A New Metal-Mediated Cyclization: Conversion of a Metallacyclobutene and Alkyne Substrates to η^4-Cyclopentadiene Products

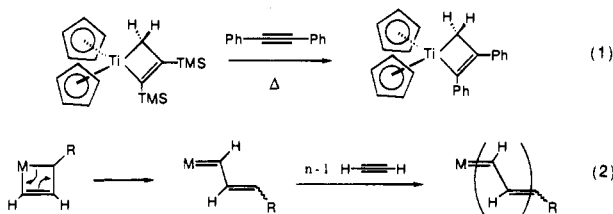Joseph M. O'Connor,* Bella S. Fong, Hong-Li Ji,[†] and Kristin Hübner

Department of Chemistry and Biochemistry (0358)
9500 Gilman Drive, University of California, San Diego
La Jolla, California 92093-0358

Arnold L. Rheingold*

Department of Chemistry, University of Delaware
Newark, Delaware 19716

Metallacyclopentadienes and metallacyclopentenes have been widely developed as reagents and reactive intermediates for the synthesis of carbocycles.[1,2] In principle, metallacyclobutene complexes should undergo analogous reactions to provide five-membered carbocycles. The only previous literature report of well-defined metallacyclobutene−alkyne chemistry is Tebbe's alkyne exchange reaction (1).[3] There is also evidence that metallacyclobutenes and their vinylalkylidene isomers are key intermediates in alkyne polymerization reactions (2).[4] Herein we demonstrate the unprecedented reaction of a metallacyclobutene with alkyne substrates to generate η^4-cyclopentadiene complexes.

(1)

(2)

Previously we have reported the reaction of carbon monoxide and cobaltacyclobutene $(\eta^5\text{-}C_5H_5)(PPh_3)\overline{Co[C(SO_2Ph)=C}$-$(TMS)CH(CO_2Et)]$ (1)[5a] to give vinylketene complex **2**, which

Scheme 1

is converted in high yield to the corresponding furan and $(\eta^5\text{-}C_5H_5)Co(CO)_2$.[5b] We have now determined that **1** undergoes a highly regioselective reaction with a range of alkyne substrates to give η^4-cyclopentadiene products (**3**) in good to excellent yields (Scheme 1).

When a benzene solution of **1** (0.42 mmol, 0.01 M) and methyl propiolate (0.82 mmol) is heated for 72 h at 75 °C, the η^4-cyclopentadiene product *exo*-**3a** (R = H, R^1 = CO_2Me) is generated and isolated as an analytically pure black crystalline solid in 90% yield.[6] In the ^1H NMR spectrum ($CDCl_3$) of *exo*-**3a**, singlets at δ 3.61 and 6.60 are assigned to the cyclopentadiene ring hydrogens. The indicated stereochemistry is supported by the observation of a NOE at the δ 3.61 singlet upon irradiation of the η^5-cyclopentadienyl hydrogen resonance in the ^1H NMR spectrum. In the $^{13}C(^1H)$ NMR spectrum ($CDCl_3$), resonances at 41.0 ($^1J_{CSi^{29}}$ = 63 Hz), 104.7, 84.3 ($^1J_{CH}$ = 187 Hz), 45.3, and 58.5 ($^1J_{CH}$ = 147 Hz) ppm are assigned to the η^4-cyclopentadiene ring carbons C(1)−C(5), respectively. The proposed regio- and stereochemistry were verified by an X-ray crystal structure analysis of *exo*-**3a**.[6]

As listed in Table 1, a range of alkynes undergo this new cyclization reaction.[6] Both terminal and internal alkynes which bear the sterically nondemanding methoxycarbonyl substituent give excellent yields of η^4-cyclopentadiene product as a single diastereomer in each case (*exo*-**3a**−**c**). Notably, the electron-rich alkyne, ethyl ethynyl ether, provides cyclopentadiene complex *exo*-**3d** in excellent yield. Also of interest with respect to subsequent elaboration of the cyclopentadiene products is the observation that primary halides are tolerated in the alkyne substituent **3h**. In the case of terminal alkynes bearing alkyl or phenyl substituents, the yields are sensitive to the steric bulk of the alkyl group, varying from 100% in the case of phenylacetylene (**3f**) to 67% for *tert*-butylacetylene (**3k**). There is a remarkable dependence of diastereoselectivity on the size of the alkyne substituent. Alkynes with small substituents give only *exo* product (**3a**−**e**), phenyl and most alkyl substituent result in both *exo* and *endo* product (**3f,h**−**j**), and the bulky *tert*-butylacetylene gives only *endo* product (**3k**).[7] For disubstituted alkynes, diastereoselectivity is influenced by both substituents. Thus, phenylacetylene gives **3f** as a 67:33 ratio of *exo* to *endo* isomers, whereas 4-phenyl-3-butyn-2-one gives only endo isomer **3g**.[7]

The formation of **3** from **1** and alkyne presumably involves loss of phosphine to give **4**, followed by alkyne addition to the metallacycle to give η^4-metallacyclohexadiene intermediate **5**, and subsequent reductive elimination to **3** (Scheme 2). Based on related coupling reactions of **1** with CO, isocyanide, and ethyl diazoacetate, we believe that the alkyne initially reacts at the cobalt−vinyl bond in preference to the sp³-carbon−cobalt
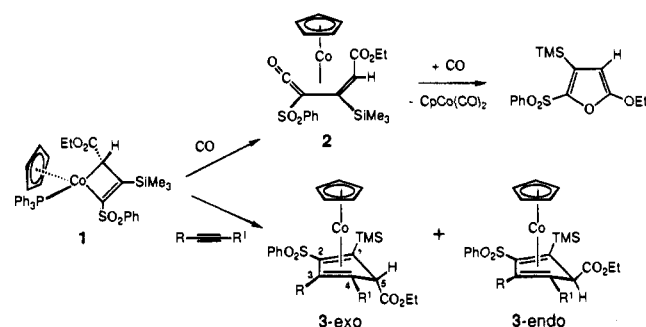
[†] Department of Chemistry, University of Nevada, Reno, NV 89557.

(1) For leading references to cobalt systems: (a) Boese, R.; Harvey, D. F.; Malaska, M. J.; Vollhardt, K. P. C. *J. Am. Chem. Soc.* **1994**, *116*, 11153. (b) Saa, C.; Crotts, D. D.; Hsu, G.; Vollhardt, K. P. C. *Synlett* **1994**, 487. (c) Grotjahn, D. B.; Vollhardt, K. P. C. *Synthesis* **1993**, 579. (d) Vollhardt, K. P. C. *Pure Appl. Chem.* **1993**, *65*, 153. (e) Vollhardt, K. P. C. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 539. (f) Schore, N. E. *Org. React. (N. Y.)* **1991**, *40*, 1. (g) Schore, N. E. *Chem. Rev.* **1988**, *88*, 1081. (h) Schore, N. E. In *Comprehensive Organic Synthesis*; Trost, B. M., Fleming, I. Eds.; Pergamon: Oxford, U.K., 1991; Chapter 9.1 and 9.4. (i) Jeong, N.; Hwang, S. H.; Lee, Y.; Chung, Y. K. *J. Am. Chem. Soc.* **1994**, *116*, 3159. (j) Hoye, T. R.; Suriano, J. A. *J. Org. Chem.* **1993**, *58*, 1659. (k) Verdaquer, X.; Moyano, A.; Pericàs, M.; Riera, A.; Benardes, U.; Greene, A. E.; Alvarez-Larena, A.; Piniello, J. F. *J. Am. Chem. Soc.* **1994**, *116*, 2153. (l) Krafft, M. E.; Scott, I. L.; Romero, R. H.; Feibelmann, S.; Van Pelt, C. E. *J. Am. Chem. Soc.* **1993**, *115*, 7199. (m) Pauson, P. L. In *Organometallics in Organic Synthesis*; de Meijere, A., tom Dieck, H., Eds.; Springer-Verlag: Berlin, 1987; p 233.

(2) For leading references to non-cobalt metals: (a) Trost, B. M.; Tanoury, G. J.; Lautens, M.; Chan, C.; MacPherson, D. T. *J. Am. Chem. Soc.* **1994**, *116*, 4255. (b) Berk, S. C.; Grossman, R. B.; Buchwald, S. L. *J. Am. Chem. Soc.* **1994**, *116*, 8593. (c) Eaton, B. E.; Rollman, B.; Kaduk, J. A. *J. Am. Chem. Soc.* **1992**, *114*, 6245. (d) Negishi, E.-I.; Holmes, S. J.; Tour, J. M.; Miller, J. A. *J. Am. Chem. Soc.* **1985**, *107*, 2568. (e) Pearson, A. J.; Dubbert, R. A. *J. Chem. Soc., Chem. Commun.* **1991**, 202. (f) Tamao, K.; Kobayashi, K.; Ho, Y. *Synlett* **1992**, 539. (g) Oppolzer, W. *Pure Appl. Chem.* **1990**, *62*, 1941. (h) Keese, R.; Guidetti-Grept, R.; Herzog, B. *Tetrahedron Lett.* **1992**, *33*, 1207. (i) Ihle, N. C.; Heathcock, C. H. *J. Org. Chem.* **1993**, *58*, 560.

(3) Tebbe, F. N.; Harlow, R. L. *J. Am. Chem. Soc.* **1980**, *102*, 6150.

(4) Fox, H. H.; Wolf, M. O.; O'Dell, R.; Liu, B. L.; Schrock, R. R.; Wrighton, M. S. *J. Am. Chem. Soc.* **1994**, *116*, 2827 and references therein.

(5) (a) O'Connor, J. M.; Ji, H.; Iranpour, M.; Rheingold, A. L. *J. Am. Chem. Soc.* **1993**, *115*, 1586. (b) O'Connor, J. M.; Ji, H.-J.; Rheingold, A. L. *J. Am. Chem. Soc.* **1993**, *115*, 9846.
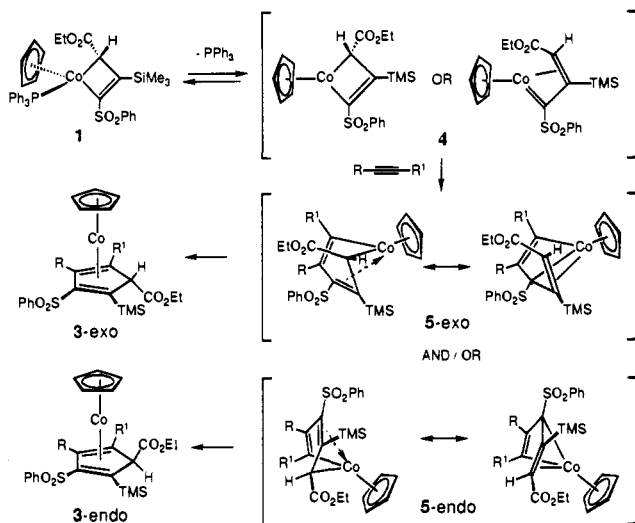
(6) See supporting information for full characterization.

(7) The *endo* assignment for the cyclopentadiene complexes **3g,k** has been confirmed by X-ray crystallographic analysis.

8030   *J. Am. Chem. Soc., Vol. 117, No. 30, 1995*

Communications to the Editor

Table 1. Cycloaddition Products **3** from Reaction of **1** with Alkyne[a]

compd	R	R[1]	% yield (exo/endo)	temp (°C)	time (h)
3a	H	CO$_2$Me	93 (exo)	75	72
3b	Me	CO$_2$Me	93 (exo)	78	30
3c	CO$_2$Me	CO$_2$Me	99 (exo)	75	48
3d	OCH$_2$CH$_3$	H	92 (exo)	60	12
3e	H	CH$_2$OMe	96 (exo)	75	12
3f	H	Ph	100 (67/33)	75	6
3g	COMe	Ph	63 (endo)	70	56
3h	H	CH$_2$CH$_2$CH$_2$Cl	87 (58/29)	60	44
3i	H	CH$_2$CH$_2$CH$_3$	93 (56/37)	40	72
3j	H	CH(Me)Et	79 (43/[36])[b]	70	27
3k	H	CMe$_3$	67 (endo)	70	24

[a] Yields by ^{1}H NMR spectroscopy relative to 1,4-C$_6$H$_4$TMS$_2$ as internal standard. For a representative procedure, see text. [b] *endo*-**3j** was not isolated.
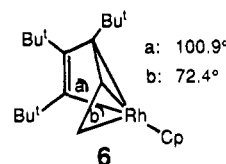
Scheme 2

bond.[5] Should the metallacyclobutene first rearrange to a vinylcarbene isomer, then this step would involve a [2 + 2]-cycloaddition of the alkyne and the cobalt–carbon double bond of a vinylcarbene.[8,9] The observed diastereoselectivity can be rationalized as due to the steric interactions at the transition state leading to **5**, or at intermediate **5** itself, should *exo*-**5**/*endo*-**5** interconversion be rapid relative to the rate of reductive cyclization (Scheme 2). For bulky alkyne substituents, *exo*-**5** is disfavored relative to *endo*-**5** due to an unfavorable steric interaction between the ester substituent and R/R[1]. For small alkyne substituents, *endo*-**5** is disfavored relative to *exo*-**5** due to steric interactions between the ester and the cyclopentadienyl ligand and the TMS substituent.

Hughes and co-workers have extensively studied η^4-cyclopentadiendiyl complexes[10] related to **5**, and the solid state

structure of rhodium complex **6** has been reported.[10c] Conver-

6

sion of **6** to an η^4-cyclopentadiene complex does not occur at 110 °C (45 days); however, the indenyl analogue gives an η^4-cyclopentadiene complex in refluxing benzene.

Oxidative decomplexation of highly substituted cyclopentadiene ligands from cobalt is well precedented.[11] In a preliminary study, oxidation of **3d** with FeCl$_3$·6H$_2$O in acetonitrile gave the cyclopentenone C(TMS)=C(SO$_2$Ph)C(=O)CH$_2$CH(CO$_2$Et) (**7**) in 62% unoptimized yield.

Metallacyclobutene **1** is formed from CpCo(PPh$_3$)-(TMSC≡CSO$_2$Ph) and ethyl diazoacetate.[5a] The formation of **3** therefore represents the metal-mediated coupling of two alkynes and a carbene. We previously reported the formation of highly substituted η^4-cyclopentadiene cobalt complexes from cobaltacyclopentadienes and ethyl diazoacetate;[12] however, the metallacyclobutene route reported here is vastly superior to the metallacyclopentadiene route in terms of both scope and yields.[13] Efforts are currently underway to extend this new chemistry to the preparation of fused ring carbocycles by reaction of cobalt alkyne complexes with diazo compounds which contain pendent ene and yne functionality.

Note Added in Proof: For the reaction of terminal alkynes with a zirconium metallacyclobutene complex to give acetylides, see: Binger, P.; Müller, P.; Herrmann, A. T.; Philipps, P.; Gabor, B.; Langhauser, F.; Krüger, C. *Chem. Ber.* **1991**, *124*, 2165.

(8) For early transition metal metallacyclobutene to vinyl carbene isomerizations, see: (a) Doxsee, K. M.; Mouser, J. K. M.; Rarahi, J. B. *Synlett* **1992**, 13. (b) Doxsee, K. M.; Juliette, J. J. J.; Mouser, J. K. M.; Zientara, K. *Organometallics* **1993**, *12*, 4742. (c) Reference 4. (d) Hofmann, P.; Hämmerle, M.; Unfied, G. *New. J. Chem.* **1991**, *15*, 769.

(9) Vinylcarbene complexes of the chromium triad react with alkynes to give cyclopentadiene or cyclopentadiene-derived products; for lead references, see: (a) Duetsch, M.; Vidoni, S.; Stein, F.; Funke, F.; Notemeyer, M.; de Meijere, A. *J. Chem. Soc., Chem. Commun.* **1994**, 1679. (b) Duetsch, M.; Lackmann, R.; Stein, F.; de Meijere, A. *Synlett* **1991**, 324. (c) Harvey, D. F.; Grenzer, E. M.; Gantzel, P. K. *J. Am. Chem. Soc.* **1994**, *116*, 6719. (d) Wulff, W. D.; Bax, B. M.; Brandvold, T. A.; Chan, K. S.; Gilbert, A. M.; Hsung, R. P.; Mitchell, J.; Clardy, J. *Organometallics* **1994**, *13*, 102. (e) Barluenga, J.; Aznar, F.; Martín, A.; García-Granda, S.; Pérez-Carreño, E. *J. Am. Chem. Soc.* **1994**, *116*, 11191. (f) Gross, M. F.; Finn, M. G. *J. Am. Chem. Soc.* **1994**, *116*, 10921.

(10) (a) Donovan, B. T.; Hughes, R. P.; Kowalski, A. S.; Trujillo, H. A.; Rheingold, A. L. *Organometallics* **1993**, *12*, 1038. (b) Donovan, B. T.; Hughes, R. P.; Trujillo, H. A. *J. Am. Chem. Soc.* **1990**, *112*, 7076. (c) Donovan, B. T.; Egan, J. W., Jr.; Hughes, R. P.; Trujillo, H. A.; Rheingold, A. L. *Isr. J. Chem.* **1990**, *30*, 351. (d) Hughes, R. P.; Robinson, D. J. *Organometallics* **1989**, *8*, 1015. (e) Egan, J. W., Jr.; Hughes, R. P.; Rheingold, A. L. *Organometallics* **1987**, *6*, 1578. (f) Grabowski, N. A.; Hughes, R. P.; Jaynes, B. S.; Rheingold, A. L. *J. Chem. Soc., Chem. Commun.* **1986**, 1694.

(11) For conversion of highly substituted CpCo(cyclopentadiene) complexes to free diene, or alternatively, to substituted η^5-cyclopentadienyl ligands, see: O'Connor, J. M.; Johnson, J. A. *Synlett* **1989**, 57. Gesing, E. R. F.; Tane, J. P.; Vollhardt, K. P. C. *Angew. Chem., Int. Ed. Engl.* **1980**, *19*, 1023. Tane, J. P.; Vollhardt, K. P. C. *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 617.

(12) O'Connor, J. M.; Pu, L.; Unrhammer, R.; Johnson, J. A. *J. Am. Chem. Soc.* **1989**, *111*, 1889.

(13) For a further comparison, cobaltacyclopentene complexes have been reported to react with alkynes to give η^4-cyclohexadiene complexes in 43−46% yield: Wakatsuki, Y.; Aoki, K.; Yamazaki, H. *J. Am. Chem. Soc.* **1979**, *101*, 1123.