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Cobalt Alkyne Complexes

X-ray Crystal Structure of an Alkene–Pentacarbonyldicobalt–Alkyne Complex: Isolation of a Stable Magnus-Type Pauson–Khand Reaction Intermediate**

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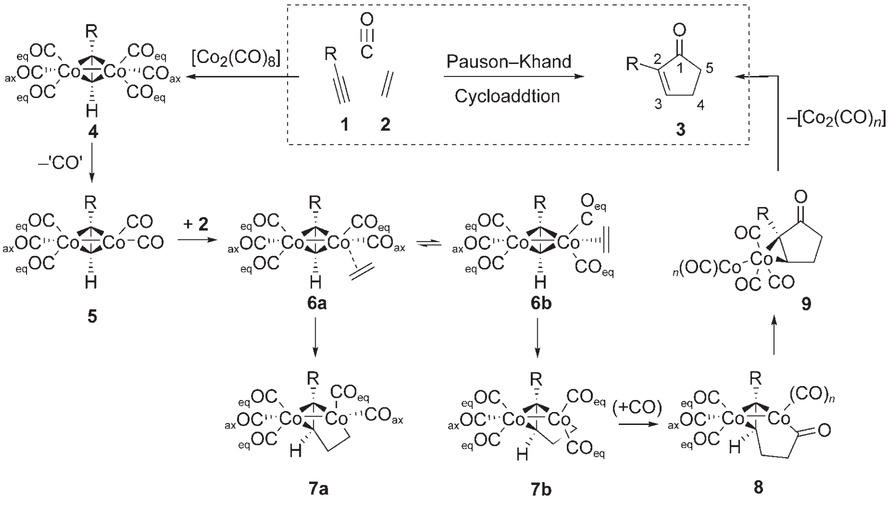
The Pauson–Khand reaction (PKR), the formal [2+2+1] cycloaddition of an alkyne **1**, an alkene **2**, and carbon monoxide, is a highly convergent method for the preparation of the important cyclopentenone ring motif **3** (Scheme 1).[1] Initially reported in 1973,[2] early examples of this process focused on the use of octacarbonyldicobalt as a reaction mediator and source of carbon monoxide, with thermal promotion. Since then, many variants have enhanced the scope and utility of the process, but the mechanism continues to attract discussion. The chemically reasonable reaction pathway proposed by Magnus and Príncipe[3] in 1985 invokes initial formation of an alkyne–hexacarbonyldicobalt tetrahedral cluster **4** that loses a ligand to generate the pentacarbonyl cluster **5**, thus allowing incorporation of the alkene moiety as in **6**. Subsequent coupling of the alkyne and alkene to form the metallocycle **7**, alkyl migration to incorporate the carbonyl group, as in **8**, and reductive elimination of the cyclopentenone from the final intermediate **9** complete the process.



Scheme 1. Proposed mechanism of the Pauson–Khand reaction. See text for details.

Since 1985, several reports concerning this mechanism have appeared, for example, **5** has been detected by using IR spectroscopy[4] and is isolable when the alkyne contains an S atom capable of coordinating, forming a chelate to the vacant site.[5] More recently, electrospray ionization mass spectrometry has been employed to detect, in one example, an alkene association complex of the type **6**.[6] However, apart from the initially formed hexacarbonyldicobalt–alkyne complex **4** none of the proposed intermediates along this pathway have previously been isolated and characterized as stable entities.

Our involvement in this area arose somewhat serendipitously as a continuation of earlier studies on metal-cluster-stabilized nonclassical or antiaromatic carbocations.[7] We chose to prepare (5-phenylethynyl-5*H*-dibenzo[*a*,*d*]cyclohepten-5-ol)hexacarbonyldicobalt (**10**) with the aim of investigating the extent of the interaction between the potential cationic center and the cobalt vertices.[8] However, when a solution of the alkynol ligand in THF was allowed to react with $[Co_2(CO)_8]$ at room temperature for 15 h, two products were isolated: the major product (73%) was the anticipated hexacarbonyl cluster **10**, and the minor product (15%), separable by flash column chromatography, proved to be the pentacarbonyldicobalt complex **11**, whereby the third ligand site on one of the cobalt centers was then occupied by the C10=C11 bond of the seven-membered ring (Scheme 2). Moreover, further investigation of this unprecedented decarbonylation/alkene-coordination process demonstrated it to be rather facile. Thus, a mixture of **10** and **11** (85:15) in [D]chloroform gradually metamorphosed into a mixture containing equal amounts of **10** and **11** after 24 h at room temperature.

The IR spectrum of the hexacarbonyl cluster **10** exhibits ν(CO) peaks at 2090, 2056, and 2029 cm^{-1}, whereas, in the pentacarbonyl complex **11** the ν(CO) absorptions are found at

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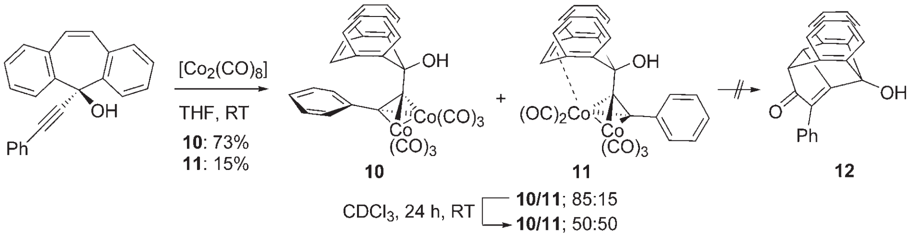

Scheme 2. Sequential formation of hexacarbonyl **10** and pentacarbonyl **11**.

2075, 2023, and 1978 cm^{-1}. These data compare well with those reported for the photolysis of [(PhC≡CH)Co$_2$(CO)$_6$] in an argon matrix that revealed strong IR peaks at 2099, 2062, 2036, and 2031 cm^{-1} for the hexacarbonyl cluster, and at 2081, 2035, 2016, and 1981 cm^{-1} after loss of a CO ligand.[4]

The molecular structures of **10** and **11**, determined by X-ray crystallography,[9,10] are shown in Figures 1 and 2, which illustrate clearly the boat conformations of the seven-membered rings.[11] The {(phenylethynyl)Co$_2$(CO)$_6$} moiety in **10** adopts a pseudoaxial position and is oriented such that the phenyl ring lies directly below the C10=C11 bond, thus shielding the attached protons, which resonate at $\delta = 6.27$ ppm (7.23 ppm in the free ligand). The carbonyl ligands in the {Co$_2$(CO)$_6$} fragment in **10** are close to the normally observed eclipsed sawhorse conformation.

In the pentacarbonyl complex **11** it is evident that rotation of the dicobalt–alkyne cluster about the C5–C12 bond has occurred, thus placing one metal center close to the C10–C11 linkage. The boat conformation is now more pronounced,[12] thus generating a distinctly avian-type structure. The alkyne carbon–carbon linkage (1.340 Å) and the C≡C-C "bend-back" angles (142.6° and 144.7°) lie within the normal ranges; as is normal, complexation to cobalt increases the C10–C11 double-bond length (from 1.336(3) Å in **10** to 1.403(7) Å in **11**).

Although the carbonyl ligands of the {Co(CO)$_3$} moiety in **11** deviate only slightly from the conventional orientation whereby one axial ligand is aligned with the midpoint of the alkyne bond, the ligands of the {Co(CO)$_2$(alkene)} moiety are staggered rather than eclipsed with respect to the {Co(CO)$_3$} tripod (see Figure 3), and the alkene is clearly in a pseudo-equatorial site.

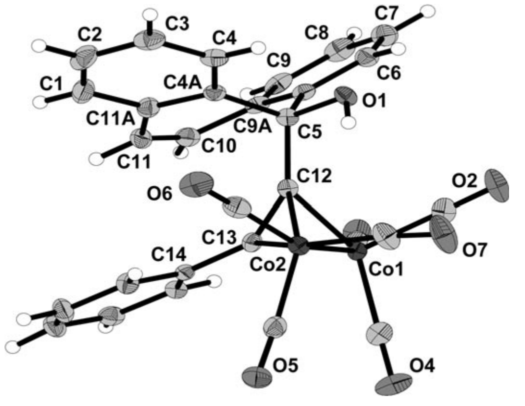

Figure 1. X-ray crystal structure of hexacarbonyl cluster **10**. Thermal ellipsoids are set at the 50% probability level.

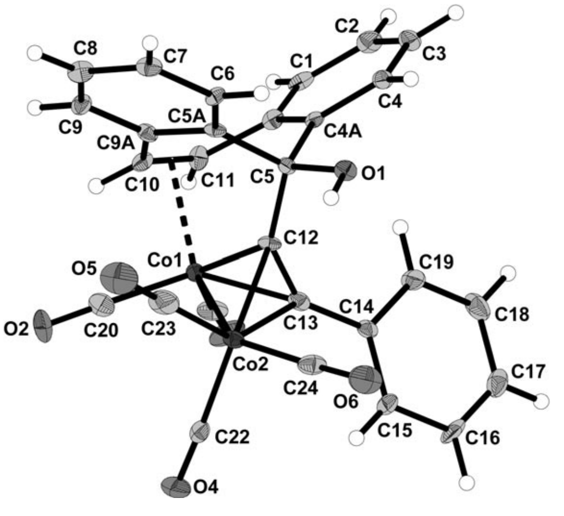

Figure 2. X-ray crystal structure of the pentacarbonyl complex **11**. Thermal ellipsoids are set at the 50% probability level.

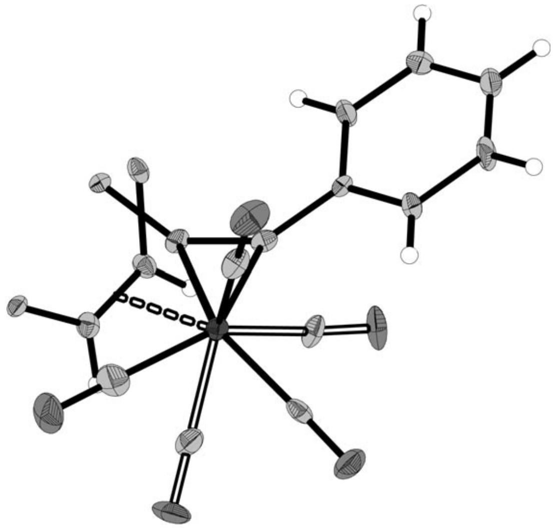

Figure 3. View along the cobalt–cobalt bond in **11**, emphasizing the staggered conformation of the {Co(CO)$_3$} and the {Co(CO)$_2$(alkene)} moieties.

The thermal instability of the hexacarbonyl cluster **10** is remarkable. Even at room temperature, decarbonylation and formation of the pentacarbonyl complex **11** is facile. This ease could be a consequence of the intramolecular character of the decarbonylation process, whereby loss of CO is compensated by chelate formation. This result is important, since **11** represents the first structurally characterized η^2-alkene–pentacarbonyldicobalt–alkyne complex, a crucial structural type in the widely invoked Magnus mechanism[3] of the Pauson–Khand cyclopentenone synthesis.

High-level density functional theory studies, in which the relative energies of the proposed Magnus intermediates have been calculated, suggest that the most energetically demanding step is the loss of a carbon monoxide ligand from **4** to form the pentacarbonyl complex **5**.[14] These studies also indicate that the two pseudoaxial carbonyl groups are more strongly bound than their pseudoequatorial counterparts, thereby implying that the alkenyl complex **6a** (Scheme 1) will be formed preferentially.[14,15] Irreversible bond migration within **6a** subsequently generates metallocycle **7a**. Milet and coworkers have considered this key carbon–carbon bond-forming step and proposed an alternative scenario whereby systems capable of undergoing rotation of the ML_3 vertex generate complex **6b**, from which position olefin insertion to form **7b** is comparatively facile energetically.[16] The calculations of Yamanaka and Nakamura[14a] indicated that the carbonyl ligands in $[(HC{\equiv}CH)Co_2(CO)_5(\eta^2\text{-}C_2H_4)]$ should be only slightly displaced from the eclipsed orientation generally observed in $[(alkyne)Co_2(CO)_6]$ systems; this finding contrasts with the experimentally observed staggered orientation in the pentacarbonyl complex **11**. However, one must recall that these experimental data are derived from an intramolecular rather than an intermolecular process. In all the calculated geometries, it was found that the ethylene ligand favors a pseudoequatorial site such that the distance between an alkene carbon atom and the nearer alkyne carbon atom is approximately 2.95 Å. Figure 4 depicts the core of the crystallographically determined structure of the η^2-alkene–pentacarbonyldicobalt–alkyne complex **11** and reveals cobalt–carbon bond lengths of 2.139 and 2.184 Å for the alkene ligand; more importantly, the alkene carbon atoms are positioned only 2.817 and 2.858 Å from the nearer alkyne carbon atom, somewhat closer than with the calculated values. The dihedral angle between the alkene plane C9A-C10-C11-C11A and the alkyne plane C5-C12-C13-C14 is 42°.

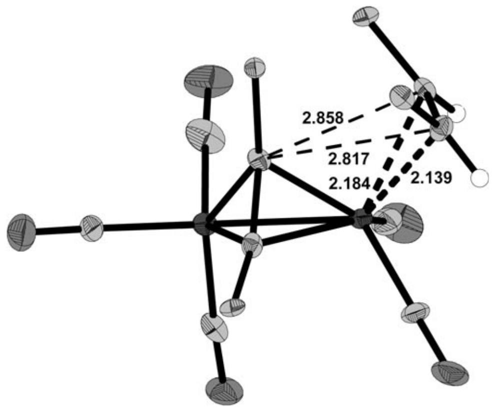

Figure 4. Cobalt–carbon bond lengths (-----) and nonbonded carbon–carbon separations (– – –) within the core of the pentacarbonyl complex **11**; values given in Å.

Thermolysis of **11** in refluxing toluene in a nitrogen atmosphere yielded dibenzosuberenone as the major organic product, and no Pauson–Khand-derived cyclopentenone product **12** (the formation of which may be precluded by molecular strain) was evident. This result may support the proposal that alkene insertion occurs preferentially from an axial position (**6b**→**7b**), and the existence of **11** as an arrested Pauson–Khand intermediate is a consequence of the rigidity of the structure. This lack of rotational freedom manifests itself in the ^{1}H and ^{13}C NMR spectra of **10** and **11**. In the hexacarbonyl cluster **10**, the time-averaged C_s symmetry of the system renders the two benzo rings equivalent, and the protons at C10 and C11 appear as a singlet at $\delta = 6.27$ ppm. In contrast, in the pentacarbonyl complex **11**, the mirror symmetry is broken, the benzo rings are now inequivalent, and the protons at C10 and C11 give rise to two doublets ($J = 9.5$ Hz) at $\delta = 5.40$ and 5.37 ppm. The gradual conversion of **10** into **11** is easily monitored by NMR spectroscopy, and the results of a kinetic study of this system and a series of related systems will be described in a future report.

Experimental Section

In a nitrogen atmosphere, a solution of (5-phenylethynyl-5*H*-dibenzo-[*a*,*d*]cyclohepten-5-ol) (720 mg, 2.34 mmol) and $[Co_2(CO)_8]$ (1.60 g, 4.67 mmol) in THF (25 mL) was stirred at room temperature for 15 h. After removal of the solvent at low temperature, the crude material was chromatographed on silica gel using pentane/dichloromethane (90:10) as eluent to yield **10** (1.02 g, 1.72 mmol, 73 %) and **11** (200 mg, 0.35 mmol, 15 %) as brown solids that were subsequently recrystallized from pentane/dichloromethane (80:20).

10: ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 8.19$ (dd, 2H, $^3J = 8.0$, $^4J = 1.2$ Hz; H4, H6), 7.42 (ddd, 2H, $^3J = 8.0$, $^3J = 7.2$, $^4J = 1.6$ Hz; H3, H7), 7.29 (td, 2H, $^3J = 7.6$, $^4J = 1.2$ Hz; H2, H8), 7.27–7.19 (m, 3H; phenyl H), 7.17 (dd, 2H, $^3J = 7.6$, $^4J = 1.6$ Hz; H1, H9), 6.80–6.76 (m, 2H; phenyl H), 6.27 (s, 2H; H10, H11), 2.84 ppm (s, 1H; OH); ^{13}C NMR (125 MHz, $CDCl_3$): $\delta = 198.7$ (CO), 141.2 (C4A, C5A), 138.0 (C_{ipso}), 132.2 (C9A, C11A), 130.2 (C10, C11), 128.8 (C1, C9), 128.7 (C_{phenyl}), 127.6 (C3, C7), 126.9 (C_{phenyl}), 126.5 (C2, C8), 126.1 (C_{phenyl}), 123.7 (C4, C6), 109.1, 93.0 (C12, C13), 75.2 ppm (C_{OH}); IR ($CDCl_3$): $\tilde{\nu} = 2090$, 2056, 2029 cm^{-1}.

11: ^{1}H NMR (500 MHz, $CDCl_3$): $\delta = 7.95$ (d, 1H, $^3J = 8.0$ Hz; H6), 7.89 (d, 1H, $^3J = 8.0$ Hz; H4), 7.58 (d, 1H, $^3J = 7.5$ Hz; H1), 7.44 (td, 1H, $^3J = 7.5$, $^4J = 1.0$ Hz; H3), 7.37 (d, 1H, $^3J = 7.5$ Hz; H9), 7.33 (t, 1H, $^3J = 7.5$ Hz; H7), 7.32 (t, 1H, $^3J = 7.5$ Hz; H2), 7.20 (t, 1H, $^3J = 7.5$ Hz; phenyl *p*-H), 7.18 (t, 1H, $^3J = 7.5$ Hz; H8), 7.14 (t, 2H, $^3J = 7.5$ Hz; phenyl *m*-H), 6.90 (d, 2H, $^3J = 7.5$ Hz; phenyl *o*-H), 5.40 (d, 1H, $^3J = 9.5$ Hz; H11), 5.37 (d, 1H, $^3J = 9.5$ Hz; H10), 2.54 ppm (s, 1H; OH); ^{13}C NMR (125 MHz, $CDCl_3$): $\delta = 197.6$ (CO), 142.6 (C5A), 142.3 (C4A), 136.4 (C_{ipso}), 135.3 (C9A), 134.4 (C11A), 129.8 (C_{ortho}), 129.7 (C1), 128.8 (C9), 128.5 (C_{meta}), 128.1, 128.0 (C3, C_{para}), 128.0 (C7), 127.4 (C2), 127.1 (C8), 123.6 (C12), 122.0 (C4), 91.3 (C13), 76.4 (C_{OH}), 74.2 (C11), 70.9 ppm (C10); IR ($CDCl_3$): $\tilde{\nu} = 2075$, 2023, 1978 cm^{-1}.

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Keywords: cobalt · density functional calculations · Pauson–Khand reaction · reaction intermediates · structure elucidation

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[1] For a very recent review of the Pauson–Khand reaction, see: N. Jeong in *Comprehensive Organometallic Chemistry III, Vol. 11* (Eds.: R. H. Crabtree, D. M. P. Mingos), Elsevier, Oxford, UK, **2006**, pp. 335–366, and references therein.
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[9] a) Crystal data for **10**: $C_{29}H_{16}O_7Co_2$ (M_r = 594.28), triclinic, space group $P\bar{1}$ (no. 2), $a = 10.5878(11)$, $b = 13.3942(13)$, $c = 18.1754(18)$ Å, $\alpha = 74.179(2)$, $\beta = 81.926(2)$, $\gamma = 89.863(2)°$, $V = 2453.6(4)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.609\ g\,cm^{-3}$, $\mu = 1.401\ mm^{-1}$, $T = 100$ K, crystal size $0.82 \times 0.40 \times 0.20\ mm^3$, $R1 = 0.0396$, $wR2 = 0.1083$, GOF = 1.035 with $I > 2\sigma(I)$. b) CCDC-629903 (**10**) and CCDC-629902 (**11**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

[10] Crystal data for **11**: $C_{28}H_{16}O_6Co_2$ (M_r = 566.27), monoclinic, space group Cc (No. 9), $a = 15.4109(17)$, $b = 13.1859(14)$, $c = 12.1179(13)$ Å, $\beta = 109.525(2)°$, $V = 2320.8(4)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.621\ g\,cm^{-3}$, $\mu = 1.473\ mm^{-1}$, $T = 100$ K, crystal size $1.00 \times 1.00 \times 0.80\ mm^3$, $R1 = 0.0547$, $wR2 = 0.1496$, GOF = 1.163 with $I > 2\sigma(I)$.[9b]

[11] The seven-membered boat is defined by C4A-C5A-C9A-C11A [plane 1], C4A-C5-C5A [plane 2] and C9A-C10-C11-C11A [plane 3]. In **10**, the interplanar angles [plane 1]–[plane 2] and [plane 1]–[plane 3] are 50.4° (49.8°) and 23.5° (22.2°), respectively, in the two independent molecules in the unit cell; the interplanar angle between the two benzo rings is 47.5° (50.3°).

[12] In **11** the interplanar angles [plane 1]–[plane 2] and [plane 1]–[plane 3] are 57.5° and 29.3°, respectively; moreover, the interplanar angle between the two benzo moieties in **11** has been increased to 59.5°, as opposed to 51.1° in the free ligand.[13]

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