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A Study of (Binap)(enyne)tetracarbonyldicobalt(0) Complexes

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Abstract: Four (binap)(enyne)tetracarbonyldicobalt(0) complexes have been synthesised and their reactivity monitored by variable temperature ^{31}P NMR spectroscopy. Formation of (binap)dicarbonylhydridocobalt(−1) **12** occurred at temperatures between 35 and 55 °C, depending on the nature of the alkene and alkyne components of the enyne. The structure of **12** was determined by X-ray crystallography, and its presence under Pauson–Khand reaction conditions was verified by NMR spectroscopy.

Keywords: alkenes · alkynes · asymmetric catalysis · cobalt

Introduction

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[1] that has found many applications in organic synthesis since it was first reported over thirty years ago.[2] Recently there has been much interest in developing asymmetric and catalytic versions of the reaction, often involving metals other than cobalt,[1d] and significant progress has been made in each of these areas. Combination of catalysis and asymmetric induction in the cobalt-catalysed reaction has been achieved by Hiroi, who employed the bisphosphane 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 step-wise construction of the product cyclopentenone on a series of di-cobalt complexes,[5] has remained scarce, although computational studies have provided interesting insights not only into the reaction pathway itself[6] but also into and the role of additives such as Lewis bases[7] and the radical promoter TEMPO.[8]

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Inspired by Hiroi's successful use of binap in the cobalt-catalysed PKR,[3] we questioned the nature of the complex formed between binap and cobalt carbonyl sources.[9] Reaction of binap with a range of cobalt carbonyl sources typically used in the PKR revealed that binap interacts with octacarbonyldicobalt(0) to form complex **1**, in which binap is chelated to one of the two cobalt atoms (Figure 1).[9] Complex **1** catalysed the PKR of a standard substrate, *N*-(prop-2-enyl)-*N*-(prop-2-ynyl)-*p*-toluenesulfonamide (**3**).[9]

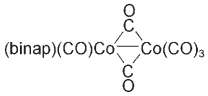

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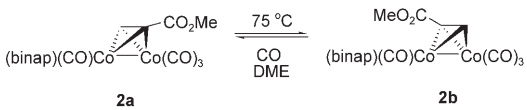
Figure 1. (Binap)hexacarbonyldicobalt(0).

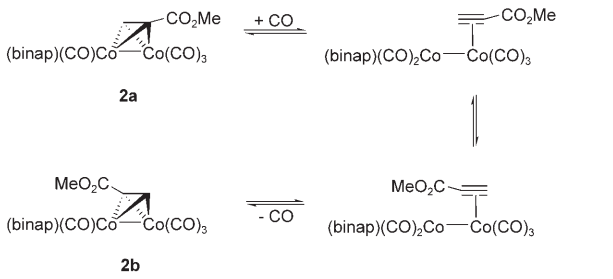
Given that alkyne coordination is the accepted first event in the PKR, we subsequently examined the reactivity of **1** towards alkynes. We found that complex **1** reacted with a range of alkynes to form mixtures of two diastereoisomeric complexes as exemplified by **2a** and **2b** (Scheme 1; structures confirmed by X-ray crystallography).[10] In the case of **2**, the two isomers were separable and ^{31}P NMR studies revealed that they interconverted without decomposition at 75 °C.[10]

One of the proposed pathways for the interconversion of the diastereoisomers of **2** is illustrated in Scheme 2.[10] The



2a **2b**

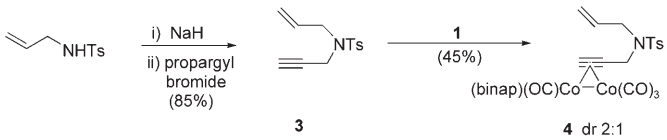
Scheme 1. Diastereoisomers of complex **2** interconvert.



Scheme 2. A proposed pathway for the interconversion of the diastereoisomers of **2**.

barrier to alkyne rotation is lowered by locating it on just one cobalt atom, the binap-free cobalt being selected for steric reasons.

To relate our studies more closely to the PKR we decided to synthesise the cobalt alkyne binap complex of the known PKR substrate **3** (Scheme 3) and study its reactivity. The results of this study, together with a discussion of how they may relate to the PKR are presented below. Some of the results have been the subject of a preliminary publication.[11]



Scheme 3. Synthesis of complex **4**.

Results and Discussion

The standard Pauson–Khand substrate, enyne **3**, was prepared by a literature method[12] that involved deprotonation of *N*-(prop-2-enyl)-*p*-toluenesulfonamide[13] and addition of propargyl bromide. A sample of complex **1** was then prepared by dissolving octacarbonyldicobalt(0) and binap in THF and stirring the mixture under nitrogen at room temperature for 30 minutes. The reaction mixture was then heated to 40 °C for a further 20 minutes before enyne **3** was added. After stirring at 40 °C for a further 2 h, purification by flash column chromatography gave complex **4** as a difficult to handle, brown air sensitive solid in 45 % yield. The IR spectrum of **4** contained three absorptions at $\tilde{\nu} = 2043$, 1980 and 1939 cm^{-1}, values typical of carbonyl ligands in cobalt(0) complexes. The molecular ion could not be seen in the mass spectrum of **4** although peaks corresponding to the molecular ion minus three and four carbon monoxide ligands could be seen together with a peak correlating to binap attached to a single cobalt atom. Characterisation of complex **4** by ^{1}H and ^{13}C NMR spectroscopy was not possible as the spectra recorded were too broad to interpret. The ^{31}P NMR of **4**, however, consisted of five clear resonances, two at δ 58.9 and 44.0 ppm corresponding to the major isomer and two at δ 53.2 and 39.2 ppm corresponding to the minor isomer. A resonance corresponding to binap at δ −14.6 ppm was also observed. The ^{31}P NMR spectrum of **4** was consistent with the ^{31}P NMR data obtained for diastereoisomers **2a** and **2b**, the structures of which had been confirmed by X-ray crystallography;[10] this, together with the X-ray characterisation obtained for complex **6** (see below), provided the necessary assurance that complex **4** was the desired binap cobalt derivative of enyne **3**. The two diastereoisomers of **3**, formed in a 2:1 ratio, could not be separated by chromatography or recrystallisation.

In a first attempt to discover the fate of complex **4** under typical Pauson–Khand conditions, it was dissolved in THF and heated to reflux under nitrogen for 1.3 h. Disappointingly, the ^{31}P NMR spectrum of the brown product contained only resonances corresponding to the bis- and monooxides of binap. It was thus decided to examine the effect of heat on complex **4** by variable temperature (VT) ^{31}P NMR spectroscopy. Complex **4** was dissolved in nitrogen-saturated 1,2-dimethoxyethane (DME) and syringed via a filter needle into a WILMAD screw cap NMR tube (with a PTFE/silicone septum) under a nitrogen atmosphere. A VT ^{31}P NMR experiment was performed between 30 and 75 °C, increasing the temperature in intervals of 5 or 10 °C. Although the quality of the spectra recorded was poor, it was clear that changes were occurring and that products other than binap and its oxides were being formed. The experiment was thus repeated under a carbon monoxide atmosphere.

Complex **4** was dissolved in carbon monoxide saturated DME and syringed into the NMR tube under a carbon monoxide atmosphere. The ^{31}P NMR spectrum was again recorded between 30 °C and 75 °C at intervals of 5 °C and a final spectrum was recorded at the end of the experiment at 30 °C. Inspection of the ^{31}P NMR spectrum of complex **4** in carbon monoxide saturated DME at 30 °C (Figure 2) showed resonances associated with the major diastereoisomer (δ 59 and 44 ppm) and minor diastereoisomer (δ 53 and 40 ppm). The spectrum of complex **4** remained essentially unchanged up to 45 °C, but increasing the temperature further to 50 °C resulted in the emergence of two new resonances at δ 54 and 43 ppm. At 60 °C these new resonances dominated the spectrum. On increasing the temperature to 75 °C and on cooling the NMR experiment to 30 °C, no further changes to the spectra were observed.

Having discovered that the effect of temperature on complex **4** was dramatically different to its effect on complex **2** (Scheme 1), it was decided to probe the role of the pendent alkene using a complex identical to complex **4** but with the propenyl substituent replaced by a propyl group.

Deprotonation of *N*-(propyl)-*p*-toluenesulfonamide[14] followed by addition of propargyl bromide gave the desired alkyne **5**. Complexation of **5** was achieved using the same procedure described above for complex **4**. Purification of the product mixture by flash column chromatography gave a brown air-sensitive solid, **6**, which was characterised by IR spectroscopy, mass spectrometry, ^{31}P NMR spectroscopy, elemental analysis and X-ray crystallography (Scheme 4).

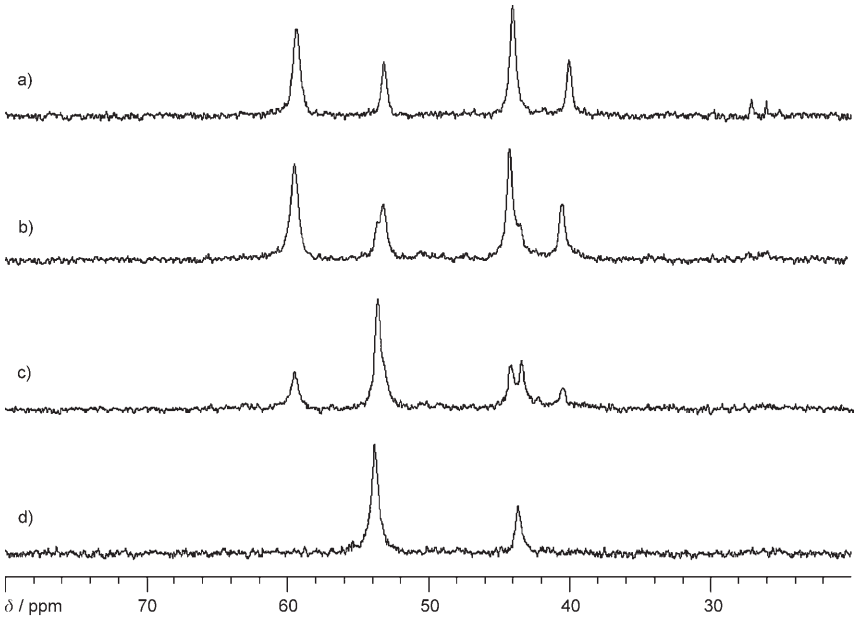
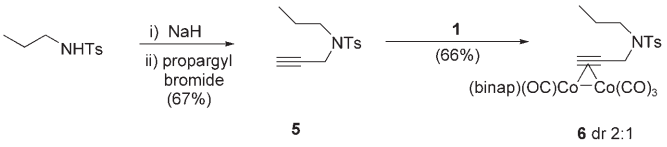


Figure 2. ^{31}P NMR spectra of complex **4** at a) 30, b) 45, c) 50 and d) 60 °C in DME under carbon monoxide.



Scheme 4. Synthesis of complex **6**.

The ^{31}P NMR spectrum of complex **6** contained five resonances, two at δ 57.9 and 43.8 ppm corresponding to the major isomer, two at δ 51.6 and 39.9 ppm corresponding to the minor isomer, and one at δ −14.99 ppm due to a trace of binap. Although repeated attempts to separate the isomers by chromatography failed, it proved possible on one occasion to obtain a sample of one of the diastereoisomers as small brown crystals from CH_2Cl_2/pentane. X-ray analysis of these crystals confirmed the structure of **6** (Figure 3).[10]

Complex **6** was dissolved in carbon monoxide saturated DME, syringed into an NMR tube and subjected to the VT ^{31}P NMR sequence described above for complex **4**. The initial spectrum recorded at 30 °C contained the four resonances associated with the two diastereoisomers of complex **6** (Figure 4). This situation remained unchanged throughout the VT sequence up to 75 °C and on cooling back to 30 °C.

It was thus clear at this point that the pendent alkene is necessary for the chemical transformation that leads to the consumption of complex **4** on heating and the appearance of the new resonances at δ 43 and 54 ppm at 50 °C (Figure 2).

In order to probe this process further, enyne complexes bearing relatively electron-rich and electron-poor alkenes were constructed. A palladium-catalysed reaction between 3-buten-2-ol and toluene sulfonyl isocyanate gave the disubstituted alkene **7**.[15] Deprotonation of **7** and reaction with propargyl bromide gave enyne **8**[16] and complexation to (binap)hexacarbonyldicobalt(0) **1** gave the required enyne complex **9** as a 2:1 ratio of diastereoisomers (Scheme 5). In addition, the known aldehyde *N*-(2-oxoethyl)-*N*-(prop-2-ynyl)-*p*-toluenesulfonamide[17] was stirred with methyl(triphenylphosphoranylidene) acetate in benzene at room tempera-

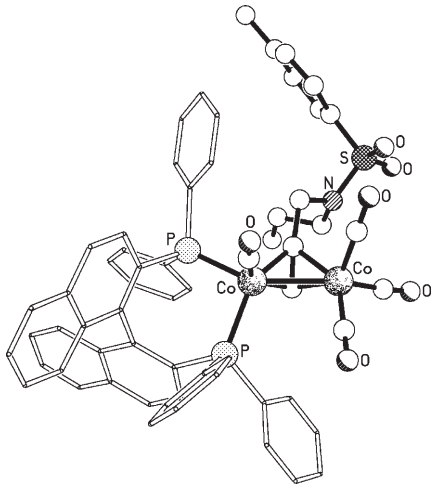


Figure 3. Molecular structure of **6**.

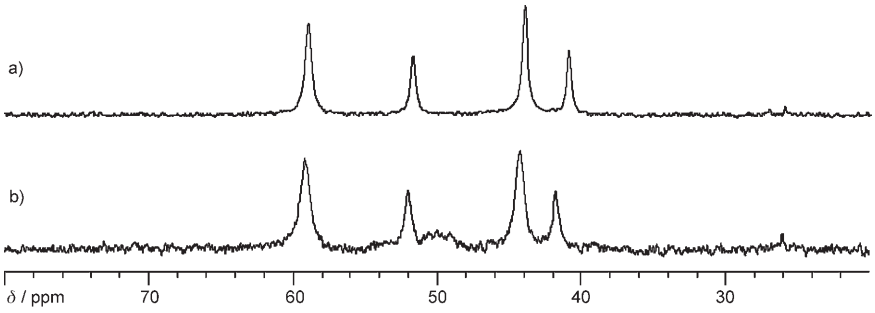
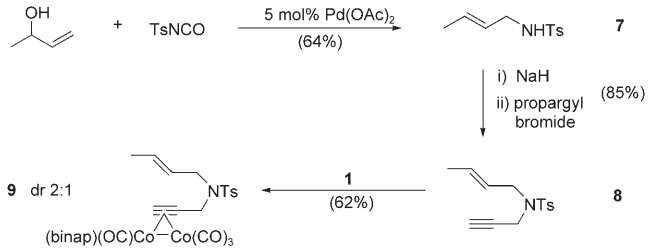
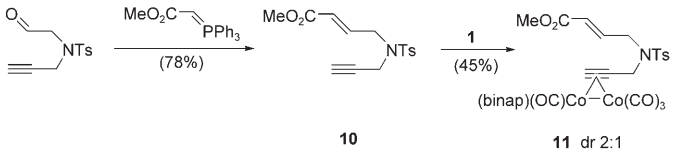


Figure 4. ^{31}P NMR spectra of complex **6** at a) 30 and b) 75 °C in DME under carbon monoxide.



Scheme 5. Synthesis of complex **9**.



Scheme 6. Synthesis of complex **11**.

ture overnight to give enyne **10**[18] as a colourless oil. Addition of **10** to **1** gave a 2:1 mixture of the diastereoisomers of the enyne cobalt complex **11** (Scheme 6).

The VT ^{31}P NMR spectra obtained from complexes **9** and **11** followed a similar pattern to those obtained from complex **4**, that is, four resonances associated with the diastereoisomers are replaced by resonances at δ 54 and 43 ppm as the temperature increases (Figures 5 and 6). Interestingly the temperature at which the contribution to the spectrum from the new resonances becomes significant alters from 50 °C in the case of complex **4** (Figure 2) to 55 °C for complex **9** and to 45 °C in the case of complex **11**. Thus the process underlying the transformation appears to be favoured by an electron-poor alkene. This is consistent with an initial alkene binding step to cobalt(0), a process favoured by a low-lying alkene LUMO.[6e]

Examination of the NMR sequences depicted in Figure 2, **5** and **6**, arising from the heating of complexes **4**, **9** and **11**, respectively, reveals that they all culminate in spectra containing resonances at δ 43 and 54 ppm. As the ^{31}P NMR spectrum of (binap)hexacarbonyldicobalt(0), **1**, in DME contains a single resonance at δ 43 ppm,[9] it was assumed that this complex is formed on heating complexes **4**, **9** and **11**. An explanation for the resonance at δ 54 ppm was provided by a combination of X-ray crystallography and a further NMR experiment. Brown crystals observed in the NMR tube after the NMR experiment on complex **4** were examined by X-ray crystallography, which revealed that they were the cobalt hydride **12** (Figure 7). Complex **12** is a trigonal bipyramidal mono cobalt species with an axial hydride, and a binap ligand spanning axial and equatorial positions.

Complex **12** is novel, although similar cobalt hydrides with achiral bidentate phosphorus ligands such as **13**,[19] **14**[20,21] and **15**[22] have been reported. Comparatively little detailed data has been collected on these complexes, presumably because of their sensitivity. Complex **16**, which has been reported in the patent literature as a hydroformylation catalyst,[23] represents the only previous example of a monocobalt-hydride containing a chiral bidentate phosphorus ligand (Figure 8).

Repetition of the VT ^{31}P NMR experiment performed on complex **4** (Figure 2) using deuterated [D_6]THF in place of DME, gave identical results and generated a final spectrum at 30 °C containing the expected resonances at δ 43 and 54 ppm. The ^{1}H NMR spectrum was then recorded and in addition to the usual broad resonances at δ 1–8, another broad resonance at δ −11.6 ppm, was observed. The newly observed broad resonance, with a shift characteristic of a cobalt-hydride species (Table 1),[24] thus provided a correlation between the solid-state structure and the solution observations.

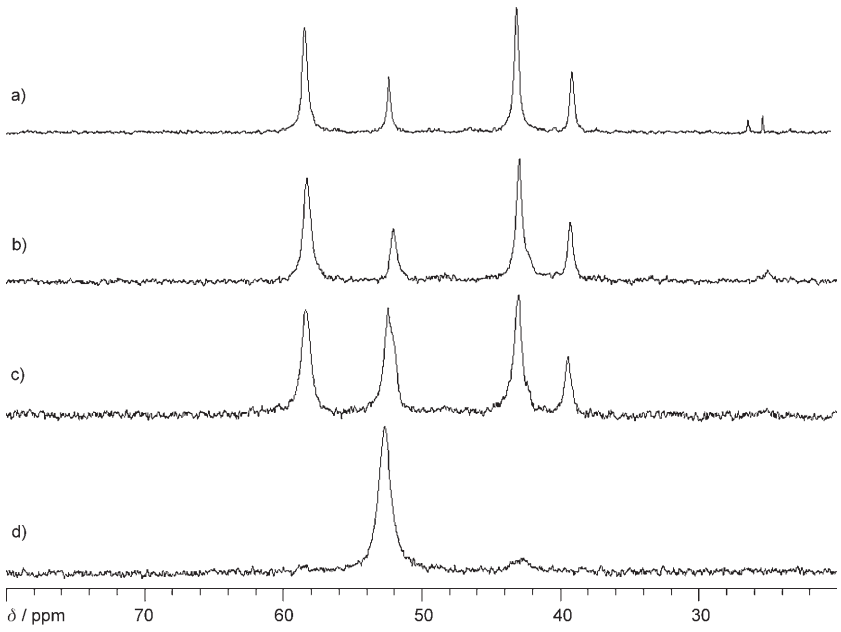


Figure 5. ^{31}P NMR spectra of complex **9** at a) 30, b) 50, c) 55 and d) 70 °C in DME under carbon monoxide.

Earlier in the project, repeated attempts to recrystallise complex **4** to obtain a diastereoisomerically pure sample had proved unsuccessful. One recrystallisation attempt from CH_2Cl_2 and petroleum spirit, however, produced small brown crystals after being left for three weeks at −10 °C. X-ray crystallographic analysis of the crystals revealed that they were a σ-bonded alkyne complex **17** (Figure 9), not the anticipated complex **4**.

The geometry at the cobalt centre is distorted trigonal bi-

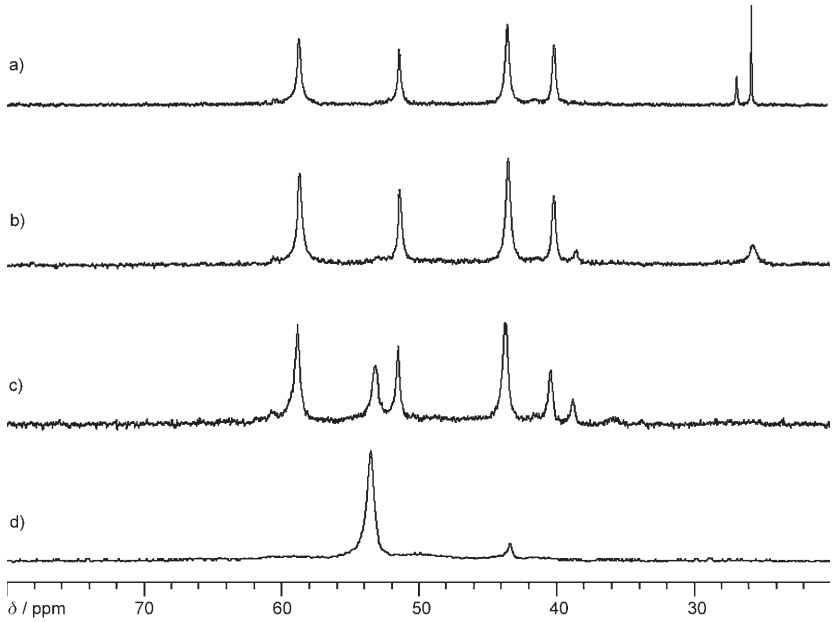


Figure 6. ^{31}P NMR spectra of complex **11** at a) 30, b) 40, c) 45 and d) 60 °C in DME under carbon monoxide.

pyramidal with the P(1) and P(2) phosphorus donors of the chelating binap ligand occupying equatorial and axial sites respectively, a situation also seen in the structure of the hydride species **12**.[11] The metal lies about 0.11 Å out of the trigonal plane in the direction of P(2), and it is noticeable that the axial Co–P(2) distance of 2.1853(10) Å is about 0.06 Å shorter than that to its equatorial counterpart [Co–P(1) 2.2488(10) Å]. In the hydride species **12** the two distances differ by only about 0.01 Å with the Co–P_{axial} bond being about 0.01 Å longer [2.1956(11) Å], and the Co–$P_{equatorial}$ bond about 0.04 Å shorter

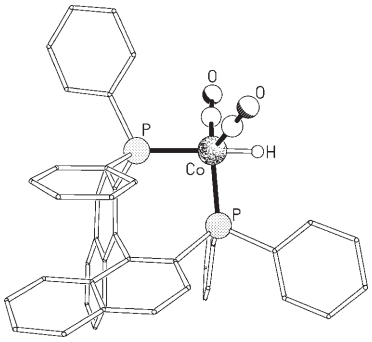


Figure 7. Molecular structure of hydride **12**.[11]

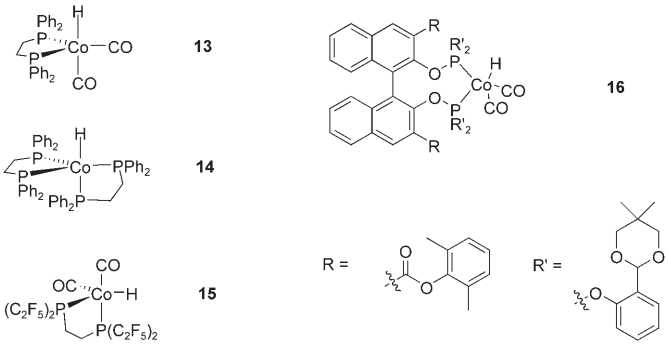


Figure 8. Cobalt hydrides with bidentate phosphorus ligands.

Table 1. Description of the hydride resonance of complex **12** and literature cobalt hydrides[24] for comparison.

Cobalt hydride	δ [ppm]	Multiplicity	Coupling to P [Hz]
$[HCo(CO)_4]$	−11.4	singlet	–
$[HCo(CO)_3P(OPh)_3]$	−11.2	doublet	54
$[HCo(CO)_2(P(OPh)_3)_2]$	−11.9	triplet	12
$[HCo(CO)_2(binap)]$ (**12**)	−11.6	broad	

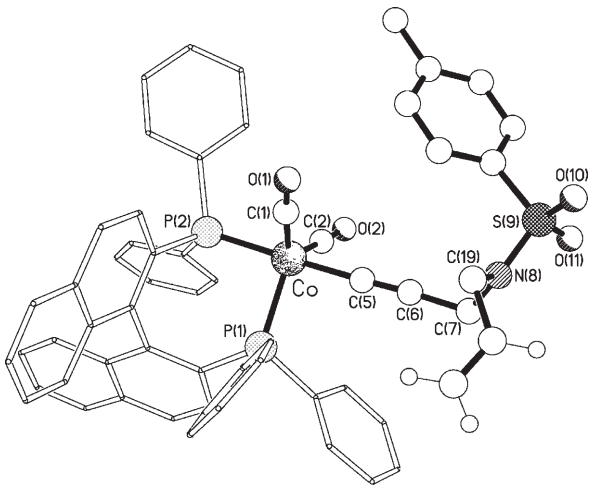


Figure 9. Molecular structure of **17**.

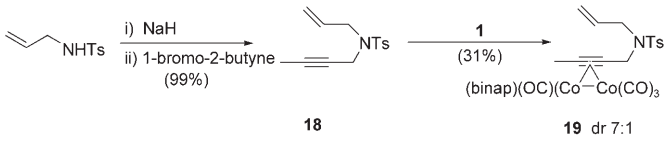
[2.2091(11) Å], than their counterparts here in **17**, respectively. The second axial site is occupied by the σ-bound alkynyl ligand which is approximately co-linear with the P(2)–Co bond, the P(2)-Co-C(5), Co-C(5)-C(6) and C(5)-C(6)-C(7) angles being 177.51(11), 177.9(4) and 176.8(5)°, respectively (Table 2). The geometry at the nitrogen centre is slightly pyramidalised, N(8) lying about 0.15 Å out of the plane of its substituents.

Our serendipitous observation of complex **17** led us to speculate that the origin of the hydride in complex **12**, formed on heating complexes **4**, **9** and **11**, was the terminal hydrogens of their monosubstituted alkynes. We thus decided to examine the reactivity of a disubstituted alkyne complex.

Table 2. Selected bond lengths [Å] and angles [°] for **17**.

Co–P(1)	2.2488(10)	Co–P(2)	2.1853(10)
Co–C(1)	1.770(4)	Co–C(2)	1.756(4)
Co–C(5)	1.904(4)	C(5)–C(6)	1.194(5)
C(6)–C(7)	1.468(6)		
P(1)-Co-P(2)	93.45(3)	P(1)-Co-C(1)	114.43(12)
P(1)-Co-C(2)	121.11(12)	P(1)-Co-C(5)	87.40(11)
P(2)-Co-C(1)	91.14(11)	P(2)-Co-C(2)	95.69(13)
P(2)-Co-C(5)	177.51(11)	C(1)-Co-C(2)	123.37(16)
C(1)-Co-C(5)	86.38(15)	C(2)-Co-C(5)	85.85(17)
Co-C(5)-C(6)	177.9(4)	C(5)-C(6)-C(7)	176.8(5)

Deprotonation of *N*-(prop-2-enyl)-*p*-toluenesulfonamide[13] and addition of 1-bromo-2-butyne generated enyne **18**[25] as a crystalline solid in 99% yield. This was then transformed into complex **19** via the standard approach used previously to synthesise the mono-substituted alkyne complexes (Scheme 7).



Scheme 7. Synthesis of complex **19**.

The ^{31}P NMR spectrum of complex **19** was examined in [D_8]toluene, since its spectrum in DME gave essentially a single broad resonance at δ 49 ppm (Figure 10). At 30 °C the spectrum in [D_8]toluene showed two stronger resonances at δ 49 and 48 ppm associated with a major diastereoisomer and two weaker resonances at δ 42 and 40 ppm associated with a minor diastereoisomer (together with resonances at δ 26–28 ppm associated with binap oxides). The ^{31}P NMR spectrum of complex **19** in carbon monoxide saturated DME was recorded at 30 °C and then the sample was subjected to the standard VT sequence. At 35 °C two new resonances started to emerge at δ 54 and 43 ppm and at 55 °C these were the only resonances in the spectrum (Figure 10). On increasing the temperature to 75 °C and on cooling of the NMR experiment to 30 °C, no further changes to the spectra were observed.

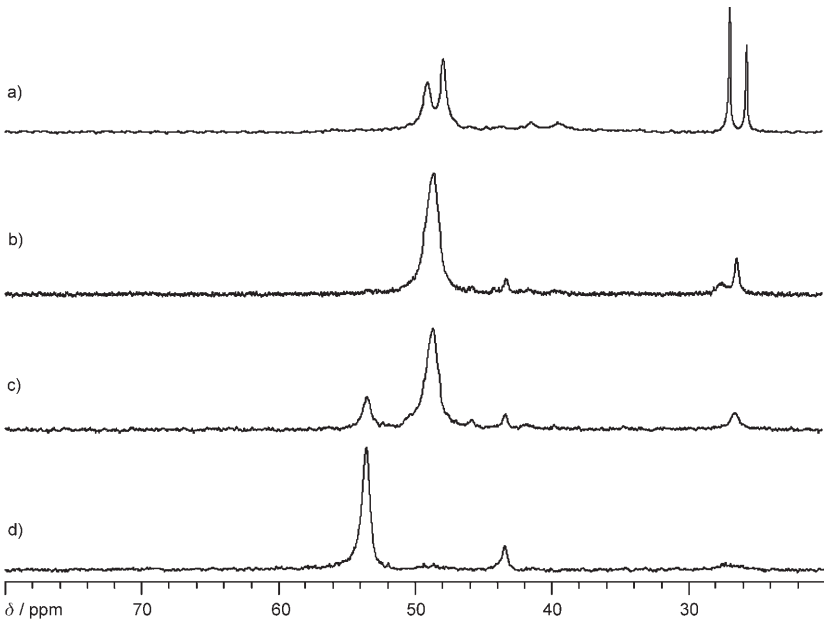


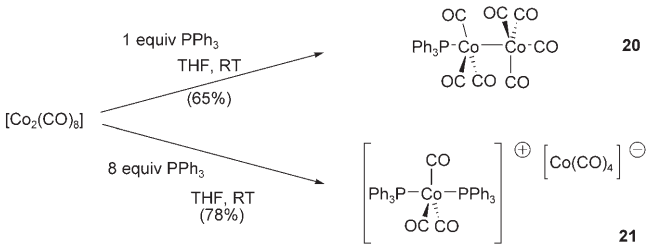
Figure 10. ^{31}P NMR spectra of complex **19** at 30 °C in a) [D_8]toluene, and b) 30, c) 35, and d) 55 °C in DME under carbon monoxide.

Observation of the resonance at δ 54 ppm during the VT ^{31}P NMR experiment on complex **19**, a derivative of a disubstituted alkyne, proved that the hypothesis that the hydrogen atom of the cobalt hydride **12** originated from the terminal hydrogen of monosubstituted alkynes was incorrect. Nevertheless this experiment did reveal that the presence of the second alkyne substituent resulted in the formation of the hydride species earlier in the VT experiment (at 35 °C for complex **19** vs 50 °C for complex **4**).

The results described above reveal that pendent alkenes promote cobalt–cobalt bond cleavage in (alkyne)-(binap)tetracarbonyldicobalt(0) complexes. The process appears to be facilitated by an electron-poor alkene and a disubstituted alkyne and disfavoured by an electron-rich alkene. These observations may be explained by a direct interaction of the alkene in complexes **4**, **9**, **11** and **19** that leads to cobalt–cobalt bond cleavage, as postulated below, but an indirect effect resulting from interactions in a downstream intermediate en route to cyclopentenone formation cannot be ruled out.

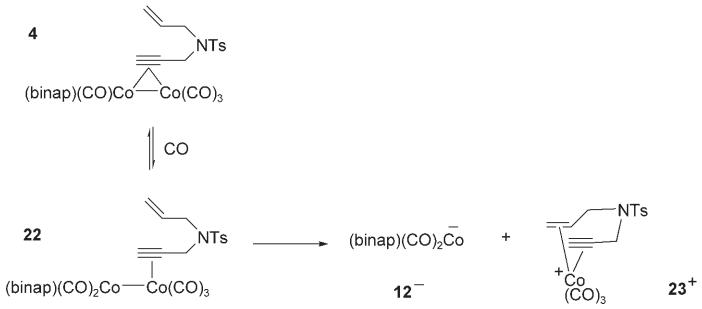
It is documented that octacarbonyldicobalt(0) is readily transformed at room temperature in THF into the monophosphane derivative **20** or the ionic diphosphane species **21** by the action of one or eight equivalents of triphenylphosphane, respectively (Scheme 8).[26] The ionic species **21** is presumably generated via the formation of **20**, followed by nucleophilic attack by a second molecule of triphenylphosphane, present in high concentration, and the displacement of the stable tetracarbonylcobaltate anion.

In light of the phosphane reactivity, it seems reasonable to postulate that the alkenes present in **4**, **9**, **11** and **19** act as internal nucleophiles leading to the cleavage of the cobalt–cobalt bonds and the generation of cobalt anions. We thus propose that carbon monoxide induces the formation of the η^2-alkyne complex **22** from complex **4** (this is consistent with



Scheme 8. Reactions of octacarbonyldicobalt(0) with triphenylphosphane.

the first step in the proposed mechanism for the interconversion of the diastereoisomers **2a** and **2b** as depicted in Scheme 2, and that this is followed by the alkene displacing the anion of **12** as depicted in Scheme 9. (The activated allylic/propargylic hydrogens in the resulting undetected cation **23** may be the source of the proton required to generate **12**, and this will be probed by future labelling studies.)



Scheme 9. Generation of the anion of **12** via displacement by alkene.

Finally, in order to relate the observations described above to catalytic PKR conditions, a series of constant temperature NMR experiments were performed using substoichiometric amounts of octacarbonyldicobalt(0) and binap with the standard PKR enyne **3**. Our established method for a catalytic PKR involves premixing sublimed octacarbonyldicobalt(0) (7.5 mol%) and binap (7.5 mol%) at room temperature for 15 minutes under carbon monoxide, before adding the substrate enyne and heating at 75 °C for 3–4 h.[9] Sublimed octacarbonyldicobalt(0) (7.5 mol%) and binap (7.5 mol%) were thus mixed in carbon monoxide saturated DME in an NMR tube for 15 minutes before addition via syringe of one equivalent of enyne **3** dissolved in carbon monoxide saturated DME. The NMR tube was then introduced into the NMR probe which had been preheated to 75 °C. ^{31}P NMR spectra were recorded at 40-minute intervals, but due to the low concentration of phosphorus species no resonances of interest were observed. Raising the concentration of octacarbonyldicobalt(0) and binap to 25 mol% led to the observation of resonances at δ 54 and 43 ppm within the first hour of the experiment. Raising the concentration of octacarbonyldicobalt(0) and binap still further to give better quality spectra and lowering the temperature to reduce the rate of the observed changes in the spectra led to the spectra depicted in Figure 11, which were recorded using 50 mol% octacarbonyldicobalt(0) and binap at 65 °C. After 15 and 30 minutes, resonances associated with enyne complex **4** were clearly visible together with resonances associated with binap (δ −13 ppm) and binap oxides (δ 26 ppm). By 60 minutes complex **4** had almost disappeared and the resonances at δ 54 and 43 ppm were starting to dominate the spectrum. At 90 minutes complex **4** was no longer observed and the spectrum was essentially the same at 120 minutes. Interestingly the binap and binap oxide resonances are only seen until 30 minutes. (The origin of the resonance at δ 41 ppm observed clearly in the final spectra is unknown but subjecting octacarbonyldicobalt(0) and binap alone to a VT ^{31}P NMR experiment in carbon monoxide saturated DME generated a major resonance at δ 43 and a minor resonance at 41 ppm at 75 °C. Thus the resonance at δ 41 ppm is not dependent on an enyne substrate and is probably a higher order binap cobalt cluster.)

The constant temperature NMR experiments described above reveal that the cobalt hydride **12** is generated under

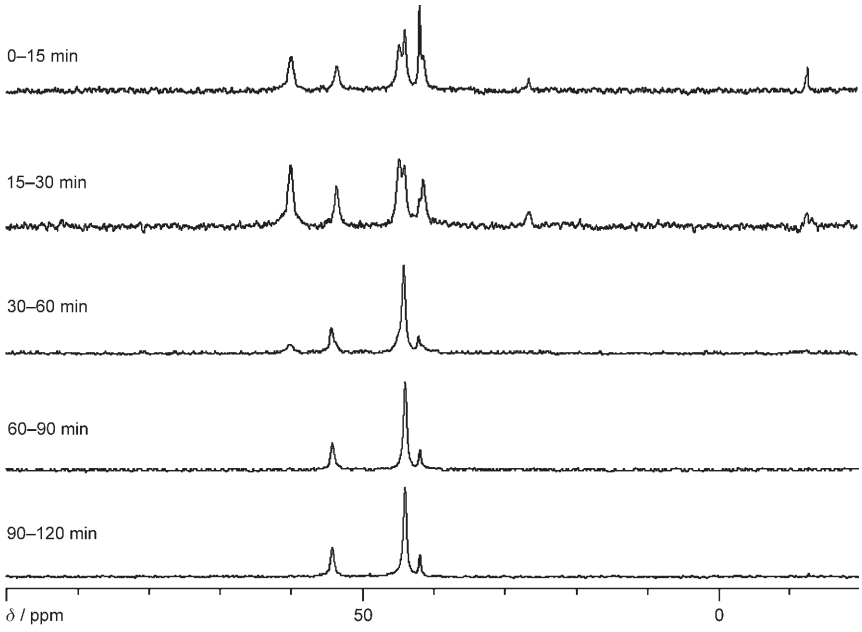
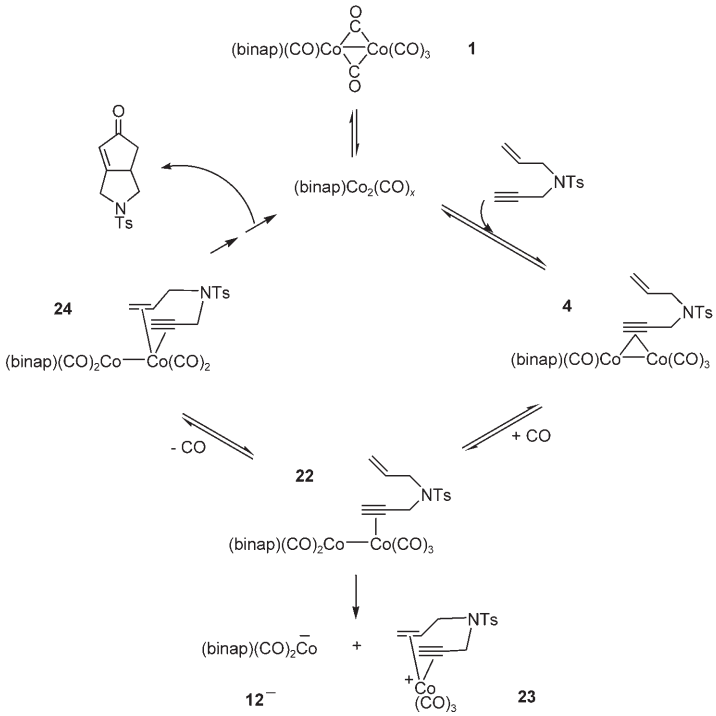


Figure 11. ^{31}P NMR spectra of octacarbonyldicobalt(0) (50 mol%), binap (50 mol%) and enyne **3** at 65 °C in carbon monoxide saturated DME with time.

sub-stoichiometric PKR conditions. On the basis of the evidence available to us at present, we postulate that it lies off the catalytic cycle, and that intermediate **22** is partitioned between i) hydride formation and ii) continuation of the catalytic cycle (Scheme 10).



Scheme 10. A proposed catalytic cycle for the binap directed PKR indicating a pathway for cobalt loss.

Conclusion

Four (binap)(enyne)tetracarbonyldicobalt(0) complexes **4**, **9**, **11** and **19**, and one (binap)(alkyne)tetracarbonyldicobalt(0) complex **6** have been synthesised and their reactivity monitored by VT ^{31}P NMR spectroscopy. Formation of (binap)dicarbonylhydridocobalt(−1) **12** occurred at temperatures between 35 and 55 °C and was facilitated by either an electron-poor alkene or a disubstituted alkyne. In the absence of a pendent alkene, complex **6** proved stable up to 75 °C. These results reveal that formation of hydride **12** requires a pendent alkene, and a mechanism involving alkene displacement of a (binap)cobaltate anion may account for the observations, although formation of **12** at a later stage in the progression of the enyne through the Pauson–Khand reaction cannot be discounted. Regardless of its origins, the appearance of hydride **12** in NMR spectra run under Pauson–Khand conditions suggests that it is of significance in this reaction and that prevention of its formation may lead to a more efficient catalytic system. It is anticipated that experiments using phosphorus labelled enynes and binap should provide further information on how the generation and fate of **12** relate to cyclopentenone formation.

Experimental Section

Syntheses were carried out under an atmosphere of nitrogen in oven-dried glassware using standard Schlenk techniques. THF and DME were distilled from sodium/benzophenone and dichloromethane was distilled from calcium hydride. *N*-(Prop-2-enyl)-*p*-toluenesulfonamide,[13] *N*-propyl-*p*-toluenesulfonamide,[13,14] and *N*-(2-oxoethyl)-*N*-(prop-2-ynyl)-*p*-toluenesulfonamide[17] were prepared according to literature procedures. All other reagents are commercially available and were used as received. NMR spectra were recorded on Bruker AM 500, Bruker AV 500, Bruker DRX 400, Bruker AV 400 and Bruker DRX 300 instruments. Some ^{31}P NMR spectra were collected in the inverse gated mode to enable peak integration. Melting points were recorded in open capillaries on a Sanyo Gallenkamp melting-point apparatus and are uncorrected. IR spectra were recorded on a Perkin-Elmer Spectrum RX FT-IR spectrometer. Mass spectra were recorded on Micromass AutoSpec-Q and Micromass Platform II spectrometers. Elemental analyses were performed by the London Metropolitan University microanalytical service.

***N*-(Prop-2-enyl)-*N*-(prop-2-ynyl)-*p*-toluenesulfonamide (3)**: [12] *N*-(Prop-2-enyl)-*p*-toluenesulfonamide[13] (5.92 g, 28 mmol) was dissolved in anhydrous DMF (50 mL) and sodium hydride (1.46 g, 36.4 mmol) was added with care. The mixture was stirred at room temperature for 30 min. Propargyl bromide (5.15 mL, 46.2 mmol) was added and the reaction was stirred for 1 h. The reaction mixture was then quenched with water (85 mL) and the product was extracted with diethyl ether (4×40 mL). The organic layer was dried over magnesium sulfate and concentrated in vacuo. The brown liquid was then loaded onto a chromatography column of silica gel and eluted with hexane/diethyl ether 5:1 to collect the title compound **3**, which was then recrystallised from diethyl ether/hexane 1:5 (5.95 g, 85 %). M.p. 63–65 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.02 (t, ^4J(H,H) = 2 Hz, 1H; *H*C≡CCH$_2$), 2.45 (s, 3H; CH$_3$), 3.85 (d, ^3J(H,H) = 6 Hz, 2H; NC*H*$_2$CH=CH$_2$), 4.11 (d, ^4J(H,H) = 2 Hz, 2H; NC*H*$_2$C≡CH), 5.26 (dd, ^3J(H,H) = 10, ^2J(H,H) = 1 Hz, 1H; CH=C*H*$_2$ (*E*)), 5.31 (dd, ^3J(H,H) = 17, ^2J(H,H) = 1 Hz, 1H; CH=C*H*$_2$ (*Z*)), 5.75 (ddt, ^3J(H,H) = 17, 10, 6 Hz, 1H; C*H*=CH$_2$), 7.32 (d, ^3J(H,H) = 8 Hz, 2H; Ar-H), 7.76 ppm (d, ^3J(H,H) = 8 Hz, 2H; Ar-H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 21.6 (CH$_3$), 35.8 (N*C*H$_2$C≡CH), 49.0 (N*C*H$_2$CH=CH$_2$), 73.7 (NCH$_2$C≡*C*H), 76.5 (NCH$_2$*C*≡CH), 120.0 (NCH$_2$CH=*C*H$_2$), 127.8 (C$_{ortho}$), 129.5 (C$_{meta}$), 131.9 (NCH$_2$*C*H=CH$_2$), 136.0 (C$_{para}$), 143.6 ppm (C$_{ipso}$); IR (CH_2Cl_2): $\tilde{\nu}$ = 3301 (s), 3081 (w, C≡C-H), 2120 (w, C≡C), 1644 (m), 992 (m), 934 (s, C=C), 1347, 1165 cm^{-1} (s, NSO$_2$); MS (FAB): *m*/*z* (%): 250 (100) [*M*+H]$^+$, 155 (23) [CH$_3$C$_6$H$_4$SO$_2$]$^+$, 91 (25) [C$_7$H$_7$]$^+$.

(Binap)tetracarbonyl[*N*-(prop-2-enyl)-*N*-(prop-2-ynyl)-*p*-toluenesulfonamide]dicobalt(0) (4): 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 230 min. Enyne **3** (56 mg, 0.226 mmol) was added and the reaction was stirred at 40 °C for 2 h. The mixture was allowed to cool to room temperature and was then adsorbed onto neutral alumina (grade II). The brown solid was loaded onto a chromatography column of silica gel 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 title compound **4** as a brown solid (109 mg, 45 %). ^{13}C NMR (125 MHz, $CDCl_3$): too broad to interpret; ^{31}P NMR (500 MHz, $CDCl_3$): δ = 58.9, 53.2, 44.0, 39.2 (CoPPh^2-Ar), −14.6 ppm (BINAP); IR ($CHCl_3$): $\tilde{\nu}$ = 2043, 1980, 1939 cm^{-1} (s, C=O); ^{1}H NMR (500 MHz, $CDCl_3$): too broad to interpret; MS (FAB): *m*/*z* (%): 1017 (11) [*M*−3CO]$^+$, 989 (40) [*M*−4CO]$^+$, 681 (100) [Co(BINAP)]$^+$, 437 (65) [BINAP-PPh$_2$]$^+$.

General experimental for VT ^{31}P NMR of complexes 4, 6, 9, 11, and 19: Complex **4**, **6**, **9**, **11** or **19** (about 75 mg) was dissolved in CO saturated DME (1 mL) and syringed via a filter needle into a WILMAD screw cap (with a PTFE/silicone septum) NMR tube under carbon monoxide. A variable temperature NMR experiment was then performed (30 to 75 °C (in 5/10 °c intervals) then in one step back to 30 °C). See Figures 2, 4–6, and 10 for selected spectra.

***N*-(Propyl)-*N*-(prop-2-ynyl)-*p*-toluenesulfonamide (5)**: *N*-Propyl-*p*-toluenesulfonamide (1.77 g, 8 mmol)[13,14] was dissolved in anhydrous DMF

(15 mL) and sodium hydride (0.43 g, 11 mmol) was added with care. The mixture was stirred at room temperature for 30 min. Propargyl bromide (1.5 mL, 14 mmol) was added and the reaction was stirred for 1 h. The reaction mixture was then quenched with water (50 mL) and the product was extracted with diethyl ether (4×30 mL). The organic layer was dried over magnesium sulfate and concentrated in vacuo. The crude mixture was then loaded onto a chromatography column of silica gel and eluted with hexane/diethyl ether 5:1 to collect the title compound **5**, which was then ground in a mortar and pestle and dried in vacuo (1.39 g, 67%). M.p. 47–49°C; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.91 (t, ^3J(H,H) = 7 Hz, 3H; CH_3), 1.58 (tq, ^3J(H,H) = 7, 7 Hz, 2H; $NCH_2CH_2CH_3$), 2.00 (t, ^4J(H,H) = 2 Hz, 1H; $NCH_2C{\equiv}CH$), 2.40 (s, 3H; CH_3), 3.14 (t, ^3J(H,H) = 7 Hz, 2H; $NCH_2CH_2CH_3$), 4.11 (d, ^4J(H,H) = 2 Hz, 2H; $NCH_2C{\equiv}CH$), 7.27 (d, ^3J(H,H) = 8 Hz, 2H; Ar-H), 7.71 ppm (d, ^3J(H,H) = 8 Hz, 2H; Ar-H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 11.0 (CH_3), 20.8 ($NCH_2CH_2CH_3$), 21.4 (CH_3), 36.1 ($NCH_2C{\equiv}CH$), 48.0 ($NCH_2CH_2CH_3$), 73.5 ($NCH_2C{\equiv}CH$), 76.6 ($NCH_2C{\equiv}CH$), 127.6 (C_{ortho}), 129.4 (C_{meta}), 136.0 (C_{para}), 143.3 ppm (C_{ipso}); IR ($CHCl_3$): $\tilde{\nu}$ = 3308 (m, C≡C-H), 1348, 1159 cm^{-1} (s, NSO_2); MS (FAB): *m*/*z* (%): 252 (100) $[M+H]^+$, 155 (18) $[CH_3C_6H_4SO_2]^+$, 91 (24) $[C_7H_7]^+$.

(Binap)tetracarbonyl[*N*-(propyl)-*N*-(prop-2-ynyl)-*p*-toluenesulfonamide]-dicobalt(0) (6): 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. Enyne **5** (57 mg, 0.226 mmol) was added and the reaction was stirred at 40°C for 2 h. The mixture was allowed to cool to room temperature and was then absorbed onto neutral alumina (grade II). The brown solid was loaded onto a chromatography column of silica gel 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 compound **6** as a brown solid (159 mg, 66%). ^{1}H NMR (500 MHz, $CDCl_3$): too broad to interpret; ^{13}C NMR (125 MHz, $CDCl_3$): too broad to interpret; ^{31}P NMR (202 MHz, $CDCl_3$): δ = 57.9, 51.6, 43.8, 39.9 ($CoPPh^2$-Ar), −14.9 ppm (BINAP); IR ($CHCl_3$): $\tilde{\nu}$ = 2044 (m), 1980 (s), 1940 cm^{-1} (w, C=O); MS (FAB): *m*/*z* (%): 1019 (18) $[M-3CO]^+$, 991 (54) $[M-4CO]^+$, 681 (16) $[Co(BINAP)]^+$, 437 (24) $[BINAP\text{-}PPh_2]^+$, 71 (100) $[CH_2NCH_2CH_2CH_3]^+$; recrystallisation from CH_2Cl_2/pentane gave a pure sample; elemental analysis calcd (%) for $C_{61}H_{49}Co_2NO_6P_2S$ (1103.92): C 66.37, H 4.47, N 1.27; found: C 66.32, H 4.41, N 1.17.

***N*-(But-2-enyl)-*p*-toluenesulfonamide (7)**:[15] *p*-Toluene sulfonyl isocyanate (0.34 mL, 2.2 mmol) and 3-buten-2-ol (0.17 mL, 2 mmol) were dissolved in THF (10 mL) and stirred at room temperature for 10 min. The reaction mixture was then concentrated in vacuo and redissolved in DMF (10 mL). Palladium (II) acetate (22 mg, 0.1 mmol) and lithium bromide (0.69 g, 8 mmol) were added and the reaction was stirred at 100°C for 22.5 h. The reaction mixture was allowed to cool before extraction with diethyl ether (200 mL) and the organic layer was washed with water (3×40 mL) and brine (3×40 mL). The crude product was dried over magnesium sulfate and concentrated in vacuo before being loaded onto a chromatography column of silica gel and eluted with hexane/ethyl acetate 7:3. The title compound **7** was collected as a white solid (288 mg, 64%). M.p. 62–64°C; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.59–1.61 (m, 3H; CH_3), 2.42 (s, 3H; CH_3), 3.50 (tt, ^3J(H,H) = 6, 1 Hz, 2H; $NCH_2CH{=}CHCH_3$), 4.46 (t, ^3J(H,H) = 6 Hz, 1H; NH), 5.36–5.29 (m, 1H; $NCH_2CH{=}CHCH_3$), 5.60–5.52 (m, 1H; $NCH_2CH{=}CHCH_3$), 7.30 (d, ^3J(H,H) = 8 Hz, 2H; Ar-H), 7.74 ppm (d, ^3J(H,H) = 8 Hz, 2H; Ar-H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 17.5 (CH_3), 21.5 (CH_3), 45.3 ($NCH_2CH{=}CHCH_3$), 125.6 ($NCH_2CH{=}CHCH_3$), 127.1 (C_{ortho}), 129.6 (C_{meta}), 129.7 ($NCH_2CH{=}CHCH_3$), 137.0 (C_{para}), 143.2 ppm (C_{ipso}); IR ($CHCl_3$): $\tilde{\nu}$ = 3380, 1496 (m, N-H), 1673 (w, C=C), 1329, 1159 cm^{-1} (s, NSO_2); MS (FAB): *m*/*z* (%): 226 (67) $[M+H]^+$, 224 (34) $[M-H]^+$, 172 (100) $[CH_3C_6H_4SO_2NH_3]^+$, 155 (50) $[CH_3C_6H_4SO_2]^+$, 91 (55) $[C_7H_7]^+$, 69 (59) $[CH_3CH{=}CHCH_2N]^+$, 55 (85) $[CH_3CH{=}CHCH_2]^+$.

***N*-(But-2-enyl)-*N*-(prop-2-ynyl)-*p*-toluenesulfonamide (8)**:[16] Sulfonamide **7** (1.70 g, 7.5 mmol) was dissolved in anhydrous DMF (15 mL) and sodium hydride (0.39 g, 9.8 mmol) was added with care. The mixture was stirred at room temperature for 30 min. Propargyl bromide (2.4 mL, 12.4 mmol) was added and the reaction was stirred for 1 h. The reaction mixture was then quenched with water (40 mL) and the product was extracted with diethyl ether (4×20 mL). The organic layer was dried over magnesium sulfate and concentrated in vacuo. The brown liquid was then loaded onto a chromatography column of silica gel and eluted with hexane/diethyl ether 5:1 to collect the title compound **8** (1.68 g, 85%). M.p. 64–66°C; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.67–1.69 (m, 3H; CH_3), 2.00 (t, ^4J(H,H) = 2 Hz, 1H; $NCH_2C{\equiv}CH$), 2.41 (s, 3H; CH_3), 3.74 (d, ^3J(H,H) = 7 Hz, 2H; $NCH_2CH{=}CHCH_3$), 4.10 (d, ^4J(H,H) = 2 Hz, 2H; $NCH_2C{\equiv}CH$), 5.38–5.31 (m, 1H; $NCH_2CH{=}CHCH_3$), 5.73–5.66 (m, 1H; $NCH_2CH{=}CHCH_3$), 7.28 (d, ^3J(H,H) = 8 Hz, 2H; Ar-H), 7.71 ppm (d, ^3J(H,H) = 8 Hz, 2H; Ar-H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 17.6 (CH_3), 21.5 (CH_3), 35.4 ($NCH_2C{\equiv}CH$), 48.2 ($NCH_2CH{=}CHCH_3$), 73.5 ($NCH_2C{\equiv}CH$), 76.7 ($NCH_2C{\equiv}CH$), 124.4 ($NCH_2CH{=}CHCH_3$), 127.7 (C_{ortho}), 129.4 (C_{meta}), 131.6 ($NCH_2CH{=}CHCH_3$), 136.1 (C_{para}), 143.4 ppm (C_{ipso}); IR ($CHCl_3$): $\tilde{\nu}$ = 3308 (s, C≡C-H), 3038 (m, C=C-H), 1673 (w, C=C), 1348, 1160 cm^{-1} (s, NSO_2); MS (FAB): *m*/*z* (%): 264 (100) $[M+H]^+$, 262 (28) $[M-H]^+$, 222 (36) $[M-CH{=}CHCH_3]^+$, 210 (72) $[CH_3C_6H_4SO_2NHCH_2CH{=}CH]^+$, 155 (41) $[CH_3C_6H_4SO_2]^+$, 108 (32) $[HC{\equiv}CCH_2NCH_2CH{=}CHCH_3]^+$, 91 (39) $[C_7H_7]^+$.

(Binap)tetracarbonyl[*N*-(but-2-enyl)-*N*-(prop-2-ynyl)-*p*-toluenesulfonamide]dicobalt(0) (9): 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. Enyne **8** (59 mg, 0.224 mmol) was added and the reaction was stirred at 40°C for 2 h. The mixture was allowed to cool to room temperature and was then adsorbed onto neutral alumina (grade II). The brown solid was loaded onto a chromatography column of silica gel and eluted under nitrogen, first with hexane/ethyl acetate 19:1 to remove unreacted octacarbonyldicobalt and then with hexane/ethyl acetate 7:3 to collect the title compound **9** as a brown solid (152 mg, 62%). ^{1}H NMR (500 MHz, $CDCl_3$): too broad to interpret; ^{13}C NMR (125 MHz, $CDCl_3$): too broad to interpret; ^{31}P NMR (202 MHz, $CDCl_3$): δ = 58.7, 53.0, 43.7, 39.0 ($CoPPh^2$-Ar), −14.7 ppm (BINAP); IR ($CHCl_3$): $\tilde{\nu}$ = 2041, 1977, 1935 cm^{-1} (s, C=O); MS (FAB): *m*/*z* (%): 1031 (20) $[M-3CO]^+$, 1003 (58) $[M-4CO]^+$, 681 (100) $[Co(BINAP)]^+$, 437 (56) $[BINAP\text{-}PPh_2]^+$.

***N*-(3-Carbomethoxyprop-2-enyl)-*N*-(prop-2-ynyl)-*p*-toluenesulfonamide (10)**:[18] *N*-(2-oxoethyl)-*N*-(prop-2-ynyl)-*p*-toluenesulfonamide[17] (1.49 g, 6 mmol) and methyl(triphenylphosphoranylidene) acetate (3.96 g, 12 mmol) were dissolved in benzene (30 mL). The solution was stirred overnight at room temperature under nitrogen. The mixture was then concentrated in vacuo and loaded onto a chromatography column of silica gel and eluted with hexane/ethyl acetate 5:1. The title compound **10** was collected as a colourless oil (1.42 g, 78%). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 2.05 (t, ^4J(H,H) = 2 Hz, 1H; $CH_2C{\equiv}CH$), 2.40 (s, 3H; CH_3), 3.71 (s, 3H; OCH_3), 3.96 (dd, ^4J(H,H) = 2 Hz, ^3J(H,H) = 6 Hz, 2H; $NCH_2CH{=}CH$), 4.07 (d, ^4J(H,H) = 2 Hz, 2H; $NCH_2C{\equiv}CH$), 6.02 (dt, ^4J(H,H) = 2, ^3J(H,H) = 16 Hz, 1H; $NCH_2CH{=}CH$), 6.78 (dt, ^3J(H,H) = 16, 6 Hz, 1H; $NCH_2CH{=}CH$), 7.29 (d, ^3J(H,H) = 8 Hz, 2H; Ar-H), 7.70 ppm (d, ^3J(H,H) = 8 Hz, 2H; Ar-H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 21.2 (CH_3), 36.7 ($NCH_2C{\equiv}CH$), 47.1 ($NCH_2CH{=}CH$), 51.7 (OCH_3), 74.5 ($NCH_2C{\equiv}CH$), 76.0 ($NCH_2C{\equiv}CH$), 124.3 ($NCH_2HC{=}CH$), 127.7 (C_{ortho}), 129.7 (C_{meta}), 135.6 (C_{para}), 141.6 ($NCH_2CH{=}CH$), 144.0 (C_{ipso}), 166.0 ppm (C=O); IR (CH_2Cl_2): $\tilde{\nu}$ = 3300 (m, C≡C-H), 1722 (s, C=O), 1664, 983 (m, C=C), 1351, 1163 (s, NSO_2), 1197, 1096 cm^{-1} (m, C−O); MS (FAB): *m*/*z* (%): 308 (100) $[M+H]^+$, 276 (34) $[M-OCH_3]^+$, 155 (46) $[CH_3C_6H_4SO_2]^+$, 91 (46) $[C_7H_7]^+$.

(Binap)tetracarbonyl[*N*-(3-carbomethoxyprop-2-enyl)-*N*-(prop-2-ynyl)-*p*-toluenesulfonamide] (11): 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. Enyne **10** (67.7 mg, 0.220 mmol) was added and the reaction was stirred at 40°C for 2 h. The mixture was allowed to cool and was then adsorbed onto neutral alumina (grade II). The brown solid was loaded onto a chromatography column of silica gel and eluted under nitrogen, first with hexane/ethyl acetate 19:1 to remove unreacted octacarbonyldicobalt and then with

hexane/ethyl acetate 7:3 to collect the title compound **11** as a brown solid (114 mg, 45%). ^{1}H NMR (500 MHz, $CDCl_3$): too broad to interpret; ^{13}C NMR (125 MHz, $CDCl_3$): too broad to interpret; ^{31}P NMR (202 MHz, $CDCl_3$): δ = 58.7, 51.7, 44.0, 40.1 ($CoPPh^2$-Ar), −14.3 ppm (BINAP); IR ($CHCl_3$): $\tilde{\nu}$ = 2044, 1981, 1941 (s, C=O), 1720 cm^{-1} (m, O-C=O); MS (FAB): *m*/*z* (%): 1075 (16) $[M-3CO]^+$, 1047 (30) $[M-4CO]^+$, 681 (100) $[Co(BINAP)]^+$, 437 (68) $[BINAP\text{-}PPh_2]^+$.

(Binap)dicarbonylhydridocobalt(I): Enyne complex **4** (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/silicon septum) NMR tube filled with carbon monoxide; ^{31}P NMR spectra were recorded between 30 °C and 75 °C. The NMR tube was then allowed to cool 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%). On storing the NMR tube in the freezer, small brown crystals appeared in the NMR tube and these were identified as hydride **12** by X-ray crystallography[11] and mass spectrometry MS (FAB): *m*/*z* (%): 710 (63) $[M-CO]^+$, 437 (100) $[BINAP\text{-}PPh_2]^+$. The early stages of the experiment were subsequently repeated in [D$_8$]THF. On cooling 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).

X-ray crystallography of complex 17: Enyne complex **4** (48 mg, 0.04 mmol) was dissolved in degassed CH_2Cl_2 (4 mL) and syringed carefully into a sealed test tube under nitrogen. Degassed petroleum spirit (15 mL) was then carefully syringed on top of the CH_2Cl_2 layer, avoiding the mixing of the two solvents. The test tube was then placed in the freezer for three weeks after which brown crystals could be observed. Crystal data: $[C_{59}H_{46}CoNO_4P_2S].0.5CH_2Cl_2$, M = 1028.36, triclinic, $P\bar{1}$ (no. 2), a = 11.1811(8), b = 13.3311(8), c = 18.3365(12) Å, α = 75.184(5), β = 84.931(5) γ = 80.246(5)°, V = 2601(3) Å^3, Z = 2, ρ_{calcd} = 1.313 g cm^{-3}, μ($Cu_{K\alpha}$) = 4.393 mm^{-1}, T = 173 K, yellow blocks, Oxford Diffraction Xcalibur PX Ultra diffractometer; 9650 independent measured reflections, F^2 refinement, R_1 = 0.0664, wR_2 = 0.1773, 8223 independent observed absorption corrected reflections [$|F_o| > 4\sigma(|F_o|)$, $2\theta_{max}$ = 142°], 654 parameters. CCDC-642 286 contains 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.

***N*-(Prop-2-enyl)-*N*-(but-2-ynyl)-*p*-toluenesulfonamide (18)**:[25] *N*-(Prop-2-enyl)-*p*-toluenesulfonamide (4.0 g, 18.9 mmol) was dissolved in anhydrous DMF (40 mL) and sodium hydride (0.99 g, 24.6 mmol) was added with care. The mixture was stirred at room temperature for 30 min. 1-Bromo-but-2-yne (2.75 mL, 31.4 mmol) was added and the reaction was stirred for 1 h. The reaction mixture was then quenched with water (100 mL) and the product was extracted with diethyl ether (3×50 mL). The organic washings were dried over magnesium sulfate and concentrated in vacuo. The brown liquid was then loaded onto a chromatography column of silica gel and eluted with hexane/diethyl ether 5:1 to collect the title compound **18** as a crystalline solid (4.95 g, 99%). M.p. 35–36 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.53 (t, ^4J(H,H) = 2 Hz, 3H; $H_3CC{\equiv}C$), 2.42 (s, 3H; CH_3), 3.79 (d, ^3J(H,H) = 6 Hz, 2H; $NCH_2CH{=}CH_2$), 4.01 (q, ^4J(H,H) = 2 Hz, 2H; $NCH_2C{\equiv}CCH_3$), 5.21 (dd, ^3J(H,H) = 10, ^2J(H,H) = 1 Hz, 1H; $CH{=}CH_2$ (E)), 5.26 (dd, ^3J(H,H) = 17, ^2J(H,H) = 1 Hz, 1H; $CH{=}CH_2$ (Z)), 5.73 (ddt, ^3J(H,H) = 17, 10, 6 Hz, 1H; $CH{=}CH_2$), 7.29 (d, ^3J(H,H) = 8 Hz, 2H, Ar-H), 7.73 ppm (d, ^3J(H,H) = 8 Hz, 2H; Ar-H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 3.2 ($C{\equiv}CCH_3$), 21.5 (CH_3), 36.3 ($NCH_2C{\equiv}CCH_3$), 48.9 ($NCH_2CH{=}CH_2$), 71.7 ($NCH_2C{\equiv}CCH_3$), 81.5 ($NCH_2C{\equiv}CCH_3$), 119.4 ($NCH_2CH{=}CH_2$), 127.9 (C_{ortho}), 129.2 (C_{meta}), 132.3 ($NCH_2CH{=}CH_2$), 136.3 (C_{para}), 143.2 ppm (C_{ipso}); IR ($CHCl_3$): $\tilde{\nu}$ = 2225 (w, C≡C), 1645, 992, 936 (m, C=C), 1348, 1160 cm^{-1} (s, NSO_2); MS (CI): *m*/*z* (%): 281 (100) $[M+NH_4]^+$, 264 (88) $[M+H]^+$, 110 (52) $[H_3CC{\equiv}CCH_2H_2NCH_2CHCH_2]^+$.

(Binap)tetracarbonyl[*N*-(prop-2-enyl)-*N*-(but-2-ynyl)-*p*-toluenesulfonamide]dicobalt(0) (19): Octacarbonyldicobalt(0) (76 mg, 0.222 mmol) and (±)-2,2′-bis(diphenylphosphino)-1,1′-binaphthalene (138 mg, 0.222 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. Enyne **18** (57 mg, 0.216 mmol) was added and the reaction was stirred at 40 °C for 2 h. The mixture was allowed to cool and was then adsorbed onto neutral alumina (grade II). The brown solid was loaded onto a chromatography column of silica gel and eluted under nitrogen, first with hexane then with hexane/ethyl acetate 19:1 to remove unreacted octacarbonyldicobalt and then with hexane/ethyl acetate 7:3 to collect title compound **19** as a brown solid (75 mg, 31%).^{1}H NMR (500 MHz, $CDCl_3$): Too broad to interpret; ^{13}C NMR (125 MHz, $CDCl_3$): Too broad to interpret; ^{31}P NMR (500 MHz, [D$_8$]toluene): δ = 49.0, 47.9, 41.4, 39.4 ($CoPPh^2$-Ar), −14.6 (BINAP); IR ($CHCl_3$): $\tilde{\nu}$ = 2040, 1977 (s), 1928 cm^{-1} (m, C=O); MS (FAB): *m*/*z* (%): 1031 (10) $[M-3CO]^+$, 1003 (47) $[M-4CO]^+$, 681 (100) $[Co(BINAP)]^+$, 437 (90) $[BINAP\text{-}PPh_2]^+$.

Examination of the PKR by ^{31}P NMR spectroscopy at 65 °C: Octacarbonyldicobalt(0) (19.3 mg, 0.06 mmol), (*S*)-BINAP (37.4 mg, 0.06 mmol) and enyne **3** (29.4 mg, 0.12 mmol) were dissolved in CO saturated DME (3 mL) and syringed via a filter needle into a WILMAD screw cap (with a PTFE/silicone septum) NMR tube under CO and the NMR tube was left at room temperature for 15 min. The NMR tube was introduced into the NMR probe which had been preheated to 65 °C and a ^{31}P NMR experiment was performed collecting a spectrum at set time intervals.

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