J. Am. Chem. Soc. 1993, 115, 9846–9847

Late Metal Metallacyclobutene Chemistry: Conversion to η^4-Vinylketene, η^4-Vinylketenimine, and Furan Products

Joseph M. O'Connor*,† and Hong-Li Ji

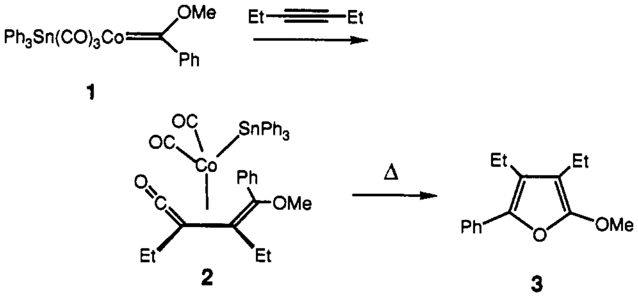
Department of Chemistry (216)
University of Nevada
Reno, Nevada 89557

Arnold L. Rheingold*

Department of Chemistry
University of Delaware
Newark, Delaware 19716

Received May 19, 1993

Metallacyclobutene complexes have been proposed as intermediates in a number of fascinating and often synthetically useful reactions of metal carbenes with alkynes.[1,2] For example, Wulff previously proposed a metallacyclobutene intermediate in the conversion of cobalt carbene complex **1** and 3-hexyne to vinylketene **2**.[2,3] At higher temperatures, 2-alkoxyfurans, **3**, are the exclusive products.[4] In fact, examples of observable[5] or isolable[6] late metal metallacyclobutenes are rare, reactivity studies have not been previously reported, and the very existence of metallacyclobutene intermediates in many reactions for which they have been proposed has been called into question by the theoretical work of Hofmann.[7] Herein we report the first reactivity studies on late metal metallacyclobutenes including direct evidence for the frequently proposed metallacyclobutene to η^4-vinylketene conversion,[1a,e,2,5b] evidence for a metallacyclobutene to furan conversion, and the formation of a η^4-vinylketenimine complex from **4** and *tert*-butylisocyanide. These results also provide for the first comparisons of late and early metal metallacyclobutene reactivity.



1

2

3

When a benzene-d_6 solution of cobaltacyclobutene ($(\eta^5$-$C_5H_5)(PPh_3)CoC(H)(CO_2Et)C(Si(CH_3)_3){=}C(SO_2Ph)$) (**4**)[8] (0.03 mmol, 0.01 M) is heated at 75 °C for 14 h under 1 atm. of carbon monoxide, η^4-vinylketene **5**, η^4-pyrone **6**, furan **7**, and $(\eta^5$-$C_5H_5)Co(CO)_2$ are formed in ca. 7:1:9:9 ratio (85% conversion), respectively, as determined by ^1H NMR spectroscopy on the crude reaction mixture (Scheme I).[9] In a preparative scale experiment, **5** and **6** were isolated in 30% and 2% yield, respectively.

The ^1H NMR spectrum of vinylketene **5** in benzene-d_6 exhibits broad singlets at δ 4.81 (5H, C_5H_5) and 4.17 (1H), the latter resonance attributed to a vinyl hydrogen syn to the trimethylsilyl substituent.[3] In $CDCl_3$ solution, the resonances for **5** remained broad down to −60 °C but sharpened at +60 °C in the variable-temperature ^1H NMR spectra. It thus appears that **5** exists in equilibrium with one or more unidentified cobalt complexes.[10]

The ^1H NMR spectrum of η^4-pyrone **6** in benzene-d_6 exhibits well-resolved resonances including a singlet at δ 4.72 (5H, C_5H_5) and a vinyl hydrogen resonance at δ 3.01 (s, 1H).[9,11] The structure of **6**, determined from an X-ray crystal structure analysis,[12] suggests that it may be a rearrangement product of vinylketene **5**. Indeed, thermolysis of either **5** or **6** in benzene-d_6 at 75 °C under 1 atm of CO leads to an equilibrium mixture of **5** and **6** (5:1 ratio), which is slowly converted to furan **7** (94% yield) and $(\eta^5$-$C_5H_5)Co(CO)_2$ in a 1:1 ratio.

Two reasonable mechanisms for the formation of furan **7** from **5** both involve deinsertion of carbon monoxide to generate a new metallacyclobutene complex (**A**). A 1,3-shift of cobalt from the sp^3 carbon to the ester oxygen leads to oxametallacycle **B**, and reductive elimination gives **7**. Alternatively, rearrangement of **A** to a vinyl carbene (**C**) and addition of the ester carbonyl to the carbene carbon (**D**) would also lead to furan **7** (Scheme II).[13,14]

When *tert*-butylisocyanide is added to a benzene solution of **4** (265 mg, 0.37 mmol, 7.5×10^{-3} M) and the mixture is heated

---

[†] Address correspondence to this author at Department of Chemistry (0358), University of California at San Diego, La Jolla, CA 92093-0506.

(1) (a) Wulff, W. D. In *Advances in Metal-Organic Chemistry*; Liebeskind, L. C., Ed.; JAI Press Inc.: Greenwich, CT, 1989; Vol. 1. (b) Dötz, K. H.; Fügen-Köster, B. *Chem. Ber.* **1980**, *113*, 1449. (c) Katz, T. J.; Lee, S. J.; Nair, M.; Savage, E. B. *J. Am. Chem. Soc.* **1980**, *102*, 7940. (d) Casey, C. P.; Polichnowski, S. W.; Shusterman, A. J.; Jones, C. R. *J. Am. Chem. Soc.* **1979**, *101*, 7282. (e) Semmelhack, M. F.; Ho, S.; Steigerwald, M.; Lee, M. C. *J. Am. Chem. Soc.* **1987**, *109*, 4397.

(2) (a) Wulff, W. D.; Gilbertson, S. R.; Springer, J. P. *J. Am. Chem. Soc.* **1986**, *108*, 420. (b) McCallum, J. S.; Kunag, F. A.; Gilbertson, S. R.; Wulff, W. D. *Organometallics* **1988**, *7*, 2346.

(3) For recent work on the synthesis, characterization, and reactivity of cobalt-coordinated vinylketenes, see: Huffman, M. A.; Liebeskind, L. S.; Pennington, W. T. *Organometallics* **1992**, *11*, 255.

(4) For the copper and rhodium acetate-mediated conversions of alkyne and diazocarbonyl substrates to furans, see: (a) Breslow, R.; Chipman, D. *Chem. Ind.* **1960**, 1105. (b) Davies, H. M. L.; Romines, K. R. *Tetrahedron* **1988**, *44*, 3343. (c) Padwa, A.; Kinder, F. R. *J. Org. Chem.* **1993**, *58*, 21 and references therein.

(5) For suggested spectroscopic observations of late metal metallacyclobutene complexes, see: (a) Foley, H. C.; Strubinger, L. M.; Targos, T. S.; Geoffroy, G. L. *J. Am. Chem. Soc.* **1983**, *105*, 3064. (b) Semmelhack, M. F.; Tamura, R.; Schattner, W.; Springer, J. *J. Am. Chem. Soc.* **1984**, *106*, 5363.

(6) (a) Calabrese, J. C.; Roe, D. C.; Thorn, D. L.; Tulip, T. H. *Organometallics* **1984**, *3*, 1223. (b) Bianchini, C.; Mealli, C.; Meli, A.; Sabat, M. *Organometallics* **1985**, *4*, 421. (c) Hemond, R. C.; Hughes, R. P.; Robinson, D. J.; Rheingold, A. L. *Organometallics* **1988**, *7*, 2239. (d) O'Connor, J. M.; Pu, L.; Woolard, S.; Chadha, R. K. *J. Am. Chem. Soc.* **1990**, *112*, 6731. (e) Casey, C. P.; Yi, C. S. *J. Am. Chem. Soc.* **1992**, *114*, 6597.

(7) (a) Hofmann, P.; Hämmerle, M. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 908. (b) Hofmann, P.; Hämmerle, M.; Unfied, G. *New J. Chem.* **1991**, *15*, 769.

(8) O'Connor, J. M.; Ji, H.-L.; Iranpour, M.; Rheingold A. L. *J. Am. Chem. Soc.* **1993**, *115*, 1586.

(9) See supplementary materials for full characterization of **5**–**8**-*anti*. For **5**: IR(C_6H_6) 1838 (s), 1713 (s) cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.52 (s, 9H, Si(CH_3)$_3$), 0.90 (br, t, *J* = 8.21 Hz, 3H, CH_3), 3.69 (m, 1H, C*H*HCH_3), 3.81 (m, 1H, CH*H*CH_3), 4.22 (s, 1H, CH), 5.26 (s, 5H, C_5H_5), 7.3–7.9 (m, 5H, Ph); $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 1.3, 13.8, 45.4, 60.4, 83.6, 86.7, 93.8, 127.6, 128.9, 133.4, 140.4, 173.1, 215.0. For **7**: IR (C_6D_6) 1587 cm^{-1}; ^1H NMR (C_6D_6) δ 0.46 (s, 9H, $SiMe_3$), 0.80 (t, *J* = 7.2 Hz, 3H, CH_3), 3.30 (q, *J* = 7.2 Hz, 2H, OCH_2) 4.94 (s, 1H, =CH), 6.84–8.08 (m, 5H, C_6H_5); $^{13}C\{H\}$ NMR (C_6D_6) δ −0.3, 14.1, 67.1, 88.2, 127.8, 129.1, 132.6, 132.8, 142.1, 142.4, 163.4. For **8**-*anti*: IR (C_6D_6) 1700 (s), 1735 (s) cm^{-1}; ^1H NMR (C_6D_6) δ 0.52 (s, 9H, Si(CH_3)$_3$), 0.66 (t, *J* = 7.2 Hz, 3H, CH_3), 1.30 (s, 9H, C(CH_3)$_3$), 3.67 (m, 1H, C*H*HCH$_,$, 3.65 (m, 1H, CH*H*CH_3), 3.80 (s, 1H, CH), 4.93 (s, 5H, C_5H_5), 6.9–7.0 (m, 3H, C_6H_5), 8.1–8.2 (m, 2H, C_6H_5); $^{13}C\{^1H\}$ NMR (C_6D_6) δ 1.4, 13.7, 29.7, 42.1, 55.7, 59.7, 63.0, 85.2, 87.8, 128.2, 128.6, 132.5, 140.7, 169.8, 173.0.

(10) In acetone-d_6 the ^1H NMR spectrum of **5** is broad at room temperature, but at −90 °C two distinct compounds are observed with cyclopentadienyl singlets at δ 5.34 and 5.21 in a 2:1 ratio. The low-temperature ^{13}C NMR spectroscopic data did not allow for a structural assignment due to inadequate signal intensities in the carbonyl region of the spectrum.

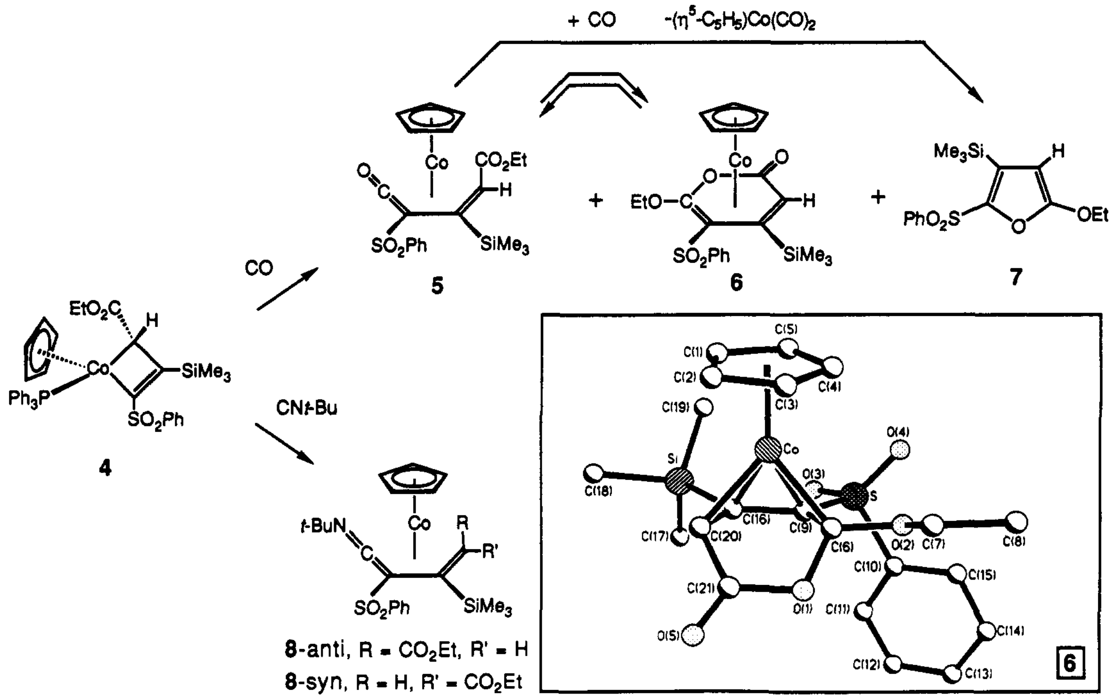
(11) For iron pyrone complexes, see: (a) Semmelhack M. F.; Tamura, R.; Schnatter, W.; Park, J.; Steigerwald, M.; Ho, S. *Stud. Org. Chem.* (*Amsterdam*) **1986**, *25*, 21. (b) Mitsudo, T.; Orino, Y.; Komiya, Y.; Watanabe, H.; Watanabe, Y. *Organometallics* **1983**, *2*, 1202. (c) Rosenblum, M.; Gatsonis, C. *J. Am. Chem. Soc.* **1967**, *89*, 5074.

(12) For **6**: $C_{21}H_{25}CoO_5SSi$, triclinic, $P\bar{1}$, $a = 8.059$, $b = 9.170(2)$, and $c = 15.344(4)$ Å, $\alpha = 79.28(2)$, $\beta = 88.39(2)$, $\gamma = 84.97(2)°$, $V = 1109.3(6)$ Å^3, $Z = 2$, μ(Mo Kα) = 9.42 cm^{-1}, $T = 296$ K. Of 5291 data collected (Siemens P4, 2θ(max) = 55°), 5100 were independent and 4108 were observed ($4\sigma F_o$). With all non-hydrogen atoms anisotropic and all hydrogen atoms idealized, $R(F) = 3.57\%$ and $R(wF) = 4.86\%$.

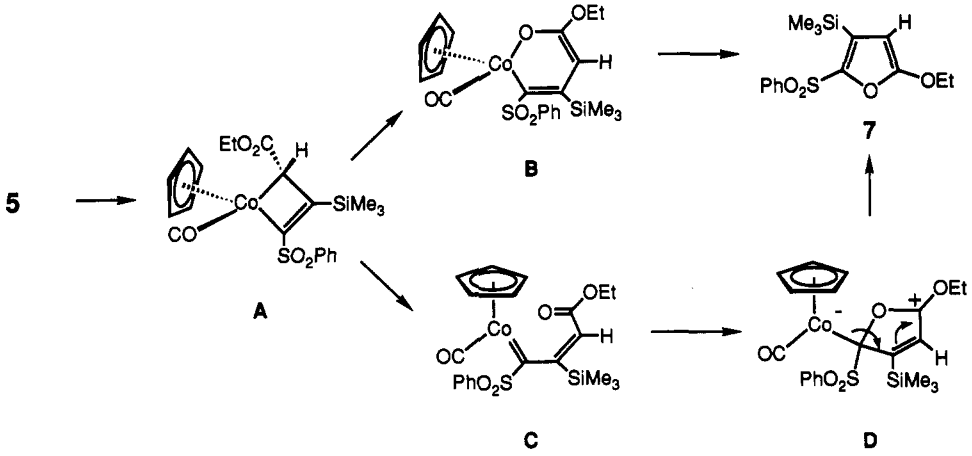
(13) The proposed **C** to **D** to furan **7** sequence is essentially identical to a portion of the mechanistic proposal suggested by Wulff for furan formation from **1**.[2a]

0002-7863/93/1515-9846$04.00/0

Scheme I



Scheme II



at 50 °C for 24 h, two vinylketenimine complexes are isolated following chromatographic workup (silica gel, 5% ethyl acetate/benzene): **8**-*anti* (79 mg, 40% yield) and **8**-*syn* (42 mg, 21% yield).[9,14,15]

To compare the structures of an analogous pair of vinylketene and vinylketenimine cobalt complexes and to confirm the proposed connectivity and stereochemistry, X-ray diffraction studies were carried out on both vinylketene **5** and vinylketenimine **8**-*anti* (see supplementary material). The structural data confirm that carbon monoxide and isocyanide have formally coupled to the sp^2 α-carbon of the metallacyclobutene ring rather than the sp^3 carbon. The mechanism of these coupling reactions may involve CO insertion or a metallacyclobutene to vinylcarbene rearrangement followed by carbene–CO ligand coupling.[14,16]

The conversion of **4** to **5** and **8** allows for the first comparisons of early and late metal metallacyclobutene reactivity patterns. Grubbs previously reported the rection of a bis(cyclopentadienyl)-titanacyclobutene complex with carbon monoxide to give an η^2-(C,O)-vinylketene and with *tert*-butylisocyanide to give an imino-acyl complex in which the isocyanide substrate has formally inserted into the (sp^3)carbon–titanium bond.[17] Although it is not known if **5** and **8** are kinetic coupling products, it is clear that the isocyanide insertion regioselectivity is complementary for the cobalt and titanium metallacyclobutenes studied to date.

Acknowledgment. Support of the National Science Foundation is gratefully acknowledged. Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial suppor of this research. We thank the American Cancer Society Junior Faculty Fellowship Program for support of our programs.

Supplementary Material Available: Characterization data, listings of fractional coordinates, bond distances, bond angles, hydrogen atom coordinates, and thermal parameters for **5**–**8** (31 pages); tables of observed and calculated structure factors (42 pages). Ordering information is given on any current masthead page.

---

(14) As pointed out by a referee, cyclopentadienyl ligand ring slippage is well precedented and may play a role in possible metallacyclobutene to η^3-vinylcarbene transformations for the **4** to **5** and **8** conversions as well as the **5** to **7** conversion. See: O'Connor, J. M.; Casey, C. P. *Chem. Rev.* **1987**, *87*, 307.

(15) For a leading reference on the synthesis and reactivity of iron vinylketenimine complexes, see: Richards, C. J.; Thomas, S. E. *Tetrahedron: Assymmetry* **1992**, *3*, 143.

(16) For selected examples of CO/sp^2 carbon coupling, see: (a) Klimes, J.; Weiss, E. *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 205. (b) Herrmann, W. A.; Planck, *J. Angew. Chem., Int. Ed. Engl.* **1976**, *15*, 615.

(17) (a) Meinhart, J. D.; Santarsiero, B. D.; Grubbs, R. H. *J. Am. Chem. Soc.* **1986**, *108*, 3318. (b) For nitrile insertions into titanacyclobutenes, see: Doxsee, K. M.; Mouser, J. K. M. *Organometallics* **1990**, *9*, 3012.