Intramolecular CH Insertion Reactions of (Pentamethylcyclopentadienyl)Rhenium Alkynylcarbene Complexes

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Thermolysis of the alkynylcarbene complex Cp*(CO)$_2$Re=C(Ph)^{13}C≡^{13}CTol (**5**) at 120 °C resulted in rapid equilibration ($t_{1/2}$ = 33 min) to a 1:1 mixture of **5** and Cp*(CO)$_2$Re=^{13}C-(Tol)^{13}C≡CPh (**7**) via a [1,3]-rhenium shift. Extended thermolysis of this mixture provided the CH insertion products {η^5:η^2-[C$_5$(CH$_3$)$_4$CH$_2$^{13}CH(Tol)^{13}C≡CPh]}Re(CO)$_2$ (**8**) and {η^5:η^2-[C$_5$(CH$_3$)$_4$CH$_2$CH(Ph)^{13}C≡^{13}CTol]}Re(CO)$_2$ (**9**). Thermolysis of the symmetrically substituted alkynylcarbene complex Cp*(CO)$_2$Re=C(Ph)C≡CPh (**6**) produced the CH insertion product {η^5:η^2-[C$_5$(CH$_3$)$_4$CH$_2$CH(Ph)C≡CPh]}Re(CO)$_2$ (**10**). The CH insertion of Cp*(CO)$_2$Re=C(Ph)-C≡CC$_6$D$_5$ (**6-HD**) was monitored at low conversion before complete equilibration with Cp*(CO)$_2$Re=C(C$_6$D$_5$)C≡CPh (**6-DH**) occurred. An excess of {η^5:η^2-[C$_5$(CH$_3$)$_4$CH$_2$CH(C$_6$D$_5$)-C≡CPh]}Re(CO)$_2$ (**13-HD**) over {η^5:η^2-[C$_5$(CH$_3$)$_4$CH$_2$CH(Ph)C≡CC$_6$D$_5$]}Re(CO)$_2$ (**13-DH**) provides evidence for site-selective CH insertion of the remote alkyne carbon into the CH bond of a Cp* methyl group.

Heteroatom-substituted alkynylcarbene complexes such as (OC)$_5$M=C(OR)C≡CR′ have become the focus of extensive research in the past 15 years. Their rich chemistry combines easy accessibility, high reactivity, and large variations in the products formed. In particular, nucleophilic additions to either the carbene carbon or the remote alkyne carbon (conjugate addition) and cycloadditions to the triple bond have been exploited synthetically.[1] Despite the large number of donor-substituted alkynylcarbene complexes, [1,3]-metal migrations such as (OC)$_5$M=C(OR)C≡CR′ ↔ (OC)$_5$M=C(R′)C≡COR have never been observed due to either a high kinetic barrier or an unfavorable equilibrium.[2,3] Recently, we began a search for [1,3]-metal shifts in non-donor-substituted rhenium alkynylcarbene complexes such as Cp(CO)$_2$Re=C(Tol)C≡CPh (**1**) and found small amounts of the [1,3]-shifted isomer Cp(CO)$_2$Re=C(Ph)C≡CTol (**2**).[4] Surprisingly, the major product was the dimeric enediyne complex **3** formed by coupling two

molecules of **1** at their remote alkyne carbon.[5,6] Mechanistic studies of the dimerization led to the hypothesis of a carbene intermediate **A** formed by a [1,1.5]-rhenium shift reacting with the triple bond of a second alkynylcarbene complex to give cyclopropene intermediate **B**, which then underwent ring opening to form the enediyne complex **3** (Scheme 1).

In an effort to accelerate the [1,3]-shift relative to dimerization, we studied the effect of para substituents on the rate of [1,3]-shifts in a series of rhenium alkynylcarbene complexes Cp(CO)$_2$Re=C(Tol)C≡CC$_6$H$_4$X (X = N(CH$_3$)$_2$, H, CF$_3$, SO$_2$CF$_3$) and found that the 1,3-shifted isomer Cp(CO)$_2$Re=C(C$_6$H$_4$X)C≡CTol formed 88 times faster with X = SO$_2$CF$_3$ than with X = H. An even more dramatic rate acceleration, 550-fold, was observed for the indenyl complex **4** compared to the cyclopentadienyl complex **1**. We proposed a mechanism for the [1,3]-rhenium shift that involves coordination of the alkyne triple bond to Re concerted with an η^5- to η^3-Cp ring slip to give the 18-electron dehydrometallacyclobutadiene intermediate **C** (Scheme 2). Ring slippage avoids a 20-electron intermediate. The acceleration of [1,3]-rhenium shifts by electron-withdrawing substitu-

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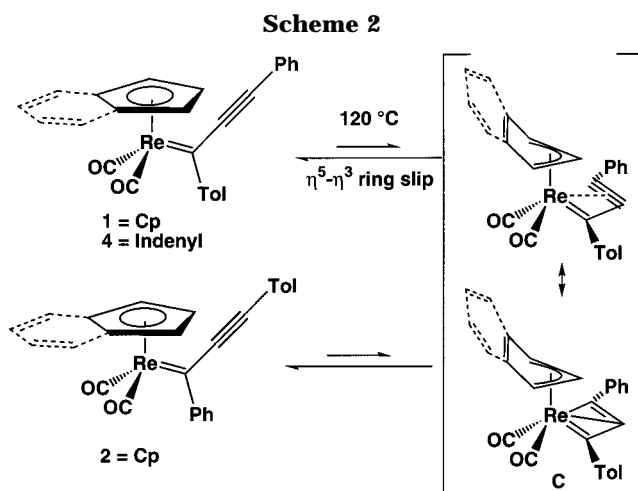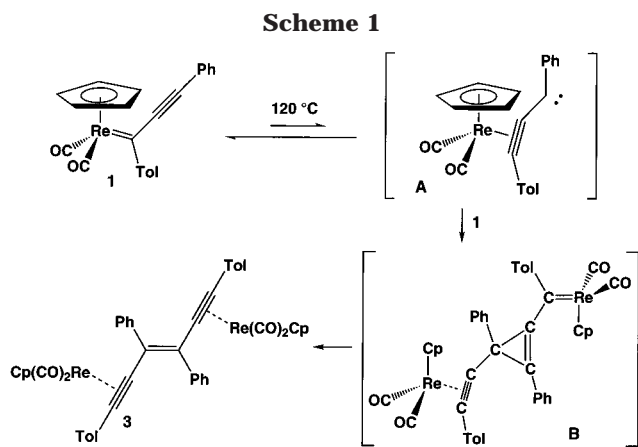
(2) A [1,3]-shift was postulated in a rhodium alkynylcarbene presumably formed in a catalytic cycle: Padwa, A.; Austin, D. J.; Gareau, Y.; Kassir, J. M.; Xu, S. L. *J. Am. Chem. Soc.* **1993**, *115*, 2637.

(3) [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. M.; 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) It was surprising to find that dimerization of **1a** occurred by coupling at the remote carbon atoms rather than the carbene carbons, since formation of symmetric alkenes by coupling of the carbene carbons of two non-heteroatom-substituted metal carbene complexes is well-known: (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.

(6) In contrast, the Pd-catalyzed dimerization of (CO)$_5$Cr=(OEt)C≡CPh gave an *E/Z* mixture of the enediyne PhC≡CC(OEt)=C(OEt)C≡CPh: Sierra, M. A.; del Amo, J. C.; Mancheño, M. J.; Gõmez-Gallego, M. *J. Am. Chem. Soc.* **2001**, *123*, 851.

Scheme 1

Scheme 2

Figure 1. X-ray crystal structure of Cp*(CO)$_2$Re=C(Ph)C≡CAr (**6**).

Scheme 3

ents was explained by invoking enhanced d–π* back-bonding to the alkyne-like dehydrometallacyclobutadiene ligand in the transition state leading to **C**.

Since electron-withdrawing substituents on the alkynylcarbene ligand accelerated the [1,3]-shift relative to dimerization, we sought to determine how the more electron-donating pentamethylcyclopentadienyl (Cp*) ligand would affect the rates of [1,3]-metal shift and dimerization. Here we report that the Cp* ligand accelerates the [1,3]-shift and, more interestingly, that a CH insertion product is formed upon thermolysis. The observation of CH insertion provides support for the formation of an intermediate with carbene like reactivity in the thermolysis of alkynylcarbene complexes.

Results and Discussion

Cp* rhenium alkynylcarbene complexes Cp*(CO)$_2$Re=C(Ph)^{13}C≡^{13}CTol (**5**) and Cp*(CO)$_2$Re=C(Ph)C≡CAr (Ar = Ph (**6**), C$_6$D$_5$ (**6-HD**)) were synthesized in moderate yield by addition of BrZn^{13}C≡^{13}CTol or BrZnC≡CAr to [Cp*(CO)$_2$Re≡CPh]BCl$_4$.[7,8] The X-ray crystal structure of **6** (Figure 1) is similar to that of Cp analogues.[4,9]

[1,3]-Rhenium Shift. When a solution of Cp*-(CO)$_2$Re=C(Ph)^{13}C≡^{13}CTol (**5**) was heated in toluene-

d_8 at 120 °C, a 1:1 equilibrium mixture of **5** and Cp*(CO)$_2$Re=^{13}C(Tol)^{13}C≡CPh (**7**) was formed within 1 h (Scheme 3). ^{13}C NMR spectroscopy provided a convenient way of monitoring the reaction. In the ^{13}C{^{1}H} NMR spectrum of **5**, intense resonances were observed at δ 110.98 (d, $^1J_{^{13}C^{13}C}$ = 172 Hz, $^{13}C≡^{13}C$Ar) and 119.37 (d, $^1J_{^{13}C^{13}C}$ = 172 Hz, $^{13}C≡^{13}C$Ar). Upon thermolysis, new resonances were observed at δ 111.1 (d, $^1J_{^{13}C^{13}C}$ = 64.4 Hz) and 249.5 (d, $^1J_{^{13}C^{13}C}$ = 64.4 Hz) and were assigned to the labeled alkyne and carbene carbons of **7**. Equilibration of the Cp* complexes (**5** ↔ **7**, k_{obs} = (3.6 ± 0.2) × 10^{-4} s^{-1}) was 84 times faster than that of the analogous Cp complexes (**1** ↔ **2**, k_{obs} = (4.3 ± 0.1) × 10^{-6} s^{-1}).

We propose that the [1,3]-rhenium shift that equilibrates **5** ↔ **7** proceeds via a ring-slipped dehydrometallacyclobutadiene complex analogous to **C** in Scheme 1. Interestingly, the faster rates seen for our Cp* complexes (**5** ↔ **7**) compared with Cp complexes (**1** ↔ **2**) contrasts with Basolo's observation that η^5 to η^3 ring slippage is 2 orders of magnitude *slower* for Cp* than for the Cp complexes in the phosphine substitution reactions of (η^5-Cp)Rh(CO)$_2$ (reaction 1).[10] These seem-

(7) For the synthesis of [Cp*(CO)$_2$Re≡CPh]BCl$_4$, see: Fischer, E. O.; Apostolidis, C.; Dornberger, E.; Filippou, A. C.; Kanellakopulos, B.; Lungwitz, B.; Müller, J.; Powietzka, B.; Rebizant, J.; Roth, W. *Z. Naturforsch., B* **1995**, *50*, 1382.

(8) We were able to obtain an X-ray crystal structure of [Cp*-(CO)$_2$Re≡CPh]BCl$_4$ (see the Supporting Information).

(9) Casey, C. P.; Kraft, S.; Powell, D. R. Submitted for publication in *J. Am. Chem. Soc.*

(10) Rerek, M. E.; Basolo, F. *J. Am. Chem. Soc.* **1984**, *106*, 5908.

Table 1. Time Course of Concentrations [6-HD], [6-DH], [13-HD], and [13-DH]

t, min	[6-HD], 10^{-1} M	[6-DH], 10^{-1} M	[13-HD], 10^{-3} M	[13-DH], 10^{-3} M	[6-HD]/{[6-HD] + [6-DH]}	[13-HD]/{[13-HD] + [13-DH]}	conversn [6] →[13], %
0	1.09	0.0116	0	0	0.99		0
2	1.04	0.0539	0.53	0.016	0.95	0.97	0.5
5	0.958	0.116	1.3	0.15	0.89	0.89	1.3
10	0.883	0.202	2.2	0.43	0.81	0.84	2.4
20	0.748	0.325	4.1	1.2	0.70	0.78	4.9
30	0.639	0.383	5.7	1.9	0.63	0.75	7.4
40	0.582	0.419	6.9	2.6	0.58	0.73	9.5

$$(\eta^5\text{-Cp})\text{Rh(CO)}_2 + \text{PR}_3 \rightarrow (\eta^3\text{-Cp})\text{Rh(CO)}_2\text{PR}_3 \rightarrow$$
$$(\eta^5\text{-Cp})\text{Rh(CO)}\text{PR}_3 + \text{CO} \quad (1)$$
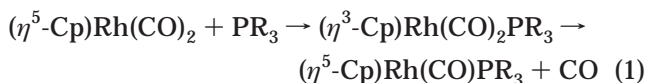
ingly conflicting observations can be reconciled by assuming that addition of a phosphine to $(\eta^5\text{-Cp})\text{Rh-}$ $(\text{CO})_2$ increases the electron density around the metal during the formation of $(\eta^3\text{-Cp})\text{Rh(CO)}_2\text{PR}_3$; the introduction of an electron-donating Cp* ligand provides an electronically unfavorable interaction. In contrast, the π coordination of a triple bond to rhenium in **C** is stabilized by enhanced $d-\pi^*$ interactions (back-bonding), effectively "diffusing" charge density from the electron-rich metal center onto the ligand. A faster [1,3]-shift in the Cp* complex **5** compared with its Cp analogue **1** is a direct consequence of an increased π-basicity at the metal center in **C**.

CH Insertion Products. Extended thermolysis of the equilibrium **5 ⇌ 7** at 120 °C for 14 h did not produce the expected dimeric enediyne complexes similar to the Cp analogue **3**. Instead, a 1:1 mixture of $\{\eta^5:\eta^2\text{-}[C_5(CH_3)_4\text{-}CH_2{}^{13}CH(Tol){}^{13}C\equiv CPh]\}\text{Re(CO)}_2$ (**8**) and $\{\eta^5:\eta^2\text{-}[C_5(CH_3)_4\text{-}CH_2CH(Ph){}^{13}C\equiv{}^{13}CTol]\}\text{Re(CO)}_2$ (**9**) was formed by a net insertion of an alkynylcarbene carbon into a CH bond of a methyl group on the Cp* ligand (Scheme 3). In the $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum, enhanced signals at δ 67.2 and 89.2 ($^1J_{^{13}\text{C}^{13}\text{C}}$ = 54 Hz) were assigned to the labeled methine and alkyne carbons of **8**. An additional splitting ($^1J_{^{13}\text{CH}}$ = 133.9 Hz) was observed for the methine carbon in the ^{1}H-coupled ^{13}C NMR spectrum. The labeled alkyne carbons in isomer **9** (δ 76.7, 86.8) showed a one-bond coupling of $^1J_{^{13}\text{C}^{13}\text{C}}$ = 111 Hz.[11]

Thermolysis of the symmetrically substituted diphenyl alkynylcarbene complex **6** cleanly formed CH insertion product **10** in 85% yield (Scheme 4). Four different methyl resonances in the ^{1}H NMR spectrum at δ 1.39, 1.95, 2.05, and 2.27 are in accordance with a C_1-symmetric molecule. The methine resonance (δ 5.13) is a triplet (^3J = 9.7 Hz) coupled to the neighboring diastereotopic methylene hydrogens at δ 2.08 (dd, ^2J = 13.5 Hz, ^3J = 9.6 Hz, H$_{anti}$) and δ 2.57 (dd, ^2J = 13.6 Hz, ^3J = 9.6 Hz, H$_{syn}$), which have a strong geminal coupling. NOE studies were undertaken to ascertain the spatial proximity of methylene and methine hydrogens to the adjacent methyl groups of the ring. Irradiation of the methine signal resulted in NOE signal enhancements for H$_{syn}$ (2.6%), H$_{anti}$ (0.6%), an adjacent ring CH$_3$ group (δ 2.26, 2.1%), and the ortho hydrogen H$_o$(1) (δ 7.21, 1.7%). Irradiation of H$_{anti}$ gave NOE enhancements for H$_{syn}$ (6.7%), a ring-CH$_3$ group (δ 1.39, 1.1%), the methine hydrogen (0.6%), and H$_o$(1) (0.6%). Irradiation of H$_o$(2) on the lower phenyl group showed only an NOE

effect for the vicinal meta hydrogen (δ 7.08, 1.8%) but no enhancement >0.2% to other hydrogens in the molecule.

We suggest that the tethered alkyne complexes **8−10** are formed by insertion of the remote alkyne carbon into a Cp* methyl group induced by a [1,1.5]-rhenium shift to give the intermediate **D** with "free carbene" character (path A, Scheme 4).[12] Previously, we provided evidence for carbene-like reactivity at the remote alkyne carbon in **11**, which formed cyclopropyl derivative **12** upon heating at 120 °C (Scheme 5).[13]

The possibility that CH insertion products might result from a net insertion of the metal-bound carbene carbon into a methyl CH bond was also considered. Such an insertion might result from an initial 1,2-addition of a CH bond across the Re=C bond to form the tuck-in complex **E**, followed by a reductive C−C elimination and alkyne complexation (path B, Scheme 4). Bercaw demonstrated the viability of an intramolecular CH addition of a Cp* methyl group across a Hf=C bond to form a tuck-in complex.[14,15] Moreover, intra- and intermolecular CH insertions have been reported for Fischer carbene complexes.[16,17]

In principle, it should be possible to identify the terminus of the alkynylcarbene that inserts into the methyl group by monitoring the conversion of the

(11) Typical one-bond CC coupling constants ($^1J_{CC}$) in alkynes range between 170 and 180 Hz. We attribute the significantly lower coupling constant in **9** to metal complexation.

(12) A similar [1,1.5]-shift has been postulated in the rearrangement of chromium alkynylcarbene complexes [(CO)$_5$Cr=C(O)(C≡COEt)]$^-$ to a cyclopropenylidene complex: Juneau, K. N.; Hegedus, L. S.; Roepke, F. W. *J. Am. Chem. Soc.* **1989**, *111*, 4762.

(13) It should be admitted that we have no direct evidence for the intermediacy of the "free carbene" shown as an intermediate in the cyclopropanation; [1,1.5]-rhenium shifts and CH insertion might proceed in a concerted fashion.

(14) (a) McDade, C.; Green, J. C.; Bercaw, J. E. *Organometallics* **1982**, *1*, 1629. (b) Bulls, A. R.; Schaefer, W. P.; Serfas, M.; Bercaw, J. E. *Organometallics* **1987**, *6*, 1219.

(15) For inter- and intramolecular CH insertions of early-transition-metal alkylidene complexes, see: (a) Adams, C. S.; Legzdins, P.; Tran, E. *J. Am. Chem. Soc.* **2001**, *123*, 612. (b) Duncalf, D. J.; Harrison, R. J.; McCamley, A.; Royan, B. W. *J. Chem. Soc., Chem. Commun.* **1995**, 2421. (c) van der Heijden, H.; Hessen, B. *J. Chem. Soc., Chem. Commun.* **1995**, 145. (d) Vilardo, J. S.; Lockwood, M. A.; Hanson, L. G.; Clark, J. R.; Parkin, B. C.; Fanwick, P. E.; Rothwell, I. P. *J. Chem. Soc., Dalton Trans.* **1997**, 3353. (e) Chamberlain, L. R.; Rothwell, I. P.; Huffman, J. C. *J. Am. Chem. Soc.* **1986**, *108*, 1502. (f) Schrock, R. R.; DePue, R. T.; Feldman, J.; Yap, K. B.; Yang, D. C.; Davis, W. M.; Park, L.; DiMare, M.; Schofield, M.; Anhaus, J.; Walborsky, E.; Evitt, E.; Krüger, C.; Betz, P. *Organometallics* **1990**, *9*, 2262. (g) van Doorn, J. A.; van der Heijden, H.; Orpen, A. G. *Organometallics* **1994**, *13*, 4271.

(16) (a) Fischer, H.; Schmid, J.; Märkl, R. *J. Chem. Soc., Chem. Commun.* **1985**, 572. (b) Wang, S. L. B.; Su, J.; Wulff, W. D.; Hoogsteen, K. *J. Am. Chem. Soc.* **1992**, *114*, 10665. (c) Barluenga, J.; Rodríguez, F.; Vadecard, J.; Bendix, M.; Fañanás, F. J.; López-Ortiz, F. *J. Am. Chem. Soc.* **1996**, *118*, 6090. (d) Barluenga, J.; Rodríguez, F.; Vadecard, J.; Bendix, M.; Fañanás, F. J.; López-Ortiz, F.; Rodríguez, M. A. *J. Am. Chem. Soc.* **1999**, *121*, 8776. (e) Barluenga, J.; Aznar, F.; Fernández, M. *Chem. Eur. J.* **1997**, *3*, 1629. (f) Wienand, A.; Reissig, H.-U. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 1129. (g) Takeda, K.; Okamoto, Y.; Nakajima, A.; Yoshii, E.; Koizumi, T. *Synlett* **1997**, 1181.

(17) Werner documented an intramolecular insertion of a carbene ligand into a CH bond of an η^5-indenyl ligand accompanied by a complete detachment from the metal (Bleuel, E.; Laubender, M.; Weberndörfer, B.; Werner, H. *Angew. Chem., Int. Ed.* **1999**, *38*, 156).

Scheme 4
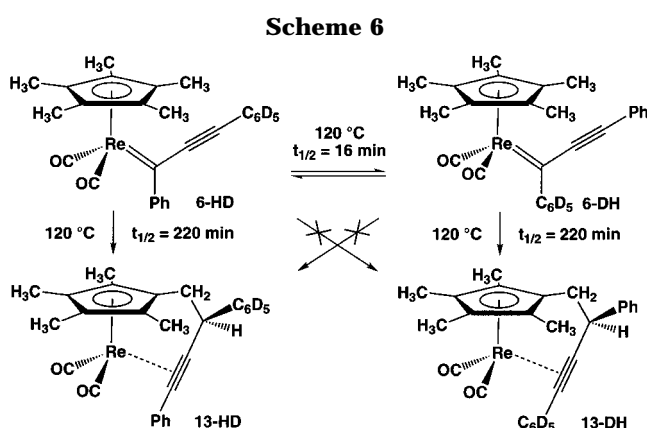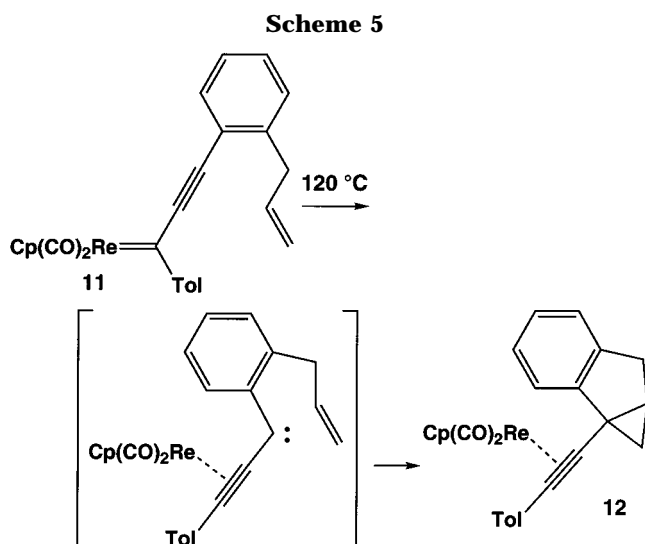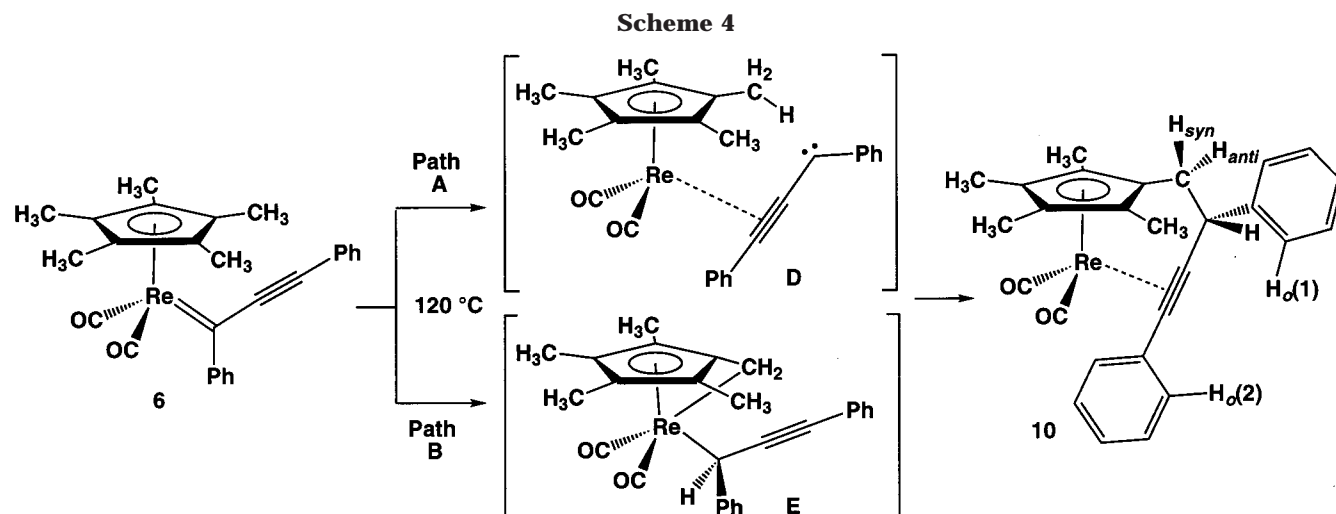
Scheme 5

Scheme 6

deuterium-labeled alkynylcarbene complex **6-HD** into either **13-HD** or **13-DH** (Scheme 6). Since the [1,3]-rhenium shift **6-HD** ⇌ **6-DH** ($k_{obs} = 7.5 \times 10^{-4}$ s^{-1}) is 14 times faster than the CH insertion step ($k_{obs} = 5.3 \times 10^{-5}$ s^{-1}), it was crucial to determine the ratio of **13-HD** to **13-DH** at less than 10% conversion to **13** to avoid complications from equilibration of **6-HD** and **6-DH**. The concentrations [**6-HD**], [**6-DH**], and [**13-HD**] were directly determined by ^{1}H NMR spectroscopy (Table 1) via their ortho hydrogens (**6-HD**, δ 8.35; **6-DH**, δ 7.55; **13-HD**, δ 7.43); [**13-DH**] was inferred from the sum of [**13-HD**] and [**13-DH**] determined by integration of a

ring methyl group (δ 2.27) common to both isomers. The comparison of the ratios [**6-HD**]/{[**6-HD**] + [**6-DH**]} and [**13-HD**]/{[**13-HD**] + [**13-DH**]} at any given point of the reaction indicated a high selectivity for the conversion of **6-HD** to **13-HD** (Table 1).

In summary, we found that replacement of a Cp ligand with the more electron rich Cp* ligand speeds up [1,3]-metal shifts in rhenium alkynylcarbene complexes by almost 2 orders of magnitude. Over several hours, new CH insertion products were identified. Site-selective CH insertion implies carbenoid reactivity at the remote alkyne carbon and supports the hypothesis of carbene intermediates such as **A** in dimerization reactions shown in Scheme 1.

Experimental Section

Cp*(CO)$_2$Re=C(Ph)^{13}C≡^{13}CTol (5). Addition of BrZn^{13}C≡^{13}CPh (from Li^{13}C≡^{13}CPh (11 mg, 0.089 mmol) and ZnBr$_2$ (20 mg, 0.089 mmol) in 1 mL of THF) to an orange solution of [Cp*-(CO)$_2$Re≡CPh]BCl$_4$ (110 mg, 0.179 mmol) in 25 mL of CH$_2$Cl$_2$ at −35 °C produced a black solution. The cold reaction mixture was poured onto a silica gel column (30 × 2 cm), and a black fraction was eluted with a 4/1 hexane/diethyl ether mixture. Evaporation of solvent under reduced pressure gave a solid which was redissolved in 2 mL of 4/1 hexane/CH$_2$Cl$_2$. Slow evaporation gave black crystals of **5** (14 mg, 0.024 mmol, 28%). ^{1}H NMR (CD$_2$Cl$_2$, 500 MHz): δ 2.16 [s, C$_5$(CH$_3$)$_5$], 2.30 (s, ArCH$_3$), 7.19 (d, ^3J = 7.9 Hz, aromatic CH), 7.29 (t, ^3J = 7.4 Hz, aromatic CH), 7.40 (t, ^3J = 7.3 Hz, aromatic CH), 7.53 (dd, ^3J = 8.1 Hz, $^3J_{^{13}CH}$ = 5.1 Hz, aromatic CH), 7.97 (d, ^3J = 7.3 Hz, aromatic CH). ^{1}H NMR (toluene-d_8, 500 MHz): δ 1.91 [s, (C$_5$(CH$_3$)$_5$], 1.97 (s, Ar—CH$_3$), 6.85 (d, ^3J = 6.9 Hz, aromatic CH), 7.15−7.18 (m, aromatic CH), 7.49−7.53 (m, aromatic CH), 8.33−8.42 (m, aromatic CH). ^{13}C{^{1}H} NMR (CD$_2$Cl$_2$, 125 MHz): δ 110.98 (d, $^1J_{^{13}C^{13}C}$ = 172 Hz, ^{13}C≡^{13}CAr), 119.37 (d, $^1J_{^{13}C^{13}C}$ = 172 Hz, ^{13}C≡^{13}CAr). IR (CH$_2$Cl$_2$): 1954, 1878 cm^{-1}. HRMS (EI): m/z calcd for C$_{26}$^{13}C$_2$H$_{27}$O$_2$Re (M$^+$) 584.1697, found 584.1636.

Kinetic Measurement of the Conversion of 5 to 7 at 120 °C. A C$_6$D$_5$CD$_3$ solution of **5** (5.0 mg, 0.0084 mmol, 0.42 mL total volume and 0.020 M at 120 °C) containing 1,4-bis-(trimethylsilyl)benzene (1.0 mg, internal NMR standard) was heated at 120 ± 0.3 °C. ^{1}H NMR spectra were acquired at room temperature after 0, 1, 15, 40, 122, and 260 min at 120 °C (**5**, δ(tolyl CH$_3$) 1.97; **7**, δ(tolyl CH$_3$) = 1.86). The decrease in the ratio **5**:(**5** + **7**) was followed (k_{obs} = (3.6 ± 0.2) × 10^{-4} s^{-1}, K_{eq} = 1.0 ± 0.1, k_1 = (1.8 ± 0.1) × 10^{-4} s^{-1}, k_{-1} = (1.8 ± 0.1) × 10^{-4} s^{-1}).

Spectroscopic characterization of **7** was undertaken without isolation. ^{1}H NMR (toluene-d_8, 500 MHz): δ 1.86 (s, C$_6$H$_4$CH_3), 1.90 [s, (C$_5$(CH$_3$)$_5$], 6.90$-$7.11 (m, aromatic CH), 8.40$-$8.45 (m, aromatic CH, partially obscured by signals from **5**). ^{13}C{^{1}H} NMR (toluene-d_8, 125 MHz): δ 111.1 (d, $^1J_{^{13}C^{13}C}$ = 64.4 Hz, ^{13}C≡C), 249.5 (d, $^1J_{^{13}C^{13}C}$ = 64.4 Hz, Re=^{13}C).

Extended Thermolysis of 5 and 7. Thermolysis of **5** and **7** for 14 h at 120 °C afforded a 5:1 mixture of (**8** + **9**) and (**5** + **7**). ^{1}H NMR (**8** + **9**, toluene-d_8, 500 MHz): δ 1.40 (s, CH$_3$), 1.41 (s, CH$_3$), 1.95 (s, CH$_3$), 1.96 (s, CH$_3$), 2.058 (s, CH$_3$), 2.061 (s, tolyl CH$_3$), 2.13 (s, tolyl CH$_3$), 2.26 (s, CH$_3$), 2.27 (s, CH$_3$), 2.50 (m, CHHCHPh and CHH^{13}CHTol), 5.12 (dtd, $^2J_{^{13}CH}$ = 11.5 Hz, ^3J = 9.5 Hz, $^3J_{^{13}CH}$ = 5.3 Hz, CHPh, **9**), 5.14 (ddt, $^1J_{^{13}CH}$ = 136.2 Hz, $^2J_{^{13}CH}$ = 11.5 Hz, ^3J = 9.5 Hz, ^{13}CHTol, **8**), 6.97 (t, ^3J = 7.3 Hz, aromatic CH), 7.08 (t, ^3J = 7.8 Hz, aromatic CH), 6.75$-$7.20 (m, aromatic CH), 7.24 (d, ^3J = 7.4 Hz, aromatic CH), 7.38 (dd, ^3J = 8.0 Hz, $^3J_{^{13}CH}$ = 5.6 Hz, aromatic CH). The signals for the CHHCHPh hydrogens of both isomers are obscured by the solvent pentet at δ 2.09. ^{13}C NMR (**8** + **9**, toluene-d_8, 125 MHz): **8**, δ 67.27 (dd, $^1J_{CC}$ = 55.5 Hz, $^1J_{CH}$ = 133.9 Hz, ^{13}CHTol), 89.21 (dt, $^1J_{CC}$ = 55.5 Hz, $^2J_{CH}$ = $^3J_{CH(\text{one of diastereotopic CH}_2)}$ = 11.0 Hz, ^{13}C≡CPh); **9**, δ 76.7 (dq, $^1J_{CC}$ = 111.7 Hz, $^3J_{CH}$ = $^3J_{CH(Tol)}$ = 4.8 Hz, ^{13}C≡^{13}CTol), 87.41 (dt, $^1J_{CC}$ = 111.6 Hz, $^2J_{CH}$ = $^3J_{CH(\text{one of diastereotopic CH}_2)}$ = 11.3 Hz, ^{13}C≡^{13}CTol).

Cp*(CO)$_2$Re=(Ph)C≡CPh (6). Addition of BrZnC≡CPh (from LiC≡CPh (71 mg, 0.66 mmol) and ZnBr$_2$ (148 mg, 0.658 mmol) in 1 mL of THF) to an orange solution of [Cp*(CO)$_2$Re≡CPh]BCl$_4$ (401 mg, 0.648 mmol) in 5 mL of THF at $-$35 °C slowly produced a black solution. After 10 min, the cold reaction mixture was poured onto a silica gel column (30 × 2 cm) and a black fraction was eluted with 5/1 hexane/diethyl ether. Evaporation of solvent under reduced pressure gave a solid which was redissolved in 2 mL of 3/1 hexane/CH$_2$Cl$_2$. Slow evaporation gave **6** as black plates (88 mg, 0.155 mmol, 24%)[18] suitable for X-ray crystal structure analysis. ^{1}H NMR (CD$_2$-Cl$_2$, 500 MHz): δ 2.17 [s, C$_5$(CH$_3$)$_5$], 7.30 (t, ^3J = 7.3 Hz, aromatic CH), 7.39 (m, aromatic CH), 7.47 (d, ^3J = 7.5 Hz, aromatic CH), 7.63 (d, ^3J = 8.0 Hz, aromatic CH), 7.99 (d, ^3J = 7.5 Hz, aromatic CH). ^{1}H NMR (toluene-d_8, 500 MHz): δ 1.89 [s, C$_5$(CH$_3$)$_5$], 7.00$-$7.20 (m, aromatic CH), 7.55 (d, ^3J = 7.3 Hz, aromatic CH), 8.35 (d, ^3J = 7.3 Hz, aromatic CH). ^{13}C{^{1}H} NMR (CD$_2$Cl$_2$, 125 MHz): δ 10.48 [C$_5$(CH$_3$)$_5$], 104.83 [C$_5$-(CH$_3$)$_5$], 110.95 (C≡CPh), 118.60 (C≡CPh), 125.75 (aromatic), 126.43 (aromatic), 128.34 (aromatic), 128.63 (aromatic), 128.70 (aromatic), 129.26 (aromatic), 129.46 (aromatic), 161.90 (aromatic), 208.34 (CO), 249.18 (Re=C). IR (CH$_2$Cl$_2$): 1956, 1880 cm^{-1}. HRMS (EI): m/z calcd for C$_{27}$H$_{25}$O$_2$Re (M$^+$) 566.1384, found 566.1395.

{η^5:η^2-[C$_5$(CH$_3$)$_4$CH$_2$CH(Ph)C≡CPh]}Re(CO)$_2$ (10). A solution of Cp*(CO)$_2$Re=C(Ph)C≡CPh (**6**; 33.1 mg, 58.3 μmol) in toluene-d_8 (0.49 mL, 0.12 M) containing 1,4-bis(trimethylsilyl)benzene (5.4 mg) as an internal NMR standard was heated at 120 °C for 14 h. ^{1}H NMR showed that more than 95% of **6** had been consumed. After the solvent was evaporated under reduced pressure, the crude product was purified by

preparative thin-layer chromatography (silica, 10/1 hexane/diethyl ether, R_f = 0.5, yellow band). A yellow solid was obtained, which was dissolved in 1.5 mL of 1/1 CH$_2$Cl$_2$/hexane. Slow evaporation gave **10** as orange-yellow needles (28.1 mg, 0.049.5 μmol, 85%). ^{1}H NMR (toluene-d_8, 500 MHz): δ 1.39 (s, CH$_3$), 1.95 (s, CH$_3$), 2.05 (s, CH$_3$), 2.08 (dd, ^2J = 13.5 Hz, ^3J = 9.6 Hz, CHHCHPh), 2.27 (s, CH$_3$), 2.57 (dd, ^2J = 13.6 Hz, ^3J = 9.6 Hz, CHHCHPh), 5.13 (t, ^3J = 9.5 Hz, CHPh), 6.97 (t, ^3J = 7.3 Hz, aromatic CH), 7.08 (t, ^3J = 7.8 Hz, aromatic CH), 7.14 (t, ^3J = 7.2 Hz, aromatic CH), 7.21 (d, ^3J = 7.7 Hz, aromatic CH), 7.43 (d, ^3J = 7.5 Hz, aromatic CH). ^{1}H NMR (CD$_2$Cl$_2$, 500 MHz): δ 1.66 (s, CH$_3$), 2.29 (s, CH$_3$), 2.34 (s, CH$_3$), 2.38 (dd, ^2J = 13.4 Hz, ^3J = 9.7 Hz, CHHCHPh), 2.56 (s, CH$_3$), 3.05 (dd, ^2J = 13.5 Hz, ^3J = 9.4 Hz, CHHCHPh), 5.30 (t, ^3J = 9.6 Hz, CHPh), 7.19$-$7.24 (m, aromatic CH), 7.25$-$7.34 (m, aromatic CH), 7.36 (t, ^3J = 7.3 Hz, aromatic CH), 7.43 (d, ^3J = 7.4 Hz, aromatic CH). ^{13}C NMR (CD$_2$Cl$_2$, 125 MHz): δ 9.23 (q, $^1J_{CH}$ = 127.9 Hz, CH$_3$), 11.25 (q, $^1J_{CH}$ = 127.9 Hz, CH$_3$), 11.61 (q, $^1J_{CH}$ = 127.9 Hz, CH$_3$), 12.24 (q, $^1J_{CH}$ = 127.3 Hz, CH$_3$), 30.34 (td, $^1J_{CH}$ = 132.8, $^2J_{CH}$ = 5.9 Hz, CH$_2$), 67.40 (d, $^1J_{CH}$ = 137.6 Hz, CHPh), 76.21 (q, $^3J_{CH}$ = $^3J_{CH(Ph)}$ = 5.4 Hz, C≡CPh), 89.71 (t, $^2J_{CH}$ = $^3J_{CH(\text{one of diastereotopic CH}_2)}$ = 11.6 Hz, C≡CPh), 91.14 (m, CCH$_3$), 99.08 (m, CCH$_3$), 100.60 (m, CCH$_3$), 103.88 (m, CCH$_3$), 115.13 (m, CCH$_3$), 127.19 (dt, $^1J_{CH}$ = 160.2 Hz, $^3J_{CH}$ = 7.1 Hz, aromatic), 127.49 (dt, $^1J_{CH}$ = 157.9 Hz, $^3J_{CH}$ = 5.4 Hz, aromatic), 127.73 (dt, $^1J_{CH}$ = 160.2 Hz, $^3J_{CH}$ = 7.7 Hz, aromatic), 128.77 (dd, $^1J_{CH}$ = 160.2 Hz, $^3J_{CH}$ = 7.9 Hz, aromatic), 130.02 (t, $^3J_{CH}$ = 7.0 Hz, aromatic), 130.90 (ddd, $^1J_{CH}$ = 160.8 Hz, $^3J_{CH}$ = 6.8 Hz, $^3J_{CH}$ = 5.4 Hz, aromatic), 143.44 (m, aromatic), 209.65 (CO), 210.16 (CO). IR (CH$_2$Cl$_2$) 1955, 1855 cm^{-1}. HRMS (EI): m/z calcd for C$_{27}$H$_{25}$O$_2$^{187}Re (M$^+$) 568.1412, found 568.1408.

Kinetic Measurement of the Conversion of 6-HD to 6-DH and of (6-HD + 6-DH) to (13-HD + 13-DH) at 120 °C. A C$_6$D$_5$CD$_3$ solution of **6-HD** (30.2 mg, 0.0527 mmol, 0.48 mL total volume and 0.11 M at 120 °C) containing 1,4-bis-(trimethylsilyl)benzene (1.0 mg, internal NMR standard) was heated at 120 ± 0.3 °C. ^{1}H NMR spectra were acquired at room temperature after 0, 2, 5, 40, 10, 20, 30, 40, 111, 216, and 375 min at 120 °C (**6-HD**, δ(CH$_{ortho}$) 8.36; **6-DH**, δ(CH$_{ortho}$) 7.55; **13-HD**, δ(CH$_{ortho}$) 7.44; **13-DH**, δ(CH$_{ortho}$) 7.21). The rate of approach to equilibrium (**6-HD** ⇌ **6-DH**) (k_{obs} = (7.5 ± 0.2) × 10^{-4} s^{-1}, K_{eq} = 1.0 ± 0.1, k_1 = (3.8 ± 0.1) × 10^{-4} s^{-1}, k_{-1} = (3.8 ± 0.1) × 10^{-4} s^{-1}) and the rate of disappearance of combined alkynylcarbene complex concentration ((**6-HD** + **6-DH**, δ(Cp*) 1.91) → (**13-HD** + **13-DH**)) (k_{obs} = (5.3 ± 0.2) × 10^{-5} s^{-1}) were determined. Ratios of [**6-HD**] to ([**6-HD**] + [**6-DH**]) and [**13-HD**] to ([**13-HD**] + [**13-DH**]) are shown in Table 1.

Supporting Information Available: Preparation of compounds, spectral data, description of kinetics, and X-ray crystal structures. This material is available free of charge via the Internet at http://pubs.acs.org.

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(18) Later we found that the yields of Cp*(CO)$_2$Re$-$alkynylcarbene complexes can be increased significantly, if the initial crude product solution is warmed from $-$35 °C to room temperature for 10 min (see preparation of **6-DH** in supporting information).