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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, (η^5 -C_5H_5)(PPh_3)Co[C(SO_2Ph)═C(TMS)CH(CO_2Et)] (**1**),[1a] which has subsequently prompted the first reactivity studies on late-metal metallacyclobutenes.[1] Here we report the conversion of metallacyclobutenes to metal−allene complexes, the first spectroscopic and X-ray crystallographic analyses of mononuclear cobalt−allene complexes,[2] 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).[3] In the ^{1}H NMR spectra (acetone-d_6), the resonances observed for H_a and H_b of the allene ligands were assigned as follows: **2**-*Z* δ 1.81 (dd, $J_{PH} = 13.2$, $J_{HH} = 2.1$ Hz, H_a) and 6.06 (dd, $J_{PH} = 4.8$, $J_{HH} = 2.1$ Hz, H_b); **2**-*E* δ 2.51 (dd, $J_{PH} = 12.0$, $J_{HH} = 2.7$ Hz, H_a) and 6.48 (t, $J_{PH} = J_{HH} = 2.7$ Hz, H_b); **3**-*E* δ 1.75 (dd, $J_{PH} = 11.7$, $J_{HH} = 1.8$ Hz, H_b) and 6.71 (t, $J_{PH} = J_{HH} = 1.8$ Hz, H_a). The observation that H_b in **2**-*Z* resonates 0.42 ppm upfield of where it is observed for **2**-*E* runs counter to literature chemical shift trends[4,5] and is presumably due to shielding of the anti hydrogen by the phenyl ring on the sulfone substituent. In the $^{13}C\{^1H\}$ NMR spectrum ($CDCl_3$) for **2**-*Z*, resonances for the allene ligand were observed at δ 35.3 ($J_{PC} = 3.6$ Hz, Co*C*H(SO_2Ph)), 118.8 (br, *C*H(CO_2Et)), and 186.7 ($J_{PC} = 15$ Hz, Co*C*(═C)C). Oxidation of **2**-*Z* with iron(III) chloride gave a 70% isolated yield of (SO_2Ph)HC═C═CH(CO_2Et) (**4**), for which allenyl carbon resonances were observed at δ 96.0, 104.7, and 213.4 in the $^{13}C\{^1H\}$ NMR ($CDCl_3$) spectrum.

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 π-systems.[4−6] For **2**-*Z* in acetone-$d_{6,}$ 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.[7] Thermolysis of either **2**-*Z* or **3**-*E* in acetone-d_6 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 [$\Delta G^\circ_{(70\,°C)} \approx 1.5$ kcal mol^{-1}] is unprecedented for metal−allene complexes.[8] An example of the typical behavior of metal−allene complexes is found for [(η^5-C_5H_5)$(CO)_2$Fe(2,3-η^2-CH_2═C═CHMe)]BF_4 which exists as a 1.95/1 equilibrium ratio of *E*/*Z* isomers at 50 °C.[5]

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^3)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^3)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°).[4]

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 (η^5-C_5D_5)-(PPh_3)Co[C(SO_2Ph)═C(TMS)CH(CO_2Et)] (**1**-*d*) and (η^5-C_5H_5)-(PPh_3)Co[C(SO_2Ph)═C(TMS)CH(CO_2R)] (**5**, R = $(CH_2)_2$-CH═CH_2) occurred without crossover to give deuterium-enriched **2**-*Z*−*d* and **3**-*E*−*d* as well as nonenriched [(η^5-C_5H_5)Co{1,2-η^2-CH(SO_2Ph)═C═CH($CO_2(CH_2)_2CH$═CH_2)}] (**6**-*Z*) and [(η^5-C_5H_5)Co{2,3-η^2-CH(SO_2Ph)═C═CH($CO_2(CH_2)_2CH$═CH_2)}] (**7**-*E*).[9] 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_3OD in acetone-d_6, all three allene complexes were deuterium-enriched only at the H_a positions (>95%-*d*). Thermal isomerization of **2**-*Z* (deuterium-enriched at H_a) in the presence of 0.1 M $NaOCH_3$ (2.8 M CH_3OH) gave a mixture of allene complexes with less than 5% deuterium at the H_a sites.

The reactions listed in Table 1[10] were carried out to determine the origin of the allene product distribution. Allene isomerization in the presence of added $NaOCH_3$ was examined since methoxide

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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 (η^5-C_5H_5)(CO)Co[η^2-(CPh_2═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.

[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.; Pombeiro, 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*, [(η^5-C_5H_5)Co{1,2-η^2-CH(SO_2Ph)═C═CH(CO_2Et)}] (**2**-*Z*−*d*), and [(η^5-C_5H_5)Co{2,3-η^2-CH(SO_2Ph)═C═CH(CO_2Et)}] (**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 ^{1}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 ^{1}H NMR spectroscopy.

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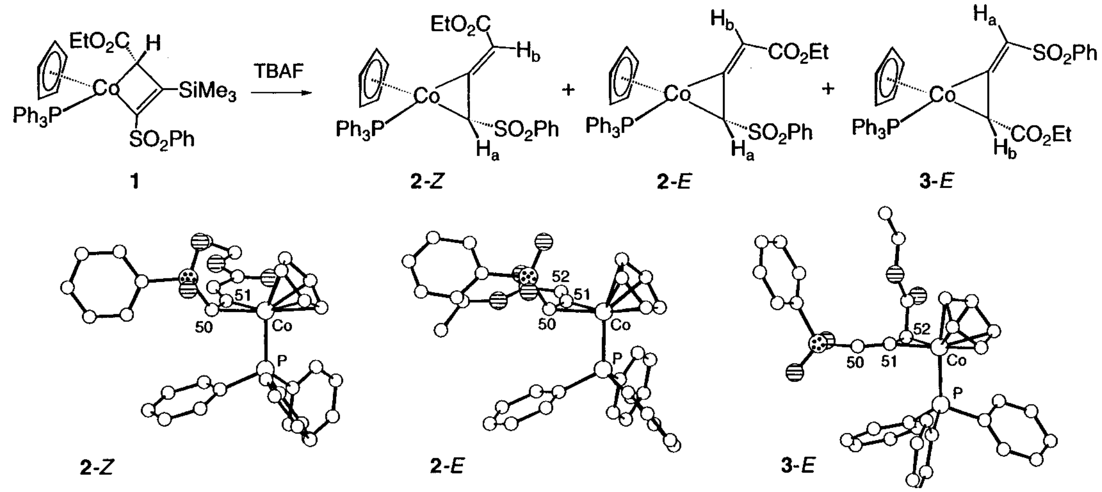
Scheme 1



2-*Z*: Co-C(50) 1.981(4) Å, Co-C(51) 1.866(5), C(50)-C(51) 1.440(6), C(51)-C(52) 1.344(6), C(50)-C(51)-C(52) 136.6(4)°
2-*E*: Co-C(50) 2.000(2) Å, Co-C(51) 1.859(3), C(50)-C(51) 1.415(4), C(51)-C(52) 1.335(4), C(50)-C(51)-C(52) 144.7(3)°
3-*E*: Co-C(52) 1.999(7) Å, Co-C(51) 1.867(6), C(50)-C(51) 1.327(8), C(51)-C(52) 1.422(7), C(50)-C(51)-C(52) 141.5(6)°

Scheme 2

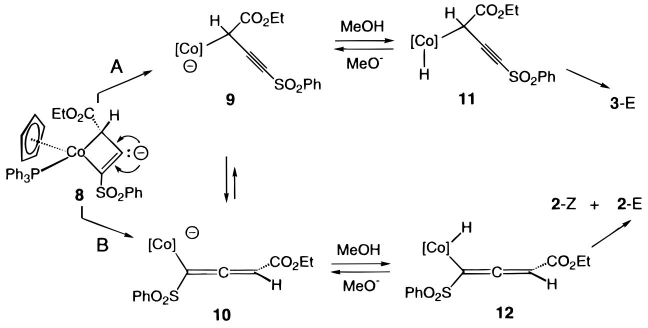


Table 1. Allene Complex Isomer Distributions[a]

entry	starting complex	reaction time (h)	added $NaOCH_3$ (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[b]	**1**	0.5		56	33	11
7[c]	**1**	0.5	0.1	82	09	09
8[d]	**2**·*Z*/**3**·*E*	336		63	29	08

[a] Reaction conditions: acetone solvent, 0.1 M starting complex, 2.8 M CH_3OH, 0.3 M TBAF, 70 °C. [b] 20% conversion of **1**. [c] 80% conversion of **1**. [d] 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 $NaOCH_3$ 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 $[CH_3O^-]$ 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.[11] Propargyl hydride **11** is converted to **3**-*E* by an intramolecular addition of the cobalt−hydride bond across the alkyne,[12] whereas reductive elimination from **12** gives **2**-*Z*/*E*. The effect of added base on product distribution is explained if **9** and **10** interconvert,[13] and each is in equilibrium with the corresponding hydrides **11** and **12**. At early reaction times (low $[CH_3O^-]$), the formation of **3**-*E* from **11** is competitive with reversion to **9**. At later reaction times (higher $[CH_3O^-]$), 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 γ 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_3OH 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-η^2-allene complex to give an η^1-allenyl complex, rather than a η^1-propargyl complex as the kinetic product.[4]

(12) For η^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.[13a] 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.