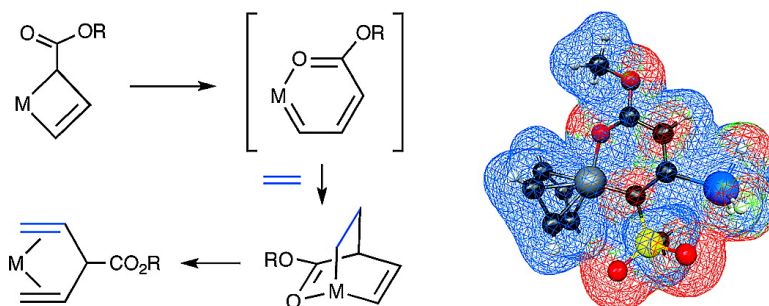Communication

# Reactions of a Metallacyclobutene Complex with Alkenes

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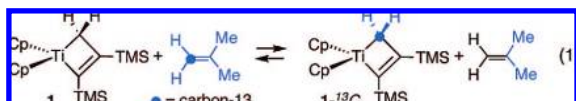
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# Reactions of a Metallacyclobutene Complex with Alkenes

Ryan L. Holland,[†] Kevin D. Bunker,[†] Christopher H. Chen,[†] Antonio G. DiPasquale,[†]
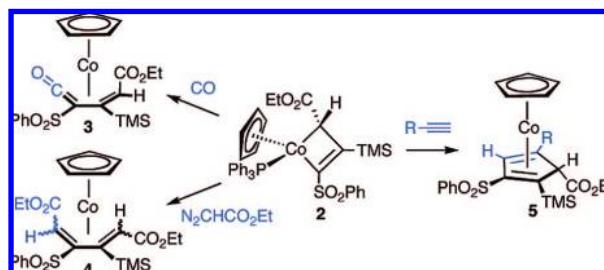Arnold L. Rheingold,*,[†] Kim K. Baldridge,*,[‡] and Joseph M. O'Connor*,[†]

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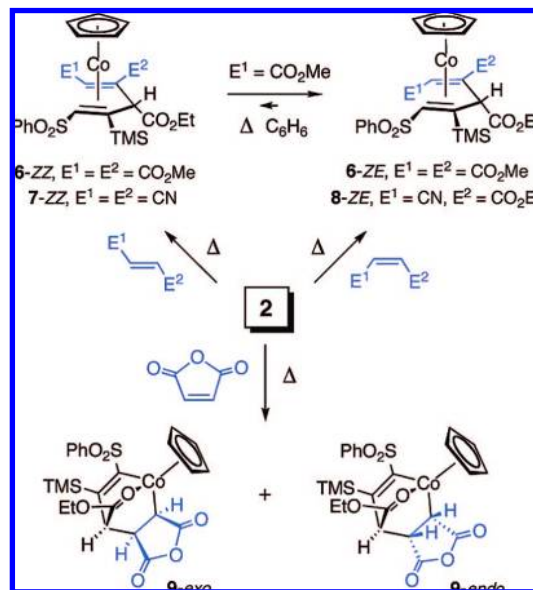Received May 18, 2008; E-mail: jmoconnor@ucsd.edu; kimb@oci.uzh.ch; arheingold@ucsd.edu

The reactions of alkenes with metallacyclopentadienes and metallacyclobutanes have been widely developed as synthetic methodology.[1] In contrast, metallacyclobutene chemistry remains largely unexplored.[2,3] Metallacyclobutenes have been proposed as unobserved intermediates in numerous metal-catalyzed reactions, including alkyne polymerization and enyne metathesis;[4] however, the only alkene reaction previously reported for a characterized metallacyclobutene is Tebbe and Harlow's 1980 observation that titanacyclobutene **1** reacts with 2-methylpropene-1-$^{13}C$ at 85 °C to give **1**-$^{13}C$ (eq 1).[5] Here we report the first productive reactions of a metallacyclobutene complex with alkenes, to give 1,4-diene complexes with excellent regio- and stereochemical control. The results are consistent with a mechanism that involves conversion of the metallacyclobutene to a vinylcarbene intermediate, which then undergoes a [4 + 2]-cycloaddition reaction with the activated alkene.

Access to the stable cobaltacyclobutene complex ($\eta^5$-$C_5H_5$)(PPh$_3$)Co[$\kappa^2$-($C,C$)-C(SO$_2$Ph)=C(SiMe$_3$)CH(CO$_2$Et)] (**2**)[3c] has permitted the first systematic investigations into the reactivity of late-metal metallacyclobutenes. For example, **2** undergoes reaction with carbon monoxide, diazocarbonyls, and alkynes to give vinylketene (**3**),[3d] 1,3-dienes (**4**),[3c] and cyclopentadienes (**5**)[3e] (Scheme 1). Of particular note, products **3** and **4** result from selective carbon–carbon bond-formation at the α-(sp$^2$)carbon of the metallacycle ring.

When a benzene solution of metallacyclobutene **2** (228 mg, 12.8 mM) and dimethyl fumarate (63 mM) was heated at 70 °C for 96 h, followed by chromatographic workup in air, the 1,4-diene complex, **6**-*ZE*, was isolated as an orange, air-stable solid in 87% yield (Scheme 2).[6,7] The $^1$H NMR spectrum (CDCl$_3$) of **6**-*ZE* exhibits two upfield singlets at δ 2.87 (H$^{anti}$, C*H*SO$_2$Ph) and 3.76 (H$^{syn}$, C*H*CO$_2$Me), suggestive of a cobalt-diene structure. For comparison, the vinyl hydrogens in the 1,3-diene complex, **4**-*ZE*, are observed at δ 1.09 (H$^{anti}$) and 3.73 (H$^{syn}$).[3c] The observation of a third singlet in the $^1$H NMR spectrum of **6**-*ZE* at δ 4.80 (1H, C*H*CO$_2$Et) is inconsistent with a 1,3-diene structure, which could have resulted from alkene coupling at the cobalt–(sp$^2$)carbon bond of **2**. When the reaction of **2** and dimethyl fumarate was monitored by $^1$H NMR

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**Scheme 1.** Established Reactions of Cobaltacyclobutene **2**

**Scheme 2.** Metallacyclobutene Reactions with Alkenes

spectroscopy, the formation of **6**-*ZZ* was observed in addition to **6**-*ZE*; however, during the course of reaction the resonances for **6**-*ZZ* were gradually replaced by those of **6**-*ZE*. Complex **6**-*ZZ* was isolated in 58% yield by terminating a reaction of **2** and dimethyl fumarate after 2.5 h at 70 °C. In the $^1$H NMR spectrum (CDCl$_3$) of **6**-*ZZ*, the three singlets assigned to the hydrogens of the pentadiene skeleton (δ 2.32, 2.58, and 4.16) resonate upfield of the corresponding resonances for **6**-*ZE*.[7]

The observation that **6**-*ZZ* was formed during the course of reaction between **2** and dimethyl fumarate suggested that the *ZZ*-isomer was thermally converted to the *ZE*-isomer under the reaction conditions. Heating a benzene-$d_6$ solution of **6**-*ZZ* and monitoring the sample by $^1$H NMR spectroscopy confirmed thermal isomer-
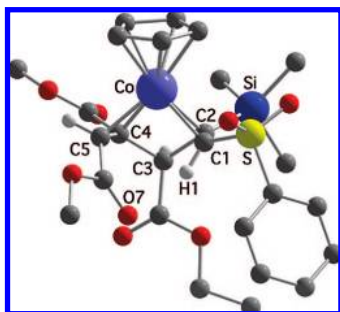
**Figure 1.** Solid-state structure of **6**-*ZE*. For clarity, only three hydrogen atoms are shown: C(1)−C(2), 1.426(4); C(2)−C(3), 1.544(4); C(3)−C(4), 1.520(4); C(4)−C(5), 1.432(4) Å.
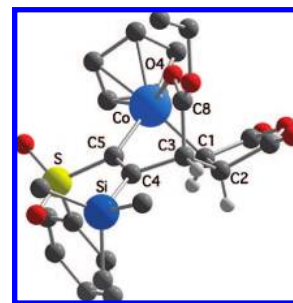


**Figure 2.** Solid-state structure of **9**-*exo*. For clarity, only three hydrogen atoms are shown: [Co−C(1), 2.030(1); C(1)−C(2) 1.522(2); C(2)−C(3), 1.546(2); C(3)−C(4), 1.541(2); C(4)−C(5), 1.356(2); C(5)−Co, 1.966(1); C(3)−C(8), 1.495(2); C(8)−O(4), 1.230(2); O(4)−Co, 1.960(1) Å].

izization. Equilibrium was established after 116 h at 70 °C, with $K_{eq}$ = [**6**-*ZE*]/[**6**-*ZZ*] = 38 ($\Delta G°$ = 2.5 kcal/mol).[8,9]

X-ray crystallographic analyses of **6**-*ZE* and **6**-*ZZ* unambiguously established the anti relationship of cobalt and the ethyl ester substituent on C(3) of the $\eta^4$-1,4-pentadiene ligand (Figure 1).[10] For both complexes, the five-carbon pentadiene ligand exhibits a pronounced fold, with 57.2(2)° (**6**-*ZE*) and 61.27(7)° (**6**-*ZZ*) dihedral angles between the mean diene plane, C(1)−C(2)−C(4)−C(5), and the C(2)−C(3)−C(4) plane. For comparison, the fold angle observed for the ($\eta^5$-C₅H₅)Co($\eta^4$-cyclopentadiene) complex, **5** (R = CO₂Me), is 34.1(6)°.[3e] The C(1)−C(5) distance in **6**-*ZE* (2.880(4) Å) is longer than in **6**-*ZZ* (2.829(2) Å), and the O(7)−H(1) distance of 2.04 Å in **6**-*ZE* is well below the sum of the van der Waals radii of hydrogen and oxygen (2.6 Å).

The reaction of **2** with dimethyl maleate in benzene-$d_6$ at 70 °C was also monitored by ¹H NMR spectroscopy and conversion to **6**-*ZE* (62% yield) was observed over the course of 70 h (Scheme 2). Only a trace amount of **6**-*ZZ* was observed during the reaction. In a similar fashion, heating a benzene-$d_6$ solution of **2** (12.7 mM) and fumaronitrile (101 mM) led to a 92% yield of **7**-*ZZ* after 11 h at 70 °C (Scheme 2).[7] Prolonged heating of an analytically pure sample of **7**-*ZZ* at 70 °C led to slow decomposition, with no evidence for formation of **7**-*ZE*.

To test regioselectivity with respect to the alkene, a dichloromethane solution of **2** (159 mg, 8.9 mM) and excess ethyl-*cis*-$\beta$-cyanoacrylate (60 mM) was heated at 70 °C for 11 h. Chromatographic workup and recrystallization led to isolation of **8**-*ZE* as orange-red crystals in 81% yield.[7]

The observation that cis alkenes form *ZE*-dienes, whereas trans alkenes generate *ZZ*-dienes, is consistent with a mechanism that involves the formation of metallacyclohexene intermediates from coupling of the alkene with the sp³-carbon of the metallacyclobutene ring (Scheme 3). Subsequent $\beta$-hydride elimination and reductive elimination would then generate the observed products. For trans alkenes, two metallacyclohexene diastereomers are possible: **I**-*exo*, from addition to the *si,si*-face of the alkene; and **I**-*endo*, from addition to the *re,re*-face (Scheme 3, top). $\beta$-Hydride elimination from **I**-*exo* leads to cobalt-hydride **II**-*exo*, followed by reductive elimination to the observed exo products (**6**-*ZZ* and **7**-*ZZ*)—with cobalt and CO₂Et on opposite faces of the diene ligand. Alternatively, the formation of **I**-*endo* would sequentially lead to **II**-*endo* and endo diene complexes—with cobalt and CO₂Et on the same face of the diene. A similar analysis applies to the reaction of **2** with cis alkenes (Scheme 3, bottom). This mechanism readily accounts for the observation that trans alkenes give ZZ-products and cis alkenes give ZE-products. Furthermore, it suggests that the metallacyclohexene intermediate formed from reaction of **2** with a

**Scheme 3.** Proposed Metallacyclohexene to 1,4-Diene Conversion of Trans Alkenes (Top) and Cis Alkenes (Bottom)
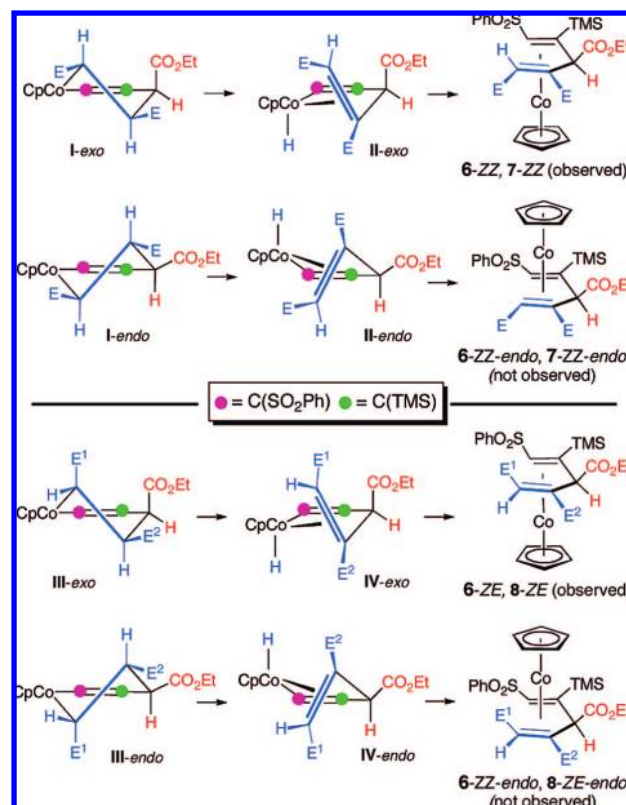


small-ring cyclic alkene will not undergo $\beta$-hydride elimination, thereby permitting observation of metallacyclohexenes related to **III**. Indeed, heating a toluene solution of **2** (12.8 mM) and excess maleic anhydride (62 mM) led to the isolation of both **9**-*exo* (50% yield) and **9**-*endo* (42%) as air-stable solids (Scheme 2, Figure 2).[7]

The observation that maleic anhydride generates a mixture of exo and endo products; whereas, dimethyl maleate and *cis*-$\beta$-cyanoacrylate give predominantly exo products indicates that subtle effects, quite possibly the reversible formation of metallacyclohexene intermediates, are influencing the observed exo/endo selectivity.

Two fundamentally distinct mechanisms for the key carbon−carbon bond-forming step in the conversion of **2** to metallacyclohexene intermediates are (1) alkene coordination and insertion into the cobalt−(sp³)carbon bond of the metallacycle ring and (2) ring-opening of the metallacyclobutene to a vinylcarbene (**10** or **11**,
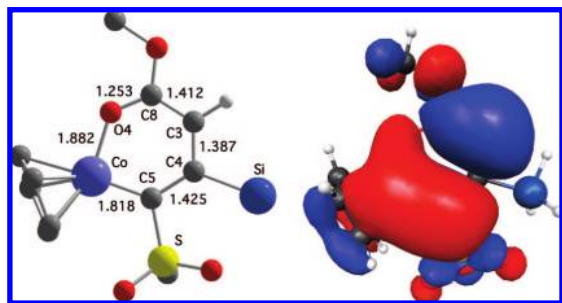
for the reactions of alkenes and alkynes with metallacyclobutenes and vinylcarbenes.

**Supporting Information Available:** Experimental details for all new compounds, computational details for **12**, and X-ray studies in CIF format. This material is available free of charge *via* the Internet at http://pubs.acs.org.



**Figure 3.** (Left) QM-computed structure for **12** (Å units); (right) HOMO of **12**, which has a primary contribution from the cobalt $d_{xy}$ and $d_{yz}$ orbitals.

**Scheme 4.** Potential Vinylcarbene Intermediates
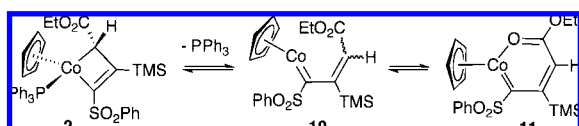


**Scheme 5.** Contrasting Behavior of Metallacyclobutenes toward Alkenes
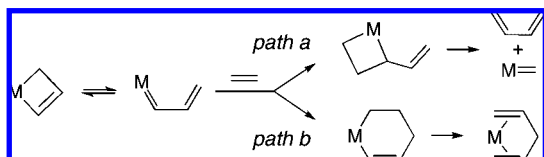


Scheme 4), which then undergoes a [4 + 2]-cycloaddition reaction with the alkene to form **I/III**. We believe the former mechanism to be unlikely since it requires that CO and carbenes insert into the cobalt−(sp$^2$)carbon bond of the metallacycle, but that alkenes insert into the cobalt−(sp$^3$)carbon bond. Alternatively, a vinylcarbene mechanism provides a reasonable explanation for the selectivity observed with CO, carbenes, and alkenes.

The tricyclic structures observed for **9** raise the intriguing possibility that the cyclic vinylcarbene intermediate **11** may play an important role in this novel alkene chemistry. We therefore examined the structure of a model complex, $(\eta^5\text{-C}_5\text{H}_5)\text{Co}[\kappa^2\text{-}(C,O)\text{-}$ C(SO$_2$Me)C(SiH$_3$)CH(CO$_2$Me)] (**12**), using quantum mechanical (QM) methods (Figure 3). Comparisons of the bond distances in **12** with those in **9**-*exo* indicate a significant degree of Co−C(5) and C(3)−C(4) double-bond character in **12**. The large orbital coefficient on cobalt in the HOMO of **12** (Figure 3, right structure) and the planar six-membered ring structure are ideally disposed for participation in a [4 + 2] cycloaddition reaction.[11−13]

To the best of our knowledge, the reactions reported herein are the first productive reactions of a characterized metallacyclobutene complex with alkenes. Reactions of metallacyclobutenes with alkenes have been widely proposed as a key step in metal-catalyzed enyne metathesis reactions, as shown in Scheme 5 (path a).[4,14] The reactions of **2** with alkenes take a much different and unexpected course, to ultimately form 1,4-diene complexes (path b). Future experimental and computational studies will be directed at understanding this dichotomy and providing a mechanistic foundation

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(7) Complexes **6**-*ZZ*, **6**-*ZE*, **7**-*ZZ*, **8**-*ZE*, **9**-*exo*, and **9**-*endo* were characterized in the solid-state by X-ray crystallography. ORTEPS are provided in Supporting Information.

(8) The mild conditions for isomerization of **6**-*ZZ* to the *ZE*-stereoisomer contrast with the behavior of $(\eta^5\text{-C}_5\text{H}_5)\text{Co}(\eta^4\text{-}(Z,Z)\text{-}1,4\text{-dideuterio-1,3-}$ butadiene) and related complexes, which are much less prone to isomerization: (a) Eaton, B.; King, J. A., Jr.; Vollhardt, K. P. C. *J. Am. Chem. Soc.* **1986**, *108*, 1359. (b) Baldridge, K. K.; O'Connor, J. M.; Chen, M.-C.; Siegel, J. S. *J. Phys. Chem. A* **1999**, *103*, 10126.

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