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Communications

[1,3]-Metal Shifts in Rhenium Alkynyl Carbene Complexes

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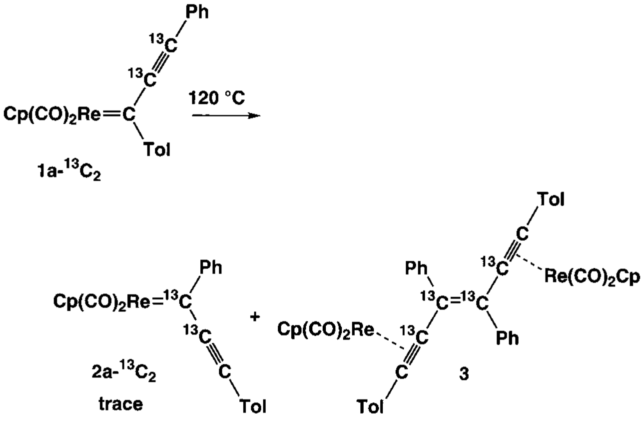
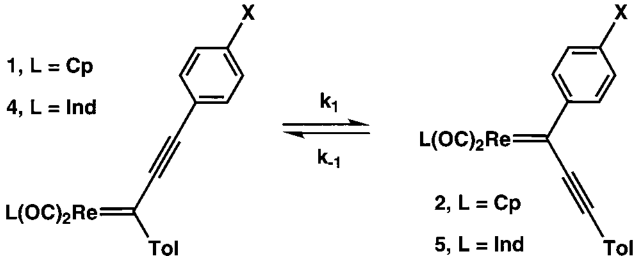
*Summary: The electron-withdrawing SO_2CF_3 substituent of $Cp(CO)_2Re{=}C(Tol)(C{\equiv}CC_6H_4\text{-}p\text{-}SO_2CF_3)$ (**1d**) greatly accelerates rearrangement via a [1,3]-rhenium shift. The [1,3]-rhenium shift is proposed to proceed via an 18-electron dehydrometallacyclobutadiene intermediate formed by alkyne coordination concerted with an $\eta^5-\eta^3$ Cp ring slip.*

Heteroatom-substituted alkynyl carbene complexes such as $(CO)_5M{=}C(OR)C{\equiv}CR'$ are highly electrophilic and synthetically versatile.[1] While many such complexes have been studied, [1,3]-shifts have not been observed because of either unfavorable equilibria or high kinetic barriers. Recently, we began a search for an unprecedented [1,3]-metal shift in a non-donor-substituted, nearly symmetric alkynyl carbene complex;[2] analogous rearrangements of σ-propargyl to σ-allenyl compounds are well-known.[3] When $Cp(CO)_2Re{=}C(Tol)(^{13}C{\equiv}^{13}CPh)$ (**1a**-$^{13}C_2$; Tol = C_6H_4-*p*-CH_3) was heated at 120 °C, only small amounts of its [1,3]-metal-shifted isomer **2a**-$^{13}C_2$ were observed (Scheme 1).[4] Surprisingly, dimerization to the *trans* enediyne complex **3** was the major reaction observed.

Scheme 1



Scheme 2



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[1] For reviews of 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, 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 but not directly observed in a rhodium alkynyl carbene complex that had 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.

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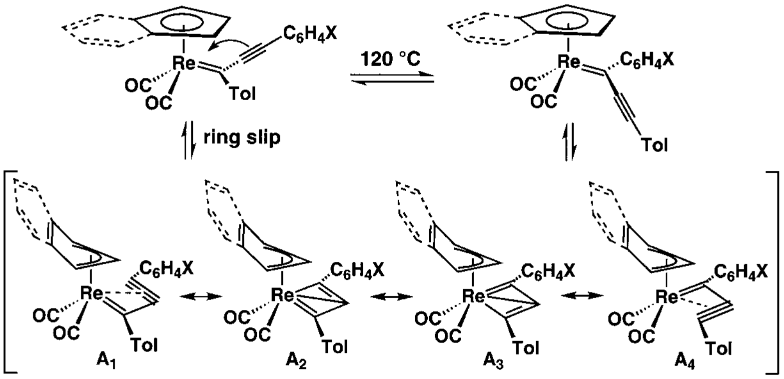
Scheme 3



In an effort to increase the ratio of [1,3]-metal shift to dimerization, we explored effects of electron-withdrawing *para* substituents on the alkynyl carbene complexes **1a**−**d** (Scheme 2). Here we report that electron-withdrawing substituents substantially increase the rate of the [1,3]-metal shift and that related rhenium indenyl complexes undergo the [1,3]-metal shift at dramatically higher rates. A mechanism involving a dehydrometallacyclobutadiene intermediate or transition state stabilized by ring slippage is proposed for the [1,3]-metal shift.

Substituted Cp alkynyl carbene complexes **1a**−**d** and related indenyl complexes **4a**−**d** were synthesized in good yields (60−70%) by addition of metal acetylides MC≡CAr (M = Li, ZnBr, Cu) to the cationic rhenium carbyne complexes [Cp(CO)$_2$Re≡CAr′]BCl$_4$[5] and [(η^5-indenyl)(CO)$_2$Re≡CAr′]BCl$_4$.[6] When a dilute solution[7] of the SO$_2$CF$_3$-substituted complex **1d** was heated at 120 °C, rapid isomerization to an 80:20 equilibrium mixture of the [1,3]-shift isomer **2d** to the starting material **1d** occurred and no dimerization was seen. **2d** was isolated by preparative thin-layer chromatography, and its structure was unambiguously determined by X-ray crystallography.[8]

Rate constants for approach to equilibrium ($k_{obsd} = k_1 + k_{-1}$) and equilibrium constants ($K_{eq} = k_1/k_{-1}$) were measured for Cp complexes **1a**−**d** at 120 °C in toluene-d_8 by ^{1}H NMR spectroscopy ($\Delta\delta \geq 0.2$ ppm for tolyl methyl groups) (Scheme 2, Table 1).[9,10] The electron-withdrawing SO$_2$CF$_3$ substituent of **1d** strongly accelerated isomerization by a [1,3]-metal shift (k_1(rel) = 88). The electron-donating NMe$_2$ substituent of **1b** slightly decreased the rate of isomerization to **2b** (k_1(rel) = 0.9). Only small solvent effects were seen on rates of isomerization of **1d** to **2d** ($k_1 = 1.9 \times 10^{-4}$ s^{-1} in toluene, 1.1×10^{-4} s^{-1} in methylcyclohexane, 4.4×10^{-4} s^{-1} in *tert*-butyl alcohol, and 9.7×10^{-4} s^{-1} in nitrobenzene), indicating similar polarities of the ground and transition states.[11]

Table 1. Equilibrium and Rate Constants for [1,3]-Rhenium Shifts in Toluene-d_8 at 120 °C

	L	X	K_{eq}	k_{obsd} (10^{-6} s^{-1})	k_1(rel)
1a	Cp	H	1.0	4.3	1.0
1b	Cp	N(CH$_3$)$_2$	1.7	3.2	0.9
1c	Cp	CF$_3$	3.3	21	7.4
1d	Cp	SO$_2$CF$_3$	4.0	240	88
4a	Ind	H	1.0	2400	550

A net [1,3]-metal shift requires a transition structure resembling a dehydrometallacyclobutadiene with carbons 1 and 3 symmetrically bound to the metal. Alkyne coordination to rhenium would generate a 20-electron intermediate unless CO dissociation or Cp ring slippage occurred.

A mechanism involving CO dissociation was excluded by the absence of ^{13}CO exchange during isomerization of **1d**. When the partial isomerization of **1d** under 0.1 atm of ^{13}CO was followed by ^{13}C NMR spectroscopy, the 60:40 mixture of **1d** and **2d** showed no Re^{13}CO signal enhancement.

Reactions involving ring slippage occur much more rapidly for indenyl than cyclopentadienyl complexes because the six-membered ring becomes more aromatic upon ring slippage.[12] To test whether ring slippage is an important component in the [1,3]-metal shifts, we measured rates of isomerization of indenyl complexes **4a**−**d**. Indenyl complex **4a** underwent a [1,3]-metal shift 550 times faster than the Cp analogue **1a** (Table 1).[13] Interestingly, the rate accelerations induced by electron-

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(3) (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) Fischer, E. O.; Clough, R. L.; Stückler, P. *J. Organomet. Chem.* **1976**, *120*, C6.

(6) Miguel, D.; Steffan, U.; Stone, F. G. A. *Polyhedron* **1988**, *7*, 443.

(7) Since dimerization is a second-order process and isomerization is a first-order process, low concentrations maximize the [1,3]-metal shift to dimerization ratio.

(8) See the Supporting Information.

(9) Wilkins, R. G. *The Study of Kinetics and Mechanism of Reactions of Transition Metal Complexes*; Allyn and Bacon: Boston, MA, 1974.

(10) The narrow range of equilibrium constants (from K_{eq} = 1.0 for [**2a**]/[**1a**] to K_{eq} = 4.0 for [**2d**]/[**1d**]) is probably related to the fact that both arene rings are conjugated with the electron-deficient carbene carbon.

(11) The 20:80 equilibrium ratio of **1d** to **2d** was solvent-independent.

(12) (a) Rerek, M. E.; Ji, L.-N.; Basolo, F. *J. Chem. Soc., Chem. Commun.* **1983**, 1208. (b) Basolo, F. *Inorg. Chim. Acta* **1984**, *100*, 33. (c) Hart-Davis, A. J.; Mawby, R. J. *J. Chem. Soc. A* **1969**, 2403. (d) Hart-Davis, A. J.; White, C.; Mawby, R. J. *Inorg. Chim. Acta* **1970**, *4*, 441. (e) White, C.; Mawby, R. J. *Inorg. Chim. Acta* **1970**, *4*, 261. (f) Jones, D. J.; Mawby, R. J. *Inorg. Chim. Acta* **1972**, *6*, 157. (f) O'Conner, J. M.; Casey, C. P. *Chem. Rev.* **1987**, *87*, 307.

(13) ^{13}C NMR evidence for a [1,3]-rhenium shift with an indenyl-substituted complex was found when (η^5-indenyl)(CO)$_2$Re=C(Tol)^{13}C≡^{13}CTol (**4e**-$^{13}C_2$) was heated to 120 °C. New signals at δ 110.39 and δ 251.50 ($^1J_{^{13}C^{13}C}$ = 64.5 Hz) indicated the formation of (η^5-indenyl)(CO)$_2$Re=^{13}C(Tol)^{13}C≡CTol (**5e**-$^{13}C_2$).

Table 2. Equilibrium and Rate Constants for [1,3]-Rhenium Shifts of Indenyl Complexes in Toluene-d_8 at 100 °C

	L	X	K_{eq}	k_{obsd} (10^{-4} s^{-1})	k_1(rel)
4a	Ind	H	1.0	5.5	1.0
4b	Ind	N(CH$_3$)$_2$	2.2	2.1	0.5
4c	Ind	CF$_3$	2.3	14	3.4
4d	Ind	SO$_2$CF$_3$	4.3	69	20

withdrawing substituents in the indenyl series **4a**−**d** (Table 2) were similar to those in the Cp series, implying that Cp and Ind compounds react by the same basic mechanism.

A plausible mechanism for the [1,3]-rhenium shifts involves coordination of the alkyne triple bond to Re parallel to the Cp plane,[14] concerted with an $\eta^5-\eta^3$ Cp ring slip to give an 18-electron dehydrometallacyclobutadiene intermediate **A** (Scheme 3). Ring slippage is strongly supported by the 550-fold indenyl rate acceleration and is required to avoid a 20-electron intermediate. While the four dehydrometallacyclobutadiene resonance structures (**A$_{1-4}$**) all look bizarre, Schrock has reported the isolation of stable Mo− and W−dehydrometallacyclobutadiene complexes and showed that the C$_3$ ligands are symmetrically bonded to the metal.[15,16]

The acceleration of [1,3]-rhenium shifts by electron-withdrawing substituents can be explained in terms of resonance structures **A$_1$** and **A$_4$**, which emphasize the similarity of dehydrometallacyclobutadienes and alkyne complexes. Electron-withdrawing substituents stabilize alkyne complexes by enhancing d−π* back-bonding. A similar stabilization of the transition state leading to **A** by electron-withdrawing substituents can be expected.

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Supporting Information Available: Text giving a description of the preparation of compounds, spectral data, and a description of kinetics and text and tables giving details of the X-ray crystal structure determinations. This material is available free of charge via the Internet at http://pubs.acs.org.

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[14] This assumes fairly unhindered rotation around the Re═C bond. The M═C rotational barrier of Cp(CO)$_2$Mn═C(CH$_3$)$_2$ was calculated to be 9 kcal mol^{-1} (Kostić, N. M.; Fenske, R. F. *J. Am. Chem. Soc.* **1982**, *104*, 3879). The ^{1}H NMR spectrum of this compound is consistent with a low barrier: Fischer, E. O.; Besl, G. Z. *Z. Naturforsch., B: Anorg. Chem., Org. Chem.* **1979**, *34*, 1186.

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[16] Dehydrometallacyclobutadienes were identified as key intermediates in the decomposition of active alkyne metathesis catalysts: (a) References 14c,d. (b) Bray, A.; Mortreux, A.; Petit, F.; Petit, M.; Szymanska-Buzar, T. *J. Chem. Soc., Chem. Commun.* **1993**, 197.