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Notes

Carbonylative Cyclization of Alkynes Using Cobalt Carbonyl Species Prepared via Reduction of $CoBr_2$ with Zn under a Carbon Monoxide Atmosphere

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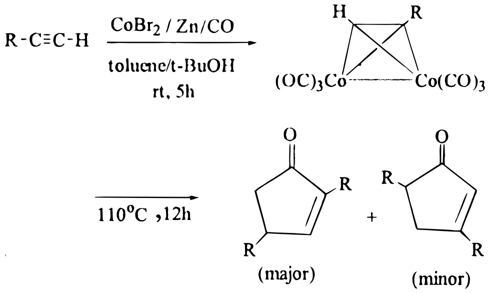
Summary: Alkyne−$Co_2(CO)_6$ complexes prepared in situ using $CoBr_2$, Zn, and CO give the corresponding cyclopentenones or cyclopentadienones on heating in toluene or in CH_2Cl_2 at 25 °C in the presence of DMSO or amines.

In recent years, metal-mediated cyclization reactions have been increasingly used in organic synthesis.[1] One of the most widely used organometallic reactions is the Pauson−Khand reaction of alkyne−$Co_2(CO)_6$ complexes.[2] Previously, we reported the generation of alkyne−$Co_2(CO)_6$ complexes in situ using $CoBr_2$, Zn, and CO in THF, CH_2Cl_2/t-BuOH, and toluene/t-BuOH solvent systems for applications in Pauson−Khand reactions.[3,4] Herein, we report the results of carbonylative cyclization of the alkynes without using externally added olefins.

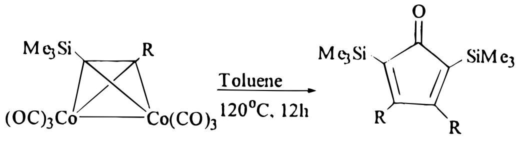
We have observed that the alkyne−$Co_2(CO)_6$ complexes, prepared in situ in toluene/t-BuOH, upon heating at 110 °C give the corresponding substituted cyclopentenones in moderate yields (Scheme 1). The results are summarized in Table 1. Two regioisomers were obtained. The regiochemistry of the major product is in line with that of cyclopentenones obtained in the Pauson−Khand reaction. However, whereas the 3-substituted cyclopentenones are not formed in the Pauson−Khand reaction, they are obtained in minor amounts here (Table 1).

In the case of the reaction with PhC≡CH, 2,5-diphenylcyclopentenone was obtained as a major product; the trimerized product of PhC≡CH was also formed in minor amounts (5%). The formation of cyclopentenones may be rationalized by the reaction of alkyne−$Co_2(CO)_6$ complexes with the olefinic intermediates, which might have formed through the cleavage of the alkyne moiety by the $HCo(CO)_4$ species formed in situ in the medium. Previously, similar results were observed in the reaction of alkyne−$Co_2(CO)_6$ complexes with CF_3COOH in THF at 80−90 °C for 24 h.[4b]

Scheme 1



Scheme 2



We have also examined the reactivity of alkynes containing trimethylsilyl substituents. Such trimethylsilyl-substituted alkynes have been used previously to change the regioselectivity in Pauson−Khand reactions.[5] The formation of corresponding substituted cyclopentadienones is observed under the present conditions (Scheme 2).

The formation of cyclopentadienones was reported in the reaction of alkynes with $CpCo(CO)_2$[6] and $Fe(CO)_5$.[7] Recently, a direct synthesis of cyclopentadienones was reported using $Co_2(CO)_8$ through reaction of cobalt-complexed alkynylsilanes with free alkynylsilanes.[8] The

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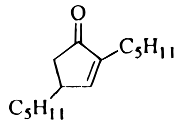
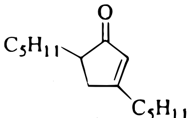
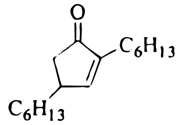
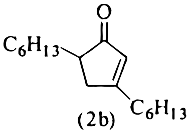
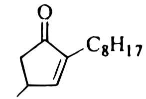
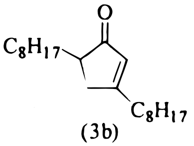
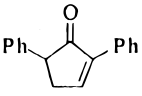
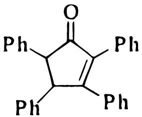
10.1021/om990534c CCC: $18.00

Table 1. Reactions of $(RC{\equiv}CR')Co_2(CO)_6$ Complexes with t-BuOH

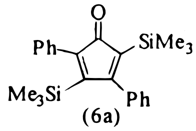
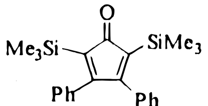
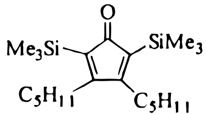
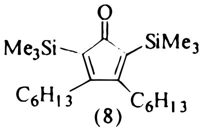
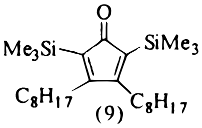
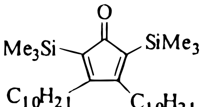
No.	alkyne	Product^{a,b}	Yield^c
1	$C_5H_{11}-C{\equiv}C-H$	 (1a)	40%
		 (1b)	10%
2	$C_6H_{13}-C{\equiv}C-H$	 (2a)	38%
		 (2b)	12%
3	$C_8H_{17}-C{\equiv}C-H$	 (3a)	39%
		 (3b)	10%
4	$Ph-C{\equiv}C-H$	 (4)	38%
5	$Ph-C{\equiv}C-Ph$	 (5)	50%

[a] All reactions were carried out using $CoBr_2$ (20 mmol), Zn (20 mmol), and alkyne (10 mmol). [b] The products were identified by IR, ^1H NMR, and ^{13}C NMR spectral data reported in the literature. [c] Yields reported here are of products separated from chromatography on a silica gel column using hexane/ethyl acetate as eluent.

present method (Scheme 2) using the simple benchtop chemicals $CoBr_2$, Zn, and CO in toluene/t-BuOH is advantageous for such synthetic applications. The results are summarized in Table 2. We have obtained symmetrical cyclopentadienones as major products in all cases except in the case of phenyl-substituted alkynylsilane. In this case, both 2,5-diphenyl- and 3,5-diphenyl-substituted isomers were obtained. The positions of the phenyl and silyl groups of the 3,5-diphenyl-substituted cyclopentadienone **6a** were also confirmed by X-ray crystal structure analysis (Figure 1).

Presumably, in the case of trimethylsilyl-substituted alkynes, the cyclopentadienones are obtained instead of cyclopentenones (Scheme 1), as the reductive cleavage of a trimethylsilyl-substituted alkyne–$Co_2(CO)_6$ complex to produce the corresponding alkenylsilane intermediate is expected to be difficult due to steric reasons. However, it may be of interest to note that the $(RC{\equiv}CSiMe_3)Co_2(CO)_6$ complexes are readily cleaved to give alkenylsilanes on heating with CF_3COOH.[4b]

Table 2. Reactions of $(RC{\equiv}CSiMe_3)Co_2(CO)_6$ Complexes in Toluene

No.	alkyne	Product^{a,b}	Yield^c
1	$Ph-C{\equiv}C-SiMe_3$	 (6a)	30%
		 (6b)	15%
2	$C_5H_{11}-C{\equiv}C-SiMe_3$	 (7)	40%
3	$C_6H_{13}-C{\equiv}C-SiMe_3$	 (8)	38%
4	$C_8H_{17}-C{\equiv}C-SiMe_3$	 (9)	35%
5	$C_{10}H_{21}-C{\equiv}C-SiMe_3$	 (10)	35%

[a] All reactions were carried out using $CoBr_2$ (20 mmol), Zn (20 mmol), and alkyne (10 mmol). [b] The products were identified by IR, ^1H NMR, and ^{13}C NMR spectral data and elemental analysis. [c] Yields reported here are of products separated from chromatography on a silica gel column using hexane/ethyl acetate as eluent.

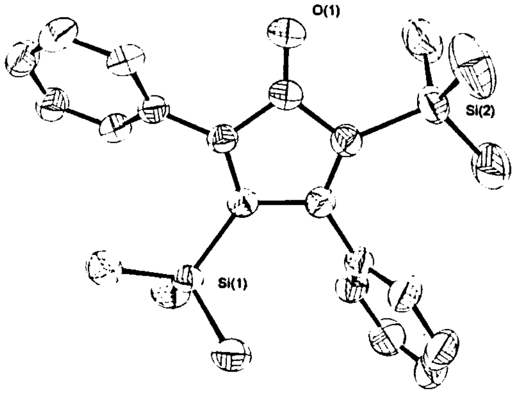
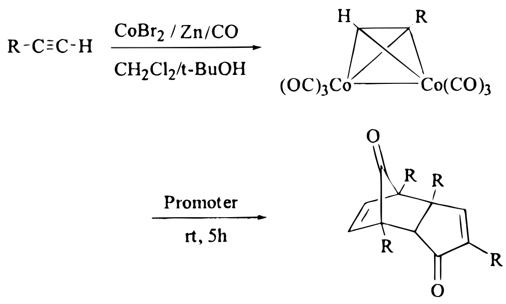


Figure 1. Ortep diagram of **6a**.

The cyclopentenones and cyclopentadienones (Tables 1 and 2) were obtained from the alkyne–$Co_2(CO)_6$ complexes under heating conditions. Previously, we have reported the use of certain amines and amides as promoters for carrying out the Pauson–Khand reaction

Scheme 3



R	Promoter	Product	Yield[11]
n-C_5H_{11}	DMSO	(11)	20%
n-C_6H_{13}	DMSO	(12)	18%
n-C_8H_{17}	DMSO	(13)	16%
n-C_5H_{11}	DMF	(11)	15%
n-C_8H_{17}	TMEDA	(13)	15%

at room temperature.[3c] Pauson and co-workers have also reported the use of DMSO for similar purposes.[9] Accordingly, we have examined the effect of these promoters on the reaction of alkyne−$Co_2(CO)_6$ complexes without using an added olefin. In all cases, the dicyclopentadienones **11−13** were obtained, along with unidentified cobalt carbonyl complexes. The results are summarized in Scheme 3. Previously, the formation of dicyclopentadienones was reported in the reaction of $Co_2(CO)_8$ in DME with a 1/1 mixture of acetylene and CO at 65 °C for 5 days under 1 atm pressure.[10]

The formation of dicyclopentadienones (Scheme 3) would most probably occur through the corresponding cyclopentadienone intermediates. However, efforts to trap the cyclopentadienone intermediate by carrying out the reaction in the presence of dienophiles such as maleic anhydride, crotonaldehyde, and dimethyl fumarate were unsuccessful. In all cases, only the dicyclopentadienones were isolated.

Experimental Section

General Methods. All reactions were carried out under an atmosphere of predried nitrogen. All transfers and manipulation of compounds were carried out under a nitrogen atmosphere. Toluene was distilled over sodium−benzophenone ketyl. All alkynes and the silyl derivatives were prepared by following reported procedures.[12] ^1H and ^{13}C NMR spectra were recorded on a Bruker AC-200 spectrometer with chloroform-*d* as solvent and TMS as reference (δ 0 ppm). All IR spectra were recorded on a JASCO FT-5300 instrument with polystyrene as reference. Elemental analysis was carried out on a Perkin-Elmer 240C elemental analyzer. Column chromatography was carried out using Aceme silica gel (100−200 mesh). Anhydrous $CoBr_2$ was prepared from the hydrated complex by keeping it in the hot-air oven at 150 °C for 5−6 h and further dried at 150 °C for 4 h under vacuum. Zn dust was activated by treating commercial Zn dust with 1% H_2SO_4, washing with water and acetone, and drying at 150 °C for 4 h under vacuum. Carbon monoxide was generated by dropwise addition of formic acid (98%) to concentrated H_2SO_4 (96%) at 90 °C using an apparatus recommended for use in the carbonylation of organoboranes.[13]

General Methods for Synthesis of Cyclopentenones and Cyclopentadienones. The cobalt carbonyl species was prepared by reducing $CoBr_2$ (4.36 g, 20 mmol) with Zn (1.43 g, 20 mmol) and alkyne/alkynylsilane (10 mmol) in toluene (50 mL)/t-BuOH (1.5 mL) while bubbling CO with stirring for 5 h at 25 °C. An additional amount of t-BuOH (2 mL) was added, and the contents were stirred at 110 °C for 10 h. The cobalt carbonyl species completely decomposed during this time. The contents were brought to room temperature. Diethyl ether (25 mL) was added and the mixture washed successively with water (20 mL) and brine solution (10 mL). The combined organic extracts were dried over anhydrous $MgSO_4$. The solvent was removed, and the residue was subjected to chromatography on silica gel using hexane/ethyl acetate as eluent. The structural assignments are based on IR, ^1H NMR, ^{13}C NMR, and mass spectral data and elemental analysis. Spectral data obtained for the cyclopentadienones are summarized below.

6a: yield 30% (1.12 g); IR (KBr) ν 1687, 1440 cm^{-1}; ^1H NMR ($CDCl_3$) δ −0.3 (s, 9H), 0.0 (s, 9H) 7.2−7.4 (m, 10H); ^{13}C NMR ($CDCl_3$) δ −0.20, 0.39, 125.2, 127.2, 127.7, 128.0, 128.1, 128.3, 129.9, 133.7, 139.6, 145.1, 155.0, 176.6, 206.6.

6b: yield 15% (0.56 g); IR (KBr) ν 1685, 1440 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.3 (s, 9H), 7.2−7.4 (m, 5H); ^{13}C NMR ($CDCl_3$) δ −0.11, 127.4, 128.0, 128.2, 135.7, 171.1, 209.9.

7: yield 40% (1.45 g); IR (neat) ν 1684, 1466 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.2 (s, 9H), 1−2.5 (m, 11H); ^{13}C NMR ($CDCl_3$) δ 0.060, 13.9, 22.4, 28.3, 30.4, 32.3, 128.2, 172.8, 210.8; MS *m*/*z* 366. Anal. Calcd for $C_{21}H_{40}Si_2O$: C, 69.23; H, 10.98. Found: C, 69.28; H, 11.00.

8: yield 38% (1.48 g); IR (neat) ν 1684, 1466 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.2 (s, 9H), 1−2.5 (m, 13H); ^{13}C NMR ($CDCl_3$) δ 0.015, 13.9, 22.5, 28.3, 29.7, 30.6, 31.5, 128.2, 172.6, 210.7; MS *m*/*z* 392. Anal. Calcd for $C_{23}H_{44}Si_2O$: C, 70.40; H, 11.20. Found: C, 70.45; H, 11.26.

9: yield 38% (1.70 g); IR (neat) ν 1684, 1466 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.2 (s, 9H), 1−2.5 (m, 17H); ^{13}C NMR ($CDCl_3$) δ 0.059, 14.0, 22.6, 28.4, 29.1, 29.3, 30.1, 30.7, 31.8, 125.3, 172.3, 210; MS *m*/*z* 449. Anal. Calcd for $C_{27}H_{52}Si_2O$: C, 72.30; 11.60. Found: C, 72.35; H, 11.65.

10: yield 35% (1.76 g); IR (neat) ν 1684, 1466 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.2 (s, 9H), 1−2.5 (m, 21H); ^{13}C NMR ($CDCl_3$) δ 0.112, 14.0, 22.7, 28.4, 28.8, 29.1, 29.3, 29.5, 30.1, 30.8, 31.9, 125.3, 172.7, 210.9.

Reaction of Alkyne−Cobalt Carbonyl Complexes in the Presence of DMSO, DMF, and TMEDA in CH_2Cl_2/t-BuOH. The cobalt carbonyl species was prepared by reducing $CoBr_2$ (4.36 g, 20 mmol) with Zn (1.43 g, 20 mmol) and alkyne (10 mmol) in CH_2Cl_2 (50 mL)/t-BuOH (1.5 mL) while bubbling CO with stirring for 5 h at 25 °C. The promoter (3 equiv) was added, and the contents were stirred for 5 h at 25 °C. The mixture was washed successively with dilute HCl (20 mL), water (2 × 20 mL), and brine solution (10 mL). The organic extracts were dried over anhydrous $MgSO_4$. The solvent was removed, and the residue was subjected to chromatography on a silica gel column using hexane/ethyl acetate as eluent. The structural assignments are based on IR, ^1H NMR, ^{13}C NMR, DEPT experiments, mass spectral data, and elemental analysis. Spectral data obtained for the dicyclopentadienones are summarized below.

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(11) All reactions were carried out using $CoBr_2$ (20 mmol), Zn (20 mmol), and alkyne (10 mmol). The products were identified by IR, ^1H NMR, and ^{13}C NMR spectral data and elemental analysis. Yields reported here are for products separated from chromatography on silica gel column using hexane/ethyl acetate as eluent. In all reactions, some amounts of unreacted cobalt carbonyl complexes were recovered.

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11: yield 20% (0.88 g); IR (neat) ν 1774, 1701, 1464 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 0.5−2.5 (m), 3.1 (s, 1H), 5.9 (d, J = 20 Hz, 1H), 6.1 (d, J = 20 Hz, 1H), 6.9 (s, 1H); ^{13}C NMR (CDCl$_3$) δ 13.9, 22.4, 23.0, 24.9, 25.2, 25.4, 25.5, 27.1, 27.5, 30.2, 31.4, 32.3, 32.5, 51.0, 55.6, 58.2, 61.8, 132.1, 133.0, 153.2, 154.6, 204.8, 208.6; MS *m*/*z* 412 (−CO).

12: yield 18% (0.89 g); IR (neat) ν 1772, 1701, 1464 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 0.5−2.5 (m), 3.1 (s, 1H), 5.9 (d, J = 20 Hz, 1H), 6.1 (d, J = 20 Hz, 1H), 6.9 (s, 1H); ^{13}C NMR (CDCl$_3$) δ 14.03 (−CH$_3$), 22.5, 23.1, 24.9, 25.5, 25.7, 25.8, 27.2, 27.8, 28.9, 29.8, 30.0, 30.3, 31.6 (−CH$_2$), 51.0 (−CH), 55.6, 58.3, 61.9 (quaternary) 132.1, 133.0, 153.2 (−CH), 154.6 (quaternary), 204.9, 208.7 (CO); MS *m*/*z* 469 (−CO).

13: yield 16% (0.97 g); IR (neat) ν 1772, 1703, 1464 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 0.5−2.5 (m), 3.1 (s, 1H), 5.9 (d, J = 20 Hz, 1H), 6.1 (d, J = 20 Hz, 1H), 6.9 (s, 1H); ^{13}C NMR (CDCl$_3$) δ 14.0, 22.6, 23.0, 24.9, 25.5, 25.7, 25.8, 27.2, 27.8, 29.2, 30.1, 30.3, 31.8, 51.0, 55.6, 58.2, 61.8, 132.1, 133.0, 153.1, 154.6, 204.8, 208.6. Anal. Calcd for $C_{42}H_{72}O_2$: C, 82.8; H, 11.8. Found: C, 83.2; H, 11.8.

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Supporting Information Available: ^{13}C NMR spectrum of the compounds **1**−**13**. This material is available free of charge via the Internet at http://pubs.acs.org.

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