

Intramolecular Cyclizations via Carbenoid Intermediates in Complexation of Alkynyltungsten Compounds with $\text{Co}_2(\text{CO})_8$: A New Route to the Pauson–Khand Reaction

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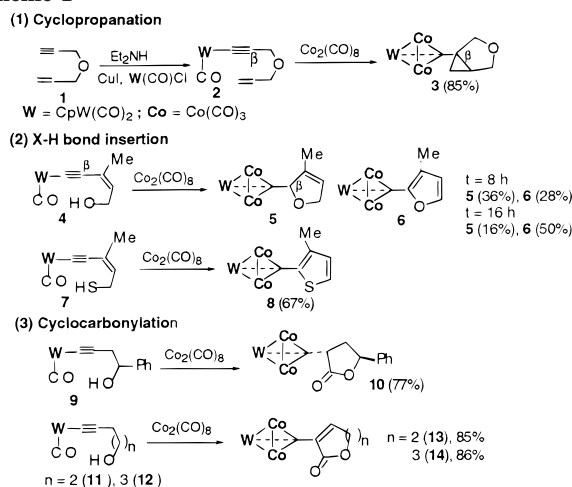
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The reactions of $\text{Co}_2(\text{CO})_8$ with alkynes RCCR' form $(\text{RCCR}')\text{Co}_2(\text{CO})_6$ complexes.¹ Organic reactions^{2–6} associated with this functionality can be grouped into three major categories: (1) [2 + 2 + 1] cyclization with alkenes to form cyclopentenones (Pauson–Khand reaction),^{2–4} (2) formation of a propargylic cation equivalent (the Nicholas reaction),^{2,5} and (3) protection of an alkyne group.⁶ The versatility of these reactions is well recognized, and they are frequently employed as a key step in synthesis of complex molecules.⁷ Organic carbenoids are useful intermediates in organic synthesis.^{8,9} Development of new synthetic method involving carbenoid intermediates has received considerable attention.⁹ Although there are numerous investigations on $(\text{RCCR}')\text{Co}_2(\text{CO})_6$ complexes,^{2–6} generation of a carbenoid intermediate from this functionality remains entirely unknown. Here we report several intramolecular cyclizations via carbenoid intermediates generated from $\text{Co}_2(\text{CO})_8$ complexation of functionalized alkynyltungsten compounds. The synthetic utility of these cyclizations is manifested by the synthesis of cyclopentenone derivatives.

A representative cyclization is shown in Scheme 1 (eq 1). Compound **2** is readily prepared¹⁰ in 78% yield from $\text{CpW}(\text{CO})_3\text{Cl}$, CuI catalyst, and its corresponding enyne **1**. Treatment of **2** with $\text{Co}_2(\text{CO})_8$ (1.0 equiv) in THF under ambient conditions (23 °C, 8 h) gave bicyclic compound **3** in 85% yield. Charac-

Scheme 1



terization of this product relied on IR, NMR, mass, elemental analysis, and X-ray diffraction studies.¹¹ The ORTEP drawing shows that $\text{Co}_2(\text{CO})_6$ is bound to the $\text{Cp}(\text{CO})_2\text{W}$ and C_α fragment to form a tetrahedral core,¹² leaving the C_β carbon like a carbenoid to capture the tethered olefin to form a cyclopropane ring. We prepared tungsten–alkynol **4** bearing a proximate hydroxyl group to capture the C_β carbenoid via insertion of the OH bond. Its reaction with $\text{Co}_2(\text{CO})_8$ (23 °C, 8 h, THF) delivered furan derivatives **5** and **6** in 36% and 28% isolated yields, respectively. After a prolonged period (16 h), the yields of **5** and **6** were 17% and 50%, respectively. The structure of **6** was also characterized by an X-ray diffraction study.¹¹ Similarly, treatment of the thiol **7** in THF (23 °C, 8 h) with $\text{Co}_2(\text{CO})_8$ produced thiophene **8** in 67% yield. Equation 3 shows a cyclocarbonylation reaction for treatment of tungsten–alkynol **9** with $\text{Co}_2(\text{CO})_8$ in THF (23 °C, 2 h); the yield of γ -lactone **10** is 77%. Similarly, unsaturated δ - and ϵ -lactones **13** and **14** were produced in 85% and 86% yields respectively from compounds **11** and **12**. The molecular structures of **10** and **13** were elucidated with X-ray diffraction studies.¹¹ The ORTEP drawing shows that compound **10** has a *trans* configuration between tetranuclear and phenyl groups.

Shown in Table 1 is generalization of the cyclopropanation reaction. To clarify the stereospecificity, we prepared alkynyltungsten species **15** and **16** (entries 1–2) containing a tethered *cis*- and *trans*-olefin, respectively. Treatment of these two species with $\text{Co}_2(\text{CO})_8$ at 23 °C only gave unstable $\text{Co}_2(\text{CO})_6$ -complexed adducts.¹³ After slight heating of the solution in THF (45 °C), both **15** and **16** afforded the same cyclopropane product **22** in 65% and 22% yields, respectively. The molecular structure of **22** is determined by an X-ray diffraction study¹¹ which reveals that the methyl group lies *trans* to the bulky tetrahedral unit to minimize steric hindrance. This stereochemical arrangement shows an opposite configuration to the *trans* geometry of compound **16**. The Pauson–Khand product can be observed here as shown in entry 3. Treatment of **17** with $\text{Co}_2(\text{CO})_8$ in benzene (25 °C, 2 h) afforded cyclopropane **23** exclusively (78% yield) in addition to cyclopentenone **24** (2% yields). Further heating of this benzene

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(11) Tables of crystal data, ORTEP drawing, atomic coordinates, bond distances and angles, and thermal parameters of compound **3**, **6**, **10**, **14**, **22**, **26**, and **27** are provided in Supporting Information.

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(13) The $\text{Co}_2(\text{CO})_6$ -complexed alkynyltungsten complexes **15** and **16** could be characterized by IR, ¹H NMR, and mass data. Purification of these two species was difficult to achieve due to its high reactivities.

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Table 1. Cyclopropanation and Pauson–Khand Reaction

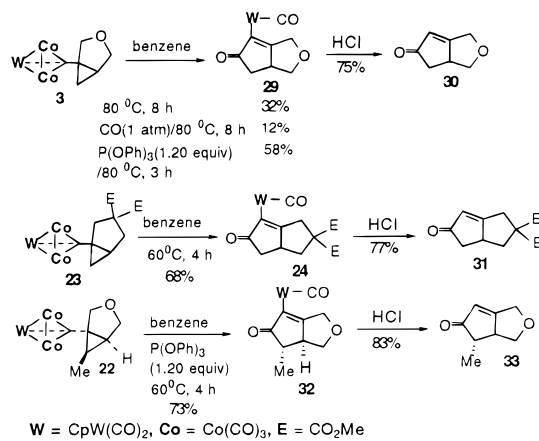
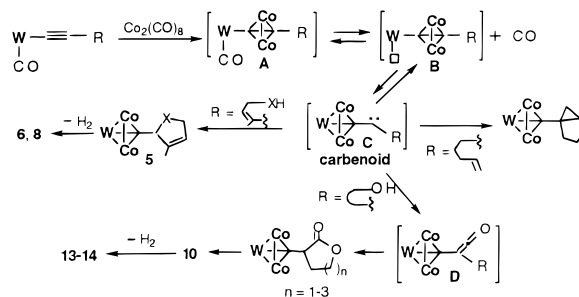
entry	alkynyl species	condition ^a	products ^{b,c}
1		THF (45 °C, 8 h)	22 (65%)
2		THF (45 °C, 16 h)	22 (22%)
3		benzene (25 °C, 2 h) benzene (60 °C, 3 h) THF (25 °C, 4 h) CO (1 atm)/THF (25 °C, 4 h)	23 (78%) 24 (2%) 23 (10%) 24 (62%) 23 (38%) 24 (44%) 23 (75%) 24 (14%)
4		benzene (45 °C, 2 h) ^d	25 (trans/cis = 2.1, 61%)
5		benzene (45 °C, 2 h) ^d	26 (trans/cis = 4.1, 72%)
6		THF (40 °C, 2 h)	27 (trans/cis = 1.8, 66%)
7		THF (25 °C, 8 h)	28 (trans/cis = 1.94, 72%)

W = CpW(CO)₂, Co = Co(CO)₃. ^aEquimolar ratios of Co₂(CO)₈ and alkynyltungsten complex were used. ^bThese organometallic products were purified on a silica column. ^cIsolated yields after chromatographic purification. ^dThe mixture was stirred in benzene for 2 h before heating.

solution at 60 °C for 3 h gave a 62% yield of cyclopentenone **24**, accompanied by loss of the cyclopropane **23** (10%). If THF was used as the solvent, the yields of **23** and **24** were 38% and 44%, respectively. The presence of CO gas (1.0 atm, THF) suppressed the Pauson–Khand reaction to give the cyclopentenone **24** in only 14% yield although one extra molecule of CO suffices for this stoichiometric reaction. In this case, the yield of cyclopropane **23** was up to 75%. Entry 4 shows an additional example for syntheses of cyclopentenones **25** in 61% yield from heating compounds **18** with Co₂(CO)₈ at 45 °C (2 h); its *trans/cis* isomeric ratio was ca. 2.1. One limitation of the Pauson–Khand reaction is its failure with styrene and electron-deficient olefins having β -hydrogen; these olefins react with RCCR'·Co₂(CO)₆ to give organic dienes exclusively in both inter- and intramolecular systems.¹⁴ But the examples in entries 5–7 indicate that bicyclic unsaturated lactones **26–28** were formed in good yields from alkynyltungsten species **19–21** in THF at ambient conditions; the *trans* isomer was formed preferably in these reactions. The structures of cyclopentenones **24** and **28** were characterized by X-ray diffraction studies.¹¹

To ascertain the role of cyclopropanes in the Pauson–Khand reaction, cyclopropanes **3** and **23** were heated in benzene (60–80 °C) in a sealed tube to yield cyclopentenones **29** and **24** in 32% and 68% yields, respectively. In case of **3**, the presence of CO (1 atm, benzene, 80 °C, 8 h) again inhibits the Pauson–Khand reaction to give a 12% yield of **29** with a 63% recovery of **3**. The transformation is improved in the presence of P(OPh)₃ (1.20 equiv) to give **29** in 58% yield. Compound **22** was also heated in benzene for 4 h to yield *trans*-cyclopentenone **32** in 73% yield. Demetalation of **29**, **24**, and **32** was achieved smoothly with concentrated HCl solution in CHCl₃ to yield free cyclopentenones **30** (75%), **31** (77%), and **33** (83%), respectively.

The cyclizations shown in Scheme 1 clearly show participation of carbenoid intermediates. Depicted in Scheme 3 is a plausible mechanism to rationalize these intramolecular cyclizations. Alkynyltungsten species first form Co₂(CO)₆-complexed species **A** upon

Scheme 2**Scheme 3**

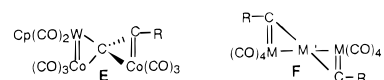
treatment with Co₂(CO)₈.¹³ After loss of one W–CO group, the Co₂(CO)₆ fragment of species **B** undergoes a 1,2-shift to form carbenoid species **C**; this transformation is driven by formation of a stable tetranuclear core. The detailed structure of species **C** remains unclear at the present stage; it is likely a cobalt carbene species.¹⁵ Capture of this carbenoid by a tethered olefin and by a proximate X–H (X = O, S) group leads to cyclopropanation and insertion reactions, respectively.⁸ If the tethered hydroxyl group is conformationally flexible as in compounds **9** and **11–12**, the carbenoid may uptake one CO to give the ketene species **D**,⁸ ultimately giving cyclocarbonylation products **10** and **13–14**.

In summary, we report the feasibility of generating a reactive carbenoid in reaction of functionalized alkynyltungsten species with Co₂(CO)₈, leading to various intramolecular cyclizations via cyclopropanation, insertion of the X–H bond (X = S, O), and cyclocarbonylations. These reaction will enhance synthetic application of (RCCR')Co₂(CO)₆ complexes. The potential utilities of these reactions is manifested by transformation of cyclopropane products into cyclopentenones upon heating in benzene. The synthesis of cyclopentenones is applicable to electron-deficient olefins such as tethered styrene, cyanoalkene, and methoxycarbonyl alkene. Realization of these reactions in intermolecular systems via metal catalyst is under current investigation.

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Supporting Information Available: Synthesis and spectral data of new compounds; tables of crystal data, atomic coordinates, bond distances and angles, and thermal parameters of **3**, **6**, **10**, **14**, **22**, **26**, and **27**. This material is available free of charge via the Internet at <http://pubs.acs.org>. JA990007K

(15) The structure of **C** in Scheme 3 represents a carbenoid equivalent, and **E** below is a plausible structure with the same formula as **C**. Several heteronuclear clusters have skeletons such as **F** are known.¹⁶



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