CHEMISTRY
A EUROPEAN JOURNAL

A Study of $[Co_2(alkyne)(binap)(CO)_4]$ Complexes (BINAP = (1,1′-Binaphthalene)-2,2′-diylbis(diphenylphosphine))

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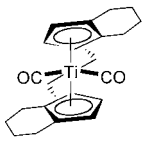
Abstract: Understanding the interaction of chiral ligands, alkynes, and alkenes with cobaltcarbonyl sources is critical to learning more about the mechanism of the catalytic, asymmetric Pauson–Khand reaction. We have successfully characterized complexes of the type $[Co_2(alkyne)(binap)(CO)_4]$ (BINAP = (1,1′-binaphthalene)-2,2′-diylbis(diphenylphosphine)) and shown that diastereomer interconversion occurs under Pauson–Khand reaction conditions when alkyne = HC≡CCO_2Me. Attempts to isolate $[Co_2(alkyne)(binap)(CO)_x]$ complexes with coordinated alkenes led to the formation of cobaltacyclopentadiene species.

Keywords: alkynes · asymmetric catalysis · cobalt · cyclopentenone · reaction mechanisms

Introduction

Methods of simultaneously introducing multiple functional groups and asymmetry are highly valued in organic synthesis. Ideally, the agent inducing the enantioselectivity is used in a catalytic quantity. The Pauson–Khand reaction (PKR), that is, the cyclocarbonylation of an alkyne and an alkene to form a cyclopentenone, is able to fulfil each of these goals.[1] Given the molecular complexity that the PKR generates, it has proven to be an invaluable tool in many total syntheses. These syntheses range from prostaglandins with a cyclopentenone core to more complex natural products in which the cyclopentenone ring is further manipulated during the course of the synthesis.[1a,d,e]

Since its initial discovery more than 30 years ago,[2] when stoichiometric amounts of cobalt were employed for cyclopentenone formation, there has been significant progress towards making the PKR either catalytic or asymmetric. Systems that are both catalytic and enantioselective, however, have only been reported since the late 1990s. The first report of a catalytic, asymmetric PKR came from Buchwald[3] in 1996. By using 5–20 mol% of complex **1**, which is generated in situ from (*S*,*S*)-[Ti(ebthi)$(Me)_2$] (EBTHI = ethylene-1,2-bis(η^5-4,5,6,7-tetrahydro-1-indenyl) under a CO atmosphere, he could obtain enantiomeric excesses (*ee*'s) as high as 96% with intramolecular PKR substrates (Scheme 1).



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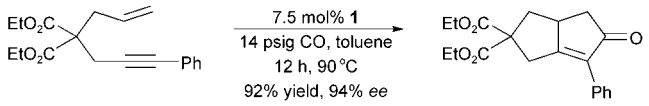
(*S*,*S*)-[Ti(ebthi)$(CO)_2$]



Scheme 1. The catalytic, asymmetric PKR employing chiral complex **1**.[3]

The bulky EBTHI ligand was, however, incompatible with some more highly substituted enynes. Buchwald[4] later went on to study the catalytic, asymmetric PKR of nitrogen-containing enynes, which proved to show large variations in *ee* depending on the substituent attached to the nitrogen atom.

The C_2 symmetry found in the EBTHI ligand has continued to play a role in subsequent reports of catalytic, asymmetric PKRs by Buchwald and others. In fact, to date, reactions giving the highest selectivities for catalytic, enantioselective PKRs all employ axially chiral ligands. Hiroi[5] was the first to use cobalt in these types of PKRs. He found the

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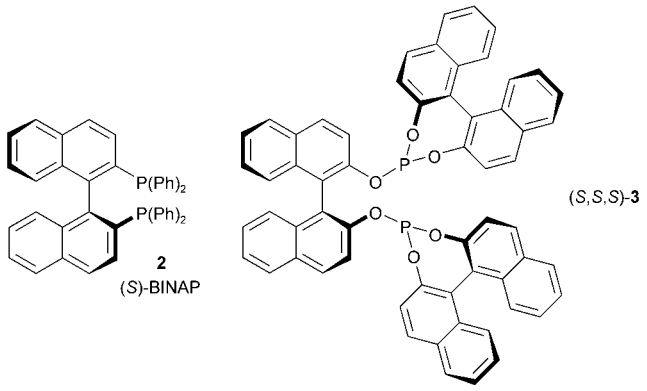
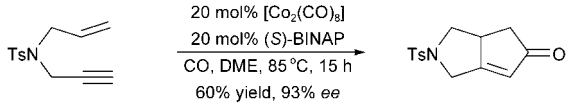
DOI: 10.1002/chem.200401210

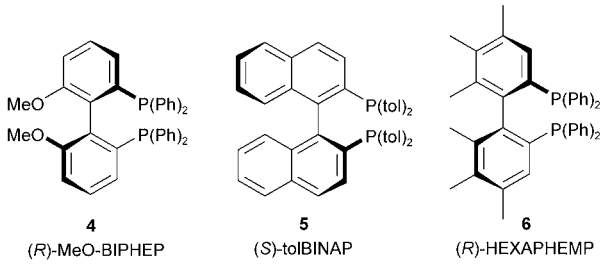


axially chiral ligand (*S*)-BINAP (**2**; BINAP = (1,1′-binaphthalene)-2,2′-diylbis(diphenylphosphine)) to be superior to other diphosphines and obtained high enantiomeric excesses with some standard intramolecular PKR substrates at 20 mol% $[Co_2(CO)_8]$ loading (Scheme 2). Buchwald[6] has

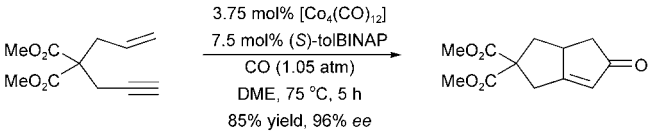


Scheme 2. Hiroi's[5] report of the cobalt-catalyzed, enantioselective PKR.

also reported conditions for the asymmetric, $[Co_2(CO)_8]$-catalyzed PKR using the binaphthyl-based phosphite **3**. He could only obtain good enantioselectivities with two intramolecular PKR substrates, however. Both Hiroi and Buchwald suggest that the bidentate phosphine ligands bridge the two cobalt centers. A recent report by Consiglio[7] extends the trend of axially chiral ligands in the PKR. The use of catalytic amounts of $[Co_2(CO)_8]$ or Co^{II} salts with a reducing agent and ligand **4** generates intramolecular PKR products with good enantiomeric excesses. Our own report[8] in which

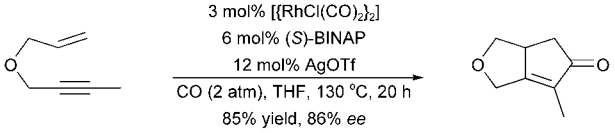


we used $[Co_4(CO)_{12}]$, an easier to handle and more reliable substitute for $[Co_2(CO)_8]$, has recently shown that catalytic, enantioselective PKRs can be carried out with lower loadings of catalyst and ligand than those reported by Hiroi to give good to excellent yields and enantiomeric excesses (Scheme 3). Again, high selectivities were only achieved with C_2-symmetric diphosphines, ligands **2**, **5**, and **6**.



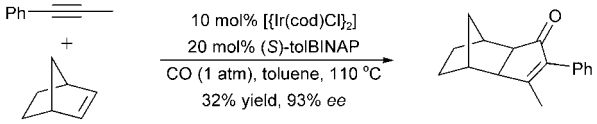
Scheme 3. Our report of improved conditions for the asymmetric, cobalt-catalyzed PKR.[8]

Initial reports of rhodium and iridium complexes being used in asymmetric, catalytic PKRs appeared in 2000. Jeong[9] found that by using $[\{RhCl(CO)_2\}_2]$ in combination with (*S*)-BINAP and AgOTf, good enantioselectivities could be obtained (Scheme 4). Even higher selectivities were ach-



Scheme 4. The enantioselective, catalytic PKR with rhodium.[9]

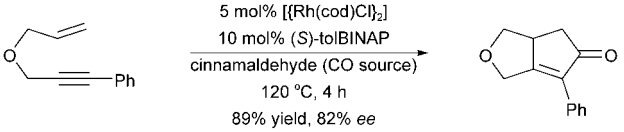
ieved by Shibata[10] by using $[\{Ir(cod)Cl\}_2]$ and (*S*)-tolBINAP (tolBINAP = 2,2′-bis(di-*p*-tolylphosphine)-1,1′-binaphthyl). In this same account, Shibata reports the first, and to date only, example of a catalytic, asymmetric, intermolecular PKR. Although the cyclocarbonylation of 1-phenyl-1-propyne and norbornene gave only a 32% yield, the enantiose-



Scheme 5. The only example of an intermolecular, catalytic, asymmetric PKR.[10]

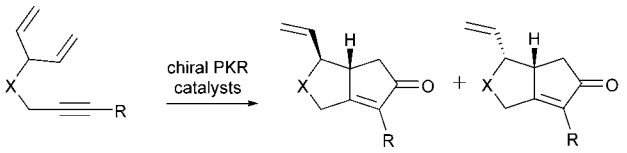
lectivity was high (93%; (Scheme 5). Both Jeong and Shibata tested a number of other chiral diphosphines, but found the binaphthyl ligands to be the best. Chung[11] studied the effectiveness of catalytic $[\{Rh(cod)Cl\}_2]$ and (*S*)-BINAP in a water/dioxane solvent system. Use of a surfactant, sodium dodecylsulfate, leads to acceleration of the PKR.

Recently, methods for the catalytic, enantioselective PKR that depend on aldehydes as a CO source rather than toxic CO gas have been developed. By using $[\{Rh(cod)Cl\}_2]$ and (*S*)-tolBINAP, Shibata[12] found moderate to good enantioselectivity with standard intramolecular PKR substrates (Scheme 6). Interestingly, he was able to achieve better re-



Scheme 6. The enantioselective, rhodium-catalyzed PKR with cinnamaldehyde as the CO source.[12]

sults with cinnamaldehyde as the CO source under solvent-free conditions than with CO gas and solvent. Finally, Jeong[13] has recently reported that the catalytic, asymmetric PKR can be used for the desymmetrization of *meso*-dienynes (Scheme 7). Rhodium- and iridium-based catalysts



Scheme 7. Desymmetrization of *meso*-dienynes by asymmetric Pauson–Khand catalysis.[13]

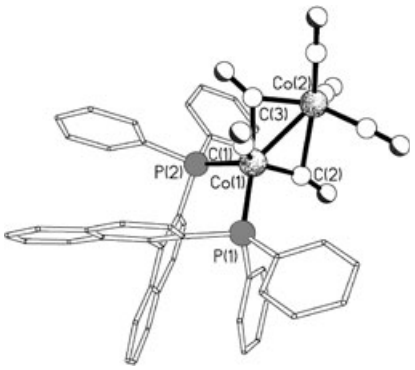


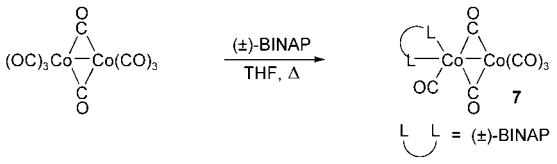
Figure 1. The molecular structure of **7**.

were used in combination with BINAP and BINAP derivatives under 1 atm of CO or with cinnamaldehyde as the CO source. Different catalyst systems give the best enantioselectivities and diastereoselectivities for different dienyne substrates.

Given the importance of developing new PKR catalysts and the success of axially chiral ligands in this chemistry, we initiated an investigation into how C_2-symmetric diphosphines direct and sustain the catalytic, enantioselective PKR. We chose to start by examining the coordination of BINAP to different cobalt carbonyl sources, cobalt carbonyls being employed in a vast majority of PKRs. We have gone on to synthesize a number of BINAP–cobalt–carbonyl complexes with coordinated alkynes, alkenes, and enynes to probe subsequent steps of the PKR mechanism. Some of the results described here have been presented in a preliminary communication.[8]

Results and Discussion

Axially chiral diphosphines coordinate to both $[Co_2(CO)_8]$ and $[Co_4(CO)_{12}]$ to form enantioselective PKR catalysts in situ,[5–8] and so it was of interest to us to establish the nature of their interactions. Experimentation with various reaction conditions eventually allowed us to isolate the complex formed on mixing $[Co_2(CO)_8]$ and (±)-BINAP (Scheme 8).[8] Complex **7** is very air sensitive and must be carefully handled under an inert atmosphere. A small number of dark red crystals of **7** were obtained and X-ray analysis revealed that BINAP is bound to just one of the two cobalt atoms (Figure 1). Phosphorus NMR analysis of crystals of complex **7** revealed a single resonance at

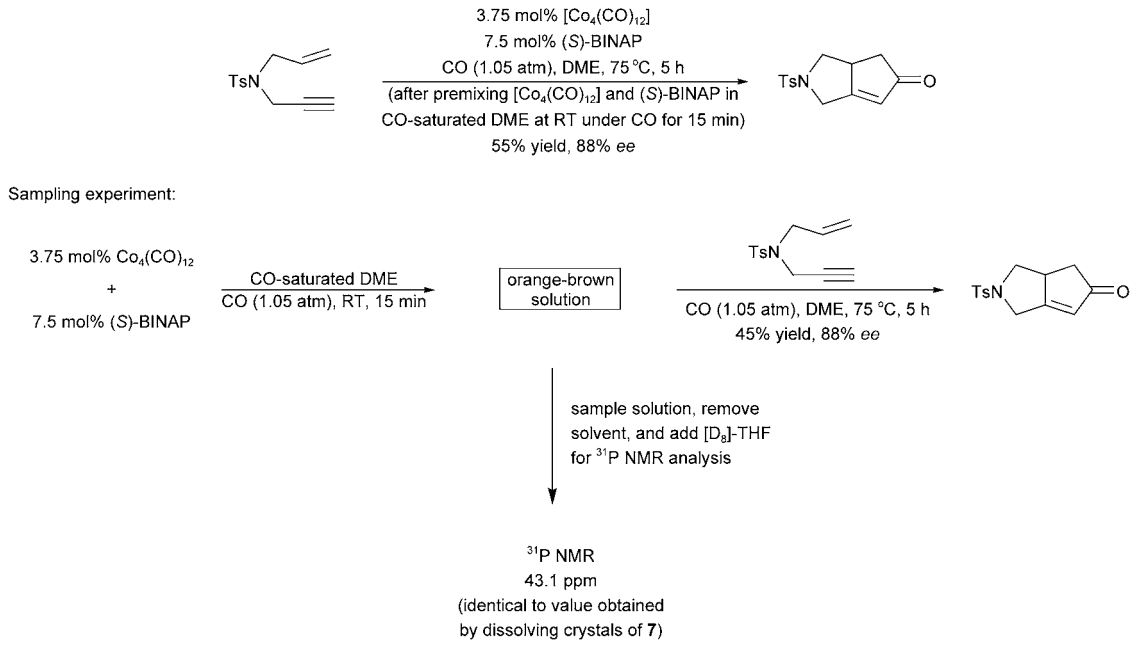


Scheme 8. Synthesis of $[Co_2(binap)(CO)_6]$.

43.1 ppm. Application of these same reaction conditions to $[Co_4(CO)_{12}]$ and (±)-BINAP gave a complex also exhibiting this same ^{31}P NMR peak at 43.1 ppm. Bands in the CO region of the IR spectra of the products formed on mixing either $[Co_2(CO)_8]$ or $[Co_4(CO)_{12}]$ with (±)-BINAP were identical.

Complex **7**, along with the structures that will be discussed later in this paper, is the only example of a molecular structure of a Co–BINAP complex with a chelating BINAP ligand. The one literature example of a Co–BINAP complex with a bridging BINAP will be discussed later in this section. The asymmetry induced by the BINAP ligand on the structure of **7** is evident upon comparison with other analogous $[Co_2(diphosphine)(CO)_6]$ structures (see Table S1 in the Supporting Information): the difference in lengths between the two Co–P bonds is greater than in $[Co_2(dppe)(CO)_6]$[14] and $[Co_2(dppp)(CO)_6]$ (DPPE = 1,2-bis(diphenylphosphino)-ethane, DPPP = 1,3-bis(diphenylphosphino)propane).[15] There is also distortion in the binding of the two bridging CO ligands. The difference in lengths between the longest $Co–CO_{bridging}$ bond length and the shortest is 0.53 Å, compared with 0.29 and 0.16 Å for the two previously mentioned $[Co_2(diphosphine)(CO)_6]$ examples, respectively. The *trans* influence of BINAP phosphorus atom, P(1), can also be seen in the fact that the Co(1)–C(3) bond is longer than those of Co(1)–C(1) or Co(1)–C(2). Given that there are few examples of crystallographically characterized transition-metal–BINAP complexes and that excellent PKR activity has been observed with rhodium complexes as described in the introduction, it is interesting to note that as a result of his interest in BINAP oxidation by dioxygen, Poë[16] has recently reported a structurally characterized [Rh(binap)(CO)(Cl)] complex, in which the BINAP occupies *cis* coordination sites in the square-planar complex.

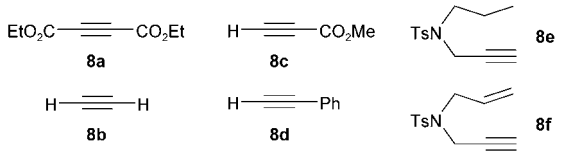
We next wished to probe whether **7** plays a role in a typical catalytic, asymmetric PKR.[8] The enantioselective, catalytic PKR shown in Scheme 9 was repeated, but just prior to adding the intramolecular PKR substrate, a sample of the solution formed from mixing $[Co_4(CO)_{12}]$ and (*S*)-BINAP was removed. Removal of solvent from this sample and analysis by ^{31}P NMR spectroscopy in $[D_8]$THF gave a spectrum containing a peak at 43.1 ppm (alongside peaks corre-



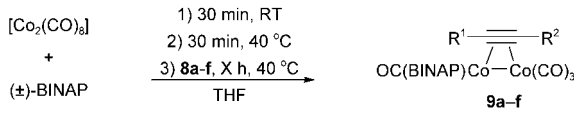
Scheme 9. A typical Pauson–Khand reaction (top) and the same reaction conducted with sampling of the precatalyst solution (bottom).

sponding to (*S*)-BINAP and (*S*)-BINAP monoxide), identical to the peak obtained from crystals of **7**. Addition of the enyne substrate to the remaining precatalyst solution and running the reaction with our standard PKR conditions gave a yield of 45% and an *ee* of 88% (compared to 55% yield and 88% *ee* when no sampling is conducted). This strongly suggests that **7** is a PKR precatalyst.

Having established the precatalytic nature of **7**, we started to investigate how **7** interacts with alkynes to begin to understand the early part of the PKR catalytic cycle. After



combining $[Co_2(CO)_8]$ and (±)-BINAP as shown in Scheme 8, alkynes **8a–f** were added and the reaction was stirred for a further 0.5–2 h at 40 °C (Scheme 10). Workup of the product mixtures gave air-sensitive brown powders that were characterized by IR, ^1H, ^{13}C, and ^{31}P NMR spectroscopy, mass spectrometry, and elemental analysis, and identified as the BINAP-containing alkyne complexes **9a–f** (Table 1).



Scheme 10. Synthesis of $[Co_2(alkyne)(binap)(CO)_4]$.

Table 1. Conversion of alkynes **8a–f** into cobalt–BINAP complexes **9a–f**.

Entry	Alkyne	*t* [h]	Isomer ratio	Yield [%][a]
1	**8a**	0.5	-	52
2	**8b**	2	-	30
3	**8c**	1	2:1	50[b]
4	**8d**	2	1:0	29
5	**8e**	2	2:1	66
6	**8f**	2	2:1	45

[a] Some samples were contaminated with a trace of BINAP. [b] Summation of yield of separated diastereoisomers (34% + 16%).

In addition, complexes **9c** and **9e** were characterized by X-ray crystallography.

The two diastereomers formed on mixing alkyne **8c** and complex **7** can be separated by column chromatography. Isolated reaction yields and inverse gated ^{31}P NMR spectroscopy both give a $\mathbf{9c}_{maj}/\mathbf{9c}_{min}$ ratio of 2:1. These isomers can be crystallized individually and both $\mathbf{9c}_{maj}$ and $\mathbf{9c}_{min}$ show that the chelating mode of coordination of the BINAP is preserved. If the chirality of the BINAP is arbitrarily selected to be *R*, the different configurations of the tetrahedral cores of $\mathbf{9c}_{maj}$ and $\mathbf{9c}_{min}$ can be readily observed (Figure 2). Figure 2 also shows schematically how the orientation of the alkyne differs between the two isomers.

Alkyne complex **9e** serves as a model of a typical enyne substrate interacting with the dicobalt species (Figure 3). One would expect a similar complex to form with the analogous enyne, **8f**, but crystallographic studies of **9f** were plagued by disorder problems (see Figures S5, S6, and S7 in the Supporting Information). Although isomer separation was not possible by column chromatography, an isomer

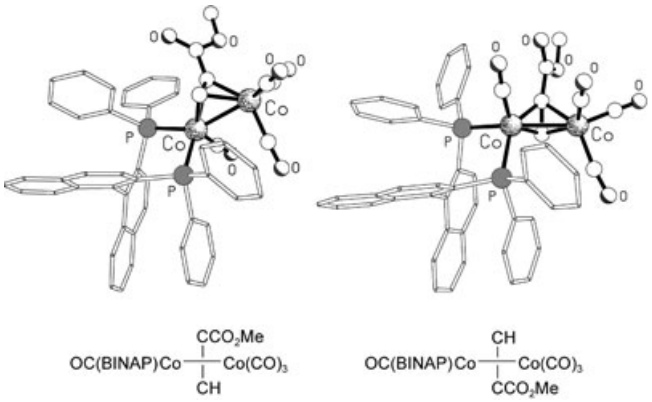


Figure 2. The molecular structures of $\mathbf{9c}_{maj}$ (left) and $\mathbf{9c}_{min}$ (right).

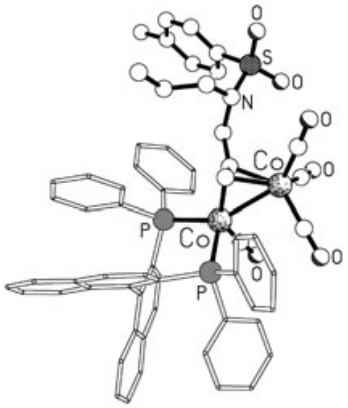
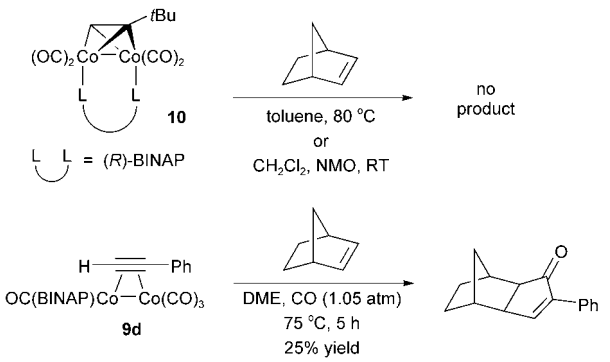


Figure 3. The molecular structure of **9e**.

ratio of 2:1 was again observed for both **9e** and **9f** by ^{31}P NMR spectroscopy.

Complexes **9a–f**, in which the BINAP ligand acts as a chelate, are different from the bridging structures predicted by Hiroi[5] and Buchwald[6] to be intermediates in their catalytic, asymmetric PKRs. Their predictions were consistent with Laschat's[17] isolation of the bridging structure **10** from the reaction between [Co_2(3,3-dimethylbutyne)$(CO)_6$] and (*R*)-BINAP.[18] Bridging structure **10** proved to be inert, however, to typical PKR conditions (Scheme 11).[17] In contrast, reaction of chelating complex **9d** from this study with norbornene gave the expected PKR product. To probe whether the order of addition of BINAP and alkyne dictated whether the chelated or bridged BINAP structure formed, **9c** was synthesized following Laschat's protocol of alkyne addition before BINAP addition. The resulting product gave a ^{31}P NMR spectrum with Co–P peaks identical to those originally obtained for **9c**. No evidence of any bridged product was detected.

It is interesting to compare the low diastereoselectivity exhibited by the BINAP system (apart from with phenylacetylene) with the high selectivities seen with some reactions pertaining to the stoichiometric, asymmetric PKR. For example, Verdaguer and Riera[19] report that coordination of a



Scheme 11. Laschat's[17] report of the inactivity of [Co_2(3,3-dimethylbutyne)$(CO)_6$] in the stoichiometric PKR (top). Our example of **9d** in the stoichiometric PKR (bottom).

chiral, bidentate phosphorus–sulfur ligand to [Co_2(3,3-dimethylbutyne)$(CO)_6$] occurs with a diastereomeric coordination ratio of 20:1. This is the highest obtained for the complexation of a chiral phosphine to a dicobaltcarbonyl complex containing a monosubstituted alkyne. Nicholas[20] also reports that, depending on the chiral alkyne used, essentially complete selectivity can be achieved when complexing triphenylphosphine to [Co_2(chiral alkyne)$(CO)_6$].

Nevertheless, the BINAP system does of course lead to PKR products with high enantioselectivities in many cases. Although a ratio of only 2:1 was obtained with complexes **9c**, and most importantly **9e** and **9f**, the enantiomeric ratio of the cyclopentenone produced from the enyne is 94:6 (88% *ee*) as shown in Scheme 9. This discrepancy in ratio could be explained by the fact that the syntheses of **9** take place at 40°C rather than the PKR temperature of 75°C. We therefore became interested in how $\mathbf{9c}_{maj}$ and $\mathbf{9c}_{min}$ would behave at 75°C under a CO atmosphere. These isomers were selected for study as they were readily separated by column chromatography.

Samples of either $\mathbf{9c}_{maj}$ or $\mathbf{9c}_{min}$ were heated in DME at 75°C for 1 h (under either a CO or nitrogen atmosphere), cooled, the DME was removed in vacuo, and the ^{31}P NMR spectrum measured in $CDCl_3$ to reveal mixtures containing both $\mathbf{9c}_{maj}$ and $\mathbf{9c}_{min}$ in all four experiments. The time required for diastereomer interconversion to lead to the equilibrium isomer ratio of 2:1 was measured at 75°C in DME in the NMR spectrometer. We have found that more time is required for $\mathbf{9c}_{maj}$ to reach this 2:1 ratio under a nitrogen atmosphere than under an atmosphere of CO (Figure 4). This same trend is observed at 60°C though, as expected, isomerization rates are slower. Variable-temperature ^{31}P NMR experiments reveal that peaks corresponding to $\mathbf{9c}_{min}$ first start to emerge at 50°C when an NMR sample of $\mathbf{9c}_{maj}$ in DME is prepared under CO and slowly heated in the spectrometer from room temperature. When the same sample is heated under nitrogen, $\mathbf{9c}_{min}$ does not appear until 65°C.

The fact that diastereomer interconversion does not prohibit high enantiomeric excesses in the intramolecular BINAP–enyne system is in contrast to many literature studies of intermolecular, stoichiometric systems in which

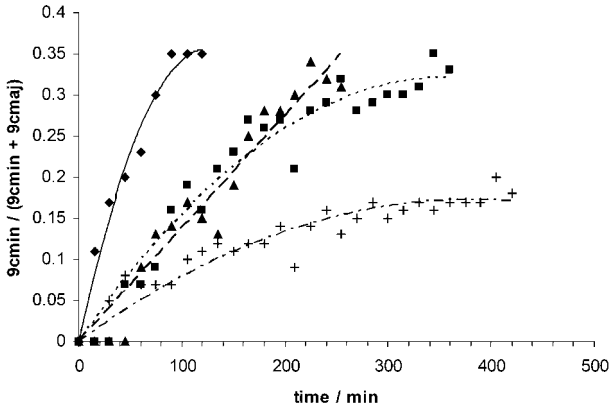
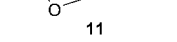


Figure 4. Inverse gated ^{31}P NMR isomerization experiments with $\mathbf{9c}_{maj}$ (◆ ——, CO/75 °C; ▲ – – –, N_2/75 °C; ■ -----, CO/60 °C; + –•–•, N_2/60 °C).

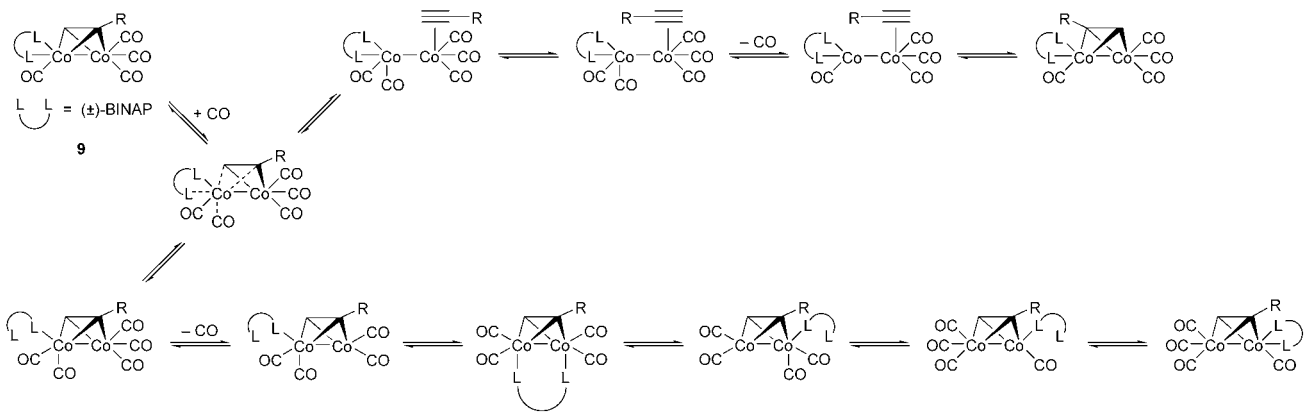
$[Co_2(phosphine)(alkyne)(CO)_x]$ complexes have had to be used at relatively low temperatures to avoid interconversion and to enable high enantiomeric excesses to be obtained in the PKR. Reports by Pauson,[21] Brunner,[21,22] and Kerr[23] using the chiral phosphine glyphos (**11**) in the asymmetric PKR with external alkenes state that diastereomer interconversion of the $[Co_2(glyphos)(alkyne)(CO)_5]$ complex takes place at elevated temperatures, thereby lowering the *ee*. Activation of the asymmetric dicobalt species possessing either chiral phosphines or chiral alkynes in the range of 0 °C to room temperature is achieved using an *N*-oxide, such as *N*-methylmorpholine *N*-oxide or trimethylamine *N*-oxide, and thus limits epimerization and allows for increased enantiomeric excesses.[19,23,24] Other literature reports note how the diastereomeric ratios of dicobaltcarbonyl–alkyne complexes containing bidentate phosphorus–sulfur ligands can be enriched through heating. For instance, heating a 1:1 isomer mixture of $[Co_2(chiral\text{-}P{-}S)(3,3\text{-}dimethylbutyne)(CO)_4]$ in toluene at 90 °C for 2 h, followed by heating under CO at 80 °C for 66 h, lead to a final ratio of 2:1.[19] In another example, heating a 1:1 isomer mixture of $[Co_2(chiral\text{-}P{-}S)(2\text{-}methyl\text{-}3\text{-}butyn\text{-}2\text{-}ol)(CO)_4]$ with a different chiral P–S ligand gave a final ratio of 4.5:1 after 17 h at 70 °C.[24c,d]



Since heating $\mathbf{9c}_{maj}$ under CO allows for faster isomerization than heating under a nitrogen atmosphere, we propose that the mechanism of isomerization begins with an associative addition of CO (Scheme 12). This can then be followed by dissociation of alkyne or phosphorus. The alkyne can rotate and recoordinate to generate the other diastereomer or the other isomer can be generated through a bridging BINAP species. We have never obtained any evidence of a bridging BINAP complex, but it could be present in solution in amounts too small to be detected.

Having examined the behavior of $[Co_2(alkyne)(binap)(CO)_4]$, we next wished to probe how alkenes react with this species during the next phase of the catalytic cycle. We hoped to isolate a complex containing bound BINAP, alkyne, and alkene ligands to model a potential PKR intermediate. Though not crystallographically characterized, Itami and Yoshida[25] have reported extensive NMR spectroscopic data for a ruthenacyclopentene PKR intermediate. Their approach of attaching a pyridylsilyl group to the olefin allowed them to characterize this complex, which has a five-membered ring derived from the metal, an alkene, and an alkyne. It was less important to us at this point to use alkynes and alkenes that are typical PKR substrates, since it was likely that these would turnover to give cyclopentenone product. Regardless of whether we added dimethyl maleate, styrene, or cyclopentene as the alkene component, the same deep red solid was isolated in low yield. X-ray crystallography confirmed that alkene had not coordinated and revealed that cobaltacyclopentadiene **12** had formed (Figure 5). Not adding alkene and increasing the equivalents of alkyne or the reaction temperature for prolonged periods of time did not improve the yield of **12** (Scheme 13).

Non-BINAP-containing cobaltacyclopentadiene complexes have been isolated as intermediates of cyclotrimerization reactions. Knox and Spicer[26] report that the yields of some cobaltacyclopentadienes can be increased by isolating $[Co_2(alkyne)(CO)_6]$ and then adding one additional equiva-



Scheme 12. Two possible isomerization pathways for complexes of type **9**.

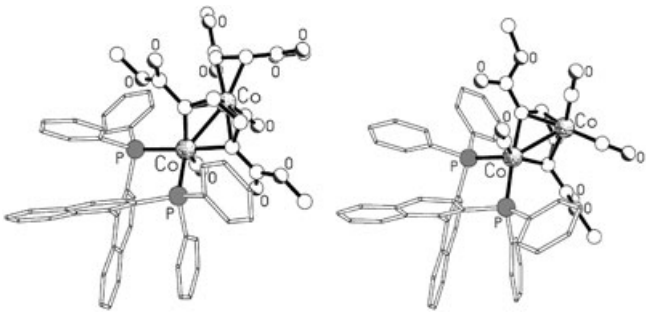
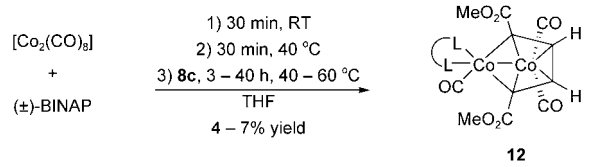
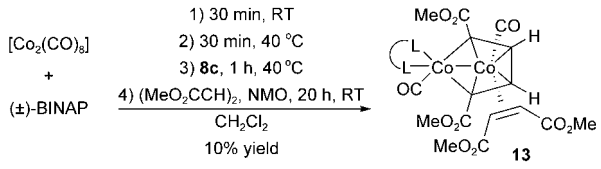


Figure 5. The molecular structures of **12** (left) and **13** (right).



Scheme 13. Synthesis of cobaltacyclopentadiene **12**.

lent of alkyne in the presence of Me_3NO at room temperature. We, too, tried adding an *N*-oxide, *N*-methylmorpholine *N*-oxide, because we thought this might generate a vacant coordination site to which the alkene could bind. As the structure of complex **13** shows, methyl maleate did indeed bind to the metal, but the five-membered cobaltacyclopentadiene ring derived from two equivalents of alkyne was still formed (Scheme 14, Figure 5). The core structure of **13** is very similar to that of **12** and other cobaltacyclopentadiene complexes.[26,27] Analogues of **12** and **13** with alkynes more electron-rich than **8c** could not be synthesized. Presumably this is a function of the propensity of electron-poor alkynes to cyclize.



Scheme 14. Synthesis of cobaltacyclopentadiene **13**.

Conclusion

Complexes of the type $[Co_2(alkyne)(binap)(CO)_4]$ have been synthesized and shown to isomerize under Pauson–Khand reaction conditions. The ease of isomerization suggests that the selectivity of initial alkyne coordination is not critical in determining the enantioselectivity of PKR products. The influence of CO on the interconversion of $[Co_2(binap)(HC{\equiv}CCO_2Me)(CO)_4$ has prompted us to propose two possible isomerization pathways. Attempts to synthesize alkene-coordinated PKR intermediates have led to the isolation of small amounts of cobaltacyclopentadiene complexes.

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. Enyne **8f** was prepared according to literature procedures;[28] the synthesis of **8e** was based on these same procedures. All other reagents are commercially available and were used as received. NMR spectra were recorded on Bruker AM500 or Avance 360 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 a Micromass AutoSpec-Q instrument. Elemental analyses were performed by the London Metropolitan University microanalytical service. HPLC analysis was performed by using a Unicam Crystal 200 pump, a Unicam Spectra 100 UV/Vis detector (set at 210 nm), and a CHIRALPAK AS column.

Synthesis of 7: In a Schlenk flask, anhydrous THF (10 mL) was added to $[Co_2(CO)_8]$ (50 mg, 0.15 mmol). After adding (±)-BINAP (93 mg, 0.15 mmol), the solution was stirred for 30 min at room temperature and 30 min at 40 °C in the dark. After cooling, nitrogen-saturated hexane (20 mL) was added and red solid precipitated. The filtrate was removed by cannula, additional hexane (10 mL) was added, and the filtrate was removed again. The red solid was dried in vacuo. IR ($CHCl_3$): $\tilde{\nu}=2053$ (s), 1985 (s), 1890 (w), 1796 cm^{-1} (m; CO); ^{31}P NMR (162 MHz, $[D_8]$THF): $\delta=43.1$, 25.4, −13.8 ppm (BINAP monoxide). On one occasion, a small sample of **7** suitable for a single-crystal structure determination was obtained by slow diffusion of petroleum ether into a solution of **7** in CH_2Cl_2 at −20 °C. IR ($CHCl_3$): $\tilde{\nu}=2053$ (s), 1986 (s), 1890 (w), 1850 (sh), 1795 cm^{-1} (m; CO); ^{31}P NMR (146 MHz, $[D_8]$THF): $\delta=43.1$ ppm. All attempts to characterize by other methods were unsuccessful due to the instability of **7**.

PKR sampling experiment as shown in Scheme 9: $[Co_4(CO)_{12}]$ (16.1 mg, 0.028 mmol) and (*S*)-BINAP (35.0 mg, 0.056 mmol) were dissolved in CO-saturated DME (3 mL) in a 10 mL round-bottomed flask fitted with a reflux condenser and stirred at room temperature under a CO atmosphere (1.05 atm) for 15 min. A sample (1 mL) of this solution was removed by syringe and injected into a different round-bottomed flask where it was dried in vacuo. ^{31}P NMR (146 MHz, $[D_8]$THF): $\delta=43.1$, 25.5, −13.8 (BINAP monoxide), −14.3 ppm (BINAP). A solution of the enyne (125 mg, 0.5 mmol) in CO-saturated DME (2 mL) was added to the original precatalyst solution and heated to 75 °C for 5 h under CO. The resulting brown mixture was cooled, filtered through a short pad of Celite, and concentrated in vacuo. The brown residue was redissolved in $CDCl_3$, and the extent of the reaction was calculated from ^1H NMR spectroscopy (82 %). Purification of the residue by flash column chromatography (hexane/ethyl acetate, 7:3, $R_f=0.12$) gave the known cyclopentenone product[29,30] as a white solid (62 mg, 45 % yield, 88 % *ee*). IR ($CHCl_3$): $\tilde{\nu}=1715$ (s, C=O), 1652 (m, C=C), 1600 (w, C−C(Ar)), 1351, 1162 cm^{-1} (s, NSO_2); ^1H NMR (360 MHz, $CDCl_3$): $\delta=2.06$ (dd, $^3J(H,H)=4$ Hz, $^2J(H,H)=18$ Hz, 1H; C*H*HCO), 2.44 (s, 3H; CH_3), 2.56–2.65 (m, 2H; CH*H*CO, NC*H*HC=), 3.16 (m, 1H; C*H*CH_2CO), 4.00–4.05 (m, 2H; NCH*H*C=, NC*H*HCH), 4.34 (d, $^2J(H,H)=17$ Hz, 1H; NCH*H*CH), 5.99 (s, 1H; C=CH), 7.35 (d, $^3J(H,H)=8$ Hz, 2H; *m*-ArH), 7.73 ppm (d, $^3J(H,H)=8$ Hz, 2H; *o*-ArH); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta=21.6$ (CH_3), 39.8 (CH_2CO), 43.9 (*C*HCH_2CO), 47.6 (N*C*H_2CH), 52.4 (N*C*H_2C=), 126.2 (C=*C*H), 127.4 (C_{ortho}), 130.0 (C_{meta}), 133.3 (C_{para}), 144.2 (C_{ipso}), 178.8 (*C*=CH), 207.4 ppm (C=O).

Representative procedure for the synthesis of complexes of type 9 and complex 12

Synthesis of 9c: In a Schlenk flask, anhydrous THF (15 mL) was added to $[Co_2(CO)_8]$ (77 mg, 0.225 mmol). After (±)-BINAP (140 mg,

0.225 mmol) was added, the solution was stirred in the dark for 30 min at room temperature and 30 min at 40 °C. Methyl propiolate (28 μL, 0.338 mmol) was added by syringe and stirring continued at 40 °C in the dark for 1 h. The flask was allowed to cool and neutral alumina (Grade II) was added before removing the solvent in vacuo. The brown solid was charged onto a chromatography column of silica and eluted under nitrogen first with hexane/diethyl ether (9:1) to remove unreacted [$Co_2(CO)_8$] and then with hexane/diethyl ether (7:3; **9c**$_{min}$ R_f = 0.24, **9c**$_{maj}$ R_f = 0.18) to collect the two diastereomers of **9c** as dark brown solids (**9c**$_{min}$: 33 mg, 16 %, **9c**$_{maj}$: 72 mg, 34 %).

Data for 9c$_{min}$: Analytically pure **9c$_{min}$** suitable for a single-crystal structure determination was obtained by slow diffusion of pentane into a solution of **9c$_{min}$** in CH_2Cl_2 at −20 °C. M.p. 214–216 °C (decomp); IR ($CHCl_3$): $\tilde{\nu}$ = 2053 (s), 1996 (s), 1947 (m), 1683 cm^{-1} (m; CO); ^{1}H NMR (500 MHz, $CDCl_3$): δ = 3.19 (s, 3H; CH_3), 5.66 (d, ^3J(P,H) = 7.4 Hz, 1H; HC≡), 6.5–7.8 ppm (m, 32H; BINAP ArH); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 51.6 (CH_3), 70.7 (d, ^2J(C,P) = 14.6 Hz, ≡*C*C), 80.9 (HC≡), 120.3–137.4 (BINAP ArC), 172.8 (C*C*O$_2$), 201.4, 210.8 ppm (C≡O); ^{31}P NMR (202 MHz, $CDCl_3$): δ = 52.0, 47.2 ($CoPPh_2Ar$); MS (FAB): *m/z* (%): 880 (4) [*M*−2CO]$^+$, 852 (31) [*M*−3CO]$^+$, 824 (90) [*M*−4CO]$^+$, 681 (100) [BINAP+Co]$^+$, 437 (80) [BINAP−PPh_2]$^+$; elemental analysis calcd (%) for $C_{52}H_{36}Co_2O_6P_2$ (936.67): C 66.68, H 3.87; found: C 66.51, H 3.75.

Data for 9c$_{maj}$: Analytically pure **9c$_{maj}$** suitable for a single-crystal structure determination was obtained by slow diffusion of light petroleum ether into a solution of **9c$_{maj}$** in CH_2Cl_2 at −20 °C. M.p. 247–250 °C (decomp); IR ($CHCl_3$): $\tilde{\nu}$ = 2054 (s), 1999 (s), 1956 (m), 1687 cm^{-1} (m, CO) cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 3.43 (s, 3H; CH_3), 5.72 (dd, ^3J(P,H) = 5.5, 2.5 Hz, 1H; HC≡), 6.4–8.0 ppm (m, 32H; BINAP ArH); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 51.7 (CH_3), 73.4 (d, ^2J(C,P) = 22.1 Hz, ≡*C*C), 73.9 (HC≡), 120.3–138.2 ppm (BINAP ArC), 172.0 (C*C*O$_2$), 200.3, 211.3 ppm (C≡O); ^{31}P NMR (202 MHz, $CDCl_3$): δ = 51.9, 40.7 ppm ($CoPPh_2Ar$); MS (FAB): *m/z* (%): 880 (2) [*M*−2CO]$^+$, 852 (12) [*M*−3CO]$^+$, 824 (62) [*M*−4CO]$^+$, 681 (100) [BINAP+Co]$^+$, 437 (94) [BINAP−PPh_2]$^+$; elemental analysis calcd (%) for $C_{52}H_{36}Co_2O_6P_2$ (936.67): C 66.68, H 3.87; found: C 66.66, H 3.79.

Synthesis of 9a: The same procedure as in the synthesis of **9c** was followed except only 0.5 h of heating was required after the addition of diethyl acetylenedicarboxylate (58 μL, 0.338 mmol) as the alkyne. The brown solid was charged onto a chromatography column of silica and eluted under nitrogen first with hexane/ethyl acetate (19:1) to remove unreacted [$Co_2(CO)_8$] and then with hexane/ethyl acetate (8:2; R_f = 0.26) to collect **9a** as a dark brown solid (119 mg, 52 %). M.p. 175–180 °C (decomp); IR ($CHCl_3$): $\tilde{\nu}$ = 2063 (s), 2010 (s), 1967 (m), 1687 cm^{-1} (m, CO); ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.08 (t, ^3J(H,H) = 7.1 Hz, 3H; CH_3), 1.19 (t, ^3J(H,H) = 7.1 Hz, 3H; CH_3), 4.04–4.22 (m, 4H; CH_2), 6.3–8.0 ppm (m, 32H; BINAP ArH); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 14.1 (CH_3), 60.6, 60.7 (CH_2), 71.7 (≡*C*C), 78.2 (d, ^2J(C,P) = 20.0 Hz, ≡*C*C), 120.3–139.1 (BINAP ArC), 171.2, 173.1 (C*C*O$_2$), 198.9, 211.4 ppm (C≡O); ^{31}P NMR (202 MHz, $CDCl_3$): δ = 48.2, 41.6 ppm ($CoPPh_2Ar$); MS (FAB): *m/z* (%): 977 (9) [*M*−OEt]$^+$, 966 (2) [*M*−2CO]$^+$, 938 (28) [*M*−3CO]$^+$, 910 (100) [*M*−4CO]$^+$, 837 (27) [*M*−4CO−CO_2Et]$^+$, 681 (60) [BINAP+Co]$^+$, 437 (54) [BINAP−PPh_2]$^+$; elemental analysis calcd (%) for $C_{56}H_{42}Co_2O_8P_2$ (1022.76): C 65.77, H 4.14; found: C 65.59, H 4.19.

Synthesis of 9b: The same procedure as in the synthesis of **9c** was followed except for the following modifications: After allowing the reaction between the [$Co_2(CO)_8$] and (±)-BINAP to cool and closing the Schlenk tap to nitrogen, acetylene gas was gently bubbled into the reaction solution through a syringe needle for 90 s. The acetylene needle was then removed, a balloon filled with nitrogen was added, and heating continued in the dark at 40 °C for 2 h. The flask was allowed to cool and neutral alumina (Grade II) was added before removing the solvent in vacuo. The brown solid was charged onto a chromatography column of silica and eluted under nitrogen first with hexane/diethyl ether (19:1) to remove unreacted [$Co_2(CO)_8$] and then with hexane/diethyl ether (8:2; R_f = 0.40) to collect **9b** as a dark brown solid (59 mg, 30 %). M.p. 176–180 °C (decomp); IR ($CHCl_3$): $\tilde{\nu}$ = 2042 (s), 1978 (s), 1923 cm^{-1} (m, CO); ^{1}H NMR (500 MHz, $CDCl_3$): δ = 5.22 (d, ^3J(P,H) = 8.1 Hz, 2H; HC≡), 6.5–7.9 ppm (m, 32H; BINAP ArH); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 72.3 (HC≡), 75.6 (d, ^2J(C,P) = 14.0 Hz, HC≡), 125.5–138.1 (BINAP ArC), 203.2, 211.1 (C≡O); ^{31}P NMR (202 MHz, $CDCl_3$): δ = 53.6, 44.9 ppm ($CoPPh_2Ar$); MS (FAB): *m/z* (%): 877 (2) [*M*−H]$^+$, 849 (1) [*M*−H−CO]$^+$, 822 (6) [*M*−2CO]$^+$, 794 (34) [*M*−3CO]$^+$, 766 (88) [*M*−4CO]$^+$, 681 (100) [BINAP+Co]$^+$, 437 (86) [BINAP−PPh_2]$^+$; elemental analysis calcd (%) for $C_{50}H_{34}Co_2O_4P_2$ (878.63): C 68.35, H 3.90; found: C 68.43, H 4.09.

Synthesis of 9d: The same procedure as in the synthesis of **9c** was followed except 2 h of heating was required after the addition of phenylacetylene (35 μL, 0.338 mmol) as the alkyne. The brown solid was charged onto a chromatography column of silica and eluted under nitrogen first with hexane/diethyl ether (9:1) to remove unreacted dicobalt octacarbonyl and then with hexane/diethyl ether (8:2; R_f = 0.38) to collect the title compound as a dark brown solid (62 mg, 29 %). M.p. 197–200 °C (decomp); IR ($CHCl_3$): $\tilde{\nu}$ = 2040 (s), 1982 (s), 1932 cm^{-1} (m, CO); ^{1}H NMR (360 MHz, $CDCl_3$): δ = 5.77 (dd, ^3J(P,H) = 6.2, 3.5 Hz, 1H; HC≡), 6.3–8.1 ppm (m, 37H; ArH, BINAP ArH); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 72.5 (HC≡), 87.8 (d, ^2J(C,P) = 20.6 Hz, ≡*C*C), 120.3–141.6 (ArC, BINAP ArC), 201.7, 213.7 ppm (C≡O); ^{31}P NMR (202 MHz, $CDCl_3$): δ = 53.5, 36.7 ppm ($CoPPh_2Ar$); MS (FAB): *m/z* (%): 870 (1) [*M*−3CO]$^+$, 842 (3) [*M*−4CO]$^+$, 681 (6) [BINAP+Co]$^+$, 655 (22) [$BINAP(O)_2$]$^+$, 453 (7) [BINAP(O)−PPh_2]$^+$, 437 (7) [BINAP−PPh_2]$^+$; elemental analysis calcd (%) for $C_{56}H_{38}Co_2O_4P_2$ (954.73): C 70.45, H 4.01; found: C 70.29, H 4.14.

Synthesis of sulfonamide precursor to 8e (*N*-(propane)-*p*-toluene sulfonamide):[28a] *p*-Toluene sulfinic acid sodium salt hydrate (7.12 g, 40 mmol) was dissolved in water (75 mL) at 5 °C and *n*-propylamine (1.6 mL, 20 mmol) and glacial acetic acid (1.1 mL, 20 mmol) were added. The reaction was stirred and sodium hypochlorite (40 mL, 30 mmol) was added dropwise over 1 h. The flask was then allowed to reach room temperature and stirred for 16 h. The reaction was acidified to pH 6 with concentrated hydrochloric acid. The precipitate was filtered, washed with water (3 × 30 mL), and dried in vacuo to give the desired product as a white crystalline solid (4.10 g, 96 %). M.p. 54–55 °C; IR ($CHCl_3$): $\tilde{\nu}$ = 3376, 1496 (m, NH), 1328, 1160 cm^{-1} (s, NSO_2); ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.50 (t, ^3J(H,H) = 7 Hz, 3H; CH_3), 1.47 (tq, ^3J(H,H) = 7, 7 Hz, 2H; $NCH_2CH_2CH_3$), 2.42 (s, 3H; CH_3), 2.88 (t, ^3J(H,H) = 7 Hz, 2H; $NCH_2CH_2CH_3$), 4.77 (s, 1H; NH), 7.30 (d, ^3J(H,H) = 8 Hz, 2H; ArH), 7.75 ppm (d, ^3J(H,H) = 8 Hz, 2H; ArH); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 11.1 (CH_3), 21.5 (CH_3), 22.9 ($NCH_2CH_2CH_3$), 44.9 ($NCH_2CH_2CH_3$), 127.1 (C_{ortho}), 129.6 (C_{meta}), 137.0 (C_{para}), 143.2 ppm (C_{ipso}); MS (FAB): *m/z* (%): 214 (100) [*M*+H]$^+$, 155 (23) [$CH_3C_6H_4SO_2$]$^+$, 91 (19) [$CH_3C_6H_4$]$^+$.

Synthesis of 8e:[28b] *N*-(Propane)-*p*-toluenesulfonamide (1.77 g, 8 mmol) was dissolved in anhydrous DMF (15 mL) at room temperature. Sodium hydride (0.43 g, 11 mmol) was added with care and the mixture was stirred for 30 minutes. Propargyl bromide (1.5 mL, 14 mmol) was added and the reaction was stirred for 1 h. It was then quenched with water (50 mL) and the product was extracted with diethyl ether (4 × 30 mL). The ethereal extracts were dried over magnesium sulfate and then concentrated in vacuo. The crude mixture was then loaded onto a chromatography column of silica and eluted with hexane/diethyl ether (5:1; R_f = 0.16) to collect **8e**, which was then ground in a mortar and dried in vacuo (1.39 g, 67 %). M.p. 47–49 °C; IR ($CHCl_3$): $\tilde{\nu}$ = 3308 (m, C≡CH), 1348, 1159 ppm (s, NSO_2); ^{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; ArH), 7.71 ppm (d, ^3J(H,H) = 8 Hz, 2H; ArH); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 11.0 (CH_3), 20.8 ($NCH_2CH_2CH_3$), 21.4 (CH_3), 36.1 ($NCH_2C{\equiv}CH$), 47.9 ($NCH_2CH_2CH_3$), 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}); MS (FAB): *m/z* (%): 252 (100) [*M*+H]$^+$, 155 (18) [$CH_3C_6H_4SO_2$]$^+$, 91 (24) [$CH_3C_6H_4$]$^+$; elemental analysis calcd (%) for $C_{13}H_{17}NO_2S$ (251.35): C 62.07, H 6.82, N 5.57; found: C 62.25, H 6.98, N 5.54.

Synthesis of 9e: The same procedure as in the synthesis of **9c** was followed except 2 h of heating was required after the addition of **8e** (57 mg,

0.226 mmol) as the alkyne. The brown solid was charged onto a chromatography column of silica and eluted under nitrogen first with hexane/ethyl acetate (19:1) to remove unreacted $[Co_2(CO)_8]$ and then with hexane/ethyl acetate (7:3; $R_f = 0.74$) to collect **9e** as an air-sensitive brown solid (159 mg, 66%). Analytically pure **9e** suitable for a single-crystal structure determination was obtained by slow diffusion of pentane into a solution of **9e** in CH_2Cl_2 at −20°C. M.p. 176–178°C; IR ($CHCl_3$): $\tilde{\nu} = 2044$ (m), 1980 (s), 1940 cm^{-1} (w, CO); ^1H NMR (500 MHz, $CDCl_3$): too broad to interpret; ^{13}C NMR (125 MHz, $CDCl_3$, major diastereomer, minor diastereomer resonances difficult to assign with confidence): $\delta =$ 11.1 (CH_3), 20.2 ($NCH_2CH_2CH_3$), 21.4 (CH_3), 49.4 ($NCH_2CH_2CH_3$), 60.3 ($NCH_2C{\equiv}CH$), 81.6 ($NCH_2C{\equiv}CH$), 83.8 ($NCH_2C{\equiv}CH$), 125.6–142.4 (ArC, BINAP ArC), 201.1, 203.2, 211.9 ppm (C≡O); ^{31}P NMR (202 MHz, $CDCl_3$): $\delta = 57.9$, 51.6, 43.8, 39.9 ($CoPPh_2Ar$), −14.9 ppm (BINAP); MS (FAB): *m/z* (%): 1019 (18) $[M-3CO]^+$, 991 (54) $[M-4CO]^+$, 681 (16) [BINAP+Co]$^+$, 437 (24) $[BINAP-PPh_2]^+$; 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.

Synthesis of 9f: The same procedure as in the synthesis of **9c** was followed except 2 h of heating was required after the addition of **8f** (56 mg, 0.226 mmol) as the alkyne. The brown solid was charged onto a chromatography column of silica and eluted under nitrogen first with hexane/ethyl acetate (19:1) to remove unreacted $[Co_2(CO)_8]$ and then with hexane: ethyl acetate (7:3; $R_f = 0.73$) to collect **9f** as an air-sensitive brown solid (109 mg, 45%). M.p. 143–144°C; IR ($CHCl_3$): $\tilde{\nu} = 2043$, 1980, 1939 cm^{-1} (s, CO); ^1H NMR (500 MHz, $CDCl_3$): too broad to interpret; ^{13}C NMR (125 MHz, $CDCl_3$, major diastereomer, minor diastereomer resonances difficult to assign with confidence): $\delta = 21.3$ (CH_3), 49.8 ($NCH_2CH{=}CH_2$), 60.2 ($NCH_2C{\equiv}CH$), 82.0 ($NCH_2C{\equiv}CH$), 83.9 ($NCH_2C{\equiv}CH$), 118.5 ($NCH_2CH{=}CH_2$), 125.4–138.4 ($ArC_{ortho,meta,para}$, BINAP ArC, $NCH_2CH{=}CH_2$), 142.4 (C_{ipso}), 201.0, 202.9, 211.6 ppm (C≡O); ^{31}P NMR (202 MHz, $CDCl_3$): $\delta = 58.9$, 53.2, 44.0, 39.2 ($CoPPh_2Ar$), −14.6 ppm (BINAP); MS (FAB): *m/z* (%): 1017 (11) $[M-3CO]^+$, 989 (40) $[M-4CO]^+$, 681 (100) [BINAP+Co]$^+$, 437 (65) $[BINAP-PPh_2]^+$.

Complex 9d in a stoichiometric PKR: Complex **9d** (382 mg, 0.4 mmol) dissolved in CO-saturated DME was syringed into a 25 mL round-bottomed flask containing norbornene (377 mg, 4.0 mmol) and fitted with a reflux condenser under CO (1.05 atm). The reaction system was stirred at 75°C for 5 h under CO. The resulting brown solution was cooled and purified twice by flash column chromatography (hexane/diethyl ether, 49:1, $R_f = 0.08$) to give the known cyclopentenone product[30,31] as a white solid (17.1 mg, 25% yield). An inverse gated ^{31}P NMR spectrum of a sample of the **9d** used is this experiment showed that 76% of the material was actually **9d**; the remainder of the sample consisted of BINAP, BINAP(O), and $BINAP(O)_2$. The reported yield is calculated based on this integration. IR ($CHCl_3$): $\tilde{\nu} = 1697$ (s, C=O) cm^{-1}; ^1H NMR (360 MHz, $CDCl_3$): $\delta = 1.00$ (d, $^2J(H,H) = 11$ Hz, 1H; $CHCHHCH$), 1.12 (d, $^2J(H,H) = 11$ Hz, 1H; $CHCHHCH$), 1.26–1.43, 1.58–1.72 (m, 4H; $CHCH_2CH_2CH$), 2.28 (br d, $^3J(H,H) = 3$ Hz, 1H; $CH_2CHCHCH{=}$), 2.37 (d, $^3J(H,H) = 5$ Hz, 1H; CHCO), 2.50 (br d, $^3J(H,H) = 3$ Hz, 1H; $CH_2CHCHCO$), 2.71 (m, 1H; $CHCH{=}$), 7.30–7.40 (m, 3H; *m*-ArH, *p*-ArH), 7.64 (d, $^3J(H,H) = 3$ Hz, 1H; CH=), 7.70 ppm (m, 2H; *o*-ArH); ^{13}C NMR (90 MHz, $CDCl_3$): $\delta = 28.4$, 29.1, 31.3 ($CHCH_2CH_2CH$, $CHCH_2CH$), 38.3, 39.4, 47.7, 54.9 ($CHCHCH_2CHCH$), 127.0, 128.4 (C_{ortho}, C_{meta}, C_{para}), 131.5 (C_{ipso}), 146.1 (PhC=), 160.2 (CH=), 209.0 (C=O).

Isomerization experiments with 9c

Type A (reaction in DME, ^{31}P NMR in $CDCl_3$): Isomer $\mathbf{9c}_{maj}$ or $\mathbf{9c}_{min}$ (25 mg, 0.027 mmol) was dissolved in DME (3 mL) in a round-bottomed flask fitted with a reflux condenser under a nitrogen or CO atmosphere. The solution was stirred at 75°C for 1 h. The solution was cooled, the DME removed in vacuo, and the ^{31}P NMR spectrum of the residue measured in $CDCl_3$.

Type B (^{31}P NMR every 15 min at 75°C or 60°C): Isomer $\mathbf{9c}_{maj}$ (25 mg, 0.027 mmol) was dissolved in DME (0.7 mL) under a nitrogen or CO atmosphere and transferred to a screw-cap NMR tube (also kept under a nitrogen or CO atmosphere) by means of a syringe. With the NMR spectrometer set at 75°C or 60°C, the NMR tube was inserted and inverse gated ^{31}P NMR spectra were taken every 15 min until either a $\mathbf{9c}_{maj}/\mathbf{9c}_{min}$ ratio of 2:1 was reached, 7 h elapsed, or decomposition occurred. Relative amounts of the two isomers were calculated by integrating the peaks at 47.2 ppm ($\mathbf{9c}_{min}$) and 40.7 ppm ($\mathbf{9c}_{maj}$).

Type C (variable-temperature ^{31}P NMR, RT→75°C): Isomer $\mathbf{9c}_{maj}$ (25 mg, 0.027 mmol) was dissolved in DME (0.7 mL) under a nitrogen or CO atmosphere and transferred to a screw-cap NMR tube (also kept under a nitrogen or CO atmosphere) by means of a syringe. ^{31}P NMR spectra were taken every 5°C from room temperature to 75°C to determine when peaks corresponding to $\mathbf{9c}_{min}$ are first observed.

Synthesis of 12: The same procedure as in the synthesis of **9c** was followed except 40 h of heating was required after the addition of methyl propiolate (60 μL, 0.675 mmol). The dark red solid was charged onto a chromatography column of silica and eluted under nitrogen first with hexane/diethyl ether (9:1) to remove unreacted $[Co_2(CO)_8]$ and then with hexane/diethyl ether (7:3; $R_f = 0.15$) to collect **12** as a dark red solid (16 mg, 7%). Analytically pure **12** suitable for a single-crystal structure determination was obtained by slow diffusion of petroleum ether into a solution of **12** in CH_2Cl_2 at −20°C. M.p. 244–248°C (decomp); IR ($CHCl_3$): $\tilde{\nu} = 2020$ (s), 1971 (s), 1676 cm^{-1} (m, CO); ^1H NMR (500 MHz, $CDCl_3$): $\delta = 2.19$ (s, 3H; CH_3), 3.21 (s, 3H; CH_3), 5.22 (s, 1H; $CHCHCCO_2$) 5.87 (d, $^4J(P,H) = 8.5$ Hz, 1H; $CHCHCCO_2$), 6.4–7.9, 8.76 ppm (m, 32H; BINAP ArH); ^{13}C NMR (125 MHz, $CDCl_3$): $\delta = 49.3$, 51.0 (CH_3), 113.0, 116.4 ($CHCHCCO_2$), 120.3–154.0 (BINAP ArC, CCO_2), 175.1, 178.0 (CCO_2), 202.4, 207.0 ppm (C≡O); ^{31}P NMR (202 MHz, $CDCl_3$): $\delta = 49.2$, 39.5 ppm ($CoPPh_2Ar$); MS (FAB): *m/z* (%): 908 (1) $[M-3CO]^+$, 681 (5) [BINAP+Co]$^+$, 655 (15) $[BINAP(O)_2]^+$, 639 (6) $[BINAP(O)]^+$, 437 (70) $[BINAP-PPh_2]^+$; elemental analysis calcd (%) for $C_{55}H_{40}Co_2O_7P_2$ (992.73): C 66.54, H 4.06; found: C 66.44, H 4.03.

Synthesis of 13: In a Schlenk flask, anhydrous dichloromethane (15 mL) was added to $[Co_2(CO)_8]$ (77 mg, 0.225 mmol). After (±)-BINAP (140 mg, 0.225 mmol) was added, the solution was stirred in the dark for 30 min at room temperature. After adding a condenser to the Schlenk flask, the mixture was stirred at 40°C in the dark for an additional 30 min. Methyl propiolate (28 μL, 0.338 mmol) was added by means of a syringe and stirring continued at 40°C in the dark for 1 h. The flask was allowed to cool and dimethyl maleate (42 μL, 0.338 mmol) and *N*-methylmorpholine *N*-oxide (158 mg, 1.35 mmol) were added. The reaction stirred for 20 h at room temperature in the dark. Neutral alumina (Grade II) was added before removing the solvent in vacuo. The dark purple-red solid was charged onto a chromatography column of silica and eluted under nitrogen first with hexane/ethyl acetate (9:1) to remove unreacted $[Co_2(CO)_8]$ and then with hexane/ethyl acetate (6:4; $R_f = 0.25$) to collect **13** as a dark purple-red solid (25 mg, 10%). Analytically pure **13** suitable for a single-crystal structure determination was obtained by slow diffusion of petroleum ether into a solution of **13** in CH_2Cl_2 at −20°C. M.p. 250–255°C (decomp); IR ($CHCl_3$): $\tilde{\nu} = 2023$ (s), 1978 (m), 1725 (m), 1681 cm^{-1} (m, CO); ^1H NMR (500 MHz, $CDCl_3$, broad peaks): $\delta = 2.17$ (s, 3H; $CHCCO_2CH_3$), 3.21 (s, 3H; $CHCCO_2CH_3$), 3.56 (s, 3H; maleate CH_3), 3.68 (s, 3H; maleate CH_3), 5.23 (s, 1H; $CHCHCCO_2$) 5.74 (s, 1H; $CHCHCCO_2$), 6.3–7.7, 8.65 ppm (m, 34H; BINAP ArH, $O_2CCHCHCO_2$); ^{13}C NMR (125 MHz, $CDCl_3$): $\delta = 44.9$, 49.5 ($O_2CCHCHCO_2$), 49.3, 51.2, 51.4, 51.7 (CH_3), 111.1, 117.7 ($CHCHCCO_2$), 120.3–165.6 (BINAP ArC, CCO_2) 173.1, 173.2, 173.8, 176.7 (CCO_2), 199.3, 207.1 ppm (C≡O); ^{31}P NMR (202 MHz, $CDCl_3$): $\delta =$ 47.0, 38.2 ppm ($CoPPh_2Ar$); MS (FAB): *m/z* (%): 1108 (1) $[M]^+$, 936 (5) $[M-CO-(MeO_2CCH)_2]^+$, 908 (76) $[M-2CO-(MeO_2CCH)_2]^+$, 681 (14) [BINAP+Co]$^+$, 655 (28) $[BINAP(O)_2]^+$, 437 (72) $[BINAP-PPh_2]^+$; elemental analysis calcd (%) for $C_{60}H_{48}Co_2O_{10}P_2$ (1108.85): C 64.99, H 4.36; found: C 64.91, H 4.47.

X-ray crystallography: Table 2 provides a summary of the crystallographic data for compounds **7**, $\mathbf{9c}_{maj}$, $\mathbf{9c}_{min}$, **9e**, **9f**, **12**, and **13**. Data were collected by using Nonius Kappa CCD (**7**), Oxford Diffraction Xcalibur 3 ($\mathbf{9c}_{maj}$ and **13**), Bruker P4 ($\mathbf{9c}_{min}$, **9e** and **12**), and Oxford Diffraction PX Ultra (**9f**) diffractometers, and the structures were refined based on F^2 by using the SHELXTL and SHELX-97 program systems.[32] CCDC 212506 (**7**), 248509 ($\mathbf{9c}_{maj}$), 248510 ($\mathbf{9c}_{min}$), 255848 (**9e**), 255847 (**9f**), 255849 (**12**), and 255850 (**13**) contain the supplementary crystallographic

Table 2. Crystal data, data collection, and refinement parameters for compounds **7**, **9c$_{maj}$**, **9c$_{min}$**, **9e**, **9f**, **12**, and **13**.[a]

	7	**9c$_{maj}$**	**9c$_{min}$**	**9e**
formula	$C_{50}H_{32}Co_2O_6P_2$	$C_{52}H_{36}Co_2O_6P_2$	$C_{52}H_{36}Co_2O_6P_2$	$C_{61}H_{49}Co_2NO_6P_2S$
solvent	$1.5\,CH_2Cl_2$	CH_2Cl_2	CH_2Cl_2	CH_2Cl_2
M_r	1035.95	1021.53	1021.53	1188.80
color, habit	red blocks	orange thin plates	orange-red plates	deep red blocky needles
crystal size [mm^{-1}]	$0.15\times0.10\times0.10$	$0.20\times0.16\times0.03$	$0.30\times0.28\times0.05$	$0.67\times0.12\times0.10$
T [K]	120	150	293	203
crystal system	monoclinic	triclinic	triclinic	monoclinic
space group	$P2_1/n$ (no. 14)	$P\bar{1}$ (no. 2)	$P\bar{1}$ (no. 2)	$P2_1/c$ (no. 14)
a [Å]	14.4575(3)	10.0063(10)	12.9966(15)	12.506(4)
b [Å]	19.3414(4)	13.1274(11)	13.229(3)	31.226(8)
c [Å]	16.2073(4)	18.7862(14)	14.5918(18)	14.528(4)
α [°]	90	73.232(7)	90.514(13)	90
β [°]	94.5540(10)	86.586(8)	96.565(11)	104.28(2)
γ [°]	90	74.004(8)	110.359(18)	90
V [Å^3]	4517.71(17)	2270.7(3)	2333.5(6)	5498(3)
Z	4	2	2	4
ρ_{calcd} [g cm^{-3}]	1.523	1.494	1.454	1.436
radiation	$Mo_{K\alpha}$	$Mo_{K\alpha}$	$Cu_{K\alpha}$	$Mo_{K\alpha}$
μ [mm^{-1}]	1.034	0.971	7.684	0.850
2θ max [°]	50	71	120	47
relfns measured	7931	18162	6881	8076
relfns observed [$\lvert F_o\rvert > 4\sigma(\lvert F_o\rvert)$]	4786	14112	4181	3728
variables	587	586	566	639
R_1/wR_2[b]	0.058/0.138	0.155/0.225	0.074/0.172	0.078/0.129

	9f	**12**	**13**
formula	$C_{61}H_{47}Co_2NO_6P_2S$	$C_{55}H_{40}Co_2O_7P_2$	$C_{60}H_{48}Co_2O_{10}P_2$
solvent	CH_2Cl_2	–	$1.5CH_2Cl_2$
M_r	1186.78	992.67	1236.17
color, habit	red plates	orange-red plates	dark orange blocks
crystal size [mm^{-1}]	$0.12\times0.11\times0.05$	$0.28\times0.18\times0.05$	$0.29\times0.28\times0.20$
T [K]	173	203	173
crystal system	monoclinic	triclinic	triclinic
space group	$P2_1/c$ (no. 14)	$P\bar{1}$ (no. 2)	$P\bar{1}$ (no. 2)
a [Å]	12.6939(12)	12.818(3)	12.9158(5)
b [Å]	30.385(2)	12.998(4)	13.1071(5)
c [Å]	14.4188(15)	15.427(4)	18.6890(7)
α [°]	90	85.936(18)	77.726(3)
β [°]	101.482(9)	75.981(16)	77.296(3)
γ [°]	90	65.772(19)	60.903(2)
V [Å^3]	5450.1(8)	2272.8(11)	2676.08(18)
Z	4	2	2
ρ_{calcd} [g cm^{-3}]	1.446	1.451	1.534
radiation	$Cu_{K\alpha}$	$Mo_{K\alpha}$	$Mo_{K\alpha}$
μ [mm^{-1}]	7.017	0.856	0.892
2θ max [°]	142	45	65
relfns measured	10336	5899	14037
relfns observed [$\lvert F_o\rvert > 4\sigma(\lvert F_o\rvert)$]	8772	3203	13236
variables	721	547	725
R_1/wR_2[b]	0.137, 0.338	0.074, 0.128	0.076, 0.196

[a] Details in common: graphite-monochromated radiation, refinement based on F^2. [b] $R_1=\Sigma\,||F_o|-|F_c||/\Sigma\,|F_o|$; $wR_2=\{\Sigma[w(F_o^2-F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$; $w^{-1}=\sigma^2(F_o^2)+(aP)^2+bP$.

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.

Acknowledgements

We thank the EPSRC and Medivir (UK) for studentship support (to K.A.C.K.), AstraZeneca and the Royal Society (Rosalind Franklin Award) for consumables support (to J.A.L.), and Peter Haycock and Jon Cobb for NMR experiments.

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Received: November 26, 2004
Published online: February 28, 2005