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Formation of *cis*-Enediyne Complexes from Rhenium Alkynylcarbene Complexes

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Abstract: Dimerization of the alkynylcarbene complex $Cp(CO)_2Re{=}C(Tol)C{\equiv}CCH_3$ (**8**) occurs at 100 °C to give a 1.2:1 mixture of enediyne complexes $[Cp(CO)_2Re]_2[\eta^2,\eta^2\text{-}TolC{\equiv}CC(CH_3){=}C(CH_3)C{\equiv}CTol]$ (**10-*E***and **10-*Z***), showing no intrinsic bias toward *trans*-enediyne complexes. The cyclopropyl-substituted alkynylcarbene complex $Cp(CO)_2Re{=}C(Tol)C{\equiv}CC_3H_5$ (**11**) dimerizes at 120 °C to give a 5:1 ratio of enediyne complexes $[Cp(CO)_2Re]_2[\eta^2,\eta^2\text{-}TolC{\equiv}C(C_3H_5)C{=}C(C_3H_5)C{\equiv}CTol]$ (**12-*E*** and **12-*Z***); no ring expansion product was observed. This suggests that if intermediate **A** formed by a [1,1.5] Re shift and having carbene character at the remote alkynyl carbon is involved, then interaction of the neighboring Re with the carbene center greatly diminishes the carbene character as compared with that of free cyclopropyl carbenes. The tethered bis-(alkynylcarbene) complex $Cp(CO)_2Re{=}C(Tol)C{\equiv}CCH_2CH_2CH_2C{\equiv}CC(Tol){=}Re(CO)_2Cp$ (**13**) dimerizes rapidly at 12 °C to give the cyclic *cis*-enediyne complex $[Cp(CO)_2Re]_2[\eta^2,\eta^2\text{-}TolC{\equiv}CC(CH_2CH_2CH_2){=}CC{\equiv}CTol]$ (**15**). Attempted synthesis of the 1,8-disubstituted naphthalene derivative $1,8\text{-}[Cp(CO)_2Re{=}C(Tol)C{\equiv}C]_2C_{10}H_6$ (**16**), in which the alkynylcarbene units are constrained to a parallel geometry, leads to dimerization to $[Cp(CO)_2Re]_2(\eta^2,\eta^2\text{-}1,2\text{-}(tolylethynyl)acenaphthylene]$ (**17**). The very rapid dimerizations of both **13** and **16** provide compelling evidence against mechanisms involving cyclopropene intermediates. A mechanism is proposed which involves rate-determining addition of the carbene center of **A** to the remote alkynyl carbon of a second alkynylcarbene complex to generate vinyl carbene intermediate **C**, and rearrangement of **C** to the enediyne complex by a [1,1.5] Re shift.

Introduction

Heteroatom-substituted alkynylcarbene complexes such as $(OC)_5M{=}C(OR)C{\equiv}CR'$ have a rich chemistry that combines high reactivity, easy accessibility, and entry into a large variety of products.[1] In particular, nucleophilic additions to either the carbene or the remote alkyne carbon and cycloadditions to the triple bond have been exploited synthetically. Despite the large number of donor-substituted alkynylcarbene complexes, [1,3] metal migrations such as from $(OC)_5M{=}C(OR)C{\equiv}CR'$ to $(OC)_5M{=}C(R')C{\equiv}COR$ were virtually unknown either due to a high kinetic barrier or due to an unfavorable equilibrium.[2,3] Recently, we began a search for [1,3] metal shifts in nondonor-substituted rhenium alkynylcarbene complexes such as $Cp(CO)_2Re{=}C(Tol)C{\equiv}CPh$ (**1**) [Tol = C_6H_4-*p*-CH_3] and found small amounts of the [1,3] shifted isomer $Cp(CO)_2Re{=}C(Ph)C{\equiv}CTol$ (**2**) upon thermolysis at 120 °C (Scheme 1).[4,5] The major product, however, was the dimeric *trans*-enediyne complex $[Cp(CO)_2Re]_2[\eta^2\text{-},\eta^2\text{-}TolC{\equiv}CC(Ph){=}C(Ph)C{\equiv}CTol]$ (**3**) formed by regioselective coupling at the remote alkynyl carbons.[6] When the conversion of **1** → **3** was followed by ^1H NMR spectroscopy, no intermediates were observed, and a second-order rate dependence on [**1**] was seen. This regioselectivity stands in contrast to the reported ability of Fischer carbene complexes (M = CRR′) to couple the carbene carbons and form alkenes.[7] Most notably, Sierra recently showed a selective "head-to-head" coupling in the Pd-catalyzed dimerization of $(CO)_5Cr{=}C(OEt)C{\equiv}CPh$ to (*E*,*Z*)-$PhC{\equiv}CC(OEt){=}C(OEt)C{\equiv}CPh$ with no evidence for "tail-to-tail" or "head-to-tail" couplings.[8]

Three types of mechanism are under consideration for dimerization of alkynylcarbene complexes. The first involves an initial

(1) For reviews of heteroatom-substituted alkynylcarbene complexes, see: (a) Aumann, R.; Nienaber, H. *Adv. Organomet. Chem.* **1997**, *41*, 163. (b) Wulff, W. D. In *Comprehensive Organometallic Chemistry II*; Abel, E. W., Stone, F. G. A., Wilkinson, G., Eds.; Pergamon Press: Oxford, 1995; Vol. 12, Chapter 5.3. (c) Herndon, J. W. *Coord. Chem. Rev.* **1999**, *181*, 177. (d) de Meijere, A.; Schirmer, H.; Duetsch, M. *Angew. Chem., Int. Ed.* **2000**, *39*, 3964.

(2) A [1.3]-shift of a rhodium alkynylcarbene complex presumed to be an intermediate in a catalytic cycle was postulated: Padwa, A.; Austin, D. J.; Gareau, Y.; Kassir, J. M.; Xu, S. L. *J. Am. Chem. Soc.* **1993**, *115*, 2637.

(3) [1.3]-Transition metal shifts are common in σ-propargyl to σ-allenyl rearrangements: (a) Keng, R.-S.; Lin, Y.-C. *Organometallics* **1990**, *9*, 289. (b) Hajela, S.; Schaefer, W. P.; Bercaw, J. E. *J. Organomet. Chem.* **1997**, *532*, 45. (c) Barluenga, J.; Trabanco, A. A.; Flórez, J.; García-Granda, S.; LLorca, M.-A. *J. Am. Chem. Soc.* **1998**, *120*, 12129. (d) Blosser, P. W.; Schimpff, D. G.; Gallucci, J. C.; Wojcicki, A. *Organometallics* **1993**, *12*, 1993. (e) Liang, K.-W.; Lee, G.-H.; Peng, S.-M.; Liu, R.-S. *Organometallics* **1995**, *14*, 2353. (f) Pu, J.; Peng, T.-S.; Arif, A.; Gladysz, J. A. *Organometallics* **1992**, *11*, 3232. (g) Caro, B.; Le Poul, P.; Robin-Le Guen, F.; Sénéchal-Tocquer, M.-C.; Saillard, J.-Y.; Kahlal, S.; Ouahab, L.; Golhen, S. *Eur. J. Org. Chem.* **2000**, 577.

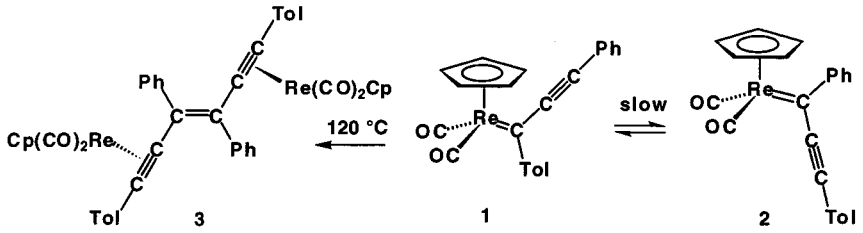
(4) Casey, C. P.; Kraft, S.; Powell, D. R. *J. Am. Chem. Soc.* **2000**, *122*, 3771.

(5) Nondonor stabilized $CpRe(CO)_2$ carbene complexes are generally less prone to decomposition than the analogous $Cr(CO)_5$ or $W(CO)_5$ carbene complexes. (a) Casey, C. P.; Vosejpka, P. C.; Askham, F. R. *J. Am. Chem. Soc.* **1990**, *112*, 3713. (b) Casey, C. P.; Czerwinski, C. J.; Powell, D. R.; Hayashi, R. K. *J. Am Chem. Soc.* **1997**, *119*, 5750. (c) Iwasawa, N.; Maeyama, K.; Saitou, M. *J. Am Chem. Soc.* **1997**, *119*, 1486.

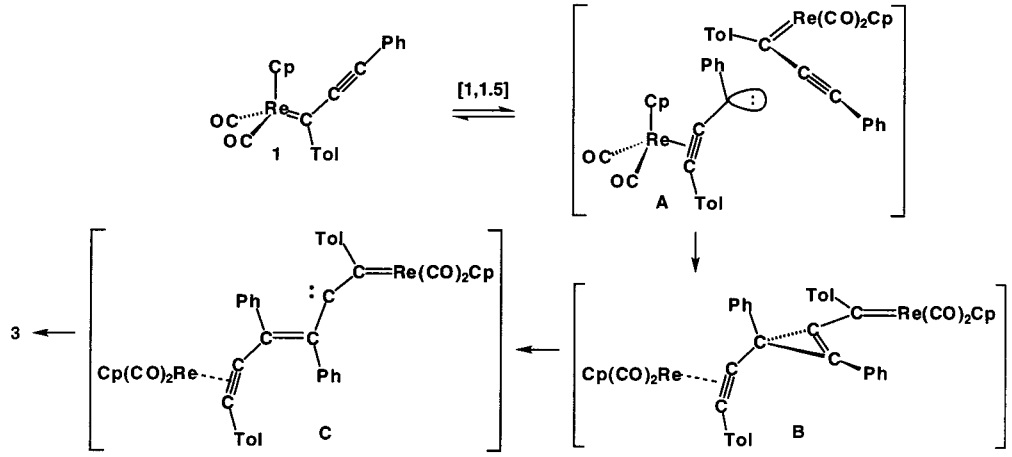
(6) Addition of dilithium or dizinc reagents to alkynylcarbene complexes has led to formation of bimetallic compounds. (a) Dötz, K. H.; Christoffers, C.; Knochel, P. *J. Organomet. Chem.* **1995**, *489*, C84. (b) Fischer, H.; Meisner, T.; Hofmann, J. *Chem. Ber.* **1990**, *123*, 1799.

10.1021/ja011962o CCC: $22.00

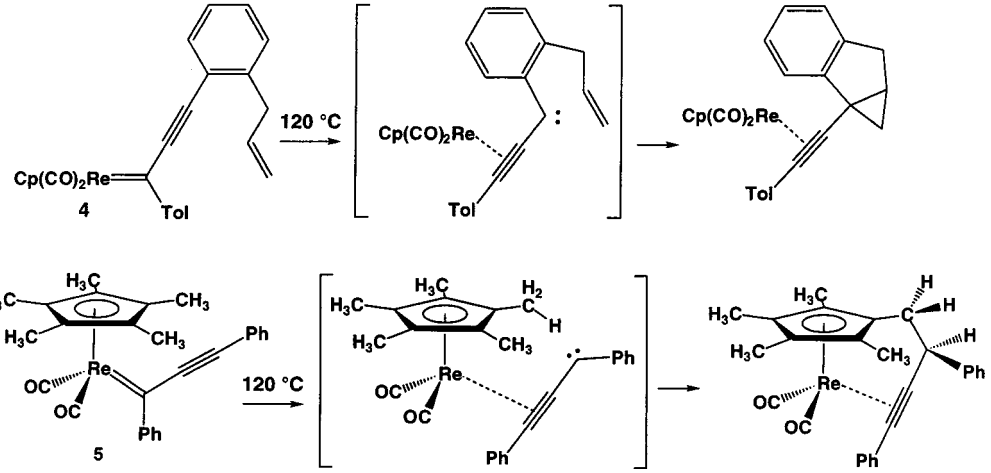
Scheme 1



Scheme 2



Scheme 3



[1,1.5] shift[9,10] of rhenium to give an intermediate **A** with enhanced electrophilic carbene character at the remote alkynyl carbon. Intermediate **A** is suggested to attack a second molecule of **1** to produce the cyclopropene intermediate **B**. Ring opening of **B** produces vinyl carbene **C**, which then rearranges via a [1,1.5] Re shift to produce enediyne complex **3** (Scheme 2).

A number of observations are consistent with this mechanistic hypothesis. The remote alkynyl carbon of **1** has electrophilic character as demonstrated by the addition of phosphines to this site.[11] The carbene character of the remote alkynyl carbon in intermediate **A** explains the intramolecular cyclopropanation of **4** and the insertion into a methyl CH bond of the Cp* complex **5** (Scheme 3).[12] As required by the mechanism shown in Scheme 2, attempted synthesis of cyclopropenyl carbene complex **6** led to immediate ring opening and formation of alkyne complex **7** (Scheme 4).

A second mechanism also involves an initial [1,1.5] shift of rhenium to give intermediate **A′**, but in this mechanism the

(7) (a) Casey, C. P.; Anderson, R. L. *J. Chem. Soc., Chem. Commun.* **1975**, 895. (b) Casey, C. P.; Burkhardt, T. J.; Bunnell, C. A.; Calabrese, J. C. *J. Am. Chem. Soc.* **1977**, *99*, 2127. (c) Casey, C. P.; Polichnowski, S. W. *J. Am. Chem. Soc.* **1977**, *99*, 6097. (d) Fischer, H.; Schmid, J. *J. Mol. Catal.* **1988**, *46*, 277. (e) Fischer, H.; Zeuner, S.; Ackermann, K.; Schmid, J. *Chem. Ber.* **1986**, *119*, 1546. (f) Fischer, H.; Zeuner, S.; Ackermann, K. *Chem. Commun.* **1984**, 684. (g) Hohmann, F.; Siemoneit, S.; Nieger, M.; Kotila, S.; Dötz, K. H. *Chem.-Eur. J.* **1997**, *3*, 853.

(8) Sierra, M. A.; del Amo, J. C.; Mancheño, M. J.; Gómez-Gallego, M. *J. Am. Chem. Soc.* **2001**, *123*, 851.

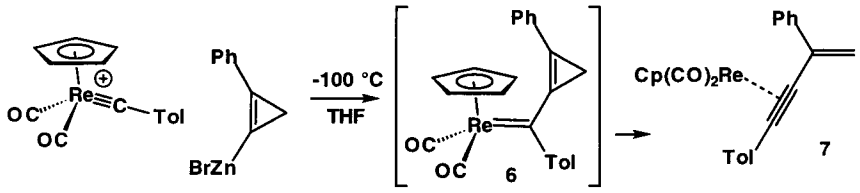
(9) We introduced the term "[1,1.5] shift" to describe the migration of rhenium from carbon 1 of carbene complex **l** to the midpoint between carbons 1 and 2 of the resulting alkyne complex **3**. See ref 4.

(10) (a) A similar [1,1.5] shift has been postulated in the rearrangement of the chromium acyl complex $[(CO)_5Cr{=}C(O)(C{\equiv}COEt)]^-$ to a cyclopropenylidene complex. Juneau, K. N.; Hegedus, L. S.; Roepke, F. W. *J. Am. Chem. Soc.* **1989**, *111*, 4762. (b) This rearrangement was recently observed in a related system. de Meijere, A.; Müller, S.; Labahn, T. *J. Organomet. Chem.* **2001**, *617*−*618*, 318.

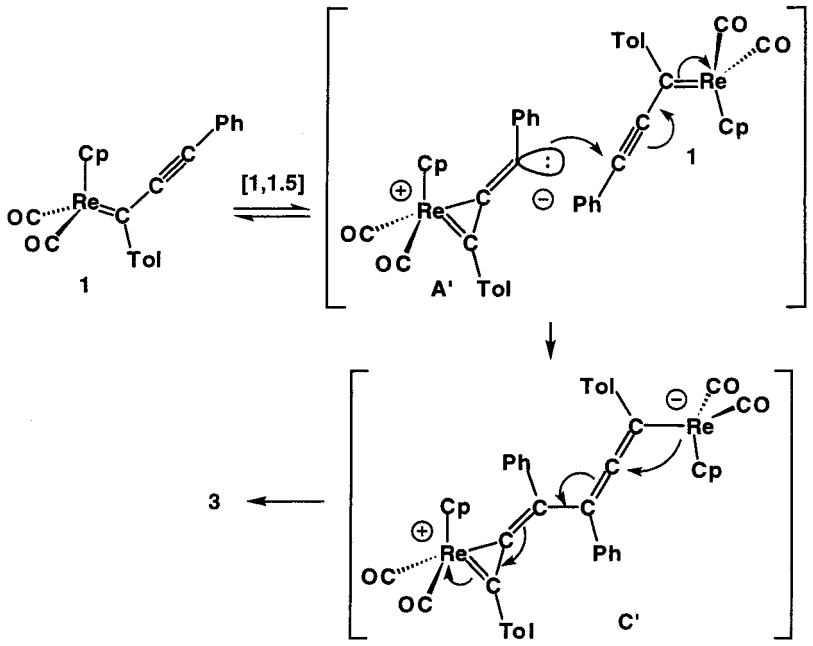
(11) Casey, C. P.; Kraft, S.; Powell, D. R.; Kavana, M. *J. Organomet. Chem.* **2001**, *617*−*618*, 723.

(12) Casey, C. P.; Kraft, S.; Powell, D. R.; Kavana, M. *Organometallics* **2001**, *20*, 3795.

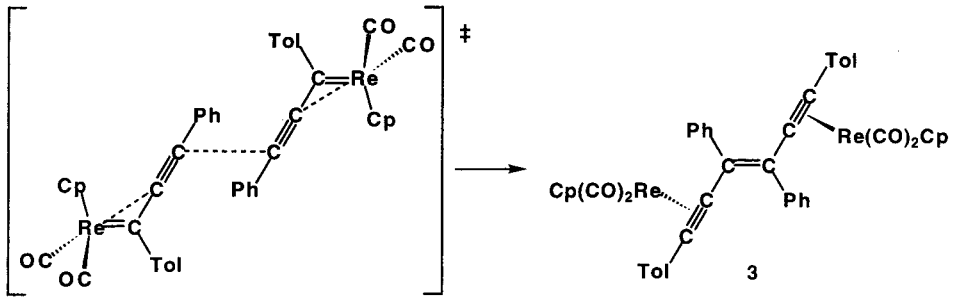
Scheme 4



Scheme 5



Scheme 6



remote alkynyl carbon is suggested to have nucleophilic character. **A′** is similar to isolated 1-metallacyclopropenes.[13,14] Nucleophilic attack on the remote alkynyl carbon of a second complex would give the zwitterionic intermediate **C′**,[15] which can then collapse to product with a second [1,1.5] Re shift (Scheme 5). It should be pointed out that **A** and **A′**, and **C** and **C′**, are resonance structures that have the same geometry but differ in their depicted polarizations and in the reactivity patterns they suggest. Protonation of alkynylcarbene complexes occurs primarily at the carbene carbon, but some protonation also occurs at the remote alkynyl carbon indicating that this center can be nucleophilic.[16] The observed insensitivity of the rate of dimerization to solvent polarity would require that the zwitterionic intermediate **C′** be similar in polarity to the starting carbene complex **1**.

A third mechanism involves no intermediate but is simply a concerted conversion of two alkynylcarbene complexes to a dimer with C=C bond formation occurring simultaneously with two [1,1.5] rhenium migrations (Scheme 6). At one extreme, where the transition state has very advanced [1,1.5] Re shifts and little C−C bond formation, this mechanism approaches dimerization of carbene-like intermediate **A**. However, a much earlier transition state would appear more likely than prior formation of two high-energy intermediates.

One distinction between these three mechanisms involves the geometry of approach of the two three-carbon units of the alkynylcarbene. In the first mechanism, the two units must approach orthogonally to produce the cyclopropene intermediate **B**. In the second mechanism, there is no geometric constraint

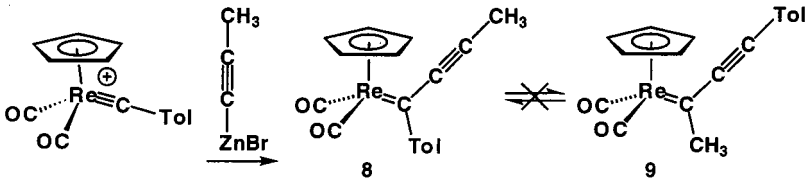
(13) For *exo*-vinylidene metallacyclopropene complexes, see: (a) Gambel, A. S.; Birdwhistell, K. R.; Templeton, J. L. *J. Am. Chem. Soc.* **1990**, *112*, 1818. (b) Feher, F. J.; Green, M.; Rodrigues, R. A. *J. Chem. Soc., Chem. Commun.* **1987**, 1206.

(14) For cationic rhenium metallacyclopropenes, see: Casey, C. P.; Brady, J. T.; Boller, T. M.; Weinhold, F.; Hayashi, R. K. *J. Am Chem. Soc.* **1998**, *120*, 12500.

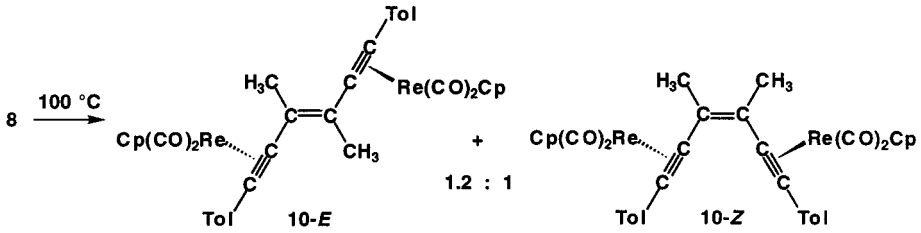
(15) For σ-allenyl complexes, see: Doherty, S.; Corrigan, J. F.; Carty, A. J.; Sappa, E. *Adv. Organomet. Chem.* **1995**, *37*, 39.

(16) Kraft, S. Ph.D. Thesis, University of Wisconsin, 2001.

Scheme 7



Scheme 8



on the first C−C bond formation to generate zwitterionic intermediate **C′**. In the third mechanism, if the transition state has some resemblance to that of carbene dimerization, then a least motion coplanar approach of the carbenes to form the new C═C bond would be symmetry forbidden;[17] geometries involving a parallel but not coplanar approach of the developing carbene centers appear favorable.

In an effort to distinguish between these mechanisms, we have synthesized bis carbene complexes in which the approach of the alkynylcarbene units is restricted by the linking unit. Here we report that intramolecular coupling of linked alkynylcarbene complexes occurs remarkably rapidly to give cyclic enediyne complexes.

Results

***cis*- and *trans*-Enediyne Complexes from Thermolysis of $Cp(CO)_2Re{=}C(Tol)C{\equiv}CCH_3$ (8).** Only the *trans*-enediyne complex **3** was observed in the coupling of **1**. To determine whether this was intrinsic to the coupling mechanism or merely due to the steric effect of large phenyl substituents on the forming double bond, we investigated the reactions of less crowded substrates. $Cp(CO)_2Re{=}C(Tol)C{\equiv}CCH_3$ (**8**) was prepared by a route similar to that used for the synthesis of $Cp(CO)_2Re{=}C(Tol)C{\equiv}CPh$ (**1**). Addition of the zinc acetylide $BrZnC{\equiv}CCH_3$ to the rhenium carbyne complex $[Cp(CO)_2Re{\equiv}CTol]BC1_4$ in THF at −35 °C gave the black alkynylcarbene complex $Cp(CO)_2Re{=}C(Tol)C{\equiv}CCH_3$ (**8**), which was isolated in 22% yield following column chromatography (Scheme 7).

The structure of **8** was established spectroscopically; the ^{13}C NMR spectrum established the presence of a carbene ligand (δ 258.1). Evidence for an aryl group bound to the carbene carbon comes from a high-frequency aromatic resonance at δ 157.2 assigned to the ipso-carbon bound to the carbene carbon. This assignment is based on ^{13}C NMR spectra of **1** and the labeled derivative $Cp(CO)_2Re{=}C(Tol)(C{\equiv}^{13}CPh)$ (**1-^{13}C**). Therefore, no [1,3] rhenium shift to give $Cp(CO)_2Re{=}C(CH_3)C{\equiv}CTol$ (**9**) occurred during synthesis or isolation of **8**.

When a solution of **8** was heated at 100 °C in toluene-d_8, the Cp ^1H NMR resonance of **8** at δ 5.7 decreased, and a 1.2:1 ratio of two new Cp resonances at δ 5.5 and 5.3 grew in. Thin-layer chromatography gave partial separation of the two products, and the major isomer was isolated in pure form after exposure of the mixture in CH_2Cl_2 to air.[18] No evidence was found for isomerization via a [1,3] rhenium shift to $Cp(CO)_2Re{=}C(CH_3)C{\equiv}CTol$ (**9**). A [1,1.5] shift of **8** would generate a carbene-like intermediate similar to **A** in Scheme 2. Such an intermediate might undergo a 1,2 hydrogen shift to form $Cp(CO)_2Re(\eta^2\text{-}TolC{\equiv}CCH{=}CH_2)$. However, no evidence for formation of such an eneyne complex was obtained.

The structures of the products were assigned as the *trans*- and *cis*-enediyne complexes $[Cp(CO)_2Re]_2[\eta^2,\eta^2\text{-}TolC{\equiv}CC(CH_3){=}C(CH_3)C{\equiv}CTol]$ (**10-*E*** and **10-*Z***) on the basis of spectroscopy (Scheme 8). Mass spectrometry established that both complexes were dimers. There are six possible dimers: cis- and trans-isomers arising from tail-to-tail, head-to-head, and head-to-tail combinations. Both ^1H and ^{13}C NMR established the symmetric nature of the products, ruling out head-to-tail isomers. The formation of a cis head-to-head isomer with tolyl groups on the C═C bond seems unlikely on steric grounds and such cis isomers were not observed from coupling of **1**. The ^{13}C NMR chemical shifts of the methyl groups of **10-*E*** and **10-*Z***, both at δ 21.73, are consistent with their assignment as vinyl methyl groups of the tail-to-tail isomers. If head-to-head isomers were formed, the chemical shifts of the complexed $CH_3C{\equiv}CR$ unit would have been expected to be in the δ 10 region; for example, the chemical shift of $(CH_3C{\equiv}CCH_3)Re(CO)_2Cp$ is δ 14.2.[19] The major isomer was assigned as **10-*E*** on the basis of the observation of a 1.0% nOe signal enhancement of the resonance at δ 7.59 (assigned to aromatic CH ortho to the alkynyl substituent) upon irradiation of the allylic methyl resonance at δ 1.96. For the minor isomer assigned as **10-*Z***, only a 0.1% nOe enhancement of the resonance at δ 7.23 (assigned to aromatic CH ortho to the alkynyl substituent) was seen upon irradiation of the allylic methyl resonance at δ 2.24.

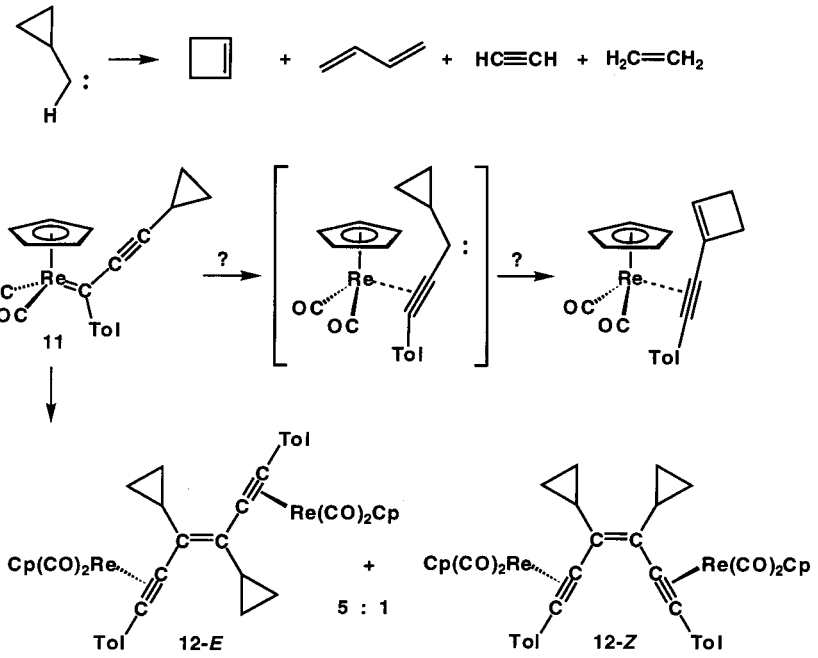
The kinetics of dimerization of **8** in toluene-d_8 were followed by ^1H NMR spectroscopy between 80 and 120 °C. NMR yields of >95% based on conversion of **8** were determined using 1,4-bis-trimethylsilylbenzene as an internal NMR standard. Clean second-order kinetics for disappearance of starting material were

(17) Hoffmann, R.; Gleiter, R.; Mallory, F. B. *J. Am. Chem. Soc.* **1970**, *92*, 1460. Ohta, K.; Davidson, E. R.; Morokuma, K. *J. Am. Chem. Soc.* **1985**, *107*, 3466. Alder, R. W.; Blake, M. E.; Oliva, J. M. *J. Phys. Chem. A* **1999**, *103*, 11200.

(18) Isomerization in air at room temperature was unexpected since the compounds are stable at 120 °C in the absence of air. We speculate that isomerization occurs via a reversibly formed radical cation $\mathbf{10\text{-}Z}^+\ \mathbf{O_2}^-$ in which the bonding character of the central C═C bond is weakened.

(19) Alt, H. G.; Engelhardt, H. E. *J. Organomet. Chem.* **1988**, *342*, 235.

Scheme 9



observed. Activation parameters ($\Delta H^{\ddagger} = 18.3 \pm 0.4$ kcal mol^{-1}, $\Delta S^{\ddagger} = -19.8 \pm 1.2$ eu) were determined from an Eyring plot. The rate of dimerization of **8** ($25.4 \pm 0.2 \times 10^{-3}$ M^{-1} s^{-1}) which has an alkynyl methyl group was about 17 times faster at 120 °C than was the rate of dimerization of **1** ($1.8 \pm 0.05 \times 10^{-3}$ M^{-1} s^{-1}) which has an alkynyl phenyl group.[4] Thus, the effect of replacing the phenyl group of **1** by a methyl group in **8** is to increase the rate of dimerization and to allow the formation of both *cis*- and *trans*-enediynes.

The observation of *cis*-enediyne product **10-*Z*** indicates that the coupling mechanism has no intrinsic bias toward *trans*-enediyne complexes. The previously observed selective formation of only *trans*-enediyne **3** from dimerization of phenyl-substituted alkynylcarbene complex **1** is more likely related to steric effects. While we cannot rigorously exclude the possibility that [1,3] isomerization of **8** to **9** is rapid and reversible and favors **8**, this seems highly unlikely. In the case of aryl-substituted alkynylcarbene complexes, we found that electron-withdrawing substituents sped up interconversion of isomers but did not greatly affect the equilibrium constants.[20] For example, $Cp(CO)_2Re{=}C(Tol)C{\equiv}CC_6H_4$-*p*-$SO_2CF_3$ equilibrates with the [1,3] shift isomer $Cp(CO)_2Re{=}C(C_6H_4$-*p*-$SO_2CF_3)C{\equiv}$CTol 88 times more rapidly than equilibration of **1** with **2**, but the equilibrium constants for the two systems are similar, 4 and 1, respectively. We are trying to devise a synthesis of $Cp(CO)_2Re{=}C(CH_3)C{\equiv}$CTol (**9**) to test the hypothesis that isomerization is slow.

Cyclopropyl-Substituted Alkynylcarbene Complexes Dimerize without Ring Expansion. One mechanism for dimerization of alkynylcarbene complexes involves an initial [1,1.5] shift to generate intermediate **A** which is suggested to have carbene character at the remote alkynylcarbene carbon. Such a carbon center might undergo ring expansion to a cyclobutene since free cyclopropyl carbenes undergo such ring expansions (Scheme 9).[21]

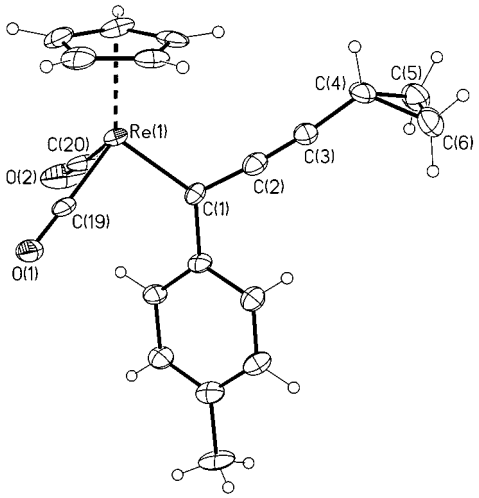


Figure 1. X-ray crystal structure of cyclopropyl-substituted alkynylcarbene complex $Cp(CO)_2Re{=}C(Tol)C{\equiv}CC_3H_5$ (**11**).

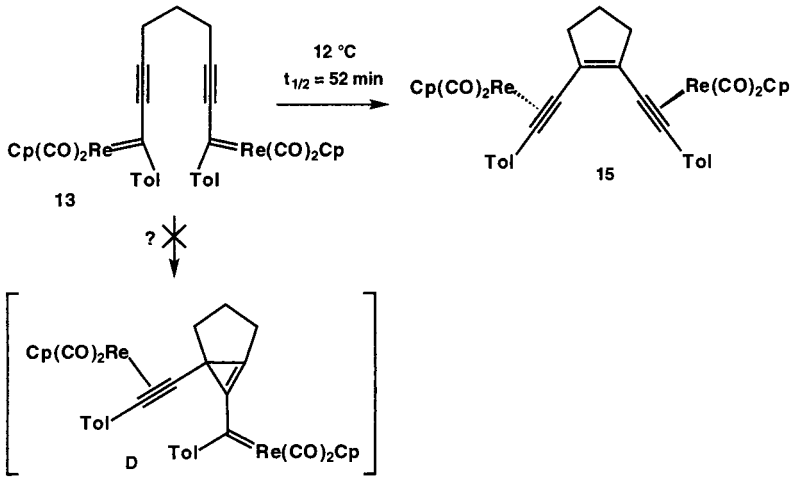
The cyclopropyl-substituted alkynylcarbene complex $Cp(CO)_2Re{=}C(Tol)C{\equiv}CC_3H_5$ (**11**) was synthesized in 64% yield by addition of the zinc cyclopropylacetylide $BrZnC{\equiv}CC_3H_5$ to the rhenium carbyne complex $[Cp(CO)_2Re{\equiv}CTol]BCl_4$ in THF at −35 °C. Complex **11** was characterized spectroscopically; the ^{13}C NMR spectrum established the presence of a carbene ligand (δ 256.67) and of an aryl group bound to the carbene (δ 156.81, t, $^3J_{CH} = 7.9$ Hz). X-ray crystallography confirmed the structural assignment (Figure 1).

When the cyclopropyl-substituted alkynylcarbene complex $Cp(CO)_2Re{=}C(Tol)C{\equiv}CC_3H_5$ (**11**) was heated at 120 °C, only dimerization to a 5:1 ratio of *trans*-:*cis*-enediyne complexes $[Cp(CO)_2Re]_2[\eta^2,\eta^2$-$TolC{\equiv}C(C_3H_5)C{=}C(C_3H_5)C{\equiv}CTol]$ [**12-*E*** and **12-*Z*]** was seen (Scheme 9). When the thermolysis was followed by ^{1}H NMR spectroscopy, a 58% yield of **12** was observed at

(20) Casey, C. P.; Kraft, S.; Powell, D. R. *Organometallics* **2001**, *20*, 2651.

(21) Cyclopropyl carbene undergoes ring expansion to cyclobutene, ring fragmentation to acetylene and ethylene, and ring opening to butadiene. Arct, J.; Brinker, U. H. In *Methoden der organischen Chemie (Houben-Weyl)*; Regitz, M., Ed.; Thieme Verlag: Stuttgart, 1989; Vol. E19b, p 337.

Scheme 10



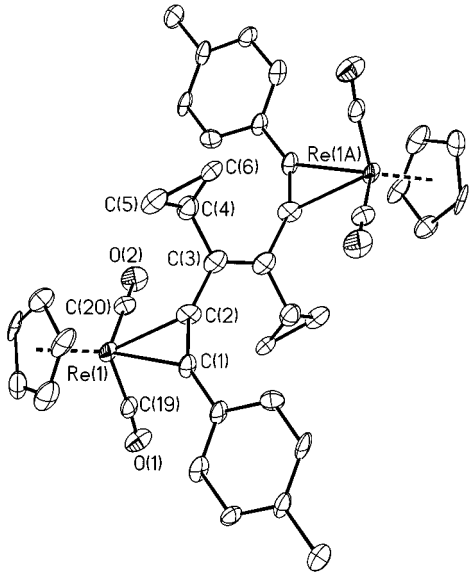


Figure 2. X-ray crystal structure of cyclopropyl-substituted enediyne complex $[Cp(CO)_2Re]_2[\eta^2,\eta^2$-(*E*)-TolC≡C($C_3H_5$)C═C($C_3H_5$)C≡CTol] (**12-*E***).

68% conversion of **11** to **12**. No ring expansion product was observed by ^{1}H or ^{13}C NMR spectroscopy. Dimer **12-*E*** was isolated as a yellow crystalline compound following thin-layer chromatography and recrystallization. The structure of **12-*E*** was established by X-ray crystallography which shows a *trans*-enediyne structure (Figure 2). The low frequency ^{1}H NMR chemical shifts (δ 0.31, 0.47, 1.51), low frequency ^{13}C NMR chemical shifts [δ 7.25 (t, $^1J_{CH}$ = 162.6 Hz, CH_2), 15.84 (d, $^1J_{CH}$ = 162.6 Hz, C═C*C*H)], and large CH coupling constants seen for **12-*E*** are typical of cyclopropanes. The second-order rate constant for disappearance of **8** at 120 °C was $k_2 = 5.33 \times 10^{-3}$ M^{-1} s^{-1}. The rate of dimerization of **11** is about 3 times faster than that of the dimerization of **1** which has a slightly larger phenyl substituent on the alkynyl unit and is about 5 times slower than the dimerization of **8** which has a smaller methyl substituent.

Cyclic *cis*-Enediynes from Tethered Bis-(alkynylcarbene) Complexes. The accessibility of alkyl-substituted *cis*-enediynes encouraged us to attempt to prepare cyclic enediynes from tethered bis-(alkynylcarbene) complexes. These substrates also allow a distinction to be made between the three dimerization mechanisms presented in the Introduction.

Table 1. Selected ^{13}C NMR Chemical Shifts of Enediyne Complexes **3**, **10-*E***, **10-*Z***, **12-*E***, **15**, and **17**

compound	TolC≡*C*	Tol*C*≡C	C═C
3[a]	79.69	85.19	134.98
10-*E*[b]	79.60	80.53	129.15
10-*Z*[b]	79.87	82.29	128.92
12-*E*[c]	77.50	85.06	133.73
15[b]	72.21	85.24	136.15
17[d]	72.52	93.45	135.19

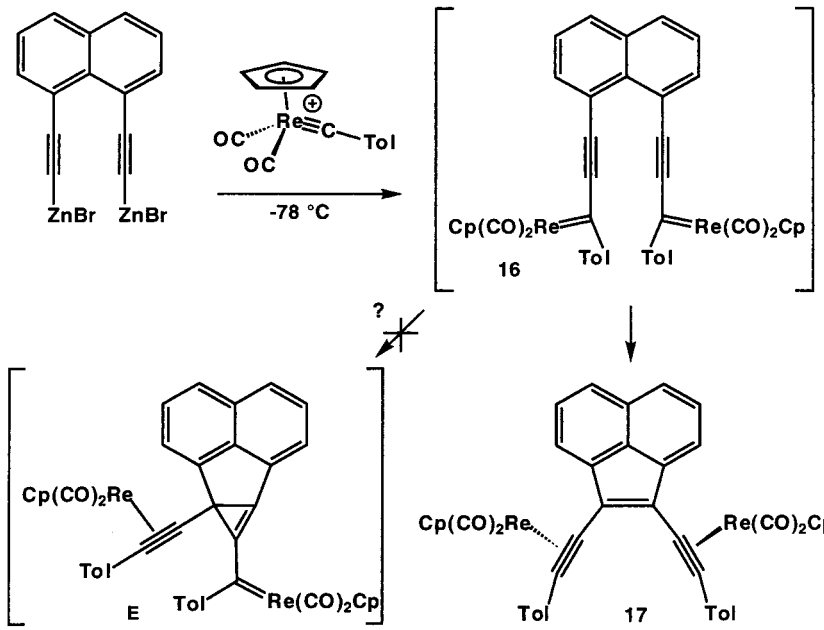
[a] In C_6D_6 at 60 °C. [b] In CD_2Cl_2 at 24 °C. [c] In $CDC1_3$ at 60 °C. [d] In THF-d_8 at 60 °C.

The tethered bis-(alkynylcarbene) complex $Cp(CO)_2Re$═C(Tol)C≡$CCH_2CH_2CH_2$C≡CC(Tol)═$Re(CO)_2Cp$ (**13**) was obtained from reaction of the bis-alkynylzinc compound BrZnC≡$CCH_2CH_2CH_2$C≡CZnBr with the carbyne complex [$Cp(CO)_2$-Re≡CTol]BCl_4. The yields of isolated **13** were significantly lower (only 8%) than for other alkynylcarbene complexes due to its temperature sensitivity which required a tedious low-temperature thin-layer chromatography workup. A major side product was the monofunctionalized complex $Cp(CO)_2Re$═C(Tol)C≡$CCH_2CH_2CH_2$C≡CH (**14**) which was formed in 20−30% isolated yield. The structure of **13** was established spectroscopically. The ^{13}C NMR spectrum established the presence of a carbene ligand (δ 254.5) and of an aryl group bound to the carbene carbon (δ 154.1 assigned to the ipso-carbon bound to the carbene carbon).

The bis-alkynylcarbene complex **13** rearranged to the cyclic *cis*-enediyne complex $[Cp(CO)_2Re]_2[\eta^2,\eta^2$-TolC≡CC($CH_2CH_2$-$CH_2$)═CC≡CTol] (**15**) below room temperature (Scheme 10). An NMR yield of >97% was determined using 1,4-bis-trimethylsilylbenzene as an internal NMR standard. The structure of **15** was determined spectroscopically (Table 1) and confirmed by X-ray crystallography (Figure 3). The X-ray crystal structure of **15** shows near C_2 symmetry broken only by the envelope conformation of the cyclopentene.[22] The cyclopentene C═C double bond is slightly twisted (the C(2)−C(3)−C(2A)−C(3A) dihedral angle is 4.4°), the complexed alkynes are bent [the C(1)−C(2)−C(3) angle is 156.8°, and the C(2)−C(3)−C(aryl) angle is 149.8°], and the two rheniums are

(22) A 50:50 disorder in the structure involves the two different envelope conformations of the cyclopentene ring.

Scheme 11



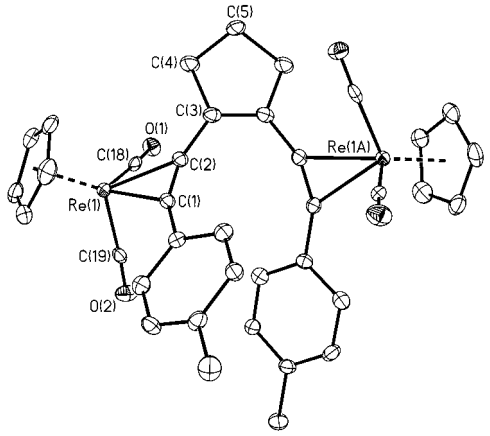


Figure 3. X-ray crystal structure of the cyclic *cis*-enediyne complex [Cp-$(CO)_2$Re][η^2,η^2-TolC≡CC($CH_2CH_2CH_2$)═CC≡CTol] (**15**).

complexed on opposite faces of the enediyne. In the room temperature ^{1}H NMR spectrum of **15**, the allylic methylene hydrogens in the five-membered ring are diastereotopic (δ 2.83, 3.11) due to the neighboring CpRe$(CO)_2$ group on one face of the enediyne. The carbonyls on Re (δ 205.15, 205.44) are diastereotopic in the ^{13}C NMR spectrum; interconversion of their environments requires both rotation of the alkyne about rhenium and passing the two alkynyl groups past one another.

The kinetics of the rearrangement of the bis-alkynylcarbene complex **13** to the *cis*-enediyne complex [$Cp(CO)_2Re]_2$[η^2,η^2-TolC≡CC($CH_2CH_2CH_2$)═CC≡CTol] (**15**) were followed by ^{1}H NMR spectroscopy in toluene at 11.9 °C. The intramolecular conversion of **13** to **15** was remarkably fast as compared to the intermolecular coupling of **8**. The half-life was 52 min at 11.9 °C as compared with the extrapolated half-life for a 0.02 M solution of **8** of 154 days. Thus at the same 0.02 M concentration, intramolecular coupling of **13** occurs 4270 times faster than does intermolecular coupling of **8**. The first-order rate constant for conversion of **13** to **15** was $k = 2.2 \pm 0.1 \times 10^{-3}$ s^{-1}, corresponding to $\Delta G^{\ddagger} = 21.43 \pm 0.03$ kcal mol^{-1}.

If we assume that the activation entropy of this intramolecular first-order process lies in the range from 0 to −12 eu, we can bracket $\Delta H^{\ddagger}$ between 21.4 and 18.0 kcal mol^{-1}.[23] This range is close to the activation enthalpy of the intermolecular reaction **8** → **10** ($\Delta H^{\ddagger} = 18.3 \pm 0.4$ kcal mol^{-1} and $\Delta S^{\ddagger} = -19.8 \pm 1.2$ eu), suggesting that in both cases the same principle mechanism is operative. Essentially, the intermolecular reaction of **8** → **10** is slowed due to an unfavorable entropy of activation as compared with that of the intramolecular conversion of **13** → **15**.

In an effort to further constrain the geometry of the linked alkynylcarbene complexes to a parallel orientation, we set out to prepare the 1,8-disubstituted naphthalene derivative 1,8-[Cp-$(CO)_2$Re═C(Tol)C≡C]$_2C_{10}H_6$ (**16**). Addition of 1,8-di-(bromozincethynyl)naphthalene to [Cp$(CO)_2$Re≡CTol]BCl_4 at −78 °C gave a deep yellow-black solution characteristic of carbene complexes. This solution underwent a subtle color change to dark purple at about −60 °C and showed no further color change upon warming to room temperature. No attempt was made to spectroscopically observe the likely intermediate 1,8-[Cp-$(CO)_2$Re═C(Tol)C≡C]$_2C_{10}H_6$ (**16**) at low temperature. When a sample taken from the −60 °C reaction mixture was immediately analyzed by thin-layer chromatography, only the coupled product [$Cp(CO)_2Re]_2$[(η^2,η^2-1,2-(tolylethynyl)acenaphthylene] (**17**) was seen; there was no evidence for a slower moving carbene complex such as **16** (Scheme 11). For comparison, when a solution of bis-alkynylcarbene complex **13** was prepared at low temperature and immediately analyzed by TLC, spots for both **13** and the *cis*-enediyne complex [$Cp(CO)_2Re]_2$-(η^2,η^2-TolC≡CC($CH_2CH_2CH_2$)═CC≡CTol) (**15**) were seen. Therefore, the rate of C═C bond formation leading to **17** must be at least as fast as that leading to **15**.

The coupled product [$Cp(CO)_2Re]_2$(η^2,η^2-1,2-(tolylethynyl)-acenaphthylene] (**17**) was isolated in 32% yield by column chromatography. The structure of **17** was determined by X-ray crystallography (Figure 4).

(23) If we assume that $\Delta H^{\ddagger}$ is the same as the 18.3 ± 0.4 kcal mol measured for the intermolecular dimerization of **3**, then $\Delta S^{\ddagger} = -10.9$ eu for the intramolecular coupling of **13**. This is a reasonable value for a first-order process that must involve an ordered intramolecular configuration for coupling.

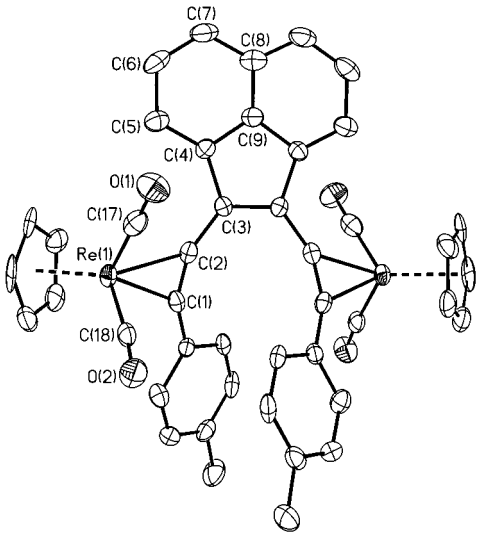


Figure 4. X-ray crystal structure of $Cp(CO)_2Re]_2$ [η^2,η^2-1,2-(tolylethynyl)-acenaphthylene] (**17**).

Discussion

Mechanism of Dimerization. One of our suggested mechanisms for alkynylcarbene complex dimerization involves an initial [1,1.5] Re shift to give a species **A** with carbene character at the remote alkynyl carbon. The ability of Re to undergo a [1,3] shift [at somewhat slower rates than dimerization for **1** and **8**, and at faster rates than dimerization of $Cp(CO)_2Re{=}C(Tol)C{\equiv}CC_6H_4$-*p*-$SO_2CF_3$] suggested that the more modest [1,1.5] shift needed to be seriously considered for the dimerization of **1**. The carbene-like reactivity of the remote alkynyl carbon seen in the cyclopropanation of **4** and in the insertion into a CH bond of the Cp* complex **5** (Scheme 3) is readily accounted for by initial [1,1.5] shifts to give carbene intermediates related to **A**.

The cyclopropyl-substituted alkynylcarbene complex **11** was prepared as a test for carbene-like reactivity of the remote alkynyl carbon. The cyclopropyl substituent should be able to intercept a free carbene via ring expansion. Cyclopropyl carbenes are known to quickly rearrange to cyclobutenes often accompanied by fragmentation reactions forming alkenes and alkynes.[21] The failure of complex **11** to undergo ring expansion to a cyclobutene suggests that if intermediate **A** is involved, then interaction of the neighboring Re(alkyne) complex with the carbene center greatly diminishes the carbene character as compared with that of the free cyclopropyl carbenes. Similarly, the failure of methyl-substituted alkynylcarbene complex **8** to undergo a 1,2 hydrogen shift to form $Cp(CO)_2Re(\eta^2$-$TolC{\equiv}CCH{=}CH_2)$ suggests that if intermediate **A** is involved it has diminished carbene character.

The tethered bis(alkynylcarbene) complexes **13** and **16** were studied to probe the geometric requirements for C=C bond formation. In particular, the mechanism shown in Scheme 2 requires an orthogonal approach of **A** to the alkyne unit of a second alkynylcarbene complex to produce cyclopropene intermediate **B**. Formation of cyclopropenes from either **13** or **16** would lead to the very strained intermediates **D** and **E** and would be expected to greatly retard or prevent dimerization by such a mechanism. Calculations suggest the strain energy in cyclopropenes (~54 kcal mol^{-1}) is increased by 24 kcal mol^{-1} in bicyclo[3.1.0]hex-1(6)-ene due to the extra bicyclic strain in this twisted system.[24−26] The cyclopropene intermediate **E** from the 1,8-bis(alkynyl)naphthalene system would be even more strained than cyclopropene **D** derived from the trimethylene-linked complex **13**.

However, coupling of both **13** and **16** not only occurred, but did so at much lower temperatures than intermolecular dimerizations. A fair comparison of first-order intramolecular dimerizations with second-order intermolecular dimerizations should center on $\Delta H^{\ddagger}$ of the two reactions and not simply on rates. Our estimates suggest similar $\Delta H^{\ddagger}$ for intermolecular dimerization of **8** ($\Delta H^{\ddagger}$ = 18.3 kcal mol^{-1}) and for intramolecular coupling of **13** ($\Delta H^{\ddagger}$ = 18−21 kcal mol^{-1}). The rate of formation of acenaphthylene **17** from the presumed 1,8-bis-(alkynyl)naphthalene intermediate **16** was too fast to measure but was apparently even more rapid than conversion of **13** to **15**. The extreme ease of this intramolecular coupling may be due to release of strain in the 1,8-dialkynylnaphthalene system.[27] The very rapid dimerizations of both **13** and **16** provide compelling evidence against mechanisms involving cyclopropene intermediates.

Sander recently observed that carbenes can react with alkynes to generate a new C=C double bond between the carbene carbon and one alkyne carbon and a new carbene center at the other alkyne carbon.[28] This suggests a fourth mechanism for alkynylcarbene complex dimerization that involves three steps: (1) an initial reversible [1,1.5] Re shift to give "carbene" intermediate **A**, (2) rate-determining addition of the carbene center of **A** to the remote alkynyl carbon of a second alkynylcarbene complex to generate vinyl carbene intermediate **C**, and (3) rearrangement of **C** to the enediyne complex by a [1,1.5] Re shift (Scheme 12). In the transition state, the carbene lone pair is suggested to act as a nucleophile and conjugately add to the remote alkynyl carbon, while the empty carbene orbital accepts electrons from an alkyne π-bond.[29] This mechanism avoids impossibly strained cyclopropene intermediates, makes use of the carbene-like reactivity of the remote alkynyl carbon of the

(24) Domnin, I. N.; Ponomarev, D. A.; Takhistov, V. V.; Pihlaja, K. *Russ. J. Org. Chem.* **1999**, *35*, 28.

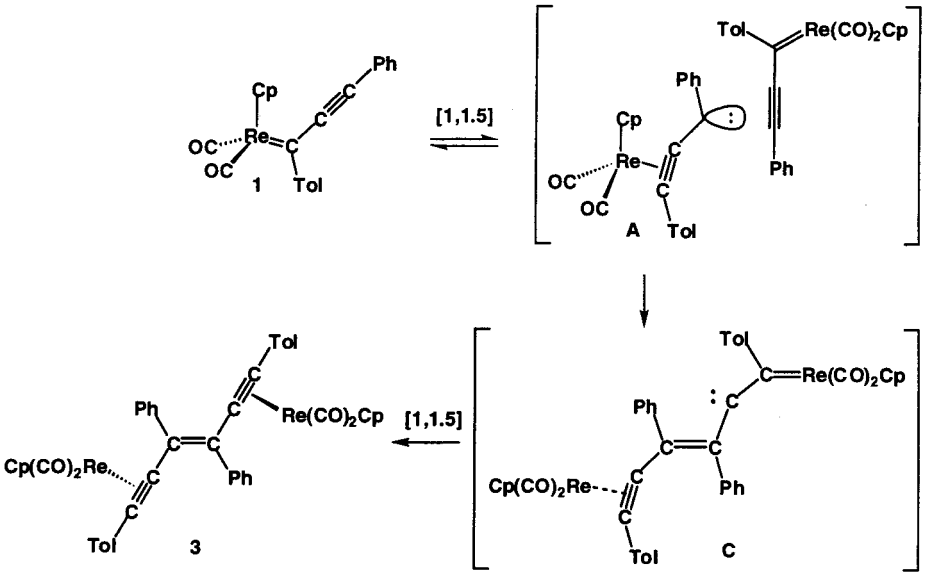
(25) Nevertheless, bicyclo[3.1.0]hex-1(16)-ene derivatives have been generated in situ, and their structures have been deduced from trapping experiments. (a) Weber, J.; Brinker, U. H. *Tetrahedron* **1996**, *52*, 14641. (b) Halton, B.; Diggins, M. D.; Kay, A. J. *J. Org. Chem.* **1992**, *57*, 4080. (c) Baird, M. S.; Netherscott, W. *Tetrahedron Lett.* **1983**, *24*, 605. (d) Coleman, B.; Jones, M., Jr. *J. Organomet. Chem.* **1979**, *168*, 393. (e) Wolff, S.; Agosta, W. C. *J. Am. Chem. Soc.* **1984**, *106*, 2363. (f) Billups, W. E.; Haley, M. M.; Lee, G.-A. *Chem. Rev.* **1989**, *89*, 1147. (g) Baird, M. S. Functionalized Cyclopropenes as Synthetic Intermediates. In *Topics in Current Chemistry*; de Meijere, A., Ed.; Springer-Verlag: Berlin, 1988; Vol. 144, p 137.

(26) Bicyclo[3.1.0]hex-1(6),3-diene-2-one has been isolated in an argon matrix at 10 K, and the cyclopropenyl moiety was identified by IR spectroscopy. Bucher, G.; Sander, W. *J. Org. Chem.* **1992**, *57*, 1346.

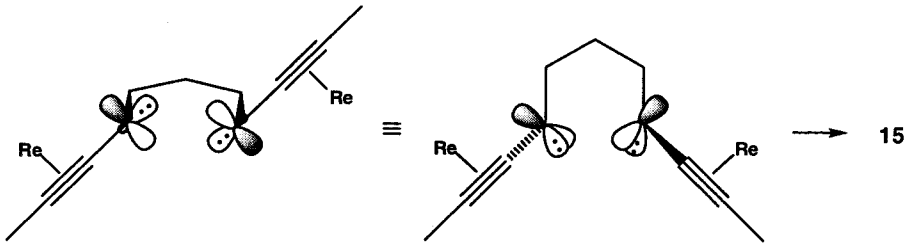
(27) 1,8-Dialkynylnaphthalenes are known to undergo cycloadditions, brominations, and hydrogenations accompanied by intramolecular C=C bond formation of the internal alkyne carbons. Release of strain is supposedly a driving force for this unique reactivity. (a) Staab, H. A.; Nissen, A.; Ipaktschi, J. *Angew. Chem., Int. Ed. Engl.* **1968**, *7*, 226. (b) Mitchell, R. H.; Sondheimer, F. *Tetrahedron* **1970**, *26*, 2141. (c) Staab, H. A.; Ipaktschi, J.; Nissen, A. *Chem. Ber.* **1971**, *104*, 1182. (d) Müller, E.; Thomas, R.; Zountsas, G. *Justus Liebigs Ann. Chem.* **1972**, *758*, 16. (e) Bossenbroek, B.; Sanders, D. C.; Curry, H. M.; Shechter, H. *J. Am. Chem. Soc.* **1969**, *91*, 371. (f) Zhou, Z.; Costa, M.; Chiusoli, G. P. *J. Chem. Soc., Perkin Trans. 1* **1992**, 1407. (g) Blum, J.; Badrieh, Y.; Shaaya, O.; Meltser, L.; Schumann, H. *Phosphorus, Sulfur Silicon Relat. Elem.* **1993**, *79*, 87. (h) Blum, J.; Baidossi, W.; Badrieh, Y.; Hoffman, R. E.; Schumann, H. *J. Org. Chem.* **1995**, *60*, 4738. (i) Eckert, T.; Ipaktschi, J. *Monatsh. Chem.* **1998**, *129*, 1035. (j) Cobas, A.; Guitián, E.; Castedo, L. *J. Org. Chem.* **1997**, *62*, 4896.

(28) Sander found that the reactive singlet vinylidene $CF_2{=}C$: adds to difluoroacetylene to form the allenylcarbene $CF_2{=}C{=}CF{-}CF$: (observed by IR in matrix isolation) without the intermediacy of a methylene cyclopropene (more stable than the allenylcarbene by 18.1 kcal mol^{-1}). Kötting, C.; Sander, W.; Senzlober, M. *Chem.-Eur. J.* **1998**, *4*, 2360.

Scheme 12



Scheme 13



alkynylcarbene complex, and is consistent with the insensitivity of the rate of dimerization to solvent polarity. This transition state for dimerization is similar to the transition states proposed for cyclopropane formation from **4**, and for CH insertion of **5**; all involve carbene-like reactivity at the remote alkynyl carbon of intermediates similar to **A**, formed by an initial reversible [1,1.5] Re shift of an alkynylcarbene complex.[30]

Our observations cannot exclude the dimerization mechanism (Scheme 6) which involves C−C bond formation between the remote alkynyl carbons concerted with two [1,1.5] Re shifts. In as much as this mechanism resembles a carbene dimerization for which a coplanar approach of the carbene units is symmetry forbidden,[17] a geometry of approach and orbital interactions as shown in Scheme 13 should be considered.

One possible way to distinguish between these two mechanisms would be to compare the rates of homo- and heterodimerization of two different alkynylcarbene complexes. The mechanism shown in Scheme 12 suggests that rates of heterodimerization of differently substituted compounds might be faster than either homodimerization since the two alkynylcarbene complexes play different roles in the rate-determining step.[31] In contrast, the symmetric mechanism shown in Scheme 6 predicts a rate of heterodimerization intermediate between the rates of the two homodimerizations.

Synthetic Potential of Intramolecular Coupling Reactions. In light of the antitumor activity of cyclic *cis*-enediynes that are able to cleave double-stranded DNA via Bergman cyclization,[32−34] we became interested in finding conditions to obtain *cis*-enediyne systems via coupling of rhenium alkynylcarbene complexes. Surprisingly, few procedures for the preparation of cyclic *cis*-enediynes are currently available and often involve multistep syntheses.[35] To enforce a cis-geometry at the central double bond, we geometrically constrained the coupling step

(29) While this mechanism is similar to our second mechanism shown in Scheme 5, intermediate **C** in Scheme 12 differs markedly from intermediate **C′** in Scheme 5 in terms of charge separations and the bond order of the newly formed C−C bond.

(30) Intermediate **A** can be considered an extreme depiction of the reactive center in the reactions.

(31) In particular, the carbene-like intermediate **A** is an electrophile and might be more reactive with electron-withdrawing groups attached, while the alkynylcarbene complex undergoing attack acts as a nucleophile and might be more reactive with electron-donor substituents attached.

(32) Jones, R. R.; Bergman, R. G. *J. Am. Chem. Soc.* **1972**, *94*, 660.

(33) Cyclic enediynes can be extremely potent anticancer antibiotics. König, B.; Pitsch, W.; Klein, M.; Vasold, R.; Prall, M.; Schreiner, P. R. *J. Org. Chem.* **2001**, *66*, 1742.

(34) For reviews of cyclic enediynes, see: (a) Grissom, J. W.; Gunawardena, G. U.; Klingberg, D.; Huang, D. *Tetrahedron* **1996**, *52*, 6453. (b) Nicolaou, K. C.; Smith, A. L. In *The Enediyne Antibiotics* in *Modern Acetylene Chemistry*; Stang, P. D., Diederich, F., Eds.; VCH: Weinheim, 1995; Chapter 7, p 203. (c) Maier, M. E. *Synlett* **1995**, 13. (d) Smith, A. L.; Nicolaou, K. C. *J. Med. Chem.* **1996**, *39*, 2103. (e) Suffert, J.; Abraham, E.; Raeppel, S.; Brückner, R. *Liebigs Ann.* **1996**, 447. (f) Sander, W. *Acc. Chem. Res.* **1999**, *32*, 669. (g) Nicolaou, K. C.; Dai, W.-M. *Angew. Chem., Int Ed. Engl.* **1991**, *30*, 1387.

(35) (a) Nicolaou, K. C. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 1377. (b) Brandstetter, T.; Maier, M. E. *Tetrahedron* **1994**, *50*, 1435. (c) Iida, K.-I.; Hirama, M. *J. Am. Chem. Soc.* **1994**, *116*, 10310. (d) Wender, P. A.; Beckham, S.; Mohler, D. L. *Tetrahedron Lett.* **1995**, *36*, 209. (e) Magnus, P.; Fortt, S. M. *J. Chem. Soc., Chem. Commun.* **1991**, 544. (f) Nicolaou, K. C.; Zuccarello, G.; Ogawa, Y.; Schweiger, E. J.; Kumazawa, T. *J. Am. Chem. Soc.* **1988**, *110*, 4866. (g) Wender, P. A.; McKinney, J. A.; Mukai, C. *J. Am. Chem. Soc.* **1990**, *112*, 5369. (h) Shair, M. D.; Yoon, T. Y.; Mosny, K. K.; Chou, T. C.; Danishefsky, S. J. *J. Am. Chem. Soc.* **1996**, *118*, 9509. (i) Funk, R. L.; Young, E. R. R.; Williams, R. M.; Flanagan, M. F.; Cecil, T. L. *J. Am. Chem. Soc.* **1996**, *118*, 3291. (j) Jones, G. B.; Huber, R. S.; Mathews, J. E.; Li, A. *Tetrahedron Lett.* **1996**, *37*, 3643. (k) Wright, J. M.; Jones, G. B. *Tetrahedron Lett.* **1999**, *40*, 7605. (l) Jones, G. B.; Mathews, J. E. *Tetrahedron* **1997**, *53*, 14599.

by tethering two alkynylcarbene units. The successful conversion of **13** → **14** illustrates the viability of this concept.

The transformation of our initial observation of the synthesis of cyclic *cis*-enediyne rhenium complexes into a viable synthetic procedure faces many challenges. Rhenium is too expensive for a stoichiometric reaction, and the high kinetic stability of rhenium alkyne complexes poses a problem for metal release. The synthesis of alkynylcarbene complexes is limited by the functional group compatibility of the precursor metal acetylides and metal carbyne complexes. Extension to carbyne precursors other than aryl carbyne complexes, extensions to allow use of two different alkyne precursors, and extensions to unsymmetric diyne precursors are all needed. Our initial efforts to improve this new route to cyclic *cis*-enediynes will center on analogous manganese compounds[36] since their use would be more economical and metal decomplexation from π-complexes is expected to be facile.

Experimental Section

$Cp(CO)_2Re{=}C(Tol)C{\equiv}CCH_3$ (8). Addition of $BrZnC{\equiv}CCH_3$ [prepared from $LiC{\equiv}CCH_3$ (14 mg, 0.30 mmol) and $ZnBr_2$ (66 mg, 0.29 mmol) in 1 mL of THF] to an orange solution of $[Cp(CO)_2Re{\equiv}CTol]BCl_4$ (151 mg, 0.287 mmol) in 5 mL of THF at −35 °C produced a black color immediately. After 10 min, the cold reaction mixture was poured onto a silica gel column (30 × 2 cm), and a black fraction was eluted with 4:1 hexane:diethyl ether. Evaporation of solvent under reduced pressure produced a solid material which was redissolved in 2 mL of 3:1 hexane:CH_2Cl_2. Slow evaporation gave black needles of **8** (28 mg, 0.0623 mmol, 22%). ^{1}H NMR (CD_2Cl_2, 500 MHz): δ 1.90 (s, $C{\equiv}CH_3$), 2.14 (s, $ArCH_3$), 5.73 (s, C_5H_5), 7.11 (d, ^3J = 8.4 Hz, aromatic CH), 7.97 (d, ^3J = 8.4 Hz, aromatic CH). ^{13}C{^{1}H} NMR (CD_2Cl_2, 125 MHz): δ 7.3 ($C{\equiv}CCH_3$); 21.9 ($ArCH_3$); 94.9 (C_5H_5); 103.1 ($C{\equiv}CCH_3$); 120.5 ($C{\equiv}CCH_3$); 127.6, 129.6, 140.7, 157.2 (aromatic); 205.4 (CO); 258.1 (Re=C). IR (CH_2Cl_2): 1961, 1885 cm^1. HRMS(El) *m*/*z*: calcd for $C_{18}H_{15}O_2Re$ (M^+), 456.0630; found, 456.0628.

$[Cp(CO)_2Re]_2[\eta^2,\eta^2$-(*E*)-TolC≡C($CH_3$)C=C($CH_3$)C≡CTol] (10-*E*). Thermolysis of $Cp(CO)_2Re{=}C(Tol)C{\equiv}CCH_3$ (**8**) (80.8 mg, 0.180 mmol) in 0.75 mL of toluene-d_8 at 100 °C for 55 min and subsequent preparative thin-layer chromatography (silica, 9:1 hexane:diethyl ether, R_f = 0.3, yellow band) gave a yellow powder consisting of a 1.2:1 mixture of **10-*E***:**10-*Z***. The mixture was dissolved in CH_2Cl_2:hexane; slow evaporation of solvent under air exposure gave yellow needles of **10-*E*** (40.1 mg, 0.0446 mmol, 50%). For **10-*E***, ^{1}H NMR (CD_2Cl_2, 500 MHz): δ 1.95 (s, $C{=}CCH_3$), 2.40 (s, $ArCH_3$), 5.49 (s, C_5H_5), 7.24 (d, ^3J = 8.1 Hz, aromatic CH), 7.54 (d, ^3J = 8.1 Hz, aromatic CH). ^{13}C NMR ($CDCl_3$, 125 MHz): δ 21.40 (qt, $^1J_{CH}$ = 125.6 Hz, $^3J_{CH}$ = 4.6 Hz, $ArCH_3$), 21.73 (q, $^1J_{CH}$ = 127.7 Hz, $C{=}CCH_3$), 79.59 (s, $C{\equiv}CAr$), 80.50 (s, $C{\equiv}CAr$), 88.76 (dp, $^1J_{CH}$ = 179.0 Hz, $^2J_{CH}$ = $^3J_{CH}$ = 6.7 Hz, C_5H_5), 128.14 (t, $^3J_{CH}$ = 6.7 Hz, aromatic), 129.16 (q, $^3J_{CH}$ = 7.1 Hz, C=C), 129.44 (d, $^1J_{CH}$ = 157.8 Hz, aromatic), 132.46 (dd, $^1J_{CH}$ = 159.1 Hz, J_{CH} = 4.7 Hz, aromatic), 138.06 (sext, $^2J_{CH}$ = $^3J_{CH}$ = 6.2 Hz, aromatic), 205.38 (s, CO). IR (CH_2Cl_2): 1966, 1885 cm^{-1}. MS(FAB) *m*/*z*: calcd for $C_{36}H_{30}O_4Re_2$ (M^+), 898.1; found, 898.1.

For **10-Z**, ^{1}H NMR (CD_2Cl_2, 500 MHz): δ 2.19 (s, $C{=}CCH_3$), 2.28 (s, $ArCH_3$), 5.28 (s, C_5H_5), 6.92 (d, ^3J = 7.8 Hz, aromatic), 7.18 (d, ^3J = 8.0 Hz, aromatic). ^{13}C NMR ($CDCl_3$, 125 MHz): δ 21.36 (qt, $^1J_{CH}$ = 125.6 Hz, $^3J_{CH}$ = 4.6 Hz, $ArCH_3$), 21.73 (q, $^1J_{CH}$ = 127.6 Hz, $C{=}CCH_3$), 79.87 (s, $C{\equiv}CAr$), 82.29 (s, $C{\equiv}CAr$), 88.35 (dp, $^1J_{CH}$ = 179.0 Hz, $^2J_{CH}$ = $^3J_{CH}$ = 6.3 Hz, C_5H_5), 128.92 (broad s, C=C), 128.99 (dt, $^1J_{CH}$ = 158.5 Hz, $^3J_{CH}$ = 6.3 Hz, aromatic), 129.38 (t, $^3J_{CH}$ = 7.5 Hz, aromatic), 132.74 (dd, $^1J_{CH}$ = 160.2 Hz, $^3J_{CH}$ = 4.7 Hz, aromatic), 137.46 (sextet, $^2J_{CH}$ = $^3J_{CH}$ = 6.2 Hz, aromatic), 204.81 (broad s, CO), 205.93 (broad s, CO).

$Cp(CO)_2Re{=}C(Tol)C{\equiv}CC_3H_5$ (11). Addition of $BrZnC{\equiv}CC_3H_5$ [from $LiC{\equiv}CC_3H_5$) (22 mg, 0.31 mmol) and $ZnBr_2$ (70 mg, 0.31 mmol) in 1 mL of THF] to an orange solution of $[Cp(CO)_2Re{\equiv}CTol]BCl_4$ (162 mg, 0.307 mmol) in 5 mL of THF at −35 °C produced a black color immediately. After 10 min, the cold reaction mixture was poured onto a silica gel column (30 × 2 cm), and a black fraction was eluted with 4:1 hexane:diethyl ether. Evaporation of solvent under reduced pressure produced a solid material which was redissolved in 2 mL of 3:1 hexane:CH_2Cl_2. Slow evaporation gave black needles of **11** (93 mg, 0.20 mmol, 64%) suitable for X-ray crystal structure analysis. ^{1}H NMR (CD_2Cl_2, 500 MHz): δ 0.98 (AA′ part of AA′BB′X pattern, CH*H*CH*H*), 1.10 (BB′ part of AA′BB′X pattern, C*H*HC*H*H), 1.70 (tt, $^3J_{cis}$ = 8.3 Hz, $^3J_{trans}$ = 4.9 Hz, $C{\equiv}CCH$), 2.15 (s, $ArCH_3$), 5.67 (s, C_5H_5), 7.11 (d, ^3J = 8.3 Hz, aromatic CH), 7.91 (d, ^3J = 8.3 Hz, aromatic CH). ^{13}C NMR (CD_2Cl_2, 125 MHz): δ 3.65 (dpent, $^1J_{CH}$ = 170.5 Hz, $^2J_{CH}$ = $^{2'}J_{CH}$ = 2.8 Hz, $C{\equiv}CCH$), 10.51 (dm, $^1J_{CH}$ = 164.9 Hz, CH_2), 21.84 (qt, $^1J_{CH}$ = 126.5 Hz, $^3J_{CH}$ = 4.5 Hz, $ArCH_3$), 94.72 (dpent, $^1J_{CH}$ = 179.6 Hz, $^2J_{CH}$ = $^3J_{CH}$ = 6.7 Hz, C_5H_5), 99.73 (d, $^3J_{CH}$ = 3.5 Hz, $C{\equiv}CCH$), 127.45 (dd, $^1J_{CH}$ = 159.2 Hz, $^3J_{CH}$ = 5.7 Hz, aromatic), 129.59 (dpent, $^1J_{CH}$ = 159.1 Hz, $^2J_{CH}$ = $^3J_{CH}$ = 5.6 Hz, aromatic), 131.17 (m, $C{\equiv}CCH$), 140.69 (q, $^2J_{CH}$ = 6.8 Hz, aromatic), 156.81 (t, $^3J_{CH}$ = 7.9 Hz, aromatic), 205.40 (s, CO), 256.67 (s, Re=C). IR (CH_2Cl_2): 1959, 1884 cm^{-1}. HRMS(EI) *m*/*z*: calcd for $C_{20}H_{17}O_2{}^{185}Re$ (M+), 474.0758; found, 474.0745.

$[Cp(CO)_2Re]_2[\eta^2,\eta^2$-(E)-TolC≡C($C_3H_5$)C=C($C_3H_5$)C≡CTol] (12-*E*). Thermolysis of $Cp(CO)_2Re{=}C(Tol)C{\equiv}C(C_3H_5)$ (**11**) (19.8 mg, 0.0416 mmol) and 1,4-bis-trimethylsilylbenzene (2 mg, internal NMR standard) in 0.58 mL of toluene-d_8 at 120 °C for 281 min produced a yellow precipitate. The conversion of starting material as determined by ^{1}H NMR integration was 82% (with 95% mass balance). A ^{1}H NMR spectrum taken after 91 min (with no precipitate formed at this point) indicated a mixture of 45% starting material and 55% of a 5:1 ratio of **12-*E***:**12-*Z***. [^{1}H NMR (toluene-d_8, 500 MHz) **12-*E***: δ 0.49 (d, $^3J_{cis}$ = $^3J_{trans}$ = 6.0 Hz, CH_2), 1.74 (pent, $^3J_{cis}$ = $^3J_{trans}$ = 6.0 Hz, $C{\equiv}CCH$), 2.15 (s, $ArCH_3$), 4.93 (s, C_5H_5), 7.07 (d, ^3J = 8.0 Hz, aromatic CH), 7.77 (d, ^3J = 8.0 Hz, aromatic CH). **12-*Z***: δ 4.78 (s, C_5H_5), 6.95 (d, ^3J = 8.0 Hz, aromatic CH), all other peaks overlap with peaks from **12-*E*** and solvent.] Preparative thin-layer chromatography (silica, 3:1 hexane: diethyl ether, R_f = 0.3, yellow band) gave a yellow powder. Recrystallization from $CHCl_3$ afforded yellow crystals of **(12-*E*)$_2$•$CHCl_3$** (10.1 mg, 0.00499 mmol, 48%) suitable for X-ray crystal structure analysis. ^{1}H NMR ($CDCl_3$, 500 MHz, 60 °C): δ 0.31 (AA′ part of AA′BB′X pattern, CH*H*CH*H*), 0.47 (BB′ part of AA′BB′X pattern, CH*H*CH*H*), 1.51 (tt, $^3J_{cis}$ = 7.6 Hz, $^3J_{trans}$ = 5.2 Hz, $C{\equiv}CCH$), 2.38 (s, $ArCH_3$), 5.45 (s, C_5H_5), 7.18 (d, ^3J = 8.0 Hz, aromatic CH), 7.50 (d, ^3J = 8.0 Hz, aromatic CH). ^{13}C NMR ($CDCl_3$, 125 MHz, 60 °C): δ 7.25 (t, $^1J_{CH}$ = 162.6 Hz, CH_2), 15.84 (d, $^1J_{CH}$ = 162.6 Hz, $C{=}CCH$), 21.41 (qt, $^1J_{CH}$ = 126.5 Hz, $^3J_{CH}$ = 4.6 Hz, $ArCH_3$), 77.50 (d, $^3J_{CH}$ = 5.6 Hz, $C{\equiv}CAr$), 85.06 (s, $C{\equiv}CAr$), 86.68 (d, $^1J_{CH}$ = 179.5 Hz, C_5H_5), 129.38 (t, $^3J_{CH}$ = 3.1 Hz, aromatic), 129.49 (dt, $^1J_{CH}$ = 157.5 Hz, $^3J_{CH}$ = 5.6 Hz, aromatic), 131.75 (dd, $^1J_{CH}$ = 159.3 Hz, $^3J_{CH}$ = 6.6 Hz, aromatic), 133.73 (m, C=C), 138.03 (q, $^2J_{CH}$ = 5.5 Hz, aromatic), 206.28 (s, CO). IR (CH_2Cl_2): 1966, 1878 cm^{-1}. MS(EI) *m*/*z*: calcd for $C_{40}H_{34}O_4Re_2$ (M^+ + 1), 951.2; found, 951.2.

$Cp(CO)_2Re{=}C(Tol)C{\equiv}CCH_2CH_2CH_2C{\equiv}CC(Tol){=}Re(CO)_2Cp$ (13). Addition of $BrZnC{\equiv}CCH_2CH_2CH_2C{\equiv}CZnBr$ [from $LiC{\equiv}CCH_2CH_2CH_2C{\equiv}CLi$ (5 mg, 0.05 mmol) and $ZnBr_2$ (22 mg, 0.098 mmol, sublimed) in 0.2 mL of THF] to $[Cp(CO)_2Re{\equiv}CTol]BCl_4$ (78 mg, 0.15 mmol) in 0.2 mL of THF at −35 °C produced a black solution. The cold reaction mixture was poured onto a silica thin-layer chromatography plate which was precooled to −40 °C. While maintaining this temperature with solid dry ice underneath the plate, the solvent was evaporated under a gentle stream of cold N_2. The plate was placed

(36) The synthesis of an analogous Mn alkynylcarbene complex $Cp(CO)_2Mn{=}CPhC{\equiv}CTol$ has recently been reported. The interconversion of dimanganese compounds $Cp(CO)_2Mn{=}CPh\{\eta^2$-$C{\equiv}CTol[Mn(CO)_2Cp]\}$ by two [1, 1.5] shifts was also observed. Ortin, Y.; Coppel, Y.; Lugan, N.; Mathieu, R.; McGlinchey, M. J. *Chem. Commun.* **2001**, 1690.

into a precooled chamber, and a black band was eluted (4:1 pentane: diethyl ether, $R_f = 0.3$). After extraction with CH_2Cl_2 and evaporation of the solvent under reduced pressure at 0 °C, **13** (4 mg, 8%) was obtained as a black solid. A faster moving band containing $Cp(CO)_2Re{=}C(Tol)C{\equiv}CCH_2CH_2CH_2C{\equiv}CH$ (**14**) was also observed. For **13**, ^{1}H NMR (CD_2Cl_2, 500 MHz, −80 °C): δ 2.05 (s, CH_3), 2.42 (m, $CH_2CH_2CH_2$), 5.70 (s, C_5H_5), 7.08 (d, $^3J = 8.2$ Hz, aromatic CH), 8.03 (d, $^3J = 8.3$ Hz, aromatic CH). ^{13}C NMR (CD_2Cl_2, 125 MHz): δ 21.3 (t, $^1J_{CH} = 131.1$ Hz, $CH_2CH_2CH_2$), 21.45 (q, $^1J_{CH} = 126.7$ Hz, $ArCH_3$), 26.6 (t, $^1J_{CH} = 129.1$ Hz, $CH_2CH_2CH_2$), 94.9 (d, $^1J_{CH} = 179.5$ Hz, C_5H_5), 101.9 (s, C≡CAr), 122.2 (s, C≡CAr), 127.8 (d, $^1J_{CH} = 159.9$ Hz, aromatic), 129.2 (d, $^1J_{CH} = 159.1$ Hz, aromatic), 140.8 (s, aromatic), 154.1 (s, aromatic), 205.6 (s, CO), 254.5 (s, Re=C).

$[Cp(CO)_2Re]_2[\eta^2,\eta^2$-TolC≡CC($CH_2CH_2CH_2$)=CC≡CTol] (15). The bis-zincacetylide $BrZnC{\equiv}CCH_2CH_2CH_2C{\equiv}CZnBr$ [from $LiC{\equiv}CCH_2CH_2CH_2C{\equiv}CLi$ (12 mg, 0.12 mmol) and $ZnBr_2$ (52 mg, 0.23 mmol, sublimed) in 1 mL of THF] was added to $[Cp(CO)_2Re{\equiv}CTol]BCl_4$ (125 mg, 0.237 mmol) in 2 mL of THF at −35 °C. The cold black reaction mixture was poured onto a silica gel column (30 × 2 cm), and a black band was eluted with 4:1 hexane:diethyl ether. Evaporation of solvent under reduced pressure gave a dark solid which was redissolved in 1 mL of CH_2Cl_2 and stirred for 2 h. Preparative thin-layer chromatography (silica, 4:1 hexane:diethyl ether) gave **15** (36 mg, 35%) as an orange band ($R_f = 0.4$) and **14** (17 mg, 0.034 mmol, 29%) as a black band ($R_f = 0.5$).

For **15**, ^{1}H NMR (CD_2Cl_2, 500 MHz): δ 2.08 (pent, $^3J = 7.5$ Hz, $CH_2CH_2CH_2$), 2.23 (s, CH_3), 2.83 [broad, $\omega_{1/2} = 35$ Hz, $CHHCH_2$-CHH], 3.11 (broad, $\omega_{1/2} = 35$ Hz, $CHHCH_2CHH$), 5.44 (s, C_5H_5), 6.89 (d, $^3J = 7.9$ Hz, aromatic), 7.00 (d, $^3J = 7.9$ Hz, aromatic). ^{13}C NMR (CD_2Cl_2, 125 MHz): δ 21.29 (q, $^1J_{CH} = 125.3$ Hz, $ArCH_3$), 23.24 (t, $^1J_{CH} = 132.2$ Hz, $CH_2CH_2CH_2$), 40.06 (t, $^1J_{CH} = 133.8$ Hz, CH_2-CH_2CH_2), 72.21 (br s, C≡CAr), 85.24 (s, C≡CAr), 88.56 (dpent, $^1J_{CH} = 179.5$ Hz, $^2J_{CH} = {}^3J_{CH} = 6.5$ Hz, C_5H_5), 128.83 (d, $^1J_{CH} = 159.2$ Hz, aromatic), 128.87 (s, aromatic), 136.15 (s, C=C), 137.34 (q, $^2J_{CH} = 6.8$ Hz, aromatic), 205.15 (s, CO), 205.44 (s, CO). IR (CH_2Cl_2): 1964, 1881 cm^{-1}. MS(FAB) *m*/*z*: calcd for $C_{37}H_{30}O_4Re_2$ (M^+), 910.1; found, 910.1.

$[Cp(CO)_2Re]_2[\eta^2,\eta^2$-1,2-$(TolC{\equiv}C)_2C_{12}H_6$] (17). Sequential addition of *n*-butyllithium (0.48 mL, 1.6 M, 0.30 mmol) and $ZnBr_2$ (68 mg, 0.30 mmol) to 1,8-$(HC{\equiv}C)_2C_{10}H_6$ (25 mg, 0.14 mmol) in 3 mL of THF at −78 °C produced a solution of 1,8-$(BrZnC{\equiv}C)_2C_{10}H_6$. Upon addition of a solution of $[Cp(CO)_2Re{\equiv}CTol]BCl_4$ (147 mg, 0.280 mmol) in 1 mL of THF, the solution turned black immediately. After warming to 24 °C, the reaction mixture was poured onto a silica gel column (30 × 2 cm), and a purple black fraction was eluted with 2:1 hexane:diethyl ether. Evaporation of solvent under reduced pressure produced a solid material which was redissolved in 2 mL of 2:1 CH_2Cl_2:hexane. Slow evaporation gave fine black crystals of **17** (45 mg, 32%) suitable for X-ray crystallography. ^{1}H NMR (CD_2Cl_2, 300 MHz): δ 2.29 (s, $ArCH_3$), 5.44 (s, C_5H_5), 6.93 (d, $^3J = 8.0$ Hz, aromatic CH), 7.22 (d, $^3J = 7.8$ Hz, aromatic CH), 7.64 (dd, $^3J = 8.2$ Hz, $^3J = 7.0$ Hz, aromatic CH), 7.85 (d, $^3J = 7.0$ Hz, aromatic CH), 7.90 (d, $^3J = 8.2$ Hz, aromatic CH). ^{13}C{^{1}H} NMR (THF-d_8, 125 MHz, 60 °C): δ 21.30 ($ArCH_3$); 72.52 ($C{\equiv}CTol$); 89.65 (C_5H_5); 93.45 ($C{\equiv}CTol$); 123.33, 127.78, 128.66, 129.29, 129.85, 130.36, 131.15, 132.97, 135.19, 137.82, 141.36 (aromatic); 205.06 (broad, $\omega_{1/2} = 48$ Hz, CO). IR (CH_2Cl_2): 1970, 1885 cm^{-1}. MS(FAB) *m*/*z*: calcd for $C_{44}H_{30}O_4Re_2$ (M^+), 994.1; found, 994.1.

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Supporting Information Available: General experimental procedures, description of kinetics of the conversion of **8** to **10-*E*/10-Z** and of **13** to **15**, spectra of **14**, and X-ray crystal structures of **11**, **(12-*E*)$_2$•CHCl$_3$**, **15**, and **17** (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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