Intramolecular Cyclizations via Carbenoid Intermediates in Complexation of Alkylkynyltungsten Compounds with Co$_2$(CO)$_6$: A New Route to the Pauson–Khand Reaction

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The reactions of Co$_2$(CO)$_6$ with alkynes RCCR' form (RCCR')-Co$_5$(CO)$_6$ complexes. Organic reactions associated with this functionality can be grouped into three major categories: (1) [2 + 2 + 1] cyclization with alkynes to form cyclopentenones (Pauson–Khand reaction), (2) formation of a propargyl cation equivalent (the Nicholas reaction), and (3) protection of an alkylene group. The versatility of these reactions is well recognized, and they are frequently employed as a key step in synthesis of complex molecules. Organic carbenoids are useful intermediates in organic synthesis. Development of new synthetic method involving carbenoid intermediates has received considerable attention. Although there are numerous investigations on (RCCR')-Co$_5$(CO)$_6$ complexes, generation of a carbenoid intermediate from this functionality remains entirely unknown. Here we report several intramolecular cyclizations via carbenoid intermediates generated from Co$_2$(CO)$_6$ complexation of functionalized alkynes. The synthetic utility of these cyclizations is shown by the synthesis of cyclopentenone derivatives.

A representative cyclization is shown in Scheme 1 (eq 1). Compound 2 is readily prepared in 78% yield from CpW(CO)$_3$Cl, CuI catalyst, and its corresponding enyne 1. Treatment of 2 with Co$_2$(CO)$_6$ (1.0 equiv) in THF under ambient conditions (23 °C, 8 h) gave bicyclic compound 3 in 85% yield. Characterization of this product relied on IR, NMR, mass, elemental analysis, and X-ray diffraction studies. The ORTEP drawing shows that Co$_2$(CO)$_6$ is bound to the CpCoW and Cp fragment to form a tetrahedral core, leaving the Cp 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 Cp carbond via insertion of the OH bond. Its reaction with Co$_2$(CO)$_6$ (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. Similarly, treatment of the thiol 7 in THF (23 °C, 8 h) with Co$_2$(CO)$_6$ produced thiophene 8 in 67% yield. Equation 3 shows a cyclocarbonylation reaction for treatment of tungsten–alkynol 9 with Co$_2$(CO)$_6$ 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.

The ORTEP drawing shows that compound 10 has a trans configuration between tetranuclear and phenyl groups. Shown in Table 1 is a 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 Co$_2$(CO)$_6$ at 23 °C only gave unstable Co$_5$(CO)$_6$-complexed adducts. 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 study 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 Co$_2$(CO)$_6$ in benzene (25 °C, 2 h) afforded cyclopropane 23 exclusively (78% yield) in addition to cyclopentene 24 (2% yields). Further heating of this benzene
derivative...
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)8 to give organic dienes exclusively in both inter- and intramolecular synthesis. 18 But the examples in entries 5–7 indicate that bicyclic unsaturated lactones 26–28 were formed in good yields from alkylalkyltungsten 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 (1.2 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 carbonyl intermediates. Depicted in Scheme 3 is a plausible mechanism to rationalize these intramolecular cyclizations. Alkylalkyltungsten species first form Co2(CO)8-complexed species A upon treatment with Co2(CO)8. 13 After loss of one W–CO group, the Co2(CO)8 fragment of species B undergoes a 1,2-shift to form carbonyl 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. 15 Capture of this carbonyl by a tethered olefin and by a proximate X–H (X = O, S) group leads to cyclopropanation and insertion reactions, respectively. 12 If the tethered hydroxyl group is conformationally flexible as in compounds 9 and 11–12, the carbonyl may uptake one CO to give the ketene species D, ultimately giving cyclocarbonylation products 10 and 13–14.

In summary, we report the feasibility of generating a reactive carbonyl in reaction of functionalized alkylalkyltungsten species with Co2(CO)8, leading to various intramolecular cyclizations via cyclopropanation, insertion of the X–H bond (X = S, O), and cyclocarbonylations. These reactions will enhance synthetic applications of (RCCR′)Co2(CO)8 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 carbonyl 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