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## Communications

# Diazoketones Undergo Reaction with a Cobalt Alkyne Complex To Give Highly Functionalized Conjugated Dienes

Joseph M. O'Connor,* Ming-Chou Chen, and Michael Frohn

*Department of Chemistry and Biochemistry, University of California at San Diego,*
*La Jolla, California 92093-0358*

Arnold L. Rheingold* and Ilia A. Guzei

*Department of Chemistry, University of Delaware, Newark, Delaware 19716*

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*Summary: The reaction of a cobalt alkyne complex with 2 equiv of diazo ketone led to the synthesis of highly substituted 1,3-diene complexes with an excellent control of diene stereochemistry.*

The rapid and selective construction of highly functionalized, conjugated dienes represents an ongoing challenge for the organic and organometallic chemist.[1−4] A fascinating and highly promising conceptual approach to this problem is the metal-mediated addition of two carbenes across an alkyne (Scheme 1). This class of reaction is exceedingly rare, having precedent only in the reactions of $(\eta^5\text{-}C_5H_5)Co(PPh_3)(\eta^2\text{-}PhC{\equiv}CPh)$[2] and $(\eta^5\text{-}C_5H_5)Co(PPh_3)(\eta^2\text{-}TMSC{\equiv}CSO_2Ph)$ (**1**)[1a,3] with diazo esters. To illustrate, when a benzene-$d_6$ solution of **1** and ethyl diazoacetate was heated at 70 °C for 12 h, all the starting alkyne complex was consumed to form three diene products in 81% combined yield: **2**-(*Z*,*Z*), 41%; **2**-(*Z*,*E*), 29.5%; **2**-(*E*,*Z*), 10.5%[1a] (Scheme 2).

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[⊗] Abstract published in *Advance ACS Abstracts,* November 15, 1997.

(1) For leading references of cobalt diene complexes: (a) O'Connor, J. M.; Chen, M. C.; Rheingold, A. L. *Tetrahedron Lett.* **1997**, *38*, 5241. (b) Altmann, M.; Roidl, G.; Enkelmann, V.; Bunz, U. H. F. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 1107. (c) Cammack, J. K.; Jalisatgi, S.; Matzger, A. J.; Negron, A.; Vollhardt, K. P. C. *J. Org. Chem.* **1996**, *61*, 4798. (d) Cloke, F. G. N.; Gardiner, M. G.; Raston, C. L.; Simpson, S. J. *J. Organomet. Chem.* **1996**, *507*, 245. (e) O'Connor, J. M.; Fong, B. S.; Ji, H.-L.; Hiibner, K.; Rheingold, A. L. *J. Am. Chem. Soc.* **1995**, *117*, 8029. (f) Boese, R.; Harvey, D.; Malaska, M. J.; Volllhardt, K. P. C. *J. Am. Chem. Soc.* **1994**, *116*, 11153. (g) Grotjahn, D. B.; Vollhardt, K. P. C. *J. Am. Chem. Soc.* **1990**, *112*, 5653. (h) Butenschön, H.; Betz, P. *J. Chem. Soc., Chem. Commun.* **1990**, 500. (i) Nakamura, A. *J. Organomet. Chem.* **1990**, *400*, 35. (j) King, J. A., Jr.; Vollhardt, K. P. C. *J. Organomet. Chem.* **1989**, *369*, 245. (k) O'Connor, J. M.; Pu, L.; Uhrhammer, R.; Johnson, J. A.; Rheingold, A. L. *J. Am. Chem. Soc.* **1989**, *111*, 1889. (l) O'Connor, J. M.; Johnson, J. A. *Synlett* **1989**, *1*, 57. (m) Yamazaki, H.; Wakatsuki, Y. *J. Organomet. Chem.* **1978**, *149*, 377.

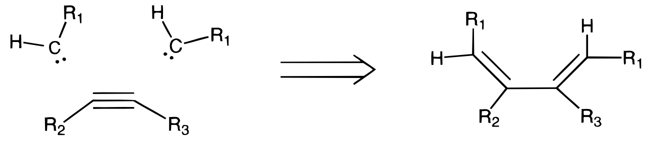
(2) Hong, P.; Aoki, K.; Yamazaki, H. *J. Organomet. Chem.* **1978**, *150*, 279.

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

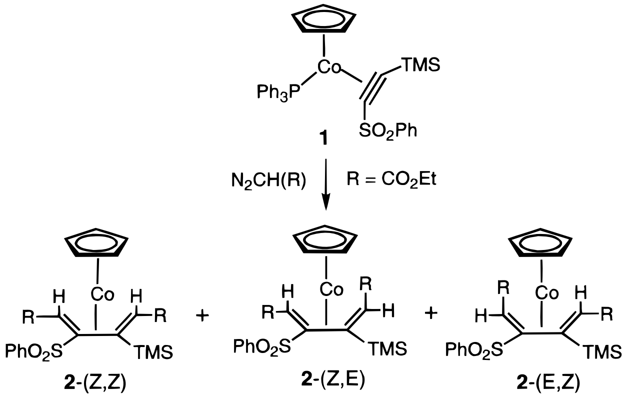
(4) NMR data for **3**-Me: $^1H$ NMR ($CDCl_3$) $\delta$ 0.45 (s, 9H, $-Si(CH_3)_3$), 0.71 (s, 1H, *anti*-H), 1.61 (s, 3H, $CH_3$), 2.22 (s, 3H, $CH_3$), 3.98 (s, 1H, *syn*-H), 5.06 (s, 5H, $C_5H_5$), 7.4−7.9 (m, 5H, $C_6H_5SO_2$); $^{13}C\{^1H\}$ NMR ($CDCl_3$) $\delta$ 1.76, 30.63, 31.49, 48.84, 53.30, 84.38, 87.29, 114.05, 128.00, 128.06, 132.48, 142.07, 204.47, 204.53. NMR data for **4**-Me: $^1H$ NMR ($CDCl_3$) $\delta$ 0.16 (s, 9H, $-Si(CH_3)_3$), 0.87 (s, 1H, *anti*-H), 2.24 (s, 3H, $CH_3$), 2.36 (s, 3H, $CH_3$), 4.82 (s, 1H, *syn*-H), 5.16 (s, 5H, $C_5H_5$), 7.4−7.9 (m, 5H, $C_6H_5SO_2$); $^{13}C\{^1H\}$ NMR ($CDCl_3$) $\delta$ 3.14, 30.43, 31.50, 50.20, 55.68, 85.31, 98.28, 101.88, 125.11, 128.94, 132.37, 143.02, 203.57, 207.31. NMR data for **5**-Me: $^1H$ NMR ($CDCl_3$) $\delta$ 0.94 (s, 1H, *anti*-H), 2.09 (s, 3H, $-CH_3$), 2.24 (s, 3H, $-CH_3$), 3.84 (d, 1H, $J = 6.6$ Hz, *syn*-H), 4.87 (s, 5H, $C_5H_5$), 5.91 (d, 1H, $J = 6.6$ Hz, $-CH{=}CH(COMe)$), 7.4−8.1 (m, 5H, $C_6H_5SO_2$); $^{13}C\{^1H\}$ NMR ($CDCl_3$) $\delta$ 30.61, 31.69, 47.20, 52.70, 82.81, 84.00, 110.30, 128.46, 131.85, 133.23, 141.45, 201.30, 204.13.

S0276-7333(97)00787-5 CCC: $14.00

**Scheme 1**



**Scheme 2**



In this communication, we demonstrate for the first time that diazo ketones can effectively serve as carbene precursors in [1 + 2 + 1] carbene/alkyne/carbene additions to form highly functionalized conjugated dienes. Remarkably, in noted contrast to diazo ester reactivity, diazo ketones give a single diene complex in reactions with **1**. The kinetic product, of (*Z*,*E*)-diene stereochemistry, is cleanly and selectively converted to either the *E*,*Z* isomer or the desilylated *Z*,*Z* or *E*,*E* isomers.

When a benzene solution of cobalt complex **1** (312 mg, 0.5 mmol, 0.017 M) and 1-diazopropan-2-one (210 mg, 2.5 mmol) was stirred under nitrogen for 12 h, the cobalt diene complex **3**-Me was isolated from the reaction mixture as a red-brown, analytically pure powder in 62% yield.[4,5] The $^1$H NMR spectrum of **3**-Me ($CDCl_3$) exhibited two singlets at $\delta$ 0.71 and 3.98, which were assigned to the *anti* and *syn* hydrogens, respectively.[6] On the basis of these two chemical shift values, we exclude the (*Z*,*Z*)- and (*E*,*E*)-diene structures for **3**-Me. Thermolysis of **3**-Me in benzene at 80 °C gave the new diene isomer **4**-Me, which exhibited vinyl hydrogen resonances as singlets in the $^1$H NMR spectrum ($CDCl_3$) at $\delta$ 0.87 (*anti*-H) and 4.82 (*syn*-H).[4–7] Irradiation of the TMS hydrogen resonance of **3**-Me resulted in a NOE at the $\delta$ 3.98 resonance but not at the $\delta$ 0.71 resonance, thereby supporting the *Z*,*E* assignment. For **4**-Me, irradiation of the TMS hydrogen signal failed to give a NOE at either the $\delta$ 0.87 or 4.82 singlet. The structures of **3**-Me and **4**-Me were conclusively established as the *Z*,*E* and *E*,*Z* isomers, respectively, by X-ray crystallographic analysis (Scheme 3).[8,9] The solid-state structures indicate substantial twisting of the *anti*-acyl group out of the diene plane. For **3**-Me, cobalt is 1.47 Å above the mean plane of the diene carbons, whereas C(7) is −1.0 Å below that plane. For **4**-Me, cobalt and C(12) deviate from the mean plane of the diene carbons by 1.5 and −1.0 Å, respectively.

Desilylation of **3**-Me with tetrabutylammonium fluoride (TBAF) in methanol/acetone (initially at −78 °C and then at 23 °C for 1 h) gave the desilylated complex **5**-Me in 84% isolated yield.[4,5] The $^1$H NMR spectrum ($CDCl_3$) of **5**-Me exhibited a singlet at $\delta$ 0.94 and two doublets at $\delta$ 3.84 ($J = 6.6$ Hz) and 5.91 ($J = 6.6$ Hz), assigned to the vinyl hydrogen resonances of the diene ligand. When **3**-Me and TBAF were stirred in methanol/acetone solution at room temperature for a longer period of time (24 h), diene isomerization occurred to give **6**-Me (89% isolated yield), for which the $^1$H NMR spectrum ($CDCl_3$) exhibited a singlet at $\delta$ 4.45 as well as doublets at 1.32 ($J = 8.7$ Hz) and 6.61 ($J = 8.7$ Hz).[5,10] The chemical shifts and coupling constants observed for the vinyl hydrogens in **5**-Me and **6**-Me permit the structural assignment of the complexes as the *Z*,*Z* and *E*,*E* isomers, respectively (Scheme 3). The thermal isomerization of **5**-Me to **6**-Me occurred over the course of 2 days at 70 °C in 93% isolated yield.

It appears that this diene synthesis and isomerization chemistry may be general for diazo ketones. Thus, alkyne complex **1** also underwent reaction with 2-diazo-1-phenylethanone to give a single diene complex, **3**-Ph, in 60% isolated yield.[5] In the $^1$H NMR spectrum ($CDCl_3$) of **3**-Ph, two singlets, assigned as *anti* and *syn* hydrogen resonances, were observed at $\delta$ 1.63 and 4.82, respectively. The *Z,E* stereochemistry for **3**-Ph was assigned on the basis of a NOE at the $\delta$ 4.82 singlet upon irradiation of the TMS hydrogen resonance. When **3**-Ph was heated at 80 °C for 2 days in benzene, the *E*,*Z* isomer **4**-Ph was formed in 51% yield.[5] Desilylation of **3**-Ph at 4 °C, followed by rapid chromatography on a short silica gel column, gave a 61% isolated yield of **5**-Ph.[5] When **3**-Ph was desilylated with TBAF (methanol/acetone, 1 h) at 23 °C, **6**-Ph was isolated in 84% yield.[5]

In summary, we have established for the first time that diazo ketones undergo reaction with an alkyne complex to give highly functionalized, conjugated dienes. The remarkable selectivity of this process, as well as the diene isomerization chemistry reported here, holds promise for the development of carbene/alkyne/carbene [1+ 2 + 1] additions as useful synthetic methodology. In addition to studies directed at the scope of this reaction with respect to the alkyne substituents, efforts are currently underway to decomplex cobalt and estab-

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[5] Full characterization data are provided in the Supporting Information.

[6] The *anti* hydrogens resonate at higher field than the *syn* hydrogens in the $^1$H NMR spectra of $\eta^4$-diene complexes: Emerson, G. F.; Mahler, J. E.; Kochhar, R.; Pettit, R. *J. Org. Chem.* **1964**, *29*, 3620.

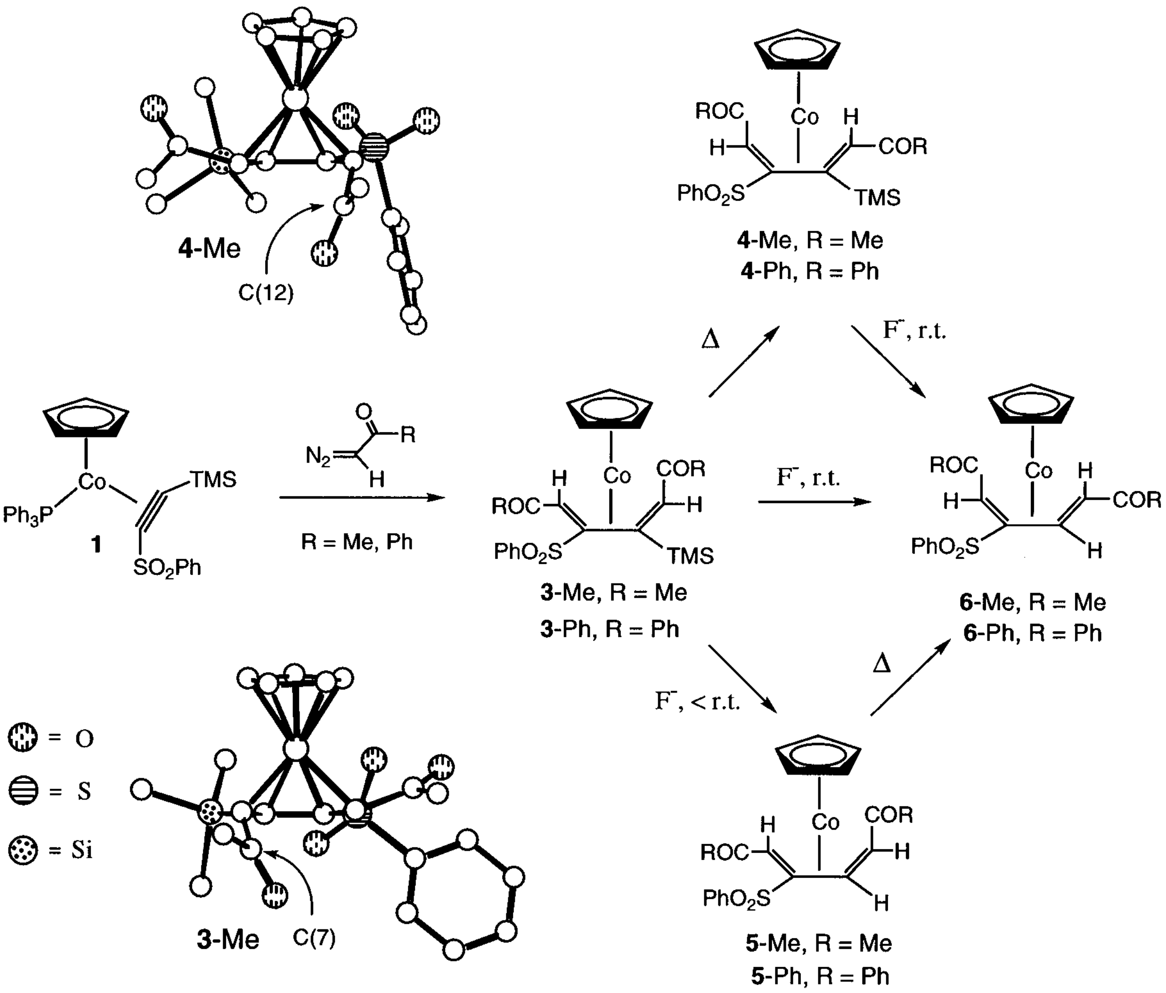
[7] For thermal and photochemical diene isomerizations of cyclopentadienyl cobalt complexes see: (a) Eaton, B.; King, J. A., Jr.; Vollhardt, K. P. C. *J. Am. Chem. Soc.* **1986**, *108*, 1359. (b) King, J. A., Jr.; Vollhardt, K. P. C. *J. Organomet. Chem.* **1993**, *460*, 91. (c) King, J. A., Jr.; Vollhardt, K. P. C. *J. Organomet. Chem.* **1994**, *470*, 207.

[8] Crystallographic data for $C_{22}H_{27}CoO_4SSi$ (**3**-Me): $M_r = 474.52$, triclinic, $P\bar{1}$, $a = 7.86950(10)$ Å, $b = 8.79770(10)$ Å, $c = 16.3646(2)$ Å, $\alpha = 91.9630(10)°$, $\beta = 102.9570(10)°$, $\gamma = 92.6580(10)°$, $V = 1101.78(2)$ Å$^3$, $Z = 2$, $D$(calc) = 1.430 g/cm$^3$, $\mu$(Mo K$\alpha$) = 9.53 cm$^{-1}$, Mo K$\alpha$ radiation ($\lambda = 0.710\ 73$Å), $T = 173(2)$ K, $R(F) = 5.55\%$, $R_w(F^2) = 15.32\%$. Crystallographic data for $C_{22}H_{27}CoO_4SSi$ (**4**-Me): $M_r = 474.52$, triclinic, $P2_1/c$, $a = 14.2164(3)$ Å, $b = 10.9545(2)$ Å, $c = 16.08480(10)$ Å, $\beta = 112.5150(4)°$, $V = 2314.01(7)$ Å$^3$, $Z = 4$, $D$(calc) = 1.362 g/cm$^3$, $\mu$(Mo K$\alpha$) = 9.08 cm$^{-1}$, Mo K$\alpha$ radiation ($\lambda = 0.710\ 73$ Å), $T = 173(2)$ K, $R(F) = 3.52\%$, $R_w(F^2) = 9.54\%$.

[9] For structural characterization of cobalt diene complexes see: Wakatsuki, Y.; Aoki, K.; Yamazaki, H. *J. Chem. Soc., Dalton Trans.* **1982**, 89.

[10] Base- and acid-catalyzed diene isomerizations are known for tricarbonyliron diene complexes: Frederiksen, J. S.; Graf, R. E.; Gresham, D. G.; Lillya, C. P. *J. Am. Chem. Soc.* **1979**, *101*, 3863.

**Scheme 3**



lish the reactivity patterns for these highly functionalized dienes.[11-12]

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**Supporting Information Available:** Tables of the X-ray crystal structure determination data, atomic coordinates, anisotropic thermal parameters, and bond lengths and angles and ORTEP diagrams for **3**-Me and **4**-Me and a table giving full characterization data for **3**-R–**6**-R (R = Me, Ph) (16 pages). Ordering information is given on any current masthead page.

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[11] For iron complexes of 2-phenylsulfonyl 1,3-dienes see: Chou, S.-S. P.; Hsu, C.-H.; Yeh, M.-C. *Tetrahedron Lett.* **1992**, *33*, 643. Yeh, M.-C. P.; Chou, T.-S.; Tso, H.-H.; Tsai, C.-Y. *J. Chem. Soc., Chem. Commun.* **1990**, 897.

[12] 2-Phenylsulfonyl 1,3-dienes are versatile synthetic intermediates. For recent leading references see: (a) Hentemann, M. F.; Fuchs, P. L. *Tetrahedron Lett.* **1997**, *38*, 5615. (b) Bäckvall, J.-E.; Ericsson, A. *J. Org. Chem.* **1994**, *59*, 5850. (c) Bäckvall, J.-E.; Ericsson, A.; Juntunen, S. K.; Nájera, C.; Yus, M. *J. Org. Chem.* **1993**, *58*, 5221. (d) Hiroi, K.; Arinaga, Y. *Tetrahedron Lett.* **1994**, *35*, 153. (e) Padwa, A.; Filipkowski, M. A. *Tetrahedron Lett.* **1993**, *34*, 813.