp*(CO)$_2$Re(μ-η^1,η^3-HC=CHCO)Re(CO)Cp* (**4**) and Cp*(CO)$_2$Re(μ-η^1,η^3-C(CH$_3$)=C(CH$_3$)CO)Re(CO)Cp* (**13**) are both fluxional molecules. Variable-temperature ^{1}H NMR spectroscopy of **4** showed coalescence of the Cp* resonances at 70 °C ($\Delta G^‡$ = 16.8 kcal mol^{-1}). Magnetization transfer experiments on **4** showed that the methine protons exchanged environments with an activation barrier ($\Delta G^‡$ = 16.9 kcal mol^{-1}) similar to that for the Cp* exchange. Substantially lower barriers were seen for coalescence of the Cp* resonances ($\Delta G^‡$ = 13.6 ± 0.3 kcal mol^{-1}) and the methyl resonances ($\Delta G^‡$ = 14.6 ± 1.0 kcal mol^{-1}) of **13**. While an η^2-alkyne complex such as **2** could account for interchange of methyl environments, a symmetric intermediate such as dimetallacyclobutene **B** or dimetallabicyclobutane **C** are required to explain the simultaneous interchange of both the Cp* and dimetallacyclopentenone substituent environments (Scheme 3).

Scheme 3



(16) Protonation of the dimetallabicyclobutane complex Cp*(CO)$_2$Re(μ-η^2,η^2-CH$_3$O$_2$CC≡CCO$_2$CH$_3$)Re(CO)$_2$Cp* with CF_3CO_2H also produced μ-vinyl complex **22**.

(17) Boag, N. M.; Green, M.; Stone, F. G. A. *J. Chem. Soc., Chem. Commun.* **1980**, 1281.

Variable-temperature ^{1}H NMR spectroscopy experiments on $Cp^*(CO)_2Re(\mu\text{-}\eta^1,\eta^3\text{-}CH{=}CCH_3CO)Re(CO)Cp^*$ (**5**) allowed us to rule out dimetallabicyclobutanes as intermediates in the isomerization of regioisomeric dimetallacyclopentenones and the fluxional process that interchanges the environments of Cp* ligands in **4** and **13**. No excess line broadening ($\omega_{1/2}$ = 1.0 Hz) in the Cp* resonances of **5** was observed at 100 °C. Assuming a maximum excess line broadening of 0.2 Hz at 100 °C allowed calculation of a maximum rate of exchange of 3 s^{-1} and a minimum barrier of $\Delta G^{\ddagger}$ = 23 kcal mol^{-1} for the interchange of Cp* environments. If propyne-derived dimetallacyclopentenone **5** interconverts with its regioisomer **11** via a dimetallabicyclobutane, then the barrier for Cp* interchange would be expected to be intermediate between that of the HC≡CH derived dimetallacyclopentenone **4** ($\Delta G^{\ddagger}$ = 16.8 kcal mol^{-1}) and that of the $CH_3C{\equiv}CCH_3$ derived dimetallacyclopentenone **13** ($\Delta G^{\ddagger}$ = 13.6 kcal mol^{-1}). Since the barrier for Cp* interchange must be higher than 23 kcal mol^{-1}, a dimetallabicyclobutane can be excluded as an intermediate.

Crude estimates of the half-life for the conversion of $Cp^*(CO)_2Re(\mu\text{-}\eta^1,\eta^3\text{-}CCH_3{=}CHCO)Re(CO)Cp^*$ (**11**) to its regioisomer **5**[18] allowed us to calculate $\Delta G^{\ddagger}$ = 15 kcal mol^{-1} for the process. This barrier is intermediate between the barriers measured for the Cp* coalescence of **4** (16.8 kcal mol^{-1}) and **13** (13.6 kcal mol^{-1}). We suggest that conversion of **11** to its regioisomer **5** proceeds via the same process which equilibrates the Cp* signals in **4** and **13** and that these processes all involve dimetallacyclobutene intermediates.

Relative Stability of (η^2-Alkyne)dirhenium Complexes, Dirhenacyclobutenes, and Dirhenacyclopentenones. $Cp^*(CO)_2Re{=}Re(CO)_2Cp^*$ (**1**) reacts with various alkynes to give a fascinating array of products including (η^2-alkyne)dirhenium complexes, dimetallacyclopentenones, dimetallacyclobutenes, and dimetallabicyclobutanes (Scheme 1). The dimetallacyclopentenone **4** derived from acetylene was stable at 105 °C for over 10 min, but the dimetallacyclopentenone **13** derived from 2-butyne fragmented to $Cp^*Re(CO)_3$ and the 4-electron donor alkyne complex $Cp^*Re(CO)(CH_3C{\equiv}CCH_3)$ at room temperature. These results prompted us to further investigate the factors which determine the chemoselectivity of the reaction of **1** with alkynes and the factors which control the stability of dimetallacyclopentenones.

Overall, our observations on the reactions of **1** with alkynes suggest that (η^2-alkyne)dirhenium complexes, dirhenacyclobutenes, and dirhenacyclopentenones are all readily interconverted. The least stable of these species are the η^2-alkyne dirhenium complexes such as propyne complex **12** and 2-butyne complex **2**; these kinetically formed products rearranged to dimetallacyclopentenones well below room temperature. Earlier we suggested the possibility that the decomposition of the dimetallacyclopentenone **13** occurred by initial reversal to the less stable η^2-alkyne complex **2** followed by fragmentation to $Cp^*Re(CO)_3$ and $Cp^*Re(CO)(CH_3C{\equiv}CCH_3)$. The reaction of DMAD with **1** produced the dirhenacyclobutene **3**, the formal product of a symmetry-forbidden 2 + 2 cycloaddition; we suggested that **3** is formed in a stepwise manner by initial formation of an unstable η^2-alkyne dirhenium complex followed by rearrangement.

The fluxional behavior of dirhenacyclopentenones **4** and **13** taken together with the rearrangement of **11** to its regioisomer **5** provides compelling evidence for an equilibrium between dirhenacyclopentenones and dirhenacyclobutenes and for the greater stability of dirhenacyclopentenones derived from most alkynes. Two ester substituents are apparently required to invert the normally greater stability of the dimetallacyclopentenones as seen in the formation of dimetallacyclobutene **3** from reaction of DMAD with **1**. Even alkynes with a single ester substituent such as $HC{\equiv}CCO_2Me$ and $MeC{\equiv}CCO_2Me$ form only dimetallacyclopentenones **9** and **10**. Apparently, the strongly electron-withdrawing ester substituents selectively stabilize dirhenacyclobutenes relative to dirhenacyclopentenones. The stabilizing effect of electron-withdrawing substituents on a dirhenacyclobutene are readily explained; a μ-DMAD unit is electronically similar to a μ-CO group and can effectively remove electron density from the electron rich rhenium centers. There are numerous examples of dimetallacyclobutenes with electron-withdrawing CF_3 or CO_2R substituents.[8] Electron-withdrawing substituents apparently have less influence on the stability of dirhenacyclopentenones.

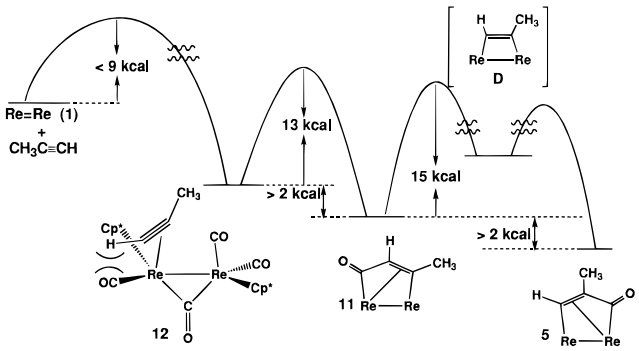
Electronic effects are apparently unimportant in controlling the stability of dimetallacyclopentenones with respect to fragmentation to 4-electron donor alkyne complexes $Cp^*Re(CO)$(alkyne). Dimetallacyclopentenones with a single electron-withdrawing ester substituent (**9** and **10**) or an electron donor alkoxy substituent (**8**) are thermally stable. The fact that dirhenacyclopentenone **13** derived from 2-butyne fragmented at room temperature while adducts of terminal alkynes were stable suggested that steric factors may determine the stability of the dirhenacyclopentenones. Examination of molecular models revealed that a substituent on the carbon α to the ketone was in a relatively uncrowded environment while a substituent on the β carbon bridging the two rhenium was in close proximity to the Cp* ligands on both metals. In dimetallacyclopentenones derived from terminal alkynes a proton occupies the more crowded β site, but this option does not exist for dimetallacyclopentenone **13** derived from 2-butyne.

It is curious that the internal alkyne methyl 2-butynoate forms the stable dimetallacyclopentenone **10**. One could argue that the ester group is small enough to occupy the crowded β site without significant interaction with the Cp* ligands. It is also possible that the electron-withdrawing group stabilizes the product with respect to fragmentation. One possible reason that the 2-butyne adduct fragments is that the product $Cp^*Re(CO)(CH_3C{\equiv}CCH_3)$ contains an alkyne acting as a four-electron donor. A less electron-releasing alkyne such as methyl 2-butynoate may not be able to stabilize a similar product.

Regioselectivity of the Reaction of 1 with Propyne. Any explanation of the regioselectivity of the addition of propyne to **1** is necessarily complicated by the low barrier to interconversion of dirhenacyclopentenones and dirhenacyclobutenes, either of which might be the kinetic product of rearrangement of the initially

(18) Assuming a first-order rate constant for the conversion of **11** to **5** allowed estimation of a rate constant $k = 9.6 \times 10^{-4}$ s^{-1} and an activation barrier of $\Delta G^{\ddagger}$ = 15 kcal mol^{-1}.

Scheme 4

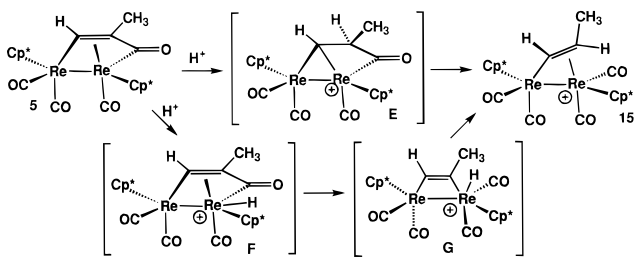


observed η^2-propyne complex **12**. The most straightforward explanation for the course of the reaction of **1** with propyne involves initial formation of η^2-propyne complex **12**, followed by conversion to the more crowded kinetic regioisomeric dimetallacyclopentenone **11**, and finally isomerization to the less crowded thermodynamically favored dimetallacyclopentenone **5** via dimetallacyclobutene intermediate **D** (Scheme 4). A possible rationale for the selective formation of kinetic regioisomer **11** is that carbon−carbon bond formation between CO and the less crowded terminal alkyne carbon is preferred even though it leads to the less stable regioisomer.

Another route to the kinetic regioisomer **11** that cannot be excluded involves initial conversion of η^2-propyne complex **12** to dimetallacyclobutene intermediate **D** which then undergoes highly selective rearrangement to **11** in preference to **5**. Eventually, **11** could be converted to **5** via **D**.

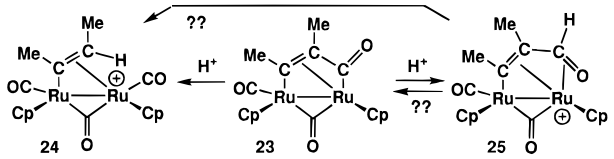
Mechanism of (μ-Vinyl)dirhenium Complex Formation. Any mechanism for the conversion of dimetallacyclopentenones to μ-vinyl cations must account for the regiospecific protonation of the regioisomeric dimetallacyclopentenones **5** and **11** derived from propyne and for the stereospecific deuteration of the dimetallacyclopentenone **4** derived from acetylene. The interconversion of dimetallacyclopentenones and dimetallacyclobutenes also complicates the determination of the mechanism of these protonations. The net transformation involving cleavage of a carbon−carbon bond α to a ketone by H^+ is unusual.

Scheme 5



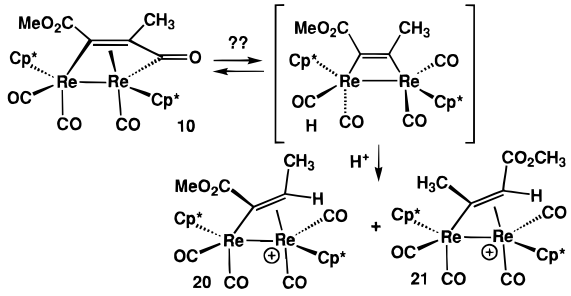
One possible mechanism involves stereospecific protonation of the carbon alpha to the ketone from the side opposite Re to give **E**, followed by ring opening (Scheme 5). Such a protonation for an organic ketone is unprecedented. A second possible mechanism involves protonation at rhenium bound to the ketone carbonyl to give **F**, followed by ring contraction of the dimetallacyclopentenone to give a protonated dimetallacyclobutene **G** and reductive elimination of the vinyl unit. Rearrangement of the dimetallacyclopentenone to a dimetallacyclobutene prior to protonation can be excluded since it is inconsistent with the regioselective cleavage of the regioisomeric dimetallacyclopentenones **5** and **11**. The observation that the dimetallacyclobutene **3** derived from DMAD is cleaved by acid to give a (μ-vinyl)-dirhenium cation is consistent with the latter mechanism.

Knox found that diruthenacyclopentenone **23** is cleaved by acid to give a μ-vinyl cation **24**.[6f] The reaction proceeds via the isolable intermediate **25**. It is not clear whether **25** is converted directly to the μ-vinyl cation **24** or whether it first reverts to the starting dimetallacyclopentenone **23**.



Protonation of the dimetallacyclopentenone **10** derived from methyl 2-butynoate was nonregiospecific and gave a mixture of the regioisomeric (μ-vinyl)dirhenium cations **20** and **21**. In this case, it is possible that the reaction proceeds by prior rearrangement to dimetallacyclobutene **H**, followed by protonation at either rhenium and elimination to give μ-vinyl cations **20** and **21** (Scheme 6). The ability of ester substituents to stabilize dimetallacyclobutenes makes this mechanism plausible for protonation of **10** than for dimetallacyclopentenones without ester substituents.

Scheme 6



Experimental Section

General Methods. ^{1}H NMR spectra were obtained on a Bruker WP200, AC300, or AM500 spectrometer. $^{13}C\{^1H\}$ spectra were obtained on a Bruker AM500 spectrometer (126 MHz). Infrared spectra were measured on a Mattson Polaris (FT) or a Mattson Genesis (FT) spectrometer. High resolution mass spectra were obtained on a Kratos MS-80. LSIMS was performed on a VG Autospec M using a 3-nitrobenzyl alcohol matrix.

Toluene-d_8, THF-d_8, THF, C_6D_6, ether, and pentane were distilled from purple solutions of sodium benzophenone ketyl immediately prior to use. CH_2Cl_2 was distilled from CaH_2. CD_2Cl_2 was dried over P_2O_5 and distilled from CaH_2. Air-sensitive materials were manipulated by standard Schlenk techniques or in an inert-atmosphere glovebox. Propyne was purified by fractional distillation under vacuum at −78 °C to remove acetylene. Phenylacetylene, methyl propynoate, ethyl ethynyl ether, and methyl 2-butynoate were purchased from Aldrich and freeze−pump−thaw degassed.

Cp*(CO)$_2$Re[μ-η^1,η^3-CH=C(CH$_3$)CO]Re(CO)Cp* (5). Excess propyne (0.12 mmol) was condensed onto a solution of **1** (30 mg, 40 μmol) in THF (10 mL) at −196 °C. The mixture

was warmed to room temperature, and the resulting red solution was concentrated under vacuum. Hexane was added, and the solution was cooled to −78 °C to give **5** (23 mg, 29 μmol, 73%) as an orange solid. ^{1}H NMR (300 MHz, C_6D_6): δ 8.04 (s, ReCH), 1.83 (s , CH_3), 1.80 (s, Cp*), 1.69 (s, Cp*). ^{13}C-{^{1}H} NMR (126 MHz, C_6D_6): δ 211.1, 210.4, 208.8, 208.0 (CO's); 124.4 (CH); 98.6, 98.1 (s, C_5Me_5); 46.7 (s, CCH_3); 21.6 (CCH_3); 10.8, 10.0 (Cp*CH_3). IR (toluene): 1944 (s), 1899 (vs), 1849 (s), 1700 (m) cm^{-1}. HRMS calcd (found) for $C_{26}H_{34}O_4{}^{187}Re_2$: m/z 796.157 (796.159).

General Procedure for Preparation of Dimetallacyclopentenones 6 and 8−10. At room temperature, a green solution of **1** (25−50 mg, 33−66 μmol) in C_6H_6 (1 mL) was titrated with a colorless solution containing one drop of alkyne (∼10 mg, ∼100 μmol) in C_6H_6 (2 mL) until the color changed (about 30−60% of benzene solution) from green to orange (**6**), red (**8**, **9**), or purple (**10**). Volatiles were evaporated under vacuum and the solid residue was suspended in 6 mL of pentane with minimal THF added to nearly dissolve the remaining solids. The suspensions were filtered, cooled to −40 °C overnight, and filtered cold to give the dimetallacyclopentenones as powders which were washed twice with 2 mL of pentane and dried.

Cp*(CO)$_2$Re[μ-η^1,η^3-CH=C(C$_6$H$_5$)CO]Re(CO)Cp* (6). Phenylacetylene and **1** (20 mg, 27 μmol) gave **6** (11 mg, 48%) as an orange solid. ^{1}H NMR (300 MHz, THF-d_8): δ 8.70 (s, ReCH), 7.71 (dd, J = 7.8, 1.0 Hz, H_o), 7.35 (td, J = 7.2, 1.0 Hz, H_m), 7.22 (tt, J = 7.5, 1.2 Hz, H_p), 1.88 (s, Cp*), 1.71 (s, Cp*). ^{13}C{^{1}H} NMR (126 MHz, C_6D_6): δ 211.0, 209.6, 208.4, 208.2 (CO's); 138.2 (C_{ipso}); 130.2, 129.0 (C_m, C_o); 127.9 (C_p); 114.6 (ReCH); 99.3, 98.8 (C_5Me_5); 52.2 [$C(C_6H_5)$]; 10.9, 9.8 (Cp*CH_3). IR (KBr): 1951 (s), 1902 (vs), 1851 (s), 1699 (m) cm^{-1}. HRMS calcd (found) for $C_{32}H_{36}O_4{}^{187}Re_2$: m/z 858.173 (858.176). Anal. Calcd for $C_{32}H_{36}O_4Re_2$: C, 44.85; H, 4.23. Found: C, 44.68; H, 4.16.

Cp*(CO)$_2$Re[μ-η^1,η^3-CH=C(OCH$_2$CH$_3$)CO]Re(CO)Cp* (8). Ethyl ethynyl ether and **1** (50 mg, 66 μmol) gave **8** (37 mg, 68%) as a red solid. ^{1}H NMR (300 MHz, C_6D_6): δ 7.98 (s, CH); 4.25 and 4.10 (two dq, J = 10.2, 7.2 Hz, diastereotopic CH_2); 1.81 (s, Cp*); 1.79 (s, Cp*); 1.20 (t, J = 7.2 Hz, CH_3). ^{13}C {^{1}H} NMR (126 MHz, C_6D_6): δ 213.6, 210.8 208.6, 206.2 (CO); 112.3 (ReCH); 99.2, 98.1 (C_5Me_5); 91.5 [C(OEt)]; 63.2 (CH_2); 15.8 (CH_2CH_3); 10.9, 9.7 (Cp*CH_3). IR (THF): 1943 (s), 1899 (vs), 1848 (s), 1676 (m) cm^{-1}. HRMS calcd (found) for $C_{28}H_{36}O_5{}^{187}Re_2$: m/z 826.163 (826.163). Anal. Calcd for $C_{28}H_{36}O_5Re_2$: C, 40.77; H, 4.40. Found: C, 40.69; H, 4.28.

Cp*(CO)$_2$Re[μ-η^1,η^3-CH=C(CO$_2$CH$_3$)CO]Re(CO)Cp* (9). Methyl propynoate and **1** (40 mg, 48 μmol) gave **9** (30 mg, 70%) as a red-orange solid. ^{1}H NMR (500 MHz, CD_2Cl_2, −10 °C): δ 8.92 (s, CH), 3.77 (s, OCH_3), 1.88 (s, Cp*), 1.84 (s, Cp*). ^{13}C{^{1}H} NMR (126 MHz, CD_2Cl_2, −30 °C): δ 208.1, 207.1, 206.8, 205.7 (CO); 173.4 (CO_2); 124.8 (CH); 99.1, 98.2 (C_5Me_5); 52.1 (OCH_3); 34.7 (CCO_2); 10.6, 9.5 (Cp*CH_3). IR (THF): 1953 (s), 1906 (vs), 1869 (s), 1704 (m) cm^{-1}. HRMS calcd (found) for $C_{28}H_{34}O_6{}^{187}Re_2$: m/z 840.147 (840.153).

Cp*(CO)$_2$Re[μ-η^1,η^3-(CO$_2$CH$_3$)C=C(CH$_3$)CO]Re(CO)-Cp* (10). Methyl 2-butynoate and **1** (50 mg, 66 μmol) gave **10** (35 mg, 62%) as a purple solid. ^{1}H NMR (300 MHz, C_6D_6): δ 3.64 (s, OCH_3), 1.93 (s, CH_3), 1.79 (s, Cp*), 1.77 (s, Cp*). ^{13}C {^{1}H} NMR (126 MHz, C_6D_6): δ 211.3, 207.3, 206.0, 205.8 (CO); 176.4 (CO_2); 135.9 (ReCCO_2); 101.0, 99.2 (C_5Me_5); 50.7 (OCH_3); 41.4 (CCH_3); 17.2 (CCH_3); 10.4, 10.2 (Cp*CH_3). IR (THF): 1944 (s), 1909 (vs), 1867 (s), 1701 (m) cm^{-1}.

General Procedure for Preparation of Bridging Vinyl Complexes (14−20). Dimetallacyclopentenones were prepared from a solution of Cp*(CO)$_2$Re=Re(CO)$_2$Cp* (**1**) in toluene (3 mL) and the appropriate alkyne. The resulting solutions were evaporated to remove excess alkyne. A flask containing the dimetallacyclopentenone was attached to a reversible frit apparatus, and toluene (3 mL) was added. Addition of excess CF_3CO_2H by vacuum-transfer at −78 °C and warming to room temperature gave yellow-orange to dark orange solutions containing some toluene-insoluble material. Volitile materials were evaporated to give oily residues. Et_2O (4 mL) was added by vacuum-transfer and stirring gave yellow orange to orange precipitates which were filtered out, washed with Et_2O (2 × 4 mL), and dried. Alternatively, isolated dimetallacyclopentenones **4**−**6**, and **8**−**10** were used as starting materials. The yields from the two methods were comparable.

[Cp*(CO)$_2$Re(μ-η^1,η^2-CH=CH$_2$)Re(CO)$_2$Cp*]$^+$CF$_3$CO$_2^-$ (14). Addition of CF_3CO_2H to isolated and purified **4** (48 mg, 61 μmol) gave **14** (30 mg, 55%) as a yellow-orange solid. ^{1}H NMR (300 MHz, CD_2Cl_2): δ 7.92 (dd, J = 11.8, 9.2 Hz, CH), 4.07 (dd, J = 9.3, 1.4 Hz, =CHH), 2.63 (dd, J = 12.0, 1.4 Hz, =CHH), 2.06 (s, Cp*), 2.05 (s, Cp*). ^{13}C {^{1}H} NMR (126 MHz, CD_2Cl_2): δ 201.8, 198.8, 198.3, 198.2 (CO); 132.5 (ReC=); 104.2, 103.7 (C_5Me_5); 53.0 (CH_2); 10.8, 9.8 (Cp*CH_3). IR (CH_2-Cl_2): 2011 (m), 1981 (vs), 1939 (s), 1910 (m) cm^{-1}.

[Cp*(CO)$_2$Re(μ-η^1,η^2-(*E*)-CH=CHCH$_3$)Re(CO)$_2$-Cp*]$^+$CF$_3$CO$_2^-$ (15). Addition of CF_3CO_2H to isolated and purified **5** (10 mg, 13 μmol) in C_6H_6 (300 μL) gave **15** (7 mg, 62%) as a brown oil . ^{1}H NMR (300 MHz, CD_2Cl_2): δ 7.50 (d, J = 11.4 Hz, ReCH), 3.06 (dq, 11.6, 6.2 Hz, 1 H, =CHCH$_3$), 2.11 (s, Cp*), 2.05 (s, Cp*), 1.90 (d, J = 6.2 Hz, =CHCH_3). ^{13}C{^{1}H} NMR (126 MHz, CD_2Cl_2): δ 202.2, 201.3, 200.7, 199.4 (CO); 129.8 (ReC=); 104.2, 103.7 (C_5Me_5); 76.8 (CHCH$_3$); 25.4 (CHCH$_3$); 10.6,10.5 (Cp*CH_3). IR (CH_2Cl_2): 2002 (m), 1978 (vs), 1924 (s), 1879 (m) cm^{-1}.

[Cp*(CO)$_2$Re(μ-η^1,η^2CCH$_3$=CH$_2$)Re(CO)$_2$Cp*]$^+$-CF$_3$CO$_2^-$ (16). In a reversible frit apparatus, a green solution of **1** (38 mg, 50 μmol) in toluene (5 mL) was treated with excess propyne at −60 °C for 5 min to give an orange solution. CF_3-CO_2H (excess) was condensed into the solution. Solvent and excess propyne were evaporated under vacuum to give a brown oil. CH_2Cl_2 (1 mL) and pentane (5 mL) were condensed into the flask to give an orange precipitate. The solution was filtered cold and washed once with cold pentane to give **16** (24 mg, 52%) as a yellow-orange powder that was >95% pure by ^{1}H NMR spectroscopy. ^{1}H NMR (300 MHz, CD_2Cl_2): δ 4.09 (d, J = 0.8 Hz, =CHH), 3.13 (br s, CH_3), 2.07 (s, Cp*), 2.03 (s, Cp*), 1.95 (d, 0.8 Hz, =CHH). ^{13}C{^{1}H} NMR (126 MHz, CD_2-Cl_2): δ 204.0, 200.6, 200.2, 199.8 (CO); 145.6 (ReC=); 105.8, 103.9 (C_5Me_5); 53.5 (CH_2); 42.6 (CH_3); 10.0, 9.7 (Cp*CH_3). IR (CH_2Cl_2): 2006 (s), 1976 (vs), 1935 (vs), 1903 (m) cm^{-1}. LSIMS calcd (found) for $C_{27}H_{33}O_4{}^{187}Re_2$: m/z 797.2 (797.1).

{Cp*(CO)$_2$Re[μ-η^1,η^2-(*E*)-CH=CH(C$_6$H$_5$)]Re(CO)$_2$-Cp*}$^+$CF$_3$CO$_2^-$ (17). Orange **6** was prepared from **1** (54 mg, 71 μmol) and excess phenylacetylene in toluene (3 mL). Crude **6** was washed with ether to remove black ether-soluble impurities and was dissolved in toluene. Addition of CF_3CO_2H gave **17** as an orange powder (22 mg, 37%). ^{1}H NMR (300 MHz, CD_2Cl_2): δ 8.37 (d, J = 12.5 Hz, ReCH), 7.51 (d, J = 7.0 Hz, H_o), 7.43 (t, J = 7.0 Hz, H_m), 7.39 (d, J = 7.0 Hz, H_p), 4.42 (d, J = 12.2 Hz, =CHC$_6$H$_5$), 2.09 (s, Cp*), 1.86 (s, Cp*). ^{13}C{^{1}H} NMR (126 MHz, CD_2Cl_2): δ 202.0, 201.5, 199.0, 198.0 (CO); 138.5 (C_{ipso}); 130.3 (C_p); 129.3 and 127.3 (C_o and C_m); 122.7 (ReCH=); 104.4, 104.0 (C_5Me_5); 79.4 (=CHC$_6$H$_5$); 10.7, 10.0 (Cp*CH_3). IR (CH_2Cl_2): 2004 (s), 1988 (vs), 1932 (vs), 1894 (m) cm^{-1}. LSIMS calcd (found) for $C_{32}H_{37}O_4{}^{187}Re_2$: m/z 859.18 (859.2) M$^+$.

{Cp*(CO)$_2$Re[μ-η^1,η^2-(*E*)-CH=CH(OCH$_2$CH$_3$)]Re(CO)$_2$-Cp*}$^+$CF$_3$CO$_2^-$ (18). Purple **8** was prepared from **1** (64 mg, 85 μmol) and excess ethyl ethynyl ether in toluene (3 mL). Addition of CF_3CO_2H gave **18** as an orange powder (40 mg, 50%). ^{1}H NMR (300 MHz, CD_2Cl_2): δ 7.17 (d, J = 9.6 Hz, ReCH=), 5.32 (d, J = 9.0 Hz, =CHO), 4.04 (qd, J = 7.0, 1.5 Hz, OCH_2), 2.08 (s, 2 Cp*), 1.33 (t, J = 6.9 Hz, CH_2CH_3). ^{13}C {^{1}H} NMR (126 MHz, CD_2Cl_2): δ 203.4, 202.0, 198.9, 197.8 (CO); 119.4 (ReCH=); 106.2 (=CHO); 104.2, 103.4 (C_5Me_5); 70.0 (OCH_2); 15.1 (CH_2CH_3); 10.9, 10.2 (Cp*CH_3). IR (CH_2-Cl_2): 1956 (m), 1924 (vs), 1887 (s), 1863 (m) cm^{-1}. LSIMS calcd (found) for $C_{28}H_{36}O_5{}^{187}Re_2$: m/z 827.176 (827.2).

{Cp*(CO)$_2$Re[μ-η^1,η^2-(*E*)-CH=CH(CO$_2$CH$_3$)]Re(CO)$_2$-

Cp*}$^+$CF$_3$CO$_2^-$ (19). Red-orange **9** was prepared from **1** (60 mg, 79 μmol) and excess methyl propynoate in toluene (3 mL). Addition of CF_3CO_2H gave **19** (44 mg, 65%) as an orange powder. ^{1}H NMR (300 MHz, CD_2Cl_2): δ 8.24 (d, J = 11.2 Hz, ReCH), 3.79 (s, OCH_3), 2.95 (d, J = 11.0 Hz, =C*H*CO$_2$CH$_3$), 2.10 (s, Cp*), 2.06 (s, Cp*). ^{13}C{^{1}H} NMR (126 MHz, CD_2Cl_2): δ 200.8, 198.6, 196.80, 196.76 (CO); 171.9 (CO_2); 128.5 (ReCH=); 105.3, 104.3 (C_5Me_5); 59.5 (OCH_3); 53.0 (=*C*HCO$_2$CH$_3$); 10.6, 10.0 (Cp*CH_3). IR (CH_2Cl_2): 2013 (m), 1991 (vs), 1937 (s), 1898 (m), 1726 (m) cm^{-1}. LSIMS calcd (found) for $C_{28}H_{35}O_6{}^{187}Re_2$: m/z 841.16 (841.2).

{Cp*(CO)$_2$Re[μ-η^1,η^2-(*E*)-C(CO$_2$CH$_3$)=CH(CH$_3$)]Re(CO)$_2$Cp*}$^+$CF$_3$CO$_2^-$ (20) and {Cp*(CO)$_2$Re[μ-η^1,η^2-(*E*)-C(CH$_3$)=CH(CO$_2$CH$_3$)]Re(CO)$_2$Cp*}$^+$CF$_3$CO$_2^-$ (21). **10** was prepared from **1** (54 mg, 71 μmol) and excess methyl 2-butynoate in 3 mL of toluene. The purple solution of **10** was evaporated to remove excess alkyne. Toluene (3 mL) and excess CF_3CO_2H were added to give a 60:40 mixture of **20**:**21**, which was isolated as an orange powder (29 mg, 48%) and characterized as a mixture.

^{1}H NMR (300 MHz, CD_2Cl_2): Spectrum assigned to **20**, δ 3.86 (s, OCH_3), 2.47 (q, J = 6.3 Hz, =C*H*CH$_3$), 2.12 (s, Cp*), 2.04 (s, Cp*), 1.82 (d, J = 6 Hz, =CHC*H*$_3$); spectrum assigned to **21**, δ 3.76 (s, OCH_3), 3.34 (s, CH_3), 2.57 (s, =CHCO$_2$Me), 2.10 (s, Cp*), 2.05 (s, Cp*). ^{13}C{^{1}H} NMR (126 MHz, CD_2Cl_2): Spectrum assigned to **20**, δ 136.2 (Re*C*CO$_2$CH$_3$), 106.2, 103.7 (C_5Me_5), 66.9 (OCH_3), 52.6 (*C*CH$_3$), 24.0 (C*C*H$_3$), 9.8, 9.5 (Cp*CH$_3$); spectrum assigned to **21**, δ 136.2 (Re*C*CH$_3$), 105.7, 103.2 (C_5Me_5), 61.3 (OCH_3), 52.4 (*C*CO$_2$CH$_3$), 35.7 (C*C*H$_3$), 9.6, 9.2 (Cp**C*H$_3$). Unassignable: 201.2, 200.1, 199.6, 197.4, 197.1 (2), 196.3 (2) (CO's). Ester carbonyl carbons were not observed. IR (CH_2Cl_2) of mixture: 1956 (m), 1924 (vs), 1887 (s), 1863 (m) cm^{-1}. LSIMS calcd (found) for $C_{28}H_{36}O_5{}^{187}Re_2$ (cation): m/z 827.176 (827.2) M$^+$.

{Cp*(CO)$_2$Re[μ-η^1,η^2-(*E*)-(CH$_3$CO$_2$)C=CH(CO$_2$CH$_3$)]Re(CO)$_2$Cp*}$^+$ CF$_3$CO$_2^-$ (22). Addition of excess CF_3CO_2H to an orange solution of **3** (32 mg, 42 μmol) in toluene (3 mL) gave an immediate color change to yellow. Evaporation of solvent followed by washing with ether gave **22** (20 mg, 43%) as an orange solid. ^{1}H NMR (300 MHz, CD_2Cl_2): δ 3.79 (s, OCH_3), 3.75 (s, OCH_3), 2.37 (s, C=CH), 2.14 (s, Cp*), 2.06 (s, Cp*). LSIMS calcd (found) for $C_{30}H_{37}O_8{}^{187}Re_2$ (cation): m/z 899.2 (899.2).

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