Communications to the Editor

Dimerization of Rhenium Alkynyl Carbene Complexes by a Process Involving Two [1,1.5] Rhenium Shifts and Coupling of the Remote Alkynyl Carbons

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Alkynyl carbene metal complexes offer the possibility of observing unprecedented [1,3] metal shifts along the π-system to form an isomeric alkynyl carbene complex.[1,2] By using a nearly symmetrical alkynyl carbene complex **1**, the [1,3]-shifted compound **2** should have comparable stability making the [1,3] shift thermodynamically feasible (Scheme 1).[3] Here we report that in addition to a small amount of [1,3] shift, **1** undergoes an unusual dimerization that involves a [1,1.5] rhenium shift[4] and carbene-like coupling at the remote alkynyl carbon.

Rhenium alkynyl carbene complexes were prepared in good yield by addition of alkynylmetal reagents to metal carbyne complexes.[5] Addition of $C_6H_5C{\equiv}CZnBr$ to $[Cp(CO)_2Re{\equiv}C(C_6H_4\text{-}p\text{-}CH_3)]BCl_4$ gave $Cp(CO)_2Re{=}C(C_6H_4\text{-}p\text{-}CH_3)(C{\equiv}CC_6H_5)$ (**1**) as black crystals in 65% yield. A significantly higher yield was obtained from the zinc acetylide than from the corresponding lithium acetylide (<4%). The isomeric alkynyl carbene complex $Cp(CO)_2Re{=}C(C_6H_5)(C{\equiv}CC_6H_4\text{-}p\text{-}CH_3)$ (**2**) was prepared in 60% yield by a similar route. **1** and **2** were readily distinguishable by ^1H NMR spectroscopy; the tolyl methyl group of **1** appears at δ 1.78, while that of **2** appears at δ 2.11. The symmetric compound $Cp(CO)_2Re{=}C(C_6H_4\text{-}p\text{-}CH_3)(C{\equiv}CC_6H_4\text{-}p\text{-}CH_3)$ (**3**) was also synthesized and its structure confirmed by X-ray crystallography.[6]

When a 0.765 M solution of **1** in toluene-d_8 was heated at 120 °C for 4 h, little isomerization to **2** via a [1,3] rhenium shift was observed by ^1H NMR spectroscopy.[7] Instead, clean formation of a single new product **4** was seen (Scheme 1).[8] **4** was isolated in 77% yield by preparative thin-layer chromatography. MS established that **4** was a dimer ($m/e = 1024.1$). The observation of only one Cp and one methyl resonance in both the ^1H and ^{13}C NMR spectra indicated that compound **1** had dimerized symmetrically.[9]

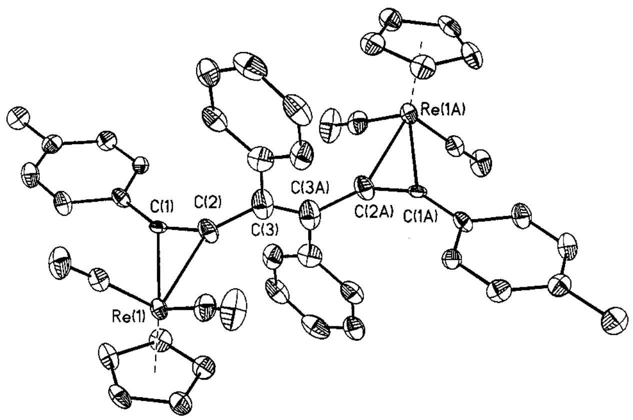
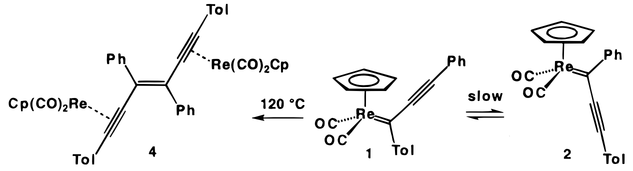


Figure 1. X-ray crystal structure of **4**.

Scheme 1



Single-crystal X-ray diffraction established the *trans*-enediyne structure of **4** (Figure 1). In the solid state, the two $Cp(CO)_2Re$ units are positioned above and below the plane of the ligand π-system. Interestingly, the X-ray structure revealed that **4** is formed by coupling of the remote alkynyl carbons.[10] Since formation of symmetric alkenes by coupling of the carbene carbons of two metal carbene complexes is well known,[11] it was surprising to find that dimerization of **1** occurred by coupling at the remote carbon atoms rather than the carbene carbons.

When the dimerization of **1** was carried out at 120 °C in an NMR probe, no intermediates were detected by ^1H NMR spectroscopy. The conversion of **1** to **4** in toluene-d_8 followed clean second-order kinetics over the concentration range from 0.171 to 0.00124 M. The second-order rate constant for dimerization was $1.45 \pm 0.2 \times 10^{-3}\ M^{-1}\ s^{-1}$ at 120 °C, which corresponds to $\Delta G^{\ddagger} = 28.3 \pm 0.1$ kcal mol^{-1}. The rate constants for dimerization showed little solvent dependence: $3.9 \times 10^{-3}\ M^{-1}\ s^{-1}$ in methylcyclohexane-d_{14}, $1.5 \times 10^{-3}\ M^{-1}\ s^{-1}$ in bromobenzene-d_5, $1.1 \times 10^{-3}\ M^{-1}\ s^{-1}$ in *o*-dichlorobenzene-d_4. This indicates that there is little polarity difference between the moderately polar carbene complexes and the transition state for dimerization.

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[1] For heteroatom-substituted alkynyl carbene complexes, see: (a) Aumann, R.; Nienaber, H. *Adv. Organomet. Chem.* **1997**, *41*, 161. (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.

[2] A [1,3] shift was postulated in a rhodium alkynyl carbene presumably formed in a catalytic cycle: Padwa, A.; Austin, D. J.; Gareau, Y.; Kassir, J. M.; Xu, S. L. *J. Am. Chem. Soc.* **1993**, *115*, 2637.

[3] Non-donor 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.

[4] We introduce the term "[1,1.5] shift" to describe the migration of rhenium from carbon 1 of carbene complex **1** to the midpoint between carbons 1 and 2 of the resulting alkyne complex **4**.

[5] For the first synthesis of a $CpRe(CO)_2$ carbyne complex, see: Fischer, E. O.; Clough, R. L.; Stückler, P. *J. Organomet. Chem.* **1976**, *120*, C6.

[6] **3** adopts a nearly C_s-symmetric geometry in which the plane of the carbene ligand is nearly perpendicular to the plane of the Cp ring. The alkynyl unit is syn to the Cp ligand. See Supporting Information.

[7] Too little isomerization of **1** to **2** occurred to be observable by ^1H NMR spectroscopy. However, compelling evidence for a [1,3] shift was found when $Cp(CO)_2Re{=}C(Tol)(^{13}C{\equiv}^{13}CPh)$ was thermolyzed at 120 °C to give small amounts of $Cp(CO)_2Re{=}^{13}C(Ph)(^{13}C{\equiv}CTol)$. See Supporting Information.

[8] The use of high concentrations of **1** produced higher yields of dimer **4** since the rate of formation of **4** depends on $[\mathbf{1}]^2$ and thermal decomposition of **4** is a first-order process.

[9] Addition of lithium or zinc reagents to alkynyl carbene 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] Prior to the X-ray structure determination, ^{13}C NMR evidence for the site of carbene ligand coupling and the trans geometry in the enediyne complex **4** was obtained from studies of the thermolysis of $Cp(CO)_2Re{=}C(Tol)(C{\equiv}^{13}CPh)$ and $Cp(CO)_2Re{=}C(Tol)(^{13}C{\equiv}^{13}CPh)$. See Supporting Information.

[11] (a) Casey, C. P.; Anderson, R. L. *J. Chem. Soc., Chem. Commun.* **1975**, 895. (b) Fischer, H.; Schmid, J. *J. Mol. Catal.* **1988**, *46*, 277. (c) Hohmann, F.; Siemoneit, S.; Nieger, M.; Kotila, S.; Dötz, K. H.; *Chem. Eur. J.* **1997**, *3*, 853.

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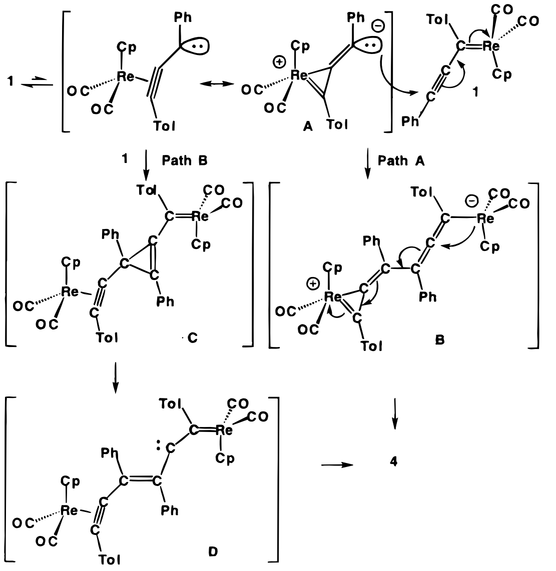
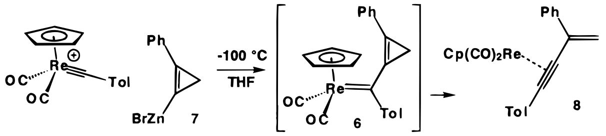
Scheme 2



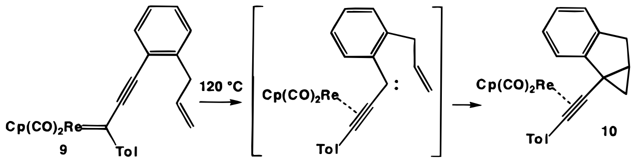
Two plausible mechanisms for dimerization are shown in Scheme 2. Both involve a rapid and reversible “[1,1.5] shift” of $CpRe(CO)_2$ along the π-system of the alkynyl carbene ligand to form **A**,[12] which has a zwitterionic and a carbenoid resonance structure. Pathway A uses the carbanionic character of C_3 in **A** to nucleophilically add to the remote alkynyl carbon of **1** to produce the zwitterionic intermediate **B**. The negatively charged rhenium center in the σ-allenyl moiety of **B** can then undergo a “[1,1.5] shift” of Re with the formation of the neutral product **4**. Pathway B uses the carbenoid character of **A** in reaction with **1** to produce cyclopropene **C**. Ring opening of the cyclopropene would produce vinyl carbene **D**,[13] which rearranges by a "[1,1.5] shift" of Re to produce the enediyne complex **4**. The observed second-order kinetics are also consistent with a concerted dimerization not involving any intermediate.

The electrophilic character of remote alkynyl carbon C_3 in **1** required in pathway A was demonstrated by the rapid conjugate addition of $PMePh_2$ to **1** to give the σ-allenyl complex $[Cp(CO)_2Re^-](C_6H_4\text{-}p\text{-}CH_3)C{=}C{=}C(PCH_3Ph_2^+)Ph$ (**5**).[14] Cationic rhenium metallacyclopropenes and anionic rhenium σ-vinyl complexes similar to the part structures in **B** are known.[3b,15] Nevertheless, the C−C bond formation between the two electrophilic atoms as the key step in this mechanism is unprecedented. The insensitivity of dimerization to solvent polarity would have to be attributed to little difference in polarity between the moderately polar rhenium carbene complex **1** and the transition state involving addition of zwitterion **A** to **1.**

Scheme 3



Scheme 4



Pathway B involves generation and ring opening of neutral cyclopropene intermediate **C** and is consistent with the small solvent effects observed. To test for the rapid cyclopropene ring opening required in pathway B, the synthesis of cyclopropene-substituted carbene complex **6** was attempted. Addition of the cyclopropenyl zinc reagent **7** to $[Cp(CO)_2Re{\equiv}C(C_6H_5\text{-}p\text{-}CH_3)]BCl_4$ at −78 °C in THF-d_8 was monitored by ^1H NMR spectroscopy at low temperature within 10 min of mixing (Scheme 3). None of the expected cyclopropenyl carbene complex **6** was observed; instead, the cyclopropene ring-opening product **8** was cleanly formed.[16] The smooth transformation **6** to **8** at low temperature supports the plausibility of a cyclopropene to vinyl carbene rearrangement in pathway B.[17]

Evidence suggesting that the remote alkynyl carbon of an alkynyl carbene can have carbenoid properties was obtained from studies of alkynyl carbene complex **9** which has a pendant allyl unit (Scheme 4). When **9** was heated at 120 °C for 30 min, intramolecular cyclopropanation occurred by addition of C_3 to the allyl double bond to form **10** in 95% yield.[18] Padwa has shown that related free alkynyl carbenes undergo similar intramolecular cyclopropanations.[2]

In conclusion, we have observed a fascinating dimerization of alkynyl carbene complexes that produces enediyne complexes. Further studies will be required to sort out the detailed mechanism of this transformation.

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Supporting Information Available: Preparation of compounds, spectral data, description of kinetics, and X-ray crystallographic data for **3** and **4** (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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[12] A similar [1,1.5] shift has been postulated in the rearrangement of chromium alkynylcarbene complexes $[(CO)_5Cr{=}C(O)(C{\equiv}C{-}OEt)]^-$ to a cyclopropenylidene complex. Juneau, K. N.; Hegedus, L. S.; Roepke, F. W. *J. Am. Chem. Soc.* **1989**, *111*, 4762.

[13] Note that **D** is a resonance structure of **B**.

[14] Compound **1** (4.38×10^{-4} M^{-1} s^{-1} at −36.0 °C) is only 115 times less reactive than methyl triflate (second-order rate constant: 5.93×10^{-2} M^{-1} s^{-1} at −36.0 °C) toward $PMePh_2$. Since alkyl triflates are approximately 10^4−10^5 times more reactive toward nucleophiles than alkyl tosylates, the electrophilicity of **1** lies between methyl triflate and methyl tosylate. (a) Stang, P. J.; Hanack, M.; Subramanian, L. R. *Synthesis* **1982**, 85. (b) Su, T. M.; Sliwinski, W. F.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1969**, *91*, 5386.

[15] Casey, C. P.; Brady, J. T.; Boller, T. M.; Weinhold, F.; Hayashi, R. K. *J. Am. Chem. Soc.* **1998**, *120*, 12500.

[16] The in situ formation of **7** was independently confirmed in a separate experiment by trapping it with trimethylsilyl chloride to form 1-(trimethylsilyl)-2-phenyl-cyclopropene. See Supporting Information.

[17] Similar rearrangements are normally observed at elevated temperatures, although sulfonyl-substituted cyclopropenes undergo ring opening at −25 °C. Franck-Neumann, M.; Lohmann, J.-J. *Angew. Chem., Int. Ed. Engl.* **1977**, *16*, 323.

[18] For a related metal-induced intramolecular cyclization via carbenoid intermediates, see: Shiu, Y.-T.; Madhushaw, R. J.; Li, W.-T.; Lin, Y.-C.; Lee, G.-H.; Peng; S.-M.; Liao, F.-L.; Wang, S.-L.; Liu, R.-S. *J. Am. Chem. Soc.* **1999**, *121*, 4066.