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Structural Isomers of Aryl-Substituted η^3-Propargyl Complexes: η^2-1-Metalla(methylene)cyclopropene and η^3-Benzyl Complexes

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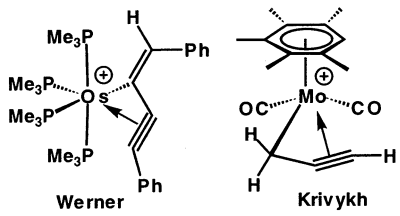
Abstract: Hydride abstraction from $C_5Me_5(CO)_2Re(\eta^2\text{-PhC}{\equiv}CCH_2Ph)$ (**1**) gave a 3:1 mixture of η^3-propargyl complex $[C_5Me_5(CO)_2Re(\eta^3\text{-PhCH}{-}C{\equiv}CPh)][BF_4]$ (**5**) and η^2-1-metalla(methylene)cyclopropene complex $[C_5Me_5(CO)_2Re(\eta^2\text{-PhC}{-}C{=}CHPh)][BF_4]$ (**6**). Observation of the η^2-isomer requires 1,3-diaryl substitution and is favored by electron-donating substituents on the C_3-aryl ring. Interconversion of η^3-propargyl and η^2-1-metalla(methylene)cyclopropene complexes is very rapid and results in coalescence of Cp* ^{1}H NMR resonances at about −50 °C. Protonation of the alkynyl carbene complex $C_5Me_5(CO)_2Re{=}C(Ph)C{\equiv}CPh$ (**22**) gave a third isomer, the η^3-benzyl complex $\{C_5Me_5(CO)_2Re[\eta^3(\alpha,1,2)\text{-}endo,syn\text{-}C_6H_5CH(C{\equiv}CC_6H_5)]\}$-$[BF_4]$ (**23**) along with small amounts of the isomeric complexes **5** and **6**. While **5** and **6** are in rapid equilibrium, there is no equilibration of the η^3-benzyl isomer **23** with **5** and **6**.

Introduction

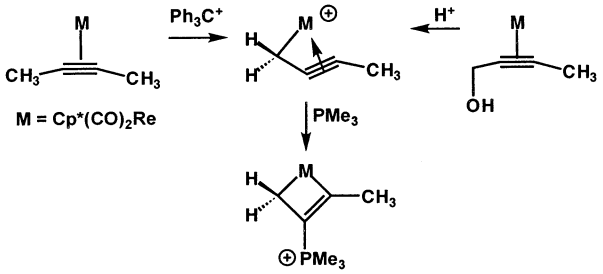
η^3-Propargyl complexes are the triple bond analogues of synthetically important η^3-allyl complexes. Werner prepared an *exo*-alkylidene-η^3-propargyl complex in 1985,[1] and Krivykh prepared the first unsubstituted η^3-propargyl complex in 1991 (Scheme 1).[2] The chemistry of η^3-propargyl complexes has been extended to many early[3,4] and late[5] transition metals, and the use of these complexes in synthesis is expanding.[6,7]

We developed efficient syntheses of η^3-propargyl rhenium complexes, both by hydride abstraction from alkyne complexes[8] and by protonation of propargyl alcohol complexes (a route pioneered by Krivykh[9]) (Scheme 2). Related η^3-allyl complexes preferentially undergo nucleophilic addition at a terminal carbon.[10] In contrast, nucleophiles normally attack the central carbon of η^3-propargyl complexes to give metallacyclobutenes. However in some cases, nucleophiles attack at either the C_1 terminus[11] to give alkyne complexes or at the C_3 terminus to give allene complexes.[12] The structures of η^3-propargyl complexes suggest that an allenyl formulation is an important resonance contributor;[6] the allenyl resonance contributor is useful in explaining the nucleophilic attack to give η^2-allene complexes.

Scheme 1



Scheme 2



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(11) Here, we define the η^3-propargyl-disubstituted carbon as C_1 and the monosubstituted carbon as C_3.

In attempting to extend the range of η^3-propargyl rhenium complexes, we initially experienced difficulty synthesizing aryl-substituted η^3-propargyl complexes because of their thermal instability. Here, we report that 1,3-diaryl-substituted η^3-propargyl rhenium complexes can be synthesized at low temperature, but surprisingly, they are in equilibrium with a second isomer, an η^2-1-metalla(methylene)cyclopropene complex. The unprecedented equilibration of η^3-propargyl and η^2-1-metalla(methylene)cyclopropene complexes is rapid and, therefore, needs to be considered in explaining the regioselectivity of nucleophilic additions to η^3-propargyl complexes. A second potential route to diaryl-substituted η^3-propargyl rhenium complexes involves protonation of alkynyl carbene complexes; however, this route led to the predominate formation of a third isomer, an η^3-benzyl complex.

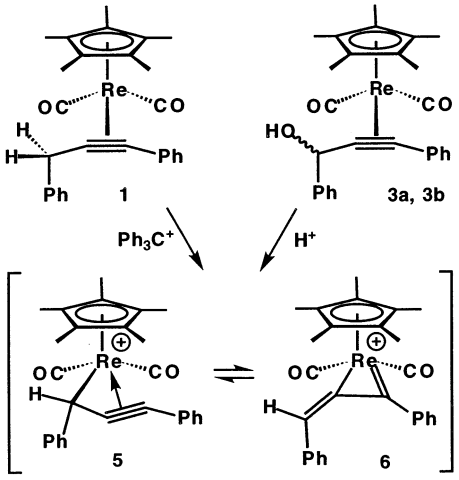
Results

Precursors of 1,3-Diaryl η^3-Propargyl Complexes. When we initiated this work, there was only one reported group 6 or 7 aryl-substituted η^3-propargyl complex.[13] The two best methods for the synthesis of cationic η^3-propargyl rhenium complexes are abstraction of a propargylic hydrogen from alkyne complexes and protonation of propargyl alcohol complexes. We have applied both to the synthesis of 1,3-diaryl η^3-propargyl complexes. The precursor for hydride abstraction, $C_5Me_5(CO)_2Re(PhC{\equiv}CCH_2Ph)$ (**1**), was prepared by reaction of the corresponding alkyne with $C_5Me_5Re(CO)_2(THF)$ (**2**). The propargyl alcohol precursor, $C_5Me_5(CO)_2Re(PhC{\equiv}CCH(OH)Ph)$ (**3a** and **b**), was prepared as a 1.1:1 mixture of diastereomers by $LiHBEt_3$ reduction of the corresponding ketone complex, $C_5Me_5(CO)_2Re[PhC{\equiv}CC(O)Ph]$ (**4**), which in turn was prepared from the alkynyl ketone and **2**.[14]

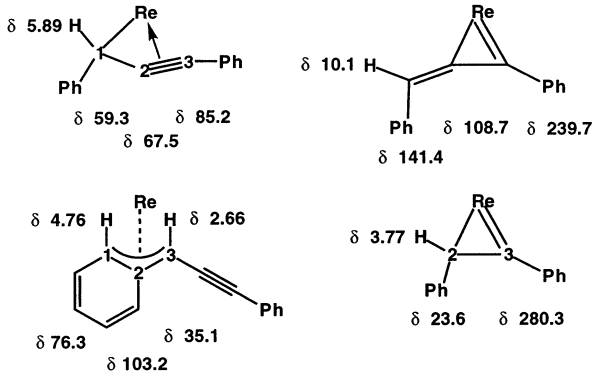
Hydride Abstraction from $C_5Me_5(CO)_2Re(PhC{\equiv}CCH_2Ph)$ (1) and Protonation of $C_5Me_5(CO)_2Re(PhC{\equiv}CCHOHPh)$ (3). Addition of $Ph_3C^+BF_4^-$ to a yellow solution of 1,3-diphenylpropyne complex **1** at 0 °C in CD_2Cl_2 led to the immediate formation of a deep green solution. The ^1H NMR spectrum at −78 °C revealed a 3:1 ratio of isomers with Cp* resonances at δ 2.07 and 2.15. In a separate reaction, 85% $HBF_4{\cdot}Et_2O$ was added to a CD_2Cl_2 solution of **3a**:**3b** at −78 °C. The ^1H NMR spectrum of the resulting green solution taken at −78 °C showed a 3:1 ratio of the same two compounds.

The ^1H and ^{13}C NMR spectra of the major isomer are consistent with its formulation as the η^3-propargyl complex $[C_5Me_5(CO)_2Re(\eta^3\text{-}PhCH{-}C{\equiv}CPh)][BF_4]$ (**5**) (Scheme 3). A singlet at δ 5.83 in the ^1H NMR spectrum was assigned to the proton on C_1. The low temperature ^{13}C NMR spectrum was crucial in validating the η^3-complexation, with the C_1, C_2, and C_3 resonances at δ 59.3, 67.5, and 85.2, respectively (Scheme 4). Related η^3-propargyl rhenium complexes[8] have similar characteristic chemical shifts: $[C_5Me_5(CO)_2Re(\eta^3\text{-}CH_2{-}C{\equiv}CH)][BF_4]$ at δ 32.0, 64.2, 65.3; $[C_5Me_5(CO)_2Re(\eta^3\text{-}CH_2{-}C{\equiv}CC(CH_3)_3)][PF_6]$ at δ 30.0, 60.5, 94.2; and $[C_5Me_5(CO)_2Re(\eta^3\text{-}CH_3CH{-}C{\equiv}CCH_3][PF_6]$ at δ 48.1, 59.8, 77.0. The $^1J_{CH}$ coupling constant 165 Hz in **5** is consistent with the sp^2 hybridization of the C_1 carbon in other η^3-propargyl complexes[8] and is inidicative of the strong contribution from an η^3-allenyl resonance form.[6]

Scheme 3



Scheme 4



The minor isomer displayed a high-frequency CH resonance at δ 10.1 and ^{13}C NMR resonances of the C_1, C_2, and C_3 carbons at δ 141.4, 108.7, and 239.7, which were consistent with the η^2-1-metalla(methylene)cyclopropene complex $[C_5Me_5(CO)_2Re(\eta^2\text{-}PhC{-}C{=}CHPh)][BF_4]$ (**6**). In particular, the δ 239.7 shift of C_3 provides evidence for a η^2-1-metallacyclopropene; very high-frequency chemical shifts are seen for the carbene-like carbon of related 1-metallacyclopropenes. In the less resonance stabilized 1-metallacylopropene $[C_5Me_5(CO)_2Re(\eta^2\text{-}PhCCHPh)][BF_4]$ (**7**), the carbene carbon appears at δ 280.3;[15] in the neutral 1-metalla(methylene)cyclopropene $C_5H_5[P(OCH_3)_3]_2Mo(E\text{-}\eta^2\text{-}PhC{-}C{=}CHPh)$ (**8**), the carbene carbon appears at δ 253.5.

η^2-1-Metalla(methylene)cyclopropene complexes are isomers of η^3-propargyl compounds in which only two carbons are bonded to the metal center. Several examples of group 6 η^2-1-metalla(methylene)cyclopropene transition metals are known. Green reported[16] that deprotonation of the cationic η^2-alkyne complex $\{C_5H_5[P(OCH_3)_3]_2Mo(\eta^2\text{-}PhC{\equiv}CCH_2Ph)][BF_4]$ (**9**) produced a 7:3 ratio of *E*:*Z* isomers of **8** (Scheme 5). The product mixture displayed fluxional ^{31}P NMR behavior (T_c = −74 °C), involving rotation of the η^2 fragment which rapidly

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(14) This two step procedure was required, since the reaction of **2** with the propargyl alcohol gave intractable mixtures or very low yields.

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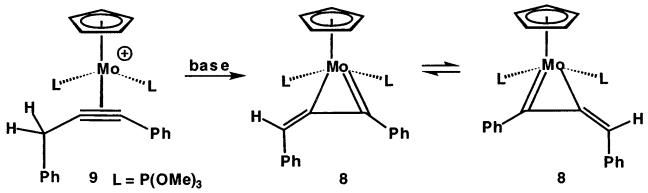
(16) Feher, F. J.; Green, M.; Rodrigues, R. A. *J. Chem. Soc., Chem. Commun.* **1987**, 1206. Green refers to η^2-1-metalla(methylene)cyclopropene as $\eta^2(3e^-)$-allenyl complexes.

Scheme 5



interchanges the environments of the phosphite ligands in **8**. Templeton reported[17] the deprotonation of a cationic η^2-alkyne tungsten complex to form the neutral η^2-1-metalla(methylene)-cyclopropene (dppe)(Me_2NCS_2)(CO)W[η^2-(CH_3O)C—C═CHPh] (**10**), which equilibrated to a mixture of two isomers via rotation of the η^2-ligand.

Variable temperature 360 MHz ^{1}H NMR spectroscopy of the mixture of **5** and **6** in CD_2Cl_2 showed rapid equilibration of these isomeric rhenium complexes. At 0 °C, a single sharp Cp* resonance was seen at δ 2.12. This fluxionality requires a rapid and reversible movement of C_1 in and out of the coordination sphere of the metal. At −100 °C,[18] interconversion of **5** and **6** was slow enough that NOE transfer to the Cp* signal at δ 2.07 was observed upon selective irradiation of the methine proton of **5** at δ 5.83; this established that the methine hydrogen was in the *endo* position. At temperatures above −90 °C, interconversion of **5** and **6** was fast enough that irradiation of the methine resonance of **5** resulted in saturation transfer to the vinylic CH of η^2-isomer **6** at δ 10.1.

The rapid interconversion of **5** and **6** makes it impossible to determine the kinetic ratio of isomers formed either from hydride abstraction or from protonation of the mixture of alcohol diastereomers.

Substituent Effects on the Equilibria between 1,3-Diaryl η^3-Propargyl Complexes and η^2-1-Metalla(methylene)cyclopropenes. In an effort to obtain equilibrium mixtures that favored either the η^3-propargyl or η^2-1-metalla(methylene)-cyclopropene, we investigated the effect of substituents on each of the aryl rings. Protonation of the 1:1 mixture of *p*-CF_3—C_6H_4-substituted alcohol complexes $C_5Me_5(CO)_2$Re[(*p*-CF_3—C_6H_4)C≡CCH(OH)Ph] (**11a** and **b**) with 85% HBF_4·Et_2O in CD_2Cl_2 at −78 °C gave an ∼50:1 ratio of η^3-propargyl (**12**): η^2-1-metalla(methylene)cyclopropene (**13**) complexes. The key features of the ^{1}H and ^{13}C NMR spectra of [$C_5Me_5(CO)_2$Re-(η^3-PhCH—C≡CC_6H_4-*p*-CF_3)][BF_4] (**12**) are the signature CH signal at δ 5.98 and resonances for C_1, C_2, and C_3 at δ 60.1 ($^1J_{CH}$ = 167 Hz), 70.2, and 83.6.

Evidence for steric crowding around the C_1 center of η^3-propargyl complexes came from low temperature ^{1}H NMR studies of **12**. The ^{1}H NMR spectrum of **12** displayed five different phenyl CH resonances at δ 6.59, 7.21, 7.29, 7.49, and 7.79, indicating asymmetry of the phenyl group due to restricted rotation about the C_1—C_{ipso} bond. At −80 °C, selective irradiation of the η^3-C*H*Ph resonance at δ 5.98 produced an NOE enhancement at the Cp* signal at δ 2.08, indicating the *endo*-orientation of the irradiated hydrogen. The ^{13}C NMR spectrum of **12** exhibited five inequivalent phenyl CH resonances at δ 122.87, 128.97, 129.19, 129.32, and 129.58.

Table 1. Electronic Effects[29] on η^3-Propargyl/η^2-1-Metalla(methylene)cyclopropene Equilibrium Ratio, Measured at −75 °C in CD_2Cl_2

η^3/η^2	C_1-ring	C_3-ring	η^3	η^2
5:**6**	H	H	75	25
12:**13**	H	*p*-CF_3	98	2
15:**16**	*p*-CH_3	*p*-CH_3	9	91
18:**19**	*p*-CH_3	H	50	50
20:**21**	*m*,*m*-CF_3	H	50	50

Protonation of the 1:1 mixture of di-*p*-tolyl-substituted alcohol complexes $C_5Me_5(CO)_2$Re[(*p*-$CH_3C_6H_4$)^{13}C≡^{13}C^{13}CHOH(C_6H_4—*p*-CH_3)] (**14a** and **b**) with 85% HBF_4·Et_2O in CD_2Cl_2 at −78 °C gave an ∼1:10 ratio of η^3-propargyl complex (**15**): η^2-1-metalla(methylene)cyclopropene (**16**). The use of triple ^{13}C-labeled material firmly established the spectral assignments of the η^2-1-metalla(methylene)cyclopropene [$C_5Me_5(CO)_2$Re[η^2-(*p*-CH_3—C_6H_4)^{13}C—^{13}C═^{13}CH(C_6H_4—*p*-CH_3)][BF_4] (**16**). At −90 °C, the key features of the ^{1}H and ^{13}C NMR spectra of **16** are a predominant Cp* resonance at δ 2.09 and a high frequency doublet for the CH at δ 9.99 ($^1J_{CH}$ = 159 Hz). The ^{13}C labels provide excellent evidence for the η^2-1-metalla(methylene)-cyclopropene bonding motif, with resonances for C_1, C_2, and C_3 at δ 141.8 (d, $^1J_{CC}$ = 85 Hz), 107.1 (dd, $^1J_{CC}$ = 85, 61 Hz), and 233.8 (d, $^1J_{CC}$ = 62 Hz).

Because of the use of triple ^{13}C-labeled material, the small amount of propargyl isomer [$C_5Me_5(CO)_2$Re[η^3-(*p*-CH_3—C_6H_4)^{13}CH—^{13}C≡^{13}C(C_6H_4—*p*-CH_3)][BF_4] (**15**) was also discernible in the ^{13}C NMR spectrum; resonances for C_1, C_2, and C_3 were observed at δ 59.8 (dd, $^1J_{CC}$ = 65 Hz, $^2J_{CC}$ = 8 Hz), 66.4 (dd, $^1J_{CC}$ = 110, 65 Hz), and 85.4 (dd, $^1J_{CC}$ = 110 Hz, $^2J_{CC}$ = 8 Hz), respectively.

The equilibrium ratio of the η^3 and η^2 products was strongly dependent on the nature of the electron-donating or -withdrawing nature of substituents on the aromatic rings (Table 1).

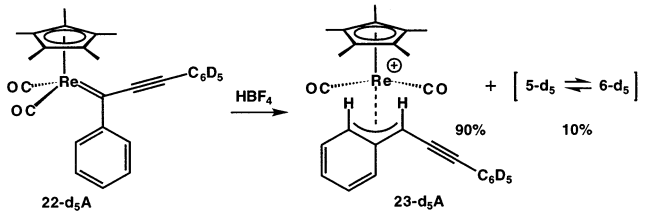
Activation Barrier for Interconversion of η^3-Propargyl and η^2-1-Metalla(methylene)cyclopropene Complexes. For a quantitative ^{13}C NMR investigation of the unique fluxional process that interconverts η^3-propargyl and η^2-1-metalla(methylene)cyclopropene complexes, we chose to study a system with a 1:1 ratio of isomers and we used ^{13}C labeling at C_1 to enhance sensitivity. Protonation of $C_5Me_5(CO)_2$Re[η^2-PhC≡C^{13}CH(OH)(C_6H_4-*p*-CH_3)] (**17a** and **b**) with HBF_4·Et_2O at −78 °C gave η^3-propargyl complex {$C_5Me_5(CO)_2$Re[η^3-(*p*-CH_3—C_6H_4)^{13}CH—C≡CPh]}[BF_4] (**18**) and η^2-1-metalla-(methylene)cyclopropene complex [$C_5Me_5(CO)_2$Re(η^2-PhC—C═^{13}CH(C_6H_4—*p*-CH_3)][BF_4] (**19**). The temperature dependence of the ^{13}C label resonances was measured over the range from −75 °C to −30 °C. Line broadening simulation of the ^{13}C spectra allowed measurement of the rates of interconversion of isomers. An Eyring plot gave activation parameters for the isomerization process: $\Delta H^‡$ = 10.8 kcal mol^{-1}, $\Delta S^‡$ = −0.5 eu, with $\Delta G^‡$ = 10.3 kcal mol^{-1} at −45 °C.

Protonation of Alkynyl Carbene Complexes as a Route to η^3-Propargyl Complexes. Recently, we reported the synthesis of rhenium alkynyl carbene complexes and their [1,3] metal shift and dimerization reactions.[19] Protonation at either the carbene carbon[20] or the remote alkynyl carbon of these

(17) Gamble, A. S.; Birdwhistell, K. R.; Templeton, J. L. *J. Am. Chem. Soc.* **1990**, *112*, 1818.

(18) The addition of 20 vol % polar solvent mixture $CDCl_2F$/$CDClF_2$ (2:1) [Siegel, J. S.; Anet, F. A. L. *J. Org. Chem.* **1988**, *53*, 2629] to a CD_2Cl_2 solution of **13**/**14** allowed NOESY1D gradient experiments at low temperature. A negative NOE peak was observed in the Cp* resonance, −26% in magnitude compared to the inverted CH signal.

Scheme 6



complexes offered a potential route to diaryl-substituted η^3-propargyl complexes. Addition of $HBF_4 \cdot Et_2O$ to a black CD_2Cl_2 solution of alkynyl carbene complex $C_5Me_5(CO)_2Re{=}C(Ph)C{\equiv}CPh$ (**22**) at −78 °C immediately produced a red solution. ^1H NMR spectroscopy at −78 °C showed the formation of a single major product (different from either **5** or **6**) containing a singlet at δ 2.66, a doublet at δ 4.76, and an asymmetric aromatic region. The ^{13}C NMR spectrum revealed an intact acetylene unit, signifying the absence of alkyne coordination to rhenium. On the basis of these spectral features, this third isomer of η^3-propargyl was assigned as the η^3-benzyl complex $\{C_5Me_5(CO)_2Re[\eta^3(\alpha,1,2)\text{-}endo,syn\text{-}C_6H_5CH(C{\equiv}CC_6H_5)]\}[BF_4]$ (**23**) (Scheme 6).

To test our proposed η^3-benzyl structure for **23**, we prepared a deuterium-labeled alkynyl carbene complex $C_5Me_5(CO)_2Re{=}C(Ph)C{\equiv}CC_6D_5$ (**22-d$_5$A**), to allow unobscured viewing of the NMR resonances of the η^3-benzyl functionality in **23-d$_5$A**. Addition of $HBF_4 \cdot Et_2O$ to a CD_2Cl_2 solution of **22-d$_5$A** at −78 °C and warming to 0 °C gave complex **23-d$_5$A** in 90% yield by ^1H NMR spectroscopy. The η^3-benzyl unit gave rise to aromatic resonances at δ 4.76, 7.33 (2H), 7.65, and 7.83. Upon cooling **23-d$_5$A** to −75 °C, ^1H NMR signals for 10% of a 3:1 mixture of **5-d$_5$**/**6-d$_5$** decoalesced and were readily detected. While **5-d$_5$** and **6-d$_5$** are in rapid equilibrium, no equilibration with η^3-benzyl isomer **23-d$_5$A** was seen, even upon warming to 25 °C. This labeling experiment also established that η^3-benzyl complex **23-d$_5$A** is predominantly formed by protonation of the carbene carbon of **22-d$_5$A** and coordination of the C_6H_5 ring.

Single crystals of a different isotopomer **23-d$_5$B** were obtained by slow diffusion of pentane into a CD_2Cl_2 solution of $\{C_5Me_5(CO)_2Re[\eta^3(\alpha,1,2)\text{-}endo,syn\text{-}C_6D_5CH(C{\equiv}CC_6H_5)]\}[BF_4]$ (**23-d$_5$B**), obtained from low temperature HBF_4 addition to $C_5Me_5(CO)_2Re{=}C(C_6D_5)C{\equiv}CC_6H_5$ (**22-d$_5$B**). While the structure was highly disordered, the trihapto coordination of the benzyl of **23-d$_5$B** was confirmed with the three carbons within bonding distance to rhenium (Figure 1).[21]

Monoaryl-Substituted η^3-Propargyl Complexes. The observation of the equilibrium between diaryl-substituted η^3-propargyl complexes and the corresponding η^2-1-metalla-(methylene)cyclopropene is unusual and had not been observed

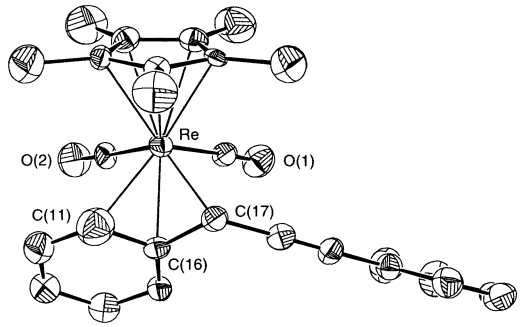
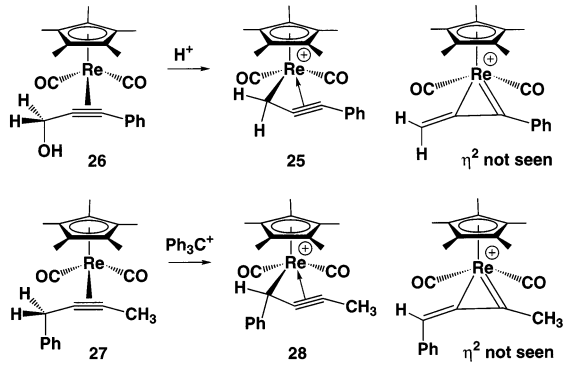


Figure 1. X-ray crystal structure of η^3-benzyl complex $\{C_5Me_5(CO)_2Re[\eta^3(\alpha,1,2)\text{-}endo,syn\text{-}C_6D_5CH(C{\equiv}CC_6H_5)]\}[BF_4]$ (**23-d$_5$B**). The molecular structure is drawn with 30% thermal probability ellipsoids, with hydrogens omitted for clarity.

Scheme 7



for alkyl-substituted η^3-propargyl complexes. This prompted us to investigate the synthesis of both 1-phenyl- and 3-phenyl-substituted η^3-propargyl complexes. Interestingly, earlier attempts to prepare such aryl-substituted complexes had been unsuccessful. A wide variety of simple alkyl and aryl groups at the C_3 carbon of the η^3-propargyl ligand are known for early and late transition metals. However, examples of aromatic substitution in group 6 and 7 metal complexes are limited.

Hydride abstraction from $C_5Me_5(CO)_2Re(\eta^2\text{-}CH_3C{\equiv}CC_6H_5)$ (**24**) with $Ph_3C^+BAr'_4{}^-$ ($BAr'_4{=}B[C_6H_3(3,5\text{-}CF_3)]_4$) in CD_2Cl_2 at 0 °C cleanly gave the desired 3-phenyl-substituted η^3-propargyl complex $[C_5Me_5(CO)_2Re(\eta^3\text{-}CH_2C{\equiv}CC_6H_5)][BAr'_4]$ (**25-BAr′$_4$**) (Scheme 7). Doublets were observed at δ 3.53 and δ 4.65 in the ^1H NMR spectrum with the characteristic geminal coupling 10.4 Hz, a signature of the coordinated CH_2 group. The 3-phenyl η^3-propargyl complex $[C_5Me_5(CO)_2Re(\eta^3\text{-}CH_2C{\equiv}CC_6H_5)][BF_4]$ (**25-BF$_4$**) was also generated by protonation of the η^2-propargyl alcohol complex $C_5Me_5(CO)_2Re(\eta^2\text{-}HOCH_2C{\equiv}CC_6H_5)$ (**26**) with 85% $HBF_4 \cdot Et_2O$ at −78 °C in CH_2Cl_2. **25-BF$_4$** was isolated in 53% yield but decomposed over hours in CH_2Cl_2 at 0 °C and rapidly as a solid at room temperature. We do not understand why phenyl-substituted η^3-propargyl complexes are less stable than their alkyl-substituted analogues.

No evidence for the η^2-isomer of **25** was observed: the ^1H NMR spectrum contained a single Cp* resonance and no $CH_2{=}C$ resonances between δ 5.5−6.5,[22] and the ^{13}C NMR spectrum exhibited no Re=C resonance.

Next, we set out to prepare the first example of a C_1-phenyl-substituted η^3-propargyl complex by hydride abstraction from

(19) (a) Casey, C. P.; Kraft, S.; Powell, D. R. *J. Am. Chem. Soc.* **2002**, *124*, 2584−2594. (b) Casey, C. P.; Kraft, S.; Powell, D. R. *Organometallics* **2001**, *20*, 2651. (c) Casey, C. P.; Kraft, S.; Powell, D. R. *J. Am. Chem. Soc.* **2000**, *122*, 3771. (d) Casey, C. P.; Kraft, S.; Kavana, M. *Organometallics* **2001**, *20*, 3795.

(20) For examples of metal carbene protonations, see: (a) Casey, C. P.; Czerwinski, C. J.; Powell, D. R.; Hayashi, R. K. *J. Am. Chem. Soc.* **1997**, *119*, 5750. (b) Casey, C. P.; Vosejpka, P. C.; Askham, F. R. *J. Am. Chem. Soc.* **1990**, *112*, 3713. (c) Klein, D. P.; Bergman, R. G. *J. Am. Chem. Soc.* **1989**, *111*, 3079. (d) Hill, A. F.; Roper, W. R.; Waters, J. M.; Wright, A. H. *J. Am. Chem. Soc.* **1983**, *105*, 5939. (e) Clark, G. R.; Roper, W. R.; Wright, A. H. *J. Organomet. Chem.* **1984**, *273*, C17.

(21) Highly idealized phenyl and Cp* units were required for refinement. See Supporting Information for bond distance tables.

(22) In a related allene complex, the terminal $CH_2{=}$ unit was observed at δ 5.48 and 6.52, with $^2J \approx 0$ Hz: Casey, C. P.; Brady, J. T. *Organometallics* **1998**, *17*, 4620.

the 1-phenyl-2-butyne complex $C_5Me_5(CO)_2Re(\eta^2\text{-}C_6H_5CH_2C{\equiv}CCH_3)$ (**27**). While hydride abstraction from a rhenium 2-pentyne complex showed only a 2.5:1 preference for abstraction from the Et group over the Me group,[8] we anticipated greater selectivity favoring abstraction of a benzylic hydride from a 1-phenyl-2-butyne rhenium complex. Addition of $Ph_3C^+BF_4^-$ to a CD_2Cl_2 solution of **27** at −78 °C led to regioselective abstraction of a secondary benzylic hydride and formation of a single new species, the 1-phenyl-substituted η^3-propargyl complex $[C_5Me_5(CO)_2Re(\eta^3\text{-}PhCH{-}C{\equiv}CCH_3)][BF_4]$ (**28**) (Scheme 7). The ^{1}H NMR spectrum at −10 °C showed a doublet at δ 2.79 and a quartet at δ 5.38, with a long range ^5J-coupling of 2.2 Hz, consistent with a 1-phenyl-substituted η^3-propargyl complex. The ^{13}C NMR spectrum with resonances for C_1, C_2, and C_3 at δ 55.6, 57.6, and 79.5 provided further support for the formulation of **28**. Decomposition of **28** occurred above 0 °C. η^3-Propargyl complexes bearing an aromatic group at C_1 were unknown prior to the work reported here.

No abstraction of a methyl hydrogen from **27** to produce an isomeric η^3-propargyl complex was observed, consistent with the expected higher reactivity of benzylic hydrogens. No evidence for formation of the η^2-isomer was observed by ^{1}H or ^{13}C NMR spectroscopy at −80 °C.

Discussion

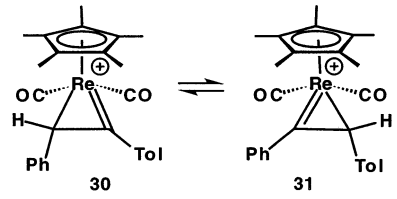
Numerous η^3-propargyl complexes have been reported, but the isomeric η^2-1-metalla(methylene)cyclopropene has never been seen in equilibrium with an η^3-propargyl complex. η^2-1-Metalla(methylene)cyclopropene complexes are limited to Mo or W compounds derived from deprotonation of η^2-alkyne precursors,[16,17,23,24] but the isomeric η^3-propargyl complexes are not seen in these systems.

In the course of investigating phenyl-substituted η^3-propargyl complexes, we discovered that 1,3-diaryl-substituted η^3-propargyl complexes such as $[C_5Me_5(CO)_2Re(\eta^3\text{-}PhCH{-}C{\equiv}CPh)][BF_4]$ (**5**) were in equilibrium with the corresponding η^2-1-metalla(methylene)cyclopropene complex $[C_5Me_5(CO)_2Re(\eta^2\text{-}PhC{-}C{=}CHPh)][BF_4]$ (**6**). Aryl substitutions at both C_1 and C_3 are apparently required for observation of an η^2-1-metalla(methylene)cyclopropene, since phenyl substitution at only the C_1 or C_3 position gave only the η^3-propargyl isomer. What steric or electronic factors might determine whether an η^2-1-metalla(methylene)cyclopropene will be stable enough to be observed?

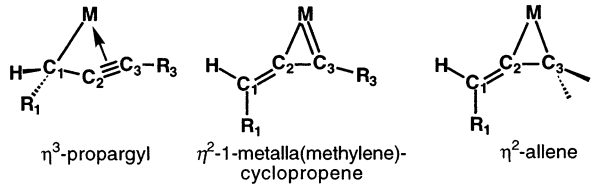
Electronic factors affect the equilibrium between η^3- and η^2-isomers. Replacement of the phenyl group at C_3 of **6** by an electron-withdrawing p-$CF_3{-}C_6H_4$ group in **13** led to a large decrease in the percentage of η^2-isomer from 25% for **6** to <2% for **13**. Replacement of the phenyl group at C_1 of **6** by an electron-donating tolyl group in **19** led to a moderate increase in the percentage of η^2-isomer from 25% for **6** to 50% for **19**. Addition of a second tolyl group to C_3 in **19** led to a still larger increase in the amount of η^2-isomer from 50% for **19** to 90% for **16**. Thus, electron donors at C_3 greatly favor the η^2-isomer, and electron donors at C_1 favor the η^2-isomer to a smaller extent.

We attribute this electronic preference for formation of the η^2-isomer to stabilization of the electrophilic carbene center at C_3 of the η^2-isomer by an electron-donating aromatic ring. The

Scheme 8



Scheme 9



C_3 site of the η^2-isomer is the most electrophilic center in either the η^3- or the η^2-isomer, and stabilization by electron donors is crucial in perturbing the equilibrium. The second most electrophilic carbon is C_1 of the η^2-isomer, which is in conjugation with the carbene-like C_3 position, with electron donors at C_1 favoring the η^2-isomer to a lesser extent than donors at the C_3 site.

We have observed similar stabilization of the electron deficient carbene center of rhenium diphenyl 1-metallacyclopropene complexes.[15] Isomeric rhenium diaryl 1-metallacyclopropene complexes equilibrate rapidly by a [1,2]-hydrogen shift. Protonation of the asymmetric η^2-alkyne complex $C_5Me_5(CO)_2Re(\eta^2\text{-}PhC{\equiv}CTol)$ (**29**) with $HBF_4{\cdot}Et_2O$ at −78 °C followed by warming to −40 °C gave a kinetic 2.3:1 ratio of the two isomeric 1-metallacyclopropene complexes $[C_5Me_5(CO)_2Re(\eta^2\text{-}PhCHCTol)][BF_4]$ (**30**)/$[C_5Me_5(CO)_2Re(\eta^2\text{-}PhCCHTol)][BF_4]$ (**31**). Upon warming to 25 °C, equilibration occurred to give a 4.5:1 mixture of **30**/**31**. The favored isomer at equilibrium has the more electron-donating tolyl group at the carbene center (Scheme 8).

Steric effects at C_1 also play a role in determining the equilibrium between η^3- and η^2-isomers. Two major structural changes occur in going from an η^3- to an η^2-isomer (Scheme 9). First, the sterically bulky C_1HPh unit moves away from the sterically large $C_5Me_5(CO)_2Re$ group in going to the η^2-isomer. Second, the C_1HR plane in the η^3-isomer, which is roughly orthogonal to the $Re{-}C_1{-}C_2{-}C_3$ plane ($R_1{-}C_1{-}C_2{-}C_3$ torsion angle 90°−100°), must rotate about 90° to become nearly coplanar in the η^2-isomer. In the η^3-isomer, C_1 is bonded to Re and there is an acute $Re{-}C_2{-}C_1$ angle (65−75° in X-ray structures[2,3a,8,16,25]). But, in the η^2-isomer, C_1 is not bonded to Re and there is an obtuse $Re{-}C_2{-}C_1$ angle (135−148° in related η^2-allene X-ray structures[26]).

Steric crowding at C_1 of η^3-propargyl complexes has been shown to lead to kinetic (and probably thermodynamic) destabilization.[8] For example, protonation of $C_5Me_5(CO)_2Re$-

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(η^2-$CH_3C{\equiv}CCH(CH_3)OH$) (**32**) at −78 °C produced a 4:1 mixture of the anti/syn η^3-propargyl complexes [$C_5Me_5(CO)_2$-Re(η^3-$CH_3C{\equiv}CCHCH_3$)][BF_4] (**33-*anti*** and **33-*syn***), which differ in the orientation of the methyl group either away or toward the Cp* ligand. Upon warming the solution above −20 °C, the less stable **33-*syn*** isomer decomposed, while the more stable **33-*anti*** isomer remained and was isolated at room temperature. Another case of steric destabilization was observed for the bulky gem-dimethyl η^3-propargyl complex [$C_5Me_5(CO)_2$-Re(η^3-$HC{\equiv}CC(CH_3)_2$][BF_4] (**34**), which decomposed above −20 °C, presumably because of the unfavorable steric interaction of the *endo*-methyl group with the Cp* fragment.

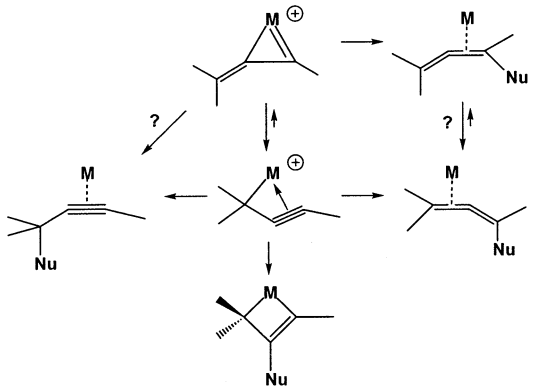
Evidence for steric crowding at the C_1HAr site in the 1,3-diaryl η^3-propargyl complexes came from low temperature ^{1}H NMR spectroscopy of the *p*-$CF_3{-}C_6H_4$-substituted η^3-propargyl complex **12**, which showed five different CH phenyl resonances for the phenyl group at C_1. This asymmetry of the phenyl group at C_1 is due to restricted rotation about the $C_1{-}C_{ipso}$ bond. We do not fully understand the origin of the steric interactions responsible for hindered phenyl rotation, but the hindered rotation strongly suggests a sterically congested site.

In summary, the combination of steric destabilization of the η^3-isomer by the large C_1HPh unit and electronic stabilization of the η^2-isomer by electron-donating aryl units at the C_3 position (and also at the C_1 position) is responsible for the observation of η^2-1-metalla(methylene)cyclopropenes only in the presence of aryl substitution at both C_1 and C_3.

Not only is the observation of an equilibrium between η^3-propargyl and η^2-1-metalla(methylene)cyclopropene isomers unprecedented, the rapid nature of this fluxional process, which involves simple, reversible π-bond complexation, is striking. Other $\eta^2{-}\eta^3$ processes (such as allylic C−H activation of iron−alkene complexes to give η^3-allyl iron hydride intermediates proposed for iron carbonyl catalyzed alkene isomerization[27]) are known but involve more complicated mechanisms than the simple, reversible π-bond complexation observed here. In the deprotonation of a molybdenum bis(alkyne) complex, Green proposed formation of an η^2-1-metalla(methylene)cyclopropene complex as an unobserved intermediate, which rearranges to an η^1-allenyl intermediate, followed by formation of a more stable η^3-propargyl complex.[13] In light of the observations reported here, a simple direct $\eta^2{-}\eta^3$ isomerization should be considered as an alternative to Green's proposed $\eta^2{-}\eta^1{-}\eta^3$ process.

Attempted entry into mixtures of $\eta^2{-}\eta^3$ isomers via protonation of alkynyl carbene complex **22** instead produced predominantly a third isomer, an η^3-benzyl complex **23**. The η^3-benzyl complex results from protonation at the carbene carbon C_1 and complexation of the aryl ring. A 16e intermediate that partitions between aryl complexation to yield η^3-benzyl complex **23** and alkyne coordination to yield η^3-propargyl complex **5** can explain the formation of two types of products. A possible variation on the mechanism involves initial protonation at rhenium to give a metal hydride, followed by hydride migration to the carbene carbon to give the 16e intermediate; however, no rhenium hydride species was observed by low temperature ^{1}H NMR spectroscopy. The small percentage of $\eta^2{-}\eta^3$ isomers in the mixture could be formed by a combination of remote protonation at the C_3 carbon to produce the η^2-allenyl isomer and C_1 carbene protonation, followed by alkyne complexation to yield the η^3-propargyl complex, with immediate equilibration for both pathways. The high selectivity of η^3-benzyl formation is attributed to a kinetic preference for protonation at the carbene center and a kinetic preference for complexation of the aryl ring versus complexation of the alkyne.

Scheme 10



The rapid nature of the $\eta^3{-}\eta^2$ equilibration needs to be considered in interpreting the regioselectivity of nucleophilic additions to η^3-propargyl systems (Scheme 10). Previously, we had observed kinetic additions of phosphines and other nucleophiles to the center carbon of η^3-propargyl rhenium complexes to give metallacyclobutenes.[12a] At higher temperature, rearrangements to η^2-allene or η^2-alkyne products were observed. These rearrangements are the result of reversible additions of phosphines and amines to the central carbon, followed by irreversible terminal addition to give η^2-allene or η^2-alkyne products. The question now arises as to whether the η^2-allene or η^2-alkyne products might arise from nucleophilic attack on the η^2-isomer rather than just the η^3-isomer, as previously assumed.

Experimental Section

$C_5Me_5(CO)_2Re(\eta^2$-PhC≡$CCH_2Ph)$ (1). A solution of $C_5Me_5(CO)_2$-Re(THF) (**2**)[8,28] (1.0 mmol) and 1,3-diphenylpropyne (1.0 g, 5.2 mmol) in 5 mL of THF was stirred overnight. Volatile material was evaporated under vacuum, and the solid residue was chromatographed (silica gel, 5:1 hexanes/Et_2O) to give **1** as a yellow powder (236 mg, 42%). ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.93 (s, C_5Me_5), 4.08 (d, J = 17.2 Hz, C*H*H), 4.33 (d, J = 17.2 Hz, CH*H*), 7.1−7.4 (m, aromatic). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 90 MHz) δ 10.75 ($C_5\mathit{Me}_5$), 35.48 ($\mathit{C}H_2$), 80.43 ($\mathit{C}{\equiv}C$), 89.83 (C≡C), 100.24 (C_5Me_5), 126.49 (aromatic CH_{para}), 126.77 (aromatic CH_{para}), 128.21, 128.79, 131.56 (aromatic $CH_{meta/ortho}$), 129.97, 140.42 (aromatic C_{ipso}), 208.82 (CO), 209.77 (CO). By ^{1}H NMR spectroscopy, the sample was >95% pure in the Cp* region δ 1.9−2.2 and >98% pure in the aromatic region δ 7.0−7.5. IR (THF) 1950.22, 1868.04. MS (ESI) Calcd (obsd) for $C_{27}H_{27}O_2Re{\cdot}Na^+$ 591.1439 (591.1420).

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$[C_5Me_5(CO)_2Re(\eta^3$-PhCHC≡CPh)][BF_4] (5) and $[C_5Me_5(CO)_2Re(\eta^2$-PhCC═CHPh)][BF_4] (6). Ph_3CBF_4 (21 mg, 0.064 mmol) was added to a solution of **1** (33 mg, 0.058 mmol) in CD_2Cl_2 at 0 °C to give a 3:1 mixture of **5**/**6**, which was characterized spectroscopically.

For $[C_5Me_5(CO)_2Re(\eta^3$-PhCH−C≡CPh)][BF_4] (**5**): ^{1}H NMR (CD_2Cl_2, 360 MHz, −75 °C) δ 2.07 (s, C_5Me_5), 5.83 (s, C*H*−C≡C), 6.57−8.12 (m, aromatic, obscured by Ph_3CH). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 90 MHz, −75 °C) δ 10.13 (C_5*Me*$_5$), 59.28 (*C*HC≡C), 67.46 (CH*C*≡C), 85.24 (CHC≡*C*), 105.79 (*C*$_5$Me$_5$), 118−132 (aromatic), 193.52 (CO), 199.36 (CO).

For $[C_5Me_5(CO)_2Re(\eta^2$-PhCC═CHPh)][BF_4] (**6**): ^{1}H NMR (CD_2Cl_2, 360 MHz, −75 °C) δ 2.15 (s, C_5Me_5), 6.56−8.21 (aromatic), 10.14 (s, C*H*═CC). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 90 MHz, −75 °C) δ 10.29 (C_5*Me*$_5$), 104.38 (*C*$_5$Me$_5$), 108.68 (CH═*C*C), 118−132 (aromatic), 141.37 (*C*H═CC), 191.64 (CO), 195.96 (CO), 239.72 (Re═*C*).

$C_5Me_5(CO)_2Re(\eta^2$-Tol^{13}CH(OH)^{13}C≡^{13}CTol) (14). Addition of $LiHBEt_3$ (0.5 mL, 1.0 M in THF, 0.5 mmol) to a red solution of $C_5Me_5(CO)_2Re(\eta^2$-Tol^{13}C(O)^{13}C≡^{13}CTol) (**37**) (60 mg, 0.098 mmol) in 10 mL of THF at 0 °C gave a yellow solution. After the solution was stirred for 30 min at room temperature, 1.0 mL of EtOH/H_2O (3:1) was added and volatile material was evaporated under vacuum. The residual solid was dissolved in diethyl ether and chromatographed (silica gel, 4:1 hexanes/Et_2O) to give a 1.1:1mixture of two diastereomers of **14** (48 mg, 80%) as a yellow oil. By ^{1}H NMR, the sample was >98% pure in the Cp* region δ 1.9−2.2.

Major diastereomer: ^{1}H NMR (CD_2Cl_2, 300 MHz) δ 1.91 (s, C_5Me_5), 2.31 (s, CH_3), 2.34 (s, CH_3), 6.08 (dq, $^1J_{CH}$ = 147.3 Hz, $^4J_{HH}$ = $^2J_{CH}$ = 4.7 Hz, C*H*OH), 6.9−7.4 (aromatic); $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 90 MHz) δ 10.22 (C_5*Me*$_5$), 72.63 (dd, $^1J_{CC}$ = 60.2 Hz, $^2J_{CC}$ = 3.3 Hz, ^{13}*C*H^{13}C≡^{13}CTol), 84.9 (dd, $^1J_{CC}$ = 99.8 Hz, $^2J_{CC}$ = 3.5 Hz, ^{13}CH^{13}C≡^{13}*C*Tol), 93.3 (dd, $^1J_{CC}$ = 100.6 Hz, $^1J_{CC}$ = 60.1 Hz, ^{13}CH^{13}*C*≡^{13}CTol).

Minor diastereomer: ^{1}H NMR (CD_2Cl_2, 300 MHz) δ 1.98 (s, C_5Me_5), 2.34 (s, CH_3), 2.39 (s, CH_3), 5.80 (dm, $^1J_{CH}$ = 147.3 Hz, $^4J_{HH}$ = $^2J_{CH}$ < 2 Hz, ^{13}C*H*OH), 6.9−7.4 (aromatic); $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 90 MHz) δ 10.41 (C_5*Me*$_5$), 71.94 (dd, $^1J_{CC}$ = 59.7 Hz, $^2J_{CC}$ = 2.3 Hz, ^{13}*C*H^{13}C≡^{13}CTol), 84.1 (dd, $^1J_{CC}$ = 98.3 Hz, $^2J_{CC}$ = 2.5 Hz, ^{13}CH^{13}C≡^{13}*C*Tol), 94.4 (dd, $^1J_{CC}$ = 98.8 Hz, $^1J_{CC}$ = 58.2 Hz, ^{13}CH^{13}*C*≡^{13}CTol).

$[C_5Me_5(CO)_2Re(\eta^3$-Tol^{13}CH^{13}C≡^{13}CTol)][BF_4] (15) and $[C_5Me_5(CO)_2Re(\eta^2$-Tol^{13}C^{13}C═^{13}CHTol)][BF_4] (16). Addition of 15 μL of 85% HBF_4·Et_2O to a dark yellow solution of **14** (17 mg, 0.03 mmol) in CD_2Cl_2 at −78 °C gave a deep green solution of a 1:10 mixture of **15**/**16**. The mixture of isomers was characterized spectroscopically.

For $[C_5Me_5(CO)_2Re(\eta^3$-Tol^{13}CH^{13}C≡^{13}CTol)][BF_4] (**15**): ^{1}H NMR (CD_2Cl_2, 500 MHz, −90 °C) δ 2.02 (s, C_5Me_5), 5.71 (d, $^1J_{CH}$ = 167 Hz, C*H*); $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 125 MHz, −90 °C) δ 59.79 (dd, $^1J_{CC}$ = 64.8 Hz, $^2J_{CC}$ = 7.8 Hz, ^{13}*C*H^{13}C≡^{13}C), 66.40 (dd, $^1J_{CC}$ = 109.8, 64.8 Hz, ^{13}CH^{13}*C*≡^{13}C), 85.42 (dd, $^1J_{CC}$ = 109.8 Hz, $^2J_{CC}$ = 7.8 Hz, ^{13}CH^{13}C≡^{13}*C*).

For $[C_5Me_5(CO)_2Re(\eta^2$-Tol^{13}C^{13}C═^{13}CHTol)][BF_4] (**16**): ^{1}H NMR (CD_2Cl_2, 500 MHz, −90 °C) δ 2.09 (s, C_5Me_5), 2.38 (s, CH_3), 2.53 (s, CH_3), 7.38 (d, ^3J = 7.8 Hz, H_{meta}), 7.62 (br s, H_{meta}), 8.05 (br s, H_{ortho}), 9.99 (d, $^1J_{CH}$ = 159.4 Hz, ^{13}C*H*═CC); $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 125 MHz, −90 °C) δ 10.30 (C_5*Me*$_5$), 104.12 (*C*$_5$Me$_5$), 107.06 (dd, $^1J_{CC}$ = 85.0, 61.0 Hz, ^{13}CH═^{13}*C*^{13}C), 141.81 (d, $^1J_{CC}$ = 85.0, ^{13}*C*H═^{13}C^{13}C), 233.81 (d, $^1J_{CC}$ = 61.9, ^{13}CH═^{13}C^{13}*C*); ^{1}H NMR (CD_2Cl_2, 360 MHz, −75 °C) δ 2.08 (s, C_5Me_5), 2.36 (s, CH_3), 2.51 (s, CH_3), 7.36 (d, ^3J = 8.0 Hz, H_{meta}), 7.63 (br, H_{meta}), 8.05 (br, H_{ortho}), 10.01 (d, $^1J_{CH}$ = 159.8 Hz, ^{13}C*H*═^{13}C^{13}C); $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 90 MHz, −75 °C) δ 10.19 (C_5*Me*$_5$), 21.95 (*C*H$_3$), 22.89 (*C*H$_3$), 103.90 (*C*$_5$Me$_5$), 106.81 (dd, $^1J_{CC}$ = 84.20, 60.7 Hz, ^{13}CH═^{13}*C*^{13}C), 141.72 (d, $^1J_{CC}$ = 84.8 Hz, ^{13}*C*H═^{13}C^{13}C), 233.54 (d, $^1J_{CC}$ = 61.8 Hz, ^{13}CH═^{13}C^{13}*C*).

{$C_5Me_5(CO)_2Re[\eta^3(\alpha,1,2)$-*endo*,*syn*-$C_6H_5CH(C≡CC_6D_5)]$}[$BF_4$] (23-$d_5$A). Addition of 8 μL of HBF_4·Et_2O to a black solution of $C_5Me_5(CO)_2Re$═C(Ph)C≡CC_6D_5 (**22-d_5A**)[19c] (23 mg, 0.04 mmol) in CD_2Cl_2 at −78 °C gave a red solution, which changed to a green solution upon warming to 0 °C. **23-d_5A** was characterized spectroscopically. ^{1}H NMR (CD_2Cl_2, 360 MHz, 0 °C) δ 2.22 (s, C_5Me_5), 2.66 (s, C*H*−C≡C), 4.76 (br d, $^3J_{HH}$ = 5.8 Hz, H_2), 7.33 (m, H_3/H_5), 7.65 (dt, $^3J_{HH}$ = 7.6 Hz, $^4J_{HH}$ < 1.5 Hz, H_4), 7.83 (br d, J = 8.5 Hz, H_6). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 90 MHz, −75 °C) δ 10.48 (C_5*Me*$_5$), 35.06 (*C*$_7$H−C≡C), 76.30 (*ortho*, *C*$_2$), 86.86 (*C*≡CC_6D_5), 91.55 (C≡*C*C_6D_5), 103.21 (*ipso*, *C*$_1$), 105.53 (*C*$_5$Me$_5$), 121.94 (*ipso*-C_6D_5), 128.38 (1:1:1 t, $^1J_{CD}$ = 24.8 Hz, C_{ortho}−D), 129.84 (C_3 or C_5), 130.68 (C_3 or C_5), 131.61 (1:1:1 t, $^1J_{CD}$ = 24.5 Hz, C_{meta}−D), 133.76 (C_4), 134.03 (C_6), 134.73 (1:1:1 t, $^1J_{CD}$ = 20.30 Hz, C_{para}−D), 193.25 (CO), 193.47 (CO). Low temperature ^{1}H NMR (CD_2Cl_2, −75 °C) for **5**: δ 2.06 (s, C_5Me_5), 5.81 (s, CH−C≡C), 6.57 (d, J = 7.6 Hz, phenyl), 7.18 (t, J = 7.1 Hz, phenyl), 7.46 (t, J = 7.6 Hz, phenyl), 8.15 (d, J = 6.4 Hz, phenyl). Low temperature ^{1}H NMR (CD_2Cl_2, −75 °C) for **6**: δ 2.11 (s, C_5Me_5), 7.0−7.9 (aromatic, obscured), 10.11 (s, CH═C).

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Supporting Information Available: General experimental procedures, spectral characterizations, dynamic NMR, and X-ray crystallographic information for **23-d_5B** (24 pages, PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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