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## Conversion of a Metallacyclobutene to Cobalt–Allene Complexes

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We recently reported the synthesis of the metallacyclobutene complex,  $(\eta^5\text{-C}_5\text{H}_5)(\text{PPh}_3)\text{Co}[\text{C}(\text{SO}_2\text{Ph})=\text{C}(\text{TMS})\text{CH}(\text{CO}_2\text{Et})]$  (**1**),<sup>1a</sup> which has subsequently prompted the first reactivity studies on late-metal metallacyclobutenes.<sup>1</sup> Here we report the conversion of metallacyclobutenes to metal–allene complexes, the first spectroscopic and X-ray crystallographic analyses of mononuclear cobalt–allene complexes,<sup>2</sup> and mechanistic studies on the cobaltacyclobutene to cobalt–allene transformation.

Desilylation of cobaltacyclobutene **1** (710 mg, 1.0 mmol, 0.1 M) with tetrabutylammonium fluoride (TBAF, 783 mg, 3.0 mmol, 0.3 M) and methanol (2.8 M) in acetone at 70 °C for 6 h produced a dark orange solution. Evaporation of the volatiles and chromatography on silica gel with 20% ethyl acetate/hexane led to the isolation of three air-stable allene complexes (Scheme 1): **2-Z** (62% isolated yield), **2-E** (6% isolated yield), and **3-E** (15% isolated yield).<sup>3</sup> In the <sup>1</sup>H NMR spectra (acetone-*d*<sub>6</sub>), the resonances observed for H<sub>a</sub> and H<sub>b</sub> of the allene ligands were assigned as follows: **2-Z**  $\delta$  1.81 (dd,  $J_{\text{PH}} = 13.2$ ,  $J_{\text{HH}} = 2.1$  Hz, H<sub>a</sub>) and 6.06 (dd,  $J_{\text{PH}} = 4.8$ ,  $J_{\text{HH}} = 2.1$  Hz, H<sub>b</sub>); **2-E**  $\delta$  2.51 (dd,  $J_{\text{PH}} = 12.0$ ,  $J_{\text{HH}} = 2.7$  Hz, H<sub>a</sub>) and 6.48 (t,  $J_{\text{PH}} = J_{\text{HH}} = 2.7$  Hz, H<sub>b</sub>); **3-E**  $\delta$  1.75 (dd,  $J_{\text{PH}} = 11.7$ ,  $J_{\text{HH}} = 1.8$  Hz, H<sub>b</sub>) and 6.71 (t,  $J_{\text{PH}} = J_{\text{HH}} = 1.8$  Hz, H<sub>a</sub>). The observation that H<sub>b</sub> in **2-Z** resonates 0.42 ppm upfield of where it is observed for **2-E** runs counter to literature chemical shift trends<sup>4,5</sup> and is presumably due to shielding of the anti hydrogen by the phenyl ring on the sulfone substituent. In the <sup>13</sup>C{<sup>1</sup>H} NMR spectrum (CDCl<sub>3</sub>) for **2-Z**, resonances for the allene ligand were observed at  $\delta$  35.3 ( $J_{\text{PC}} = 3.6$  Hz, CoCH(SO<sub>2</sub>Ph)), 118.8 (br, CH(CO<sub>2</sub>Et)), and 186.7 ( $J_{\text{PC}} = 15$  Hz, CoC(=C)C). Oxidation of **2-Z** with iron(III) chloride gave a 70% isolated yield of (SO<sub>2</sub>Ph)HC=C=CH(CO<sub>2</sub>Et) (**4**), for which allenyl carbon resonances were observed at  $\delta$  96.0, 104.7, and 213.4 in the <sup>13</sup>C{<sup>1</sup>H} NMR (CDCl<sub>3</sub>) spectrum.

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(1) (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.-L.; Rheingold, A. L. *J. Am. Chem. Soc.* **1993**, *115*, 9846. (c) O'Connor, J. M.; Fong, B.; Ji, H.-L.; Hiibner, K.; Rheingold, A. L. *J. Am. Chem. Soc.* **1995**, *117*, 8029. (d) O'Connor, J. M.; Chen, M. C.; Rheingold, A. L. *Tetrahedron Lett.* **1997**, *38*, 5241. (e) Donovan-Merkert, B.; Malik, J.; Gray, L. V.; O'Connor, J. M.; Fong, B. S.; Chen, M. C. *Organometallics*, manuscript submitted. (f) O'Connor, J. M.; Chen, M. C.; Rheingold, A. L. *Organometallics*, manuscript in press.

(2) (a) To our knowledge, the only prior report of a mononuclear cobalt allene complex is that of  $(\eta^5\text{-C}_5\text{H}_5)(\text{CO})\text{Co}[\eta^2\text{-(CPh}_2\text{=C=CPh}_2)]$ , prepared in 2% yield and characterized by mp, molecular weight, and elemental analysis: Nakamura, A.; Kim, P. J.; Hagihara, N. *J. Organomet. Chem.* **1965**, *3*, 7. (b) Cobalt(I) complexes catalyze allene polymerization to a highly regular, crystalline 1,2-polymer: Furukawa, J.; Kiji, J.; Ueo, K. *Makromol. Chem.* **1973**, *170*, 247 and references therein.

(3) For desilylation of a diene ligand to give a quaternary carbon, see: Benyunes, S. A.; Deeth, R. J.; Fries, A.; Green, M.; McPartlin, M.; Nation, C. B. *M. J. Chem. Soc., Dalton Trans.* **1992**, 3453.

(4) Pu, J.; Peng, T. S.; Arif, A. M.; Gladysz, J. A. *Organometallics* **1992**, *11*, 3232.

It has been demonstrated that metal–allene complexes undergo two fundamental fluxional processes: rotation about the metal–allene bond and migration of the metal between the orthogonal allene  $\pi$ -systems.<sup>4–6</sup> For **2-Z** in acetone-*d*<sub>6</sub>, there was no evidence of a fluxional process on the NMR time scale between –90 °C and +60 °C. However, the cobalt–allene complexes underwent thermal interconversion when observed over longer time periods.<sup>7</sup> Thermolysis of either **2-Z** or **3-E** in acetone-*d*<sub>6</sub> at 70 °C for 2 weeks gave a 64:30:7 equilibrium ratio of **2-Z**:**3-E**:**2-E**. The greater thermodynamic stability of the *Z* isomer relative to the *E* isomer [ $\Delta G^\circ_{(70^\circ\text{C})} \approx 1.5$  kcal mol<sup>–1</sup>] is unprecedented for metal–allene complexes.<sup>8</sup> An example of the typical behavior of metal–allene complexes is found for  $[(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_2\text{Fe}(2,3\text{-}\eta^2\text{-CH}_2=\text{C}=\text{CHMe})]\text{BF}_4$  which exists as a 1.95/1 equilibrium ratio of *E*/*Z* isomers at 50 °C.<sup>5</sup>

Single-crystal X-ray diffraction studies established the relative stereochemistry for the three allene complexes to be (*RRZ,SSZ*) for **2-Z**, (*RRE,SSE*) for **2-E**, and (*SRE,RSE*) for **3-E**. The Co–C(51) distance is essentially identical (1.864 Å average) in all three structures and significantly shorter than the Co–(sp<sup>3</sup>)carbon distances. Despite the presence of the sulfone substituent on C(50) of **2-E** and an ester substituent on C(52) of **3-E**, the Co–(sp<sup>3</sup>)carbon bond distances are identical (2.00 Å) within experimental error. The C(50)–C(51)–C(52) angle of 136.6(4)° in **2-Z** is at the low end of the range observed for other allene complexes (134.5–160°).<sup>4</sup>

Deuterium labeling studies were employed to address the mechanism of the metallacyclobutene to metal–allene transformation. Reaction of TBAF with a 1:1 mixture of  $(\eta^5\text{-C}_5\text{D}_5)(\text{PPh}_3)\text{Co}[\text{C}(\text{SO}_2\text{Ph})=\text{C}(\text{TMS})\text{CH}(\text{CO}_2\text{Et})]$  (**1-d**) and  $(\eta^5\text{-C}_5\text{H}_5)(\text{PPh}_3)\text{Co}[\text{C}(\text{SO}_2\text{Ph})=\text{C}(\text{TMS})\text{CH}(\text{CO}_2\text{R})]$  (**5**, R = (CH<sub>2</sub>)<sub>2</sub>CH=CH<sub>2</sub>) occurred without crossover to give deuterium-enriched **2-Z-d** and **3-E-d** as well as nonenriched  $[(\eta^5\text{-C}_5\text{H}_5)\text{Co}\{1,2\text{-}\eta^2\text{-CH}(\text{SO}_2\text{Ph})=\text{C}=\text{CH}(\text{CO}_2(\text{CH}_2)_2\text{CH}=\text{CH}_2)\}]$  (**6-Z**) and  $[(\eta^5\text{-C}_5\text{H}_5)\text{Co}\{2,3\text{-}\eta^2\text{-CH}(\text{SO}_2\text{Ph})=\text{C}=\text{CH}(\text{CO}_2(\text{CH}_2)_2\text{CH}=\text{CH}_2)\}]$  (**7-E**).<sup>9</sup> The 1,3-propendiyl ligand in **1** was therefore transformed to the allene ligand in **2-Z** and **3-E** without migration between metal centers. When the conversion of **1** and TBAF to allenes was carried out in the presence of CD<sub>3</sub>OD in acetone-*d*<sub>6</sub>, all three allene complexes were deuterium-enriched only at the H<sub>a</sub> positions (>95% *d*). Thermal isomerization of **2-Z** (deuterium-enriched at H<sub>a</sub>) in the presence of 0.1 M NaOCH<sub>3</sub> (2.8 M CH<sub>3</sub>OH) gave a mixture of allene complexes with less than 5% deuterium at the H<sub>a</sub> sites.

The reactions listed in Table 1<sup>10</sup> were carried out to determine the origin of the allene product distribution. Allene isomerization in the presence of added NaOCH<sub>3</sub> was examined since methoxide

(5) Foxman, B.; Marten, D.; Rosan, A.; Raghu, S.; Rosenblum, M. *J. Am. Chem. Soc.* **1977**, *99*, 2160.

(6) Oon, S. M.; Koziol, A. E.; Jones, W. M.; Palenik, G. J. *J. Chem. Soc., Chem. Commun.* **1987**, 491. (b) Omrcen, T.; Conti, N. J.; Jones, W. M. *Organometallics* **1991**, *10*, 913.

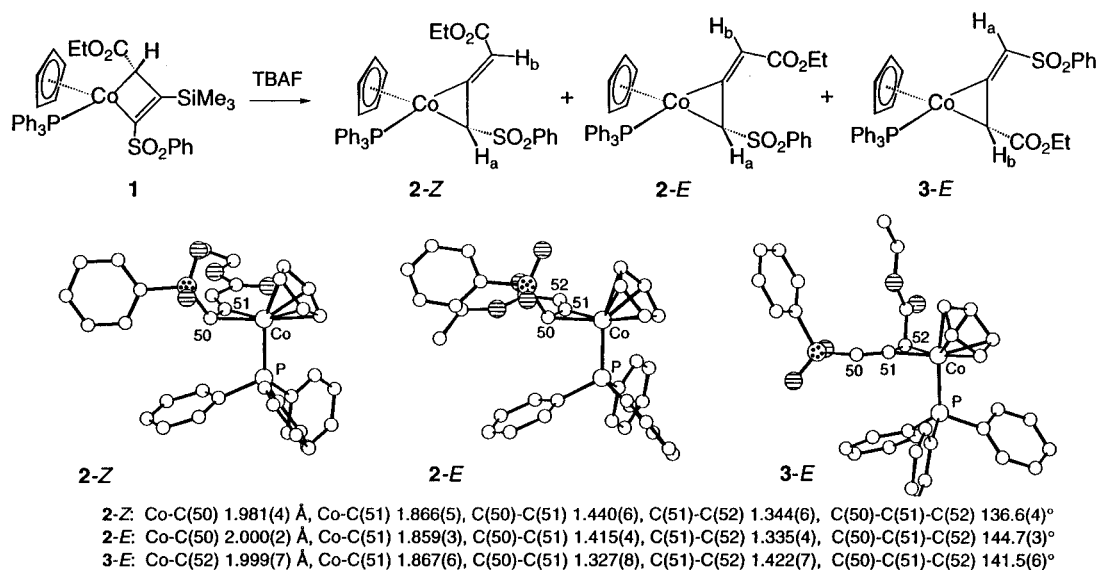
(7) Under the fluorescent laboratory lights, **2-Z** undergoes a very slow conversion (23 °C, 3 months) to a mixture of **2-E** (12%) and **3-E** (85%). A nearly identical sample of **2-Z** which was maintained in the dark showed no reaction under similar conditions.

(8) (a) Bowden, F. L.; Giles, R. *Coord. Chem. Rev.* **1976**, *20*, 81. (b) Otsuka, S.; Nakamura, A. *Adv. Organomet. Chem.* **1976**, *14*, 245. (c) Hughes, D. A.; Pombreiro, A. J. L.; Picket, C. J.; Richards, R. L. *J. Chem. Soc., Chem. Commun.* **1984**, 992. (d) Lee, L.; Wu, I. Y.; Lin, Y. C.; Lee, G. H.; Wang, Y. *Organometallics* **1994**, *13*, 2521. (e) References 4 and 5.

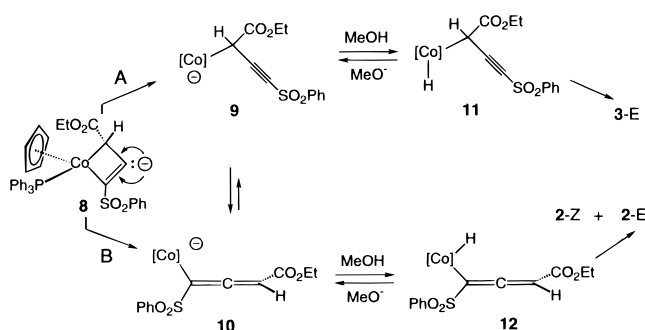
(9) **1-d**,  $[(\eta^5\text{-C}_5\text{H}_5)\text{Co}\{1,2\text{-}\eta^2\text{-CH}(\text{SO}_2\text{Ph})=\text{C}=\text{CH}(\text{CO}_2\text{Et})\}]$  (**2-Z-d**), and  $[(\eta^5\text{-C}_5\text{H}_5)\text{Co}\{2,3\text{-}\eta^2\text{-CH}(\text{SO}_2\text{Ph})=\text{C}=\text{CH}(\text{CO}_2\text{Et})\}]$  (**3-E-d**) were enriched with 85% deuterium in the Cp ligand. Attempts to convert **5** to an allene complex in the presence of added **4** were unsuccessful due to rapid decomposition of **4** upon exposure to TBAF.

(10) Severe line broadening in the <sup>1</sup>H NMR spectra precluded the use of NMR spectroscopy to directly monitor the reactions of **1**. The allene ratios were determined by filtering the crude reaction mixture through a plug of silica gel to remove paramagnetic impurities and subsequent analysis of the solution by <sup>1</sup>H NMR spectroscopy.

## Scheme 1



## Scheme 2

Table 1. Allene Complex Isomer Distributions<sup>a</sup>

entry	starting complex	reaction time (h)	added NaOCH <sub>3</sub> (M)	2-Z	3-E	2-E
1	1	6		73	18	09
2	2-Z	6		89	08	03
3	2-Z	6	0.1	73	17	10
4	3-E	6		17	83	00
5	3-E	6	0.1	45	49	06
6 <sup>b</sup>	1	0.5		56	33	11
7 <sup>c</sup>	1	0.5	0.1	82	09	09
8 <sup>d</sup>	2-Z/3-E	336		63	29	08

<sup>a</sup> Reaction conditions: acetone solvent, 0.1 M starting complex, 2.8 M CH<sub>3</sub>OH, 0.3 M TBAF, 70 °C. <sup>b</sup> 20% conversion of 1. <sup>c</sup> 80% conversion of 1. <sup>d</sup> Equilibrium ratio of allenes.

is generated from methanol in the reaction of 1 and TBAF (Table 1; entries 3 and 5). A comparison of entries 2–5 established that base accelerated the rate of allene isomerization. Entry 6 indicated that at only 0.5 h of reaction the 2-Z/3-E ratio from 1 was close to the equilibrium value (entry 8). The observation that isomerization of 2-Z (entry 3) and 3-E (entry 5) did not reach equilibrium even after 6 h indicates that neither 2-Z nor 3-E isomerization is rapid enough to account for the nearly equilibrium ratios of allene product observed from 1 at 0.5 h of reaction (entry 6). Thus it is unlikely that either 2-Z or 3-E is formed as the sole kinetic product. In addition to accelerating allene isomerization, added NaOCH<sub>3</sub> accelerated the rate of reaction for conversion of 1 to allenes (entries 6 and 7). Significantly, the 2-Z/3-E ratio of 1.7 at 0.5 h of reaction (entry 6) rapidly changed to 4.0 at 6 h of reaction (entry 1). Thus, as [CH<sub>3</sub>O<sup>−</sup>] increases during the conversion of 1 to allenes, the rate of 3-E formation becomes less competitive with the rate of 2-Z formation.

A mechanism consistent with these results is shown in Scheme 2. Desilylation of 1 leads to the anionic intermediate 8, which can then ring open to propargyl complex 9 (path A) and/or allenyl complex 10 (path B). Protonation at cobalt gives hydrides 11 and 12, respectively.<sup>11</sup> Propargyl hydride 11 is converted to 3-E by an intramolecular addition of the cobalt–hydride bond across the alkyne,<sup>12</sup> whereas reductive elimination from 12 gives 2-Z/E. The effect of added base on product distribution is explained if 9 and 10 interconvert,<sup>13</sup> and each is in equilibrium with the corresponding hydrides 11 and 12. At early reaction times (low [CH<sub>3</sub>O<sup>−</sup>]), the formation of 3-E from 11 is competitive with reversion to 9. At later reaction times (higher [CH<sub>3</sub>O<sup>−</sup>]), reversion to 9 is more competitive in the partitioning of 11. It is unlikely that the activation energy for ring opening of 8 by path A would be of similar magnitude in comparison to ring opening via path B. Preferential opening by path A is most consistent with the observation that the 2-Z/3-E ratio increases as the base concentration builds up during the course of reaction.

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**Supporting Information Available:** Tables of the X-ray crystal structure determination data, atomic coordinates, anisotropic thermal parameters, bond lengths and angles for 2-Z, 2-E, and 3-E and full characterization data for 2-Z, 2-E, 3-E, 4, 5, 6-Z, and 7-E (27 pages). See any current masthead page for ordering and Web access instructions.

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(11) Protonation at the  $\gamma$  position of a propargyl ligand gives an allene complex: Raghu, S.; Rosenblum, M. *J. Am. Chem. Soc.* **1973**, *95*, 3060. We rule out a large contribution from such a process here since added base would not retard the rate for protonation of 9 at carbon to directly give 3-E (the CH<sub>3</sub>OH concentration has not changed). Direct deprotonation of 3-E would be too slow to account entirely for the effect of added base (Table 1, entries 5–7). It is interesting to note that Gladysz has demonstrated deprotonation of a rhenium- $\eta^2$ -allene complex to give an  $\eta^1$ -allenyl complex, rather than a  $\eta^1$ -propargyl complex as the kinetic product.<sup>4</sup>

(12) For  $\eta^3$ -propargyl complexes: Casey, C. P.; Yi, C. S. *J. Am. Chem. Soc.* **1992**, *114*, 6597.

(13) Metal-propargyl to allenyl rearrangements have been suggested to involve a 1,3-metal sigmatropic shift.<sup>13a</sup> Furthermore, allenyl isomers are typically more stable than propargyl isomers: (a) Chen, M. C.; Keng, R. S.; Lin, Y. C.; Wang, Y.; Cheng, M. C.; Lee, G. H. *J. Chem. Soc., Chem. Commun.* **1990**, 1138. (b) Keng, R. S.; Lin, Y. C. *Organometallics* **1990**, *9*, 289. (c) Reference 3.