Pendant Alkenes Promote Cobalt−Cobalt Bond Cleavage in (Alkyne)(binap)tetracarbonyldicobalt(0) Complexes

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Summary: Heating (alkyne)(binap)tetracarbonyldicobalt(0) complexes bearing pendant alkenes leads to cleavage of the cobalt−cobalt bond and generation of the mononuclear hydride (binap)(CO)$_2$CoH at 45−55 °C.

The cobalt-mediated Pauson−Khand reaction (the coupling of an alkyne, an alkene, and carbon monoxide to form a cyclopentenone) is an attractive carbon−carbon bond-forming reaction that has found many applications in organic synthesis[1] since it was first reported over 30 years ago.[2] Recently, there has been much interest in developing the asymmetric and catalytic aspects of the reaction, and significant progress has been made in each of these areas. Combination of catalysis and asymmetric induction in the cobalt-catalyzed reaction has been achieved by Hiroi, who employed the bis-phosphane binap,[3] and Buchwald, who used a binaphthyl-derived phosphite.[4] Experimental evidence for the currently accepted mechanism of the stoichiometric cobalt Pauson−Khand reaction (PKR), which was proposed by Magnus in 1985 and involves the stepwise construction of the product cyclopentenone on a series of dicobalt complexes,[5] has remained scarce, although computational studies have provided interesting insights.[6]

Recently we discovered that binap reacts with cobalt carbonyl sources typically used in the PKR such as octacarbonyldicobalt(0) to form complex **1**, in which binap is chelated to one of the two cobalt atoms (Figure 1).[7] Complex **1** catalyzed the PKR of a standard substrate, *N*-(prop-2-enyl)-*N*-(prop-2-ynyl)-*p*-toluenesulfonamide.[7]

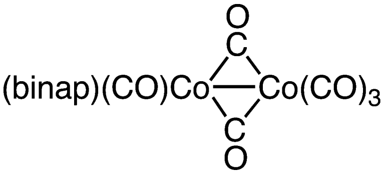

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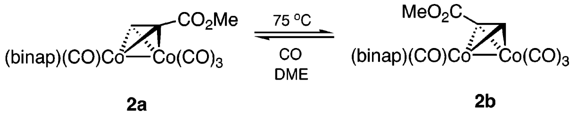
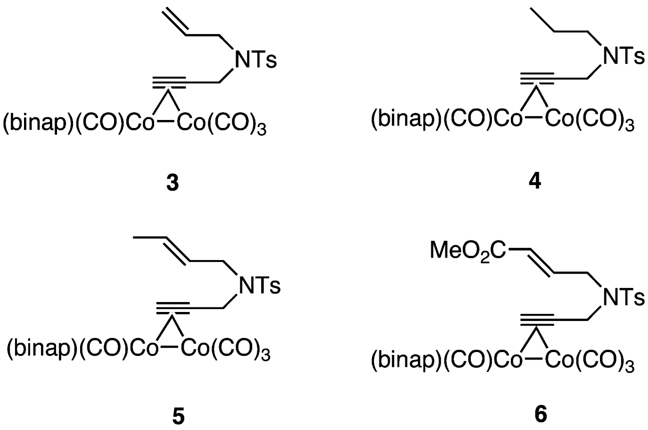
Figure 1. (binap)hexacarbonyldicobalt(0).



2a **2b**

Figure 2. Interconversion of the diastereoisomers of complex **2**.



3 **4** **5** **6**

Figure 3. Substrates for ^{31}P NMR study.

Subsequently we found that complex **1** reacted with a range of alkynes to form mixtures of two diastereoisomeric complexes, as exemplified by **2a** and **2b** (Figure 2; structures confirmed by X-ray crystallography). In the case of **2**, the two isomers were separable and ^{31}P NMR studies revealed that they interconverted without decomposition at 75 °C.[8]

We wish to report herein the results of experiments performed with alkyne complexes **3**−**6** (Figure 3), which reveal that cobalt−cobalt bond cleavage readily occurs in the presence of a pendant alkene, suggesting that monocobalt species may be formed during the course of cobalt-mediated PKRs.

To obtain **3**, octacarbonyldicobalt(0) and binap were reacted together in THF. After addition of *N*-(prop-2-enyl)-*N*-(prop-2-ynyl)-*p*-toluenesulfonamide,[9] the reaction mixture was heated at 40 °C for 2 h. Column chromatography of the resulting product mixture gave a brown solid.[10] The ^{31}P NMR spectrum

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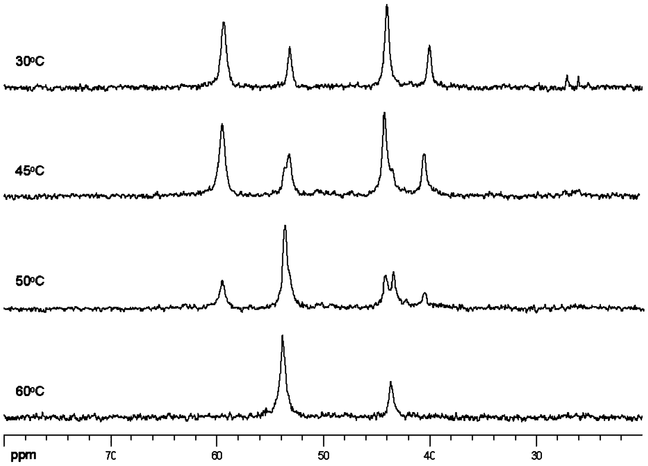

Figure 4. ^{31}P NMR spectra of complex **3** at 30, 45, 50, and 60 °C.

of the solid in DME contained two stronger resonances at δ 59 and 44, associated with one diastereoisomer of **3**, and two weaker resonances at δ 53 and 40, associated with a second diastereoisomer (Figure 4, 30 °C). These observations correlated well with those for other (alkyne)(binap)tetracarbonyldicobalt(0) complexes synthesized previously.[8]

Complex **3** proved to be relatively unstable, and so it was decided to probe its chemistry by ^{31}P NMR spectroscopy. The complex was dissolved in CO-saturated DME and its spectrum monitored at 5 °C intervals as the temperature was raised above 30 °C (see Figure 4 for key spectra). The four resonances of **3** dominated the spectrum until 45 °C, but at 50 °C two new resonances at δ 53.7 and 43.6 had appeared. At 60 °C the four resonances associated with the alkyne complex **3** had disappeared, leaving only the resonances at δ 54 and 43. This situation remained unchanged up to 75 °C and on lowering the temperature back to 30 °C.

Having discovered that the effect of temperature on complex **3** differed dramatically from its effect on complex **2** (Figure 2), we probed the role of the pendent alkene using complexes **4**−**6**. The required enynes were synthesized by drawing on standard protocols[8,11] and converted to the desired complexes **4**−**6** as outlined above for complex **3**.[10] As described for **3**, the ^{31}P NMR spectrum of each complex in CO-saturated DME was monitored between 30 and 75 °C and afterward at 30 °C. A clear dependence on the presence and nature of the pendant alkene was observed. In the case of **4**, which is identical with **3** except for the absence of the alkene, the spectrum remained unchanged throughout the sequence (Figure 5). In the case of **5**, which bears a relatively electron-rich alkene, the dominant new peak at δ 54 started to appear at 55 °C (Figure 6), while for **6**, with a relatively electron-poor alkene, the resonance at δ 54 started to emerge at 45 °C (Figure 7).

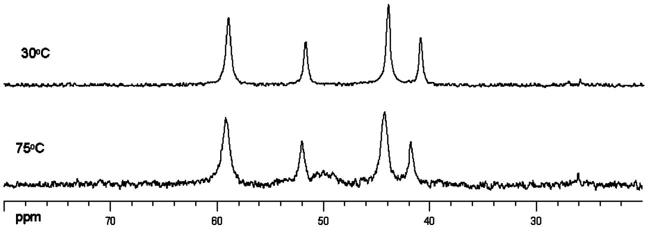

Figure 5. ^{31}P NMR spectra of complex **4** at 30 and 75 °C.

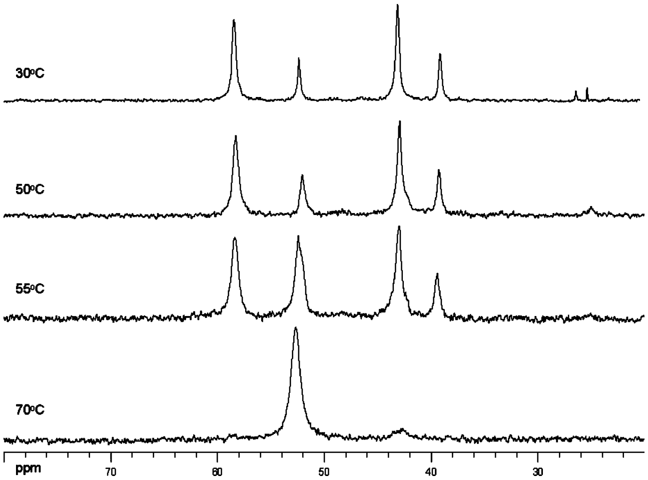

Figure 6. ^{31}P NMR spectra of complex **5** at 30, 50, 55, and 70 °C.

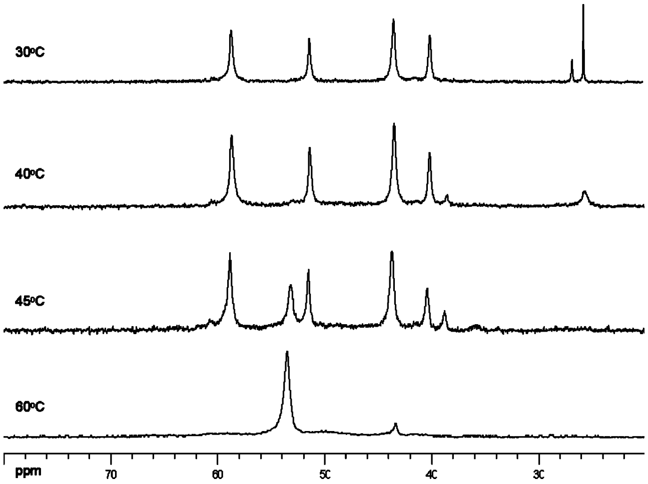

Figure 7. ^{31}P NMR spectra of complex **5** at 30, 40, 45, and 60 °C.

The ^{31}P NMR spectrum of (binap)hexacarbonyldicobalt(0) (**1**) in DME contains a single resonance at δ 43,[7] and thus it was assumed that complex **1** was formed during the NMR sequences described above. An explanation for the resonance at δ 54 was provided by a combination of X-ray crystallography and a further NMR experiment.[12] Brown crystals observed in the NMR tube after the NMR experiment on complex **3** were examined by X-ray crystallography, which revealed that they were the cobalt hydride structure **7** (Figure 8).[13] Repetition of our standard NMR sequence in d_8-THF with complex **3** led to a final ^{31}P NMR spectrum recorded at 30 °C containing resonances at δ 53 and 43. The ^{1}H NMR spectrum of this sample contained a broad resonance at δ −11.6, characteristic of a

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[10] Octacarbonyldicobalt(0) (75 mg, 0.220 mmol) and (±)-2,2′-bis(diphenylphosphino)-1,1′-binaphthalene (140 mg, 0.225 mmol) were dissolved in THF (15 mL) and stirred at room temperature for 30 min. The mixture was heated to 40 °C for 30 min. *N*-(Prop-2-enyl)-*N*-(prop-2-ynyl)-*p*-toluenesulfonamide[9] (56 mg, 0.226 mmol) was added, and the reaction mixture was stirred at 40 °C for 2 h. The mixture was cooled to room temperature and was then absorbed onto neutral alumina (grade II). The brown solid was loaded onto a chromatography column (silica) and eluted under nitrogen, first with hexane/ethyl acetate (19:1) to remove unreacted octacarbonyldicobalt(0) and then with hexane/ethyl acetate (7:3) to collect **3** as a brown solid (109 mg, 45%). IR (CHCl$_3$, cm^{-1}): ν_{CO} 2043 (s), 1980 (s), 1939 (s). ^{31}P NMR (160 MHz, DME): δ 59.4, 53.2, 44.0, 40.0 (CoPPh$_2$-Ar), −14.6 (binap; <5%). MS (FAB): *m/z* (%) 1017 (M$^+$ − 3CO, 11), 989 (M$^+$ − 4CO, 40), 681 [Co(binap)$^+$, 100], 437 [(binap − PPh$_2$)$^+$, 65].

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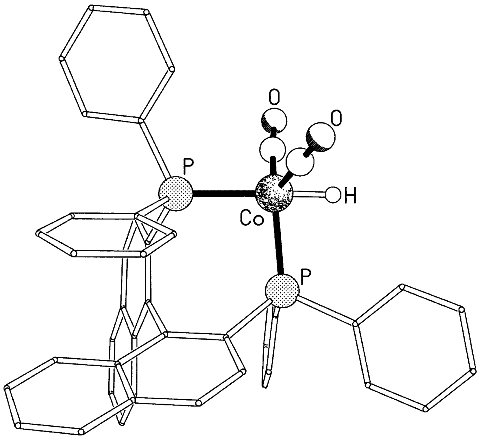
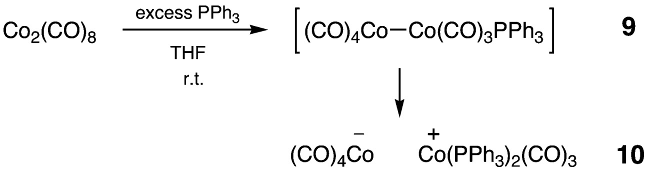


Figure 8. Molecular structure of hydride **7**.

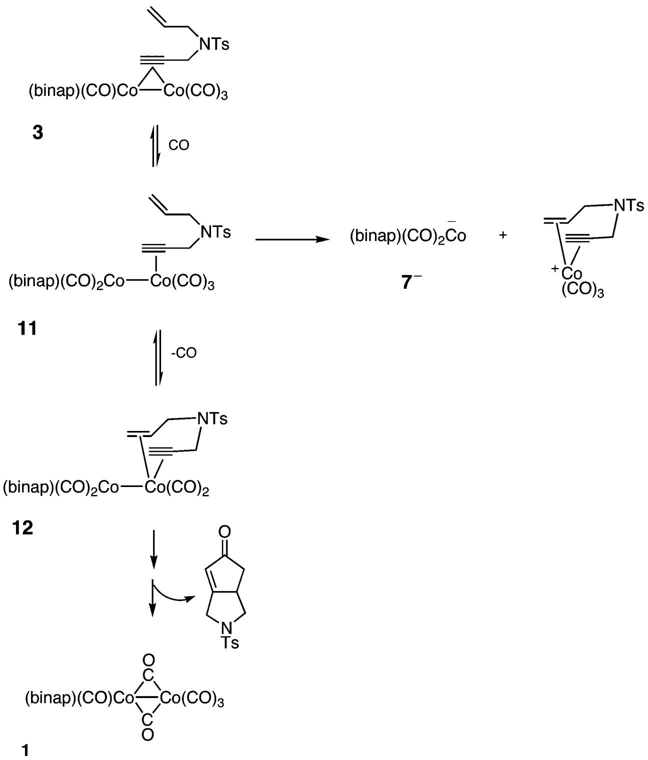
cobalt−hydride species, thus providing a correlation between the solid-state structure and the solution observations.

The results described above reveal that pendent alkenes promote cobalt−cobalt bond cleavage in (alkyne)(binap)-tetracarbonyldicobalt(0) complexes. This may be the result of a direct interaction between the alkene and the cobalt−cobalt bond, as postulated below, or an indirect effect resulting from interactions occurring in a downstream intermediate arising from Pauson−Khand activity. Given that two-electron-donor ligands have been documented to break the cobalt−cobalt bond in dicobalt carbonyl species, e.g., octacarbonyldicobalt(0) is readily transformed into the ionic species **10** presumably via nucleophilic attack of triphenylphosphane on complex **9** (Scheme 1),[14] it seems reasonable to postulate that similar nucleophilic displacements may occur in complexes **3**, **5**, and **6** driven by the pendant alkenes.

Scheme 1. Cleavage of the Cobalt−Cobalt Bond of 9 by the Two-Electron-Donor Ligand Triphenylphosphane



Scheme 2. Proposed Pathway to the Anion of 7 and How It May Relate to PK Activity



Thus, to explain the results of the NMR experiments described herein, we propose that carbon monoxide induces the formation of the η^2-alkyne complex **11** from complex **3** and that this is followed by the pendant alkene displacing the anion of **7**, as depicted in Scheme 2.

How the observed cobalt−cobalt bond cleavage relates to Pauson−Khand activity is yet to be determined,[15] but it may be speculated that the cleavage competes with carbon monoxide loss and alkene binding to give complex **12**, which in turn proceeds to the cyclopentenone product of the PKR and dicobalt complex **1**. Whether or not this speculation is correct, it is clear that cobalt−cobalt bond cleavage is a facile process in complexes of relevance to the cobalt-mediated Pauson−Khand reaction and that due consideration of this property should aid our understanding of this important synthetic process.

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Supporting Information Available: Text and figures givng detailed experimental procedures and compound characterization data and a CIF file giving crystallographic data. This material is available free of charge via the Internet at http://pubs.acs.org.

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[12] Complex **3** (35 mg) was dissolved in CO-saturated DME (0.8 mL) and syringed via a filter needle into a WILMAD screw-cap (with a PTFE/silicone septum) NMR tube filled with carbon monoxide; ^{31}P NMR spectra were recorded between 30 and 75 °C (see Figure 4). The NMR tube was then cooled to 30 °C, and the ^{31}P NMR spectrum was recorded at this temperature. ^{31}P NMR (160 MHz, DME): δ 53.4, 43.2 (CoPPh$_2$Ar), −14.2 (binap; <5%). When the NMR tube was stored in the freezer, small brown crystals appeared in the NMR tube and these were identified as hydride **7** by X-ray crystallography.[13] The early stages of the experiment were subsequently repeated in d_8-THF. When the temperature was lowered to 30 °C, the ^{31}P and ^{1}H NMR spectra were recorded. ^{31}P NMR (160 MHz, d_8-THF): δ 52.9, 42.6. ^{1}H NMR (400 MHz, d_8-THF): δ − 11.6 (broad, Co−H).

[13] Crystal data for **7**: $C_{46}H_{33}CoO_2P_2$, $M_r = 738.59$, monoclinic, $P2_1/n$ (No. 14), $a = 15.0501(7)$ Å, $b = 14.7142(7)$ Å, $c = 17.0825(8)$ Å, $\beta = 110.517(4)°$, $V = 3543.0(3)$ Å^3, $Z = 4$, $D_c = 1.385$ g cm^{-3}, μ(Mo Kα) = 0.615 mm^{-1}, $T = 173$ K, brown needles, Oxford Diffraction Xcalibur 3 diffractometer, 12 274 independent measured reflections, F^2 refinement, R1 = 0.094, wR2 = 0.114, 5717 independent observed reflections ($|F_o| > 4\sigma(|F_o|)$, $2\theta_{max} = 65°$), 464 parameters. CCDC 619746.

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[15] It is of note in this context, however, that monitoring a 1:1:3 mixture of octacarbonyldicobalt(0), binap, and *N*-(prop-2-enyl)-*N*-(prop-2-ynyl)-*p*-toluenesulfonamide in CO-saturated DME at 75 °C by ^{31}P NMR spectroscopy gave resonances at δ 54 and 43 which simplified after 2 h to a single resonance at δ 43.