J|A|C|S
COMMUNICATIONS

Published on Web 07/10/2004

Cobalt-Mediated Two-Carbon Ring Expansion of Five-Membered Rings. Electrophilic Carbon−Carbon Bond Activation in the Synthesis of Seven-Membered Rings

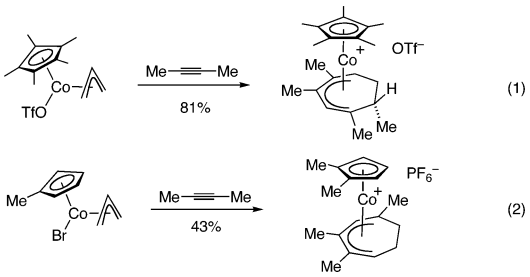
Trevor L. Dzwiniel and Jeffrey M. Stryker*

Department of Chemistry, University of Alberta, Edmonton, Alberta, Canada T6G 2G2

Received April 14, 2004; E-mail: jeff.stryker@ualberta.ca

Transition metal-mediated carbon−carbon σ-bond activation remains a fundamental challenge in organometallic chemistry, particularly for substrates not specifically imbued with structural characteristics favorable to carbon−carbon bond scission. Nonetheless, new systems and contexts continue to be uncovered, with recurrent themes of oxidative insertion and substrate predisposition (ring strain, incipient aromatic stabilization, activating functionality, and/or directing groups) complementing nonoxidative processes typically involving β-alkyl elimination.[1−3] More recently, a nonoxidative metal-assisted acidolysis pathway has been documented.[4]

We previously reported unanticipated carbon−carbon bond activation during certain cobalt-mediated allyl/alkyne cycloaddition reactions, leading in some cases to anomalously substituted η^5-cycloheptadienyl products (eq 1) and, in others, to the activation of ancillary cyclopentadienyl ligands (eq 2).[5,6]

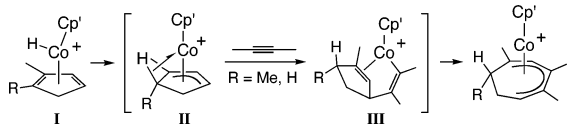


Although detailed mechanisms remain undetermined, these unusual transformations have been rationalized by invoking agostic η^3-cyclopentenyl intermediates (e.g., **II**, Scheme 1), which subsequently undergo alkyne insertion and ring expansion at or below room temperature.[5] An analogous agostic 1-ethyl-η^3-cyclopentenyl complex has been reported that converts at elevated temperature to an acyclic η^5-pentadienyl complex by carbon−carbon bond activation.[7]

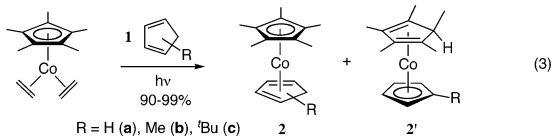
On the basis of this hypothesis, we considered that independent generation of η^3-cyclopentenyl complexes **II** in the presence of alkyne should also lead to η^5-cycloheptadienyl formation, providing new methodology to convert readily available five-membered rings to seven-membered rings, an unprecedented transformation of considerable potential utility in synthesis.

In this communication, we report the realization of this new ring expansion, accessing the required intermediates by protonation of η^4-cyclopentadiene cobalt complexes in the presence of alkyne. Thus, diene complexes **2/2′** were prepared by photochemical exchange of cyclopentadienes **1a**−**c** for the ethylene ligands of $(C_5Me_5)Co(C_2H_4)_2$[8] (eq 3);[9] thermal substitution requires elevated temperature and leads to intractable product mixtures. Photolysis provides each product as a mixture of isomers **2a**−**c**/**2′a**−**c** in a ratio highly dependent on irradiation time. The hydride migration

Scheme 1



leading to isomers **2′a**−**c** is photoinduced; no isomerization is observed in either direction at room temperature in the absence of irradiation.



Protonation of complexes **2** with $HBF_4{\cdot}OEt_2$ at low temperature in the presence of excess 2-butyne provides ring-expanded η^5-cycloheptadienyl complexes **3a**−**c** in reasonable isolated yields (Table 1, entries 1−3).[9−11] These results suggest that after protonation, hydride migration to the less substituted ring in complexes **2′** is rapid and favorable, leading to a single η^3-cyclopentenyl intermediate.[12] Similar ligand exchange using 1,2-dimethylcyclopentadiene[13] **1d** followed directly by in situ protonation in the presence of 2-butyne leads to 2,3,5,6(*exo*)-tetramethylcycloheptadienyl complex **3d**, albeit in low yield (entry 4). This product, spectroscopically identical to that obtained from allyl/2-butyne cycloaddition (eq 1), strongly supports the competency of intermediate **I** (R = Me, Cp′ = C_5Me_5) in the anomalous [3 + 2 + 2] cycloaddition.[5]

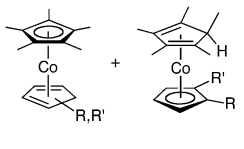
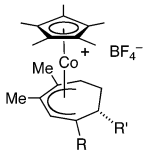
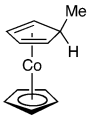
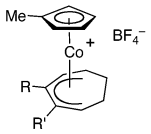
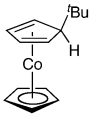
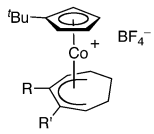
The ring expansion of complex **2** could not be generalized to other alkynes, arguably due to the limited steric accessibility of the metal center. The use of smaller ancillary ligands was thus investigated, beginning with the unsubstituted complex $(\eta^5\text{-}C_5H_5)\text{-}Co(\eta^4\text{-}C_5H_6)$.[14] All attempts to induce ring expansion by protonation of this complex in the presence of alkyne returned only cobaltocenium complex, $(\eta^5\text{-}C_5H_5)_2Co^+BF_4^-$.[15,16]

The incorporation of even one substituent into the system, however, results in a transformation of surprising generality. Thus, protonation of either the methyl- or *tert*-butyl-substituted complexes $(\eta^5\text{-}C_5H_5)Co(\eta^4\text{-}RC_5H_5)$ (R = Me, **4a**; *tert*-Bu, **4b**)[17] in the presence of a range of alkynes provides η^5-cycloheptadienyl complexes **5a**−**d** and **6a**−**f** in good to excellent yields after purification by chromatography on silica gel (Table 1).[9]

The reaction proceeds with remarkable regioselectivity, giving disubstituted η^5-cycloheptadienyl products from preferential activation of the unsubstituted cyclopentadienyl ring. The reactions of methylcyclopentadiene complex **4a** provide higher yields, but insertion of terminal alkyne leads to product mixtures arising from competitive activation of the more substituted ring (entry 8). Higher

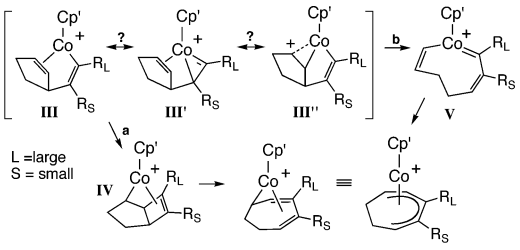
10.1021/ja047852+ CCC: $27.50

Table 1. Ring Expansion of Coordinated Cyclopentadienes[a]

Entry	Substrate	Alkyne	Product(s)	Yield[b]
				
1	**2a/2a'**	R, R' = H	**3a**	70
2	**2b/2b'**	R = Me, R' = H	**3b**	55
3	**2c/2c'**	R = H, R' = *tert*-Bu	**3c**	50
4	**2d/2d'**	R, R' = Me	**3d**	33
				
5	**4a**	R = *t*Bu, R' = Me	**5a**	85
6	**4a**	R = Me_3Si, R' = Me	**5b**	85
7	**4a**	R, R' = Me_3Si	**5c**	94
8	**4a**	R = *t*Bu, R' = H	**5d**	88[c]
				
9	**4b**	R = *t*Bu, R' = Me	**6a**	70
10	**4b**	R = Me_3Si, R' = Me	**6b**	72
11	**4b**	R, R' = Me_3Si	**6c**	74
12	**4b**	R = *t*Bu, R' = H	**6d**	66
13	**4b**	R, R' = Ph	**6e**	70
14	**4b**	R, R' = Me	**6f**	74

[a] Conditions: $HBF_4 \cdot OEt_2$, alkyne (≥2 equiv), CH_2Cl_2, −78 °C→rt.[9] [b] Yields of isolated, purified products. No significant formation of isomeric products is observed. [c] Formed as a 4:1 mixture with isomeric [(C_5H_5)Co(1-Me-3-*tert*-Bu-(1-5)η^5-cycloheptadienyl)][BF_4^-].

Scheme 2



selectivity and greater generality is observed in the *tert*-butylcyclopentadiene series (**4b**).[18]

The mechanism and regioselectivity of this reaction are consistent with the intermediacy of an agostic cyclopentenyl complex analogous to **II** (Scheme 1), provided that the (reversible) hydride migrations are accompanied by a kinetic preference for regioselective alkyne insertion to the less substituted η^3-cyclopentenyl ring. The resultant vinylcyclopentene intermediate **III** undergoes carbon−carbon bond activation, although the mechanism of this process is considerably more speculative (Scheme 2). Both indirect (path a) and direct (path b) variants can be proposed, with the indirect pathway being most conventional: migratory insertion to give strained σ,π-bicyclo[3.1.0]heptenyl intermediate **IV**, which undergoes cyclobutene ring opening[19] to give product. Less conventional pathways, involving β-carbon elimination from metallacyclopropene canonical (**III′**) or carbocation-like β-scission from an unsymmetrically bound olefin structure (**III″**), can also be considered. The mechanism of this reaction remains under investigation, both experimentally and computationally. Further optimization of the ancillary ligand and exploration of scope also remain under investigation. This unexpected new ring expansion reaction raises considerable promise for the use of electrophilic late transition metals in other synthetically valuable processes involving carbon−carbon bond activation.

Acknowledgment. Financial support from the NSERC of Canada and the University of Alberta is gratefully acknowledged. We thank Dr. Robert McDonald of the UA Structure Determination Laboratory for X-ray crystallography.

Supporting Information Available: Experimental procedures and complete characterization data for all new compounds and details of the X-ray crystallography for complex **6c** and the malonate adduct of **3a** (PDF, CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

References

(1) Reviews: (a) Murakami, M.; Ito, Y. In *Activation of Unreactive Bonds and Organic Synthesis*; Murai, S., Ed.; Topics in Organometallic Chemistry, Vol. 3; Springer: Berlin, 1999, pp 97−129. (b) Rybtchinski. B.; Milstein, D. *Angew. Chem., Int. Ed.* **1999**, *38*, 870−883.
(2) Recent references: (a) Brunkin, N. M.; Brestensky, D. M.; Jones, W. D. *J. Am. Chem. Soc.* **2004**, *126*, 3627−3641. (b) Nakazawa, H.; Kawasaki, T.; Miyoshi, K.; Suresh, C. H.; Koga, N. *Organometallics* **2004**, *23*, 117−126. (c) Datta, S.; Chang, C.-L.; Yeh, K.-L.; Liu, R.-S. *J. Am. Chem. Soc.* **2003**, *125*, 9294−9295. (d) Taw, F. L.; Mueller, A. H.; Bergman, R. G.; Brookhart, M. *J. Am. Chem. Soc.* **2003**, *125*, 9808−9813. (e) Shimada, T.; Yamamoto, Y. *J. Am. Chem. Soc.* **2003**, *125*, 6646−6647. (f) Bart, S. C.; Chirik, P. J. *J. Am. Chem. Soc.* **2003**, *125*, 886−887. (g) Jun, C.-H.; Moon, C. W.; Lee, D.-Y. *Chem. Eur. J.* **2002**, *8*, 2422−2428. (h) Xiao, N.; Zhang, S.; Qiu Z.; Li, R.; Wang, B.; Xu, Q.; Sun, J.; Chen, J. *Organometallics* **2002**, *21*, 3709−3715. (i) Mak, K. W.; Yeung, S. K. Chan, K. S. *Organometallics* **2002**, *21*, 2362−2364. (j) Müller, C.; Lachicotte, R. J.; Jones, W. D. *Organometallics* **2002**, *21*, 1975−1981. (k) Suginome, M.; Matsuda, T.; Yoshimoto, T.; Ito, Y. *Organometallics* **2002**, *21*, 1537−1539. (l) Agapie, T.; Diaconescu, P. L.; Mindiola, D. J.; Cummins, C. C. *Organometallics* **2002**, *21*, 1329−1340. (m) Müller, C.; Iverson, C. N. Lachicotte, R. J.; Jones, W. D. *J. Am. Chem. Soc.* **2001**, *123*, 9718−9719. (n) Rybtchinski, B.; Oevers, S.; Montag, M.; Vlgolak, A.; Rozenberg, H.; Martin, J. M. L.; Milstein, D. *J. Am. Chem. Soc.* **2001**, *123*, 9064−9077. (o) Miller, J. A. *Tetrahedron Lett.* **2001**, *42*, 6991−6993. (p) Murakami, M.; Tsuruta, T.; Ito, Y. *Angew. Chem., Int. Ed.* **2000**, *39*, 2484−2486.
(3) Extensive citations for σ-C−C bond activation are provided in ref 4.
(4) Older, C. M.; Stryker, J. M. *J. Am. Chem. Soc.* 2**000**, *122*, 2784−2797.
(5) Dzwiniel, T. D.; Etkin, N.; Stryker, J. M., *J. Am. Chem. Soc.* **1999**, *121*, 10640−10641.
(6) Carbon−carbon bond activation of Cp ligands: Xi, Z.; Sato, K.; Gao, Y.; Lu, J.; Takahashi, T. *J. Am. Chem. Soc.* **2003**, *125*, 9568−9569. Tillack, A.; Baumann, W.; Ohff, A.; Lefeber, C.; Spannnnberg, A.; Kempe, R.; Rosenthal, U. *J. Organomet. Chem.* **1997**, *520*, 187−193. For a comment, see: Kempe, R. *Angew. Chem., Int. Ed.* **2004**, *43*, 1463−1464.
(7) (a) Nichols, J. C.; Spencer, J. L. *Organometallics* **1994**, *13*, 1781−1787. (b) Cracknell, R. B.; Nichols, J. C.; Spencer, J. L. *Organometallics* **1996**, *15*, 446−448. Spencer observed no cyclopentenyl ring opening at 25 °C.
(8) Nicholls, J. C.; Spencer, J. L. *Inorg. Synth.* **1990**, *28*, 278−280.
(9) Complete experimental details are provided in Supporting Information.
(10) Assignment of **3a** was confirmed by alkylation with $NaCH(CO_2Me)_2$ (73% yield) and X-ray crystallography of the η^4-cycloheptadiene adduct.[9]
(11) (a) Use of triflic acid instead of HBF_4 fails to afford ring-expansion, instead producing $(C_5Me_5)Co(C_5H_5)^+OTf^-$.[11b] (b) PF_6 salt: Koelle, U.; Khouzami, F. *Angew. Chem., Int. Ed. Engl.* **1980**, *19*, 640−641.
(12) No competitive cleavage of the permethylated ring is detected. The difference in position of the *tert*-butyl and methyl substituents in **3c** and **3b** presumably reflects steric bulk-dependent positional preferences in the hydride migrations that produce the η^3-cyclopentenyl intermediates.
(13) (a) Holm, K. H.; Skatteboel, L. *Acta Chem. Scand.* **1984**, *B38*, 783−794. (b) Experimental procedures: Boag, N. M. Personal communication.
(14) Green, M. L. H.; Pratt, L.; Wilkinson, G. *J. Chem. Soc.* **1959**, 3753−3767.
(15) King, R. B.; Stone, F. G. A. *Inorg. Synth.* **1963**, *7*, 99−115.
(16) Dehydrogenation to cobaltocenium occurs either in the presence or absence of alkyne; similar transformations have been previously reported.[7a]
(17) Prepared by nucleophilic alkyation of $(C_5H_5)_2Co^+BF_4^-$: Lehmkuhl, H.; Nehl, H. F. *Chem. Ber.* **1984**, *117*, 3443−3456. Lutsenko, Z. L.; Aleksandrov, G. G.; Petrovskii, P. V.; Shubina, E. S.; Andrianov, V. G.; Struchkov, Y. T.; Rubezhov, A. Z. *J. Organomet. Chem.* **1985**, *281*, 349−364.
(18) Reactions of complex **4a** with diphenylacetylene and 2-butyne give intractable product mixtures and/or low yields. Reactions with ethyne do not involve bond activation and will be discussed elsewhere. Neither complex reacts with electron-deficient alkynes to yield ring-expanded products.
(19) *Disrotatory* ring opening of coordinated cyclobutenes: Slegeir, W.; Case, R. McKennis, J.; Pettit, R. *J. Am. Chem. Soc.* **1974**, *96*, 287−288. Pinhas, A. R.; Carpenter, B. K. *J. Chem. Soc., Chem. Commun.* **1980**, 15−17.

JA047852+