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Fluoride Induced Isomerization of Cobalt Diene Complexes

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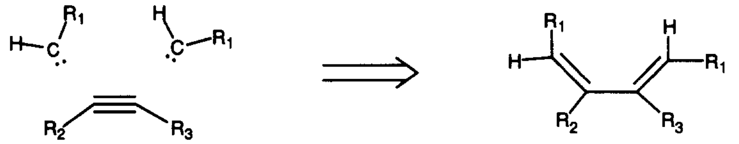
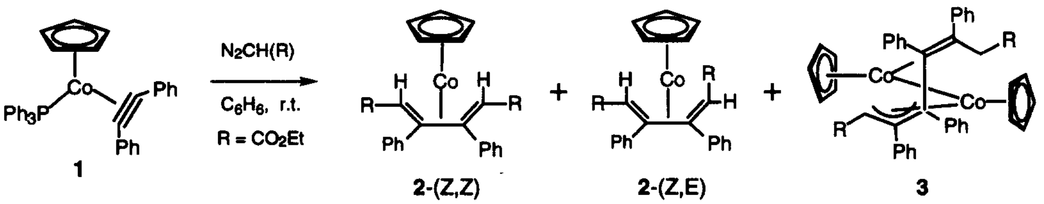
Abstract: A metal-mediated addition of two carbenes across an alkyne is employed for the synthesis of (2-phenylsulfonyl)-1,3-dienes. Control of diene stereochemistry is achieved through an unprecedented fluoride-catalyzed isomerization of the cobalt diene intermediates. © 1997 Elsevier Science Ltd.

The metal-mediated addition of two carbenes across an alkyne represents a potentially powerful route toward conjugated dienes (Scheme 1). Hong et al. first reported the reaction of cobalt-alkyne complex **1** and ethyl diazoacetate to give a mixture of cobalt diene complexes **2**-(Z,Z) and **2**-(Z,E), as well as the dicobalt complex **3** (Scheme 2).[1] The ratio of products depended on the amount of starting diazo compound, with the highest yield of dienes (12% **2**-(Z,Z), 36% **2**-(Z,E), 9% **3**) achieved at a 10:1 ratio of ethyl diazoacetate to **1**.



Scheme 1.

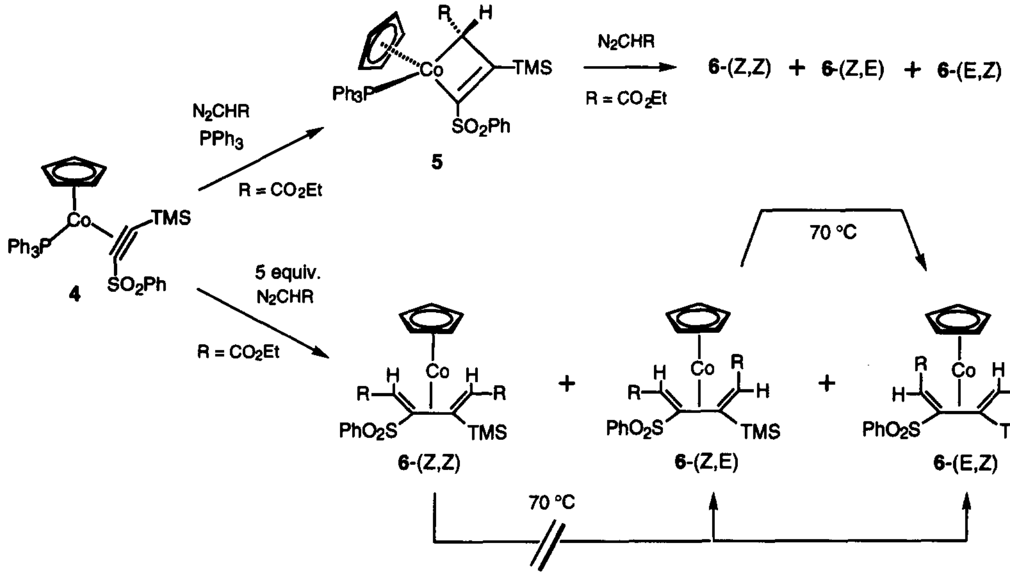


Scheme 2.

We previously reported the room temperature conversion of cobalt alkyne complex **4** and ethyl diazoacetate, in the presence of added PPh_3, to the metallacyclobutene complex **5** in 84% yield (Scheme 3).[2] Subsequent reaction of metallacycle **5** and ethyl diazoacetate at 50°C led to a mixture of diene complexes (**6**). Without added PPh_3, alkyne complex **4** and ethyl diazoacetate (1.5 equiv) gave a similar mixture of three diene products (**6**-(Z,Z), 22%; **6**-(Z,E), 11%; **6**-(E,Z), 3%), in addition to the cobaltacyclobutene complex **5** (43%).[3] The formation of three diene isomers in low yield has remained problematic for the development of this intriguing diene synthesis. Herein we report an unprecedented fluoride-catalyzed isomerization of cobalt η^4-diene complexes which greatly improves the prospects for the development of [1+2+1] carbene/alkyne additions.

In an effort to eliminate formation of metallacyclobutene **5** from the reaction of alkyne complex **4** and ethyl diazoacetate, we examined the dependence of the product distribution on the ethyl diazoacetate concentration. By increasing the concentration of ethyl diazoacetate and the reaction temperature, **4** is converted directly to a mixture of diene products in good combined yield. Thus, when a benzene-d_6 solution of **4** (0.016 mmol, 0.04 *M*), ethyl diazoacetate (5 equiv), and toluene (as an internal standard) is heated at 70 °C for 12h, all of the starting alkyne complex is consumed and three diene products are formed in 81% yield: **6**-(Z,Z), 41%; **6**-(Z,E), 29.5%; **6**-(E,Z), 10.5%. There was no spectroscopic evidence for the presence of cobaltacyclobutene **5**, dinuclear products of type **3**, or the (E,E) isomer of **6** in the reaction mixture.

In principle it should be possible to interconvert the **6**-(Z,E) and **6**-(E,Z) isomers by an envelope-flip mechanism.[4] When a sealed NMR tube containing a benzene-d_6 solution of **6**-(Z,E) is heated in an oil bath at 70 °C a slow conversion to **6**-(E,Z) is observed by ^{1}H NMR spectroscopy. After 3 months at 70 °C, the (E,Z) to (Z,E) isomer ratio is > 30:1 with no (Z,Z)-isomer observable by ^{1}H NMR spectroscopy. In contrast, thermolysis of **6**-(Z,Z) for 336 h at 70°C in benzene-d_6 did not lead to detectable (< 3%) formation of **6**-(Z,E), **6**-(E,Z), or the (E,E)-isomer.



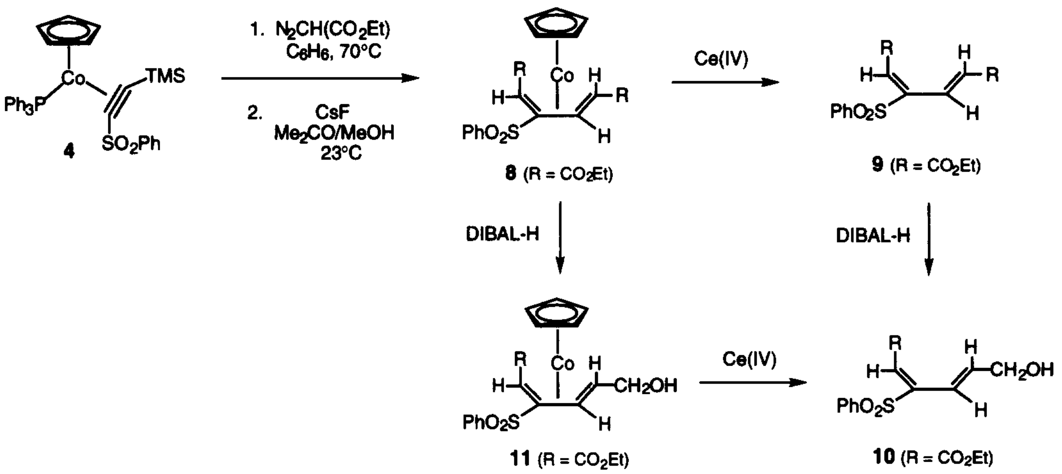
Scheme 3.

In the course of examining the desilylation reactions of **6** we discovered that fluoride ion rapidly and cleanly induces diene isomerization at room temperature to give a single diene isomer.[5] Reaction of **6**-(Z,Z) with CsF in acetone/MeOH solution at room temperature gives the desilylated (E,Z) isomer **8** in 91% yield.[6] In an effort to optimize the conversion of **4** to **8** we carried out the procedure without isolation of the three diene intermediates. Thus, a benzene solution of **4** (206 mg, 0.33 mmol, 0.03 M) and $N_2CH(CO_2Et)$ (310 mg, 2.7

mmol) was heated at 70 °C for one day. The volatiles were then removed, the residue dissolved in acetone/methanol (20 mL, 20:1), CsF (1.3 equiv) was added, and the solution stirred at room temperature for one day. Chromatographic work up in the air led to isolation of pure **8** as red-black crystals in 70% yield (Scheme 4). Treatment of **8** with two equivalents of ceric ammonium nitrate in hexane/acetonitrile (1:1), gave the (2-phenylsulfonyl)-1,3-diene **9** in 86% isolated yield.[6,7]

Reduction of **9** with diisobutylaluminum hydride leads to a mixture of products including hydroxymethyl substituted diene **10** in only 20% yield. Cobalt complexation to **9** dramatically improves the selectivity for the DIBAL-H reduction. When complex **8** is treated with DIBAL-H under similar conditions to those employed for reduction of **9**, the new diene complex **11** is formed in 72% isolated yield. Oxidation of **11** with ceric ammonium nitrate gives **10** in 97% isolated yield.[6]

The results reported herein hold promise for increased application of cobalt diene complexes in organic synthesis. Efforts are currently underway to determine the scope and mechanism of this new fluoride catalyzed diene isomerization chemistry as it applies to the cobalt mediated synthesis of diene complexes from alkynes and diazo compounds.



Scheme 4

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References and Notes

1. Hong, P.; Aoki, K.; Yamazaki, H. *J. Organomet. Chem.* **1978**, *150*, 279-293.
2. (a) O'Connor, J.M.; Ji, H-L.; Iranpour, M.; Rheingold, A.L. *J. Am. Chem. Soc.* **1993**, *115*, 1586-1588. (b) O'Connor, J.M.; Fong, B.S.; Ji, H-L.; Hiibner, K.; Rheingold, A.L. *J. Am. Chem. Soc.* **1995**, *117* 8029-8030.

3. In the ^1H NMR spectra ($CDCl_3$) of dienes **6**, the vinyl hydrogen chemical shifts are observed as follows: δ 0.06 (s, 1H), 1.10 (s, 1H) for **6**-(Z,Z); 1.09 (s, 1H), 3.73 (s, 1H) for **6**-(Z,E); and 1.13 (s, 1H), 4.55 (s, 1H) for **6**-(E,Z). The structural assignment of **6**-(Z,Z) is straightforward since the anti hydrogens resonate at higher field than the syn hydrogens in the ^1H NMR spectrum of η^4-diene complexes. We have now carried out an X-ray crystallographic analysis on **7**-(Z,E), an analogue of **6** with R = $CO_2CH_2CH_2CH{=}CH_2$. In support of the structural assignment for **6**-(Z,E), diene **7**-(Z,E) exhibits vinyl hydrogen chemical shifts at δ 1.06 and 3.74 in the ^1H NMR spectrum ($CDCl_3$).
4. For a photochemical envelope-flip see: (a) Eaton, B.; King Jr., J.A.; Vollhardt, K.P.C. *J. Am. Chem. Soc.* **1986,** *108* 1359-1360. (b) King Jr., J.A.; Vollhardt, K.P.C. *J. Organomet. Chem.* **1993,** *460,* 91-96. (c) King Jr., J.A.; Vollhardt, K.P.C. *J. Organomet. Chem.* **1994,** *470,* 207-222.
5. Base catalyzed diene isomerizations are known for tricarbonyl iron diene complexes, see Frederiksen, J.S.; Graf, R.E.; Gresham, D.G.; Lillya, C.P. *J. Am. Chem. Soc.* **1979,** *101,* 3863-3867.
6. Spectral data for **8**: m.p. 129-129.5 °C; IR (thin film) 1701 (C=O) cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.17 (t, 3H, J = 6.9 Hz, $-CH_2C\mathit{H}_3$), 1.29 (t, 3H, J = 6.9 Hz, $-CH_2CH_3$), 1.74 (d, 1H, J = 8.7 Hz, anti-H), 3.90 (q, 2H,J = 6.9 Hz, $-OC\mathit{H}_2-$), 4.13 (s, 1H, syn-H), 4.17 (q, 2H, J = 6.9 Hz, $-OC\mathit{H}_2-$), 5.11 (s, 5H, $C_5\mathit{H}_5$), 6.65 (d, 1H, J = 8.4 Hz, $-C\mathit{H}{=}CHCO_2Et$), 7.5 (m, 3H, $C_6\mathit{H}_5SO_2-$), 7.9 (m, 2H, $C_6\mathit{H}_5SO_2-$); $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 14.11 and 14.57 ($-OCH_2\mathit{C}H_3$), 35.61 and 41.49 ($={\mathit{C}}HCO_2Et$), 60.32 and 60.41 ($-O\mathit{C}H_2CH_3$), 83.80 (C_5H_5), 89.71 ($=C(SO_2Ph)\mathit{C}H=$), 98.82 ($\mathit{C}SO_2Ph$), 127.37 and 129.31 and 133.37 ($\mathit{C}_6H_5SO_2-$); 140.49 (C_i, $\mathit{C}_6H_5SO_2-$), 169.96 and 174.17 ($\mathit{C}O_2Et$); HRMS(FAB) *m/z* calcd for $C_{21}H_{23}O_6CoSNa$ (MNa^+): 485.0445, obsd: 485.0456. Anal. Calcd for $C_{21}H_{23}O_6CoS$: C, 54.55; H, 5.01. Found: C, 54.15; H, 4.96.

   Spectral data for **9**: IR (thin film): 1723 (C=O) cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.22 (m, 6H, $-CH_2C\mathit{H}_3$), 4.12 (q, 2H, J = 7.2 Hz, $-OC\mathit{H}_2CH_3$), 4.20 (q, 2H, J = 7.2 Hz, $-OC\mathit{H}_2CH_3$), 6.69 (d, 1H, J = 16.5 Hz, $-C\mathit{H}(CO_2Et){=}CH-$), 7.09 (s, 1H, $-C\mathit{H}(CO_2Et){=}CSO_2Ph-$), 7.88 (d, 1H, J = 16.5 Hz, $-CH(CO_2Et){=}C\mathit{H}-$), 7.49-7.81 (m, 5H, SO_2Ph); $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 13.69 (possibly two overlapping resonances), 60.73, 61.67, 127.88, 128.41, 129.22, 129.64, 130.99, 133.99, 137.94, 148.53, 162.99, 164.86; HRMS (FAB) *m/z* calcd for $C_{16}H_{18}O_6SNa$ (MNa^+): Calcd: 361.0722; obsd: 361.0729.

   Spectral data for **10**: IR: 3528 (br, OH), 1719 (C=O) cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.26 (t, 3H, J = 7.2 Hz, $-OCH_2C\mathit{H}_3$), 2.63 (br, s, 1H, $CH_2O\mathit{H}$), 4.15 (m, 2H, $-OC\mathit{H}_2OH$), 4.19 (q, 2H, J = 7.2 Hz, $-OC\mathit{H}_2CH_3$), 6.73 (dt, 1H, J = 16.5, 4.5 Hz, $=C\mathit{H}(CH_2OH))$, 6.88 (s, 1H, $-C\mathit{H}(CO_2Et){=}C(SO_2Ph))$, 6.96 (d, 1H, J = 16.5 Hz, $C\mathit{H}CO_2Et$), 7.49-7.81 (m, 5H, SO_2Ph); $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 13.92, 61.45, 62.54, 117.07, 124.71, 128.03, 129.20, 133.83, 138.65, 141.81, 150.72, 164.12; HRMS (FAB) m/z calcd for $C_{14}H_{16}O_5SCs$($MCs+$): Calcd: 428.9773; obsd: 428.9784.
7. (2-Phenylsulfonyl)-1,3-dienes are versatile synthetic intermediates. For recent leading references see: (a) Bäckvall, J-E.; Ericsson, A. *J. Org. Chem.* **1994,** *59,* 5850-5851. (b) Bäckvall, J-E.; Ericsson, A.; Juntunen, S.K; Nájera, C.; Yus, M. *J. Org. Chem.* **1993,** *58,* 5221-5225. (c) Hiroi, K.; Arinaga, Y. *Tetrahedron Lett.* **1994,** *35,* 153. (d) Padwa, A.; Filipkowski, M. A. *Tetrahedron Lett.* **1993,** *34,* 813.

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