Cobalt−Alkyne Complexes with Diphosphine Ligands as Mechanistic Probes for the Pauson−Khand Reaction

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Enantiomerically pure (3,3-dimethylbutyne)[(*R*)-BINAP]$Co_2(CO)_4$ (**6a**) was obtained via thermal ligand exchange in 27% yield as a single diastereomer. X-ray crystal structure analysis of **6a** revealed a basal bridged coordination of the BINAP ligand and a distorted geometry of the central Co_2C_2 core. Comparison of **6a** with the structurally related (phenylacetylene)dppm$Co_2(CO)_4$ (**7**) revealed that the geometric distortion is mainly caused by the BINAP ligand. Due to the replacement of basal CO ligands *anti* to the *tert*-butyl group in **6a** by the diphosphine, the Pauson−Khand reaction of **6a** with norbornene is completely suppressed. Comparison with (3,3-dimethylbutyne)(dppm)$Co_2(CO)_4$ (**6b**), (3,3-dimethylbutyne)(dppe)$Co_2(CO)_4$ (**6c**), **7**, (3,3-dimethylbutyne)$Co_2(CO)_6$ (**8a**), and (3,3-dimethylbutyne)$(PPh_3)Co_2(CO)_5$ (**8b**) showed a retardation of the reaction rate caused by phosphines. The mechanistic consequences for the Pauson−Khand reaction employing chiral phosphine ligands are discussed.

Since its discovery in 1973 the synthetic utility of the Pauson−Khand reaction as a powerful tool for the construction of cyclopentenones has been demonstrated in many cases.[1] Besides the classical $Co_2(CO)_8$-mediated reaction, recent results showed that several other transition-metal carbonyl complexes can be successfully employed for the cocyclization.[2] The issue of stereoselective cyclopentenone formation has been addressed in several ways. The most common approach uses chiral auxiliaries that are attached to either the alkene or alkyne moiety.[3] This methodology has been applied both intra- and intermolecularly. A very elegant catalytic and highly enantioselective method for the intramolecular cocyclization in the presence of enantiomerically pure titanocene complexes was recently introduced by Buchwald.[4] In a different approach chiral amine *N*-oxides derived from alkaloids were employed in the intermolecular Pauson−Khand reaction to remove selectively one carbon monoxide from the prochiral cobalt alkyne

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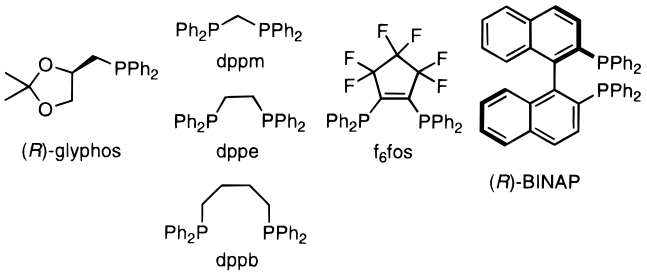
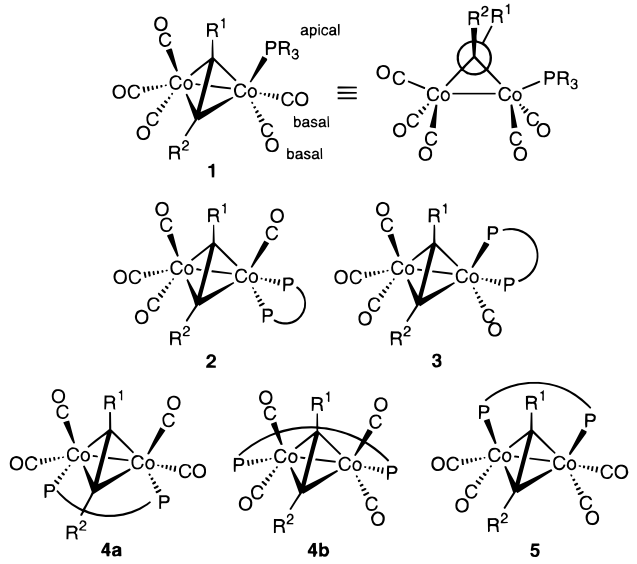
Chart 1



complex.[5] However, this procedure requires a large excess of the chiral amine *N*-oxide. Alternatively, Pauson, Brunner, and Kerr prepared enantiomerically pure cobalt alkyne complexes bearing a chiral glyphos ligand (Chart 1) via ligand exchange.[6,7] Intermolecular Pauson−Khand reactions of these modified cobalt complexes proceeded with high enantioselectivities. Unfortunately, tedious chromatographic separation of the diastereomeric cobalt complexes was a prerequisite for their application in the cocyclization. Despite its limitation, this route seemed to be particularly attractive for further investigations of enantioselective Pauson−Khand reactions. We expected that the problems associated with the use of a chiral monodentate phosphine ligand could be avoided if an enantiomerically pure C_2-symmetric diphosphine ligand is used instead. For successful realization of this concept two additional requirements have to be met. The diphosphine must have a bite angle that is large enough to form a bridged cobalt alkyne complex rather than a chelated one, to minimize the number of possible diastereomeric complexes. Earlier reports by Bonnet,[8] Bird,[9] and Cullen[10] have shown that either apical or basal carbon monoxide ligands of the cobalt alkyne complex were replaced by the phosphine, depending on the type of phosphine ligand (Chart 2). For example, monophosphines such as triphenylphosphine are usually found in the apical position (**1**).[8,10] Diphosphines with small bite angles, such as $f_6$fos, prefer the basal positions, thus forming the chelated complex **2**.[10] The apical−basal chelated geometry **3** has not been observed until now. Diphosphines with an increased bite angle and a more flexible tether such as dppm or dppe prefer a basal bridged orientation (**4a**,**b**);[9,10] diphosphines such as dppb with a very large bite angle gave the apical bridged species **5**.

For proper stereochemical control of the Pauson−Khand reaction with unsymmetrical alkynes the ligand must be attached selectively to either one of the two basal positions ($R^2 > R^1$), i.e. basal *anti* (**4a**) or basal *syn* (**4b**), or the apical position (**5**).[11] For our investigations (*R*)-BINAP was chosen as a suitable diphosphine[12]

Chart 2



and the following issues were addressed. (1) Does the ligand exchange reaction of cobalt alkyne complexes with BINAP proceed with high diastereoselectivity? (2) Can these cobalt complexes be used for the cocyclization? (3) What are the mechanistic consequences? With regard to the glyphos-mediated cocyclization, our experiments also should determine which of the two different cobalt atoms in **1**, the glyphos-bound $Co(CO)_2$ or the $Co(CO)_3$ moiety, undergoes alkene insertion. The results toward this end are described below.

Results and Discussion

The (3,3-dimethylbutyne)[(*R*)-BINAP]$Co_2(CO)_4$ complex **6a** was prepared by thermal ligand exchange reaction from (3,3-dimethylbutyne)$Co_2(CO)_6$ (**8a**) and (*R*)-BINAP in refluxing THF.[13] After workup and recrystallization from ether, brown needles were obtained in 27% yield. According to HPLC analysis of the crude product only a single diastereomer (≥98% de) was formed. Two broad singlets at 48.5 and 36.5 ppm in the ^{31}P NMR spectrum of **6a** indicated the presence of two diasterotopic tetracoordinated phosphorus atoms. Crystals of **6a** were suitable for X-ray crystal structure determination (see below).[14]

For comparison of the spectroscopic data, cobalt complexes with the achiral diphosphines dppm and dppe were prepared. (3,3-dimethylbutyne)(dppm)$Co_2(CO)_4$ (**6b**) and (3,3-dimethylbutyne)(dppe)$Co_2(CO)_4$ (**6c**) were obtained as described for **6a** in 80% and 39% yield, respectively. Both **6b** and **6c** were formed as single diastereomers (≥98% de), as confirmed by HPLC analy-

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sis. Because of the presence of two equivalent phosphorus atoms of **6b**,**c**, ^{31}P NMR spectra showed in each case only one broad singlet at 42.8 and 38.6 ppm, respectively. Thus, coordination of the more flexible ligand dppe with a larger bite angle than dppm resulted in a high-field shift of the ^{31}P NMR signal. Unfortunately, no crystals suitable for X-ray crystal structure determination could be obtained from **6b** or **6c**. Therefore, the corresponding phenylacetylene derivative (phenylacetylene)(dppm)$Co_2(CO)_4$ (**7**) was prepared in a similar way in 50% yield as a single diastereomer.[18] Again the ^{31}P NMR spectrum displayed only one broad signal at 43.4 ppm. In case of **7** X-ray crystal structure determination was successful (see below).

The X-ray data provide an unambiguous answer to the question whether apical bridged or basal bridged complexes (**5** or **4a**,**b**) were formed.[14] As shown in Figure 1a the basal bridged species was found for BINAP complex **6a**. The two phosphorus atoms are oriented *anti* with respect to the *tert*-butyl group, thus avoiding steric hindrance by the bulky alkyne substituent. The data clearly indicate that the apical Co−CO bonds (Co1−C2 = 1.767(2) Å, Co2−C4 = 1.768(2) Å) are shorter than the basal ones (Co1−C1 = 1.795(2) Å, Co2−C3 = 1.788(2) Å).

A similar *anti* basal bridged coordination of the dppm ligand was observed for complex **7** (Figure 2). Again the apical Co−CO bonds (Co2−C11 = 1.771(2) Å, Co1−C10 = 1.773(2) Å) are slightly shorter than the basal ones (Co2−C12 = 1.791(1) Å, Co1−C9 = 1.784(2) Å). This implies that apical Co−CO bonds in the BINAP complex **6a** and dppm complex **7** are stronger than the corresponding basal Co−CO bonds (see below).

The differences between apical and basal Co−CO bond lengths in **6a** and **7** are less than in the complexes (tolane)$Co_2(CO)_4$(dppm)[9] ($Co-CO_{apical}$ = 1.70, 1.71 Å, $Co-CO_{basal}$ = 1.78, 1.76 Å) and (tolane)$Co_2(CO)_6$[15] ($Co-CO_{apical}$ = 1.72, 1.71 Å, $Co-CO_{basal}$ = 1.80, 1.79 Å). Both apical and basal bonds in **6a** and **7** are approximately 0.2 Å shorter than the corresponding Co−CO bonds in (di-*tert*-butylacetylene)$Co_2(CO)_6$[16] ($Co-CO_{apical}$ = 1.786, 1.786 Å, $Co-CO_{basal}$ = 1.816, 1.803 Å). Whereas the alkyne bond length (1.34 ± 0.01 Å) seems to be quite robust to structural changes, the Co−Co bond length varies to a much greater extent in the above-mentioned cobalt clusters. The following distances were observed: 2.5007(4) Å for **6a** and 2.4858(4) Å for **7** as compared to 2.47 Å for (tolane)$Co_2(CO)_6$, 2.459 Å for (tolane)$Co_2(CO)_4$(dppm), and 2.316 Å for (di-*tert*-butylacetylene)$Co_2(CO)_6$.

Analysis of the X-ray data concerning close van der Waals contacts revealed an unsymmetric structure for **6a**;[17] the amount of steric hindrance is different for the two apical carbon monoxides C2−O2 and C4−O4 (Figure 1b). A similar difference was found between the two basal carbon monoxides C1−O1 and C3−O3. The sterically most hindered CO ligands are C2−O2 and to a lesser extent C4−O4 (distances between atoms (Å): C2−C7, 3.769; C2−C8, 3.357; C2−C10, 4.693; C4−C7, 3.369; C4−C9, 3.358; C4−C10 3.492). The distance between the basal CO ligands and the bulky *tert*-butyl group

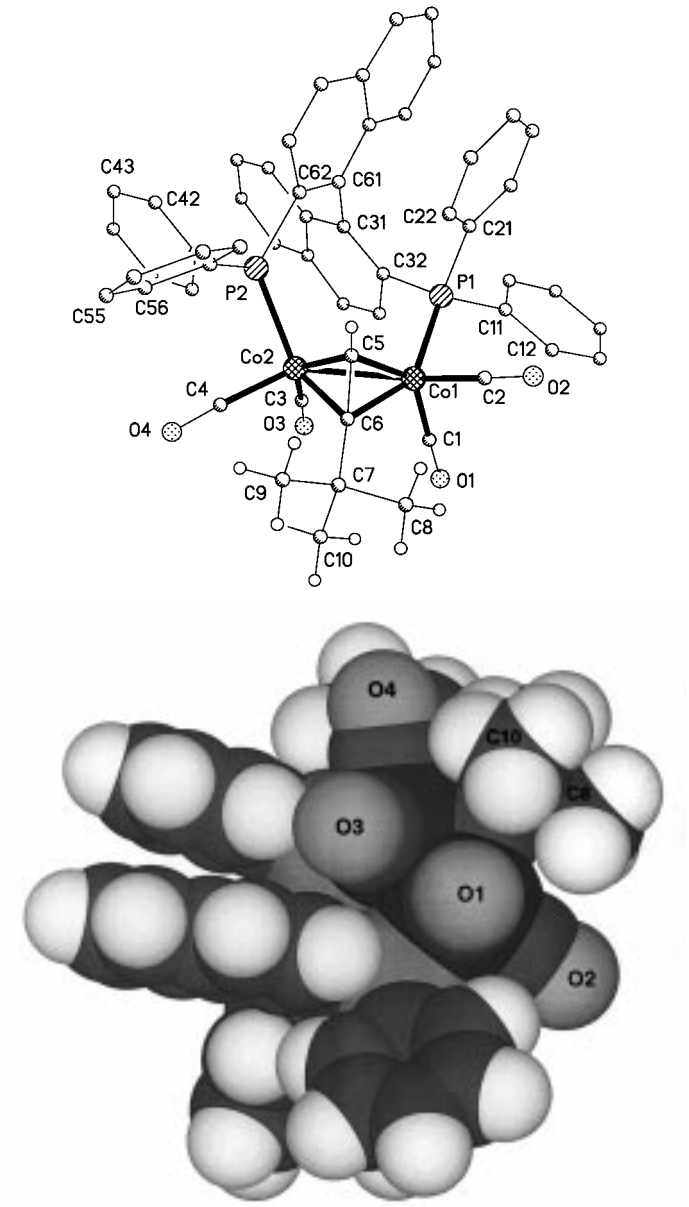

Figure 1. (a, top) X-ray crystal structure of BINAP complex **6a**. Selected bond lengths (Å) and angles (deg): Co(1)−C(2) = 1.767(2), Co(1)−C(1) = 1.795(2), Co(1)−C(6) = 1.9708(19), Co(1)−C(5) = 1.979(2), Co(1)−P(1) = 2.2349(6), Co(1)−Co(2) = 2.5007(4), Co(2)−C(4) = 1.768(2), Co(2)−C(3) = 1.788(2), Co(2)−C(5) = 1.952(2), Co(2)−C(6) = 1.9684(19), Co(2)−P(2) = 2.2741(6), C(5)−C(6) = 1.331(3), C(6)−C(7) = 1.519(3); C(2)−Co(1)−C(1) = 102.76(10), C(2)−Co(1)−C(6) = 103.06(8), C(1)−Co(1)−C(6) = 101.65(9), C(2)−Co(1)−C(5) = 95.84(9), C(1)−Co(1)−C(5) = 140.26(9), C(2)−Co(1)−P(1) = 94.32(6), C(1)−Co(1)−P(1) = 101.78(7), P(1)−Co(1)−Co(2) = 100.81(2), C(4)−Co(2)−C(3) = 93.32(10), C(4)−Co(2)−C(5) = 115.51(9), C(3)−Co(2)−C(5) = 137.79(9), C(4)−Co(2)−C(6) = 97.62(8), C(3)−Co(2)−C(6) = 110.28(9), C(4)−Co(2)−P(2) = 94.42(7), C(3)−Co(2)−P(2) = 115.69(7), P(2)−Co(2)−Co(1) = 115.987(18), C(5)−C(6)−C(7) = 138.52(19). (b, bottom) CPK model of **6a** viewed along the O1−C1 bond.

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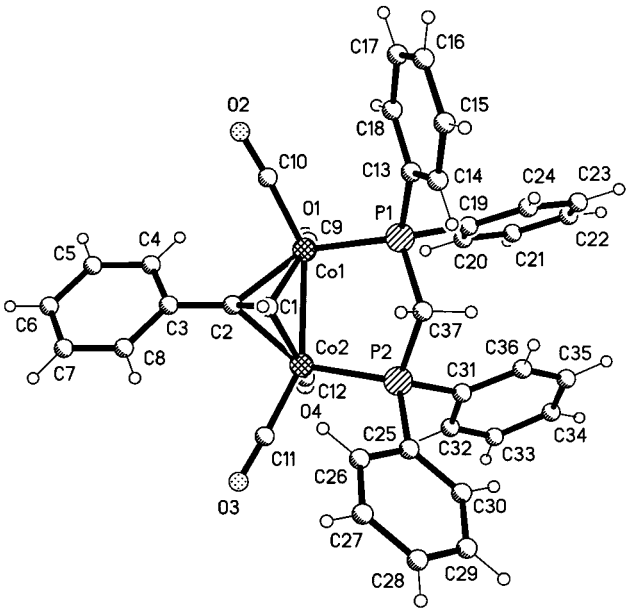


Figure 2. X-ray crystal structure of dppm complex **7**. Selected bond lengths (Å) and angles (deg): Co(1)−C(2) = 1.9513(15), Co(1)−C(1) = 1.9632(17), Co(1)−C(9) = 1.7841(17), Co(1)−C(10) = 1.7733(18), Co(1)−P(1) = 2.2330(5), Co(1)−Co(2) = 2.4858(4), Co(2)−C(11) = 1.7711(18), Co(2)−C(12) = 1.7909(18), Co(2)−C(1) = 1.9469(16), Co(2)−C(2) = 1.9742(15), Co(2)−P(2) = 2.2244(5), C(1)−C(2) = 1.350(2), C(2)−C(3) = 1.461(2); C(10)−Co(1)−C(9) = 98.99(8), C(10)−Co(1)−C(1) = 101.22(7), C(10)−Co(1)−C(2) = 98.45(7), C(9)−Co(1)−C(1) = 140.70(7) C(9)−Co(1)−C(2) = 103.50(7), C(10)−Co(1)−P(1) = 101.41(6), C(9)−Co(1)−P(1) = 111.80(5), P(1)−Co(1)−Co(2) = 96.925(16), C(11)−Co(2)−C(12) = 99.84(8), C(11)−Co(2)−C(1) = 100.24(7), C(12)−Co(2)−C(1) = 142.90(8), C(11)−Co(2)−C(2) = 101.14(7), C(12)−Co(2)−C(1) = 142.90(8), C(11)−Co(2)−P(2) = 99.57(6), C(12)−Co(2)−P(2) = 107.93(6), P(2)−Co(2)−Co(1) = 96.870(16), C(1)−C(2)−C(3) = 142.72(15).

differs by 0.2−0.4 Å, with C1−O1 much closer to the *tert*-butyl than C3−O3 (distances between atoms (Å): C1−C7, 3.674; C1−C10, 3.654; C3−C7, 4.080; C3−C10, 3.874). These structural features should have important implications for the reactivity (vide infra).

The greater geometric distortion of the central Co_2C_2 core in **6a** as compared to that in **7** can also be deduced from Co−P bond lengths. Whereas two different Co−P bond lengths (Co2−P2 = 2.2741(6) Å, Co1−P1 = 2.2349(6) Å) were found for BINAP complex **6a**, the dppm complex **7** has two Co−P bonds of almost equal length (Co2−P2 = 2.2244(5) Å, Co1−P1 = 2.2330(5) Å). The increased symmetry of **7** is in good agreement with the data observed for (tolane)$Co_2(CO)_4$(dppm)[9] (Co2−P2 = 2.210 Å, Co1−P1 = 2.215 Å).

Surprisingly, BINAP complex **6a** was completely unreactive in the attempted Pauson−Khand reaction with norbornene (Scheme 1). Neither thermal conditions (refluxing in THF or toluene) nor activation by 6 equiv of *N*-methylmorpholine *N*-oxide (NMO, CH_2Cl_2, room temperature) gave the desired product. Only starting material could be recovered.

Similar results were observed with complexes **6b**,**c** (and **7**) containing dppm or dppe as ligands. When a refluxing mixture of (3,3-dimethylbutyne)(dppm)$Co_2(CO)_4$ (**6b**) and an excess of norbornene (10 equiv) in toluene was treated with 10 equiv of NMO, only

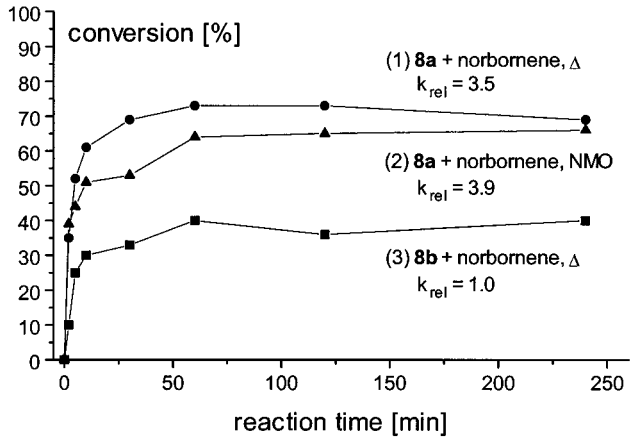


Figure 3. Reaction rate of the Pauson−Khand reaction employing (3,3-dimethylbutyne)$Co_2(CO)_5$L (**8a**,**b**) and norbornene under various conditions: (1) 1.00 equiv of **8a** (L = CO), 1.5 equiv of norbornene, toluene, 80 °C; (2) 1.00 equiv of **8a** (L = CO), 1.5 equiv of norbornene, CH_2Cl_2, 6 equiv of NMO, room temperature; (3) 1.00 equiv of **8b** (L = PPh_3), 1.5 equiv of norbornene, toluene, 80 °C. For further details see the Experimental Section.

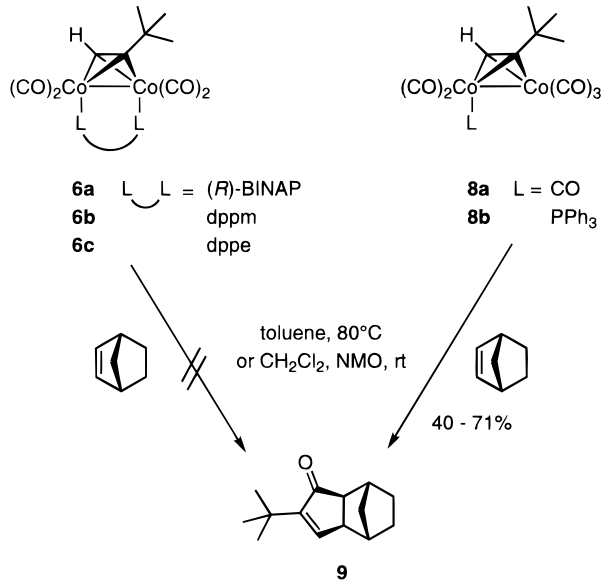
decomposition of the cobalt alkyne complex occurred. Obviously the presence of the diphosphine totally suppresses the reaction of the alkyne complex with norbornene. This outcome is in agreement with results by Pauson[18] and Jeong,[19] who observed a significant retardation of the rate (or at least a decrease of the yield) when employing phosphine-substituted cobalt carbonyl complexes for inter- and intramolecular Pauson−Khand reactions.

To compare the strong effect of the diphosphines on the reaction rate with the corresponding monophosphines, qualitative rate experiments with the parent (3,3-dimethylbutyne)$Co_2(CO)_6$ (**8a**) and the monophosphine-substituted analogue (3,3-dimethylbutyne)(PPh_3)$Co_2(CO)_5$ (**8b**) were undertaken. As can be seen in Figure 3, the NMO-promoted reaction of complex **8a** with norbornene is 1.1 times faster than the thermal reaction. In both cases a final conversion of 70% was achieved. However, the phosphine-substituted complex **8b** slowed the reaction by a factor of 4. Furthermore, the final conversion of **8b** could not be increased above 40%.[20] The decreased reaction rate of the phosphine complex is probably attributable to the replacement of a carbon monoxide by a poorer π-acceptor ligand (i.e. PPh_3). thus increasing the back-bonding between cobalt and the remaining carbon monoxides. This should lead to a retardation of the initial decarbonylation step in the Pauson−Khand reaction. According to the mechanistic scheme proposed for the cocyclization,[1f] the carbon monoxides in the basal positions *anti* to the larger substituent R^2 are usually supposed to be most prone

(19) Jeong, N.; Hwang, S. H.; Lee, Y.; Chung, Y. K. *J. Am. Chem. Soc.* **1994**, *116*, 3159−3160.

(20) One might argue that thermal reaction of **8b** yields PPh_3 as a byproduct, which is presumably a potent inhibitor, so that the maximum level of conversion should not exceed 50%. However, experiments by Pauson and Brunner[6a] have shown that thermal cocyclization of a mixture of (phenylacetylene)$Co(CO)_6$ and glyphos proceeded with much higher yield as compared to the reaction of preformed, chromatographically pure (phenylacetylene)(glyphos)Co$(CO)_5$. This means that PPh_3 only inhibits the reaction when it is directly bound to the cobalt center. In addition, it retards the reactivity of the neighboring cobalt center.

Scheme 1



to undergo decarbonylation and subsequent coordination of the alkene. The inertness of the cobalt BINAP complex **6a** and the corresponding complexes **6b**,**c** with dppm and dppe ligands toward the reaction conditions strongly supports this mechanism.[21] The only carbon monoxide ligands in complex **6a** that might be accessible for the Pauson−Khand reaction are the basal coordinated C1−O1 and C3−O3. However, the insertion step is very sensitive toward steric hindrance, and thus insertion from a basal position such as C3−O3 (or C1−O1) is disfavored due to steric interactions with the *tert*-butyl group. In contrast, the other two basal positions are occupied by the phosphine ligand and, thus, the Pauson−Khand reaction is completely suppressed. As a consequence the shutdown of the cocylization pathway is caused by the decrease of the reaction rate due to the phosphine and the coordination of the bidentate ligand at the "wrong" position, i.e., the basal *anti* instead of basal *syn* position.

These results also have important implications on the mechanism of the glyphos-containing cobalt complexes mentioned earlier. Thus, the cocyclization of (alkyne)-(glyphos)$Co_2(CO)_5$ with alkenes presumably proceeds at the cobalt center that does not contain the glyphos ligand, because this center would react much more slowly. The $Co(CO)_2$(glyphos) moiety operates as a chiral "bystander" that directs the steric outcome in the neighborhood.

Conclusion

Although (*R*)-BINAP forms cobalt alkyne complex **6a** with high diastereoselectivity, **6a** cannot be used for the Pauson−Khand reaction because of exchange of the "wrong", basal *syn* oriented carbon monoxide ligand together with an overall decrease of the reaction rate. To circumvent the problems discussed above, a chelating or nonchelating phosphine is required that should bind with high enantio- and diastereoselectivity to one of the two enantiotopic cobalt atoms. Work toward this goal is currently in progress in our laboratories.

Experimental Section

All reactions were carried out under argon by using standard Schlenk techniques. Solvents were dried and deoxygenated by standard procedures. Analytical TLC was performed on precoated Macherey-Nagel Polygram SIL G/UV_{254} plates (0.25 mm thickness), and products were visualized with a solution of phosphomolybdic acid in EtOH (5%, v/v). Flash chromatography[22] was carried out with Merck silica gel 60 (230−400 mesh). NMR spectra were performed at 400 MHz (^{1}H), 100 MHz (^{13}C), and 81 MHz (^{31}P). Melting points were uncorrected. IR spectra: Nicolet 5DXC FT-IR spectrometer. Optical rotations: 1 dm cells, 1 mL capacity, room temperature. Mass spectra were obtained at 70 eV; NH_3 was used as reactant gas for CI spectra. GC analysis: HP5-fused silica capillary column (i.d. 0.32 mm, length 30 m), a temperature program was run from 80 °C at a rate of 8 °C min^{-1} up to 280 °C. (3,3-dimethylbutyne)$Co_2(CO)_6$ (**8a**) and (3,3-dimethylbutyne)-$Co_2(CO)_5(PPh_3)$ (**8b**) were prepared as described in refs 23 and 24.

General Procedure for the Preparation of Cobalt Alkyne Phosphine Complexes. To a solution of dicobalt octacarbonyl (342 mg, 1.00 mmol) in THF (5 mL) was added dropwise alkyne (1.50 mmol), and the resulting red-brown solution was stirred for 30 min at room temperature, until the evolution of carbon monoxide ceased. Then phosphine (1.00 mmol) was added and the solution was heated for several hours at 60 °C until TLC indicated complete conversion. After the mixture was cooled to room temperature, the solvent was removed in vacuo and the crude product was purified by flash chromatography on SiO_2 and recrystallization from ether.

(3,3-Dimethylbutyne)[(*R*)-BINAP]$Co_2(CO)_4$ (6a). Purification by flash chromatography (hexanes/ethyl acetate 10:1) yielded brown crystals (40 mg, 0.04 mmol, 27%): mp 150 °C dec; $[\alpha]_D^{22}$ 198° (c = 0.05 in CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90−6.10 (m, 32H, aryl CH), 5.62 (s, br, 1H, CH), 1.22 (s, 9H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ 208.7, 207.8, 204.9, 203.8 (CO), 140.8 (d, J = 37.2 Hz, aryl CH), 139.2 (d, $J_{C,P}$ = 40.9 Hz, aryl CH), 138.0 (d, $J_{C,P}$ = 31.0 Hz, aryl C_q), 135.0−134.0 (m), 132.9−131.9 (m), 130.0 (d, $J_{C,P}$ = 15.0 Hz), 129.3−129.2 (m), 128.6−125.4 (m, 37C, aryl CH), 118.4 (Co−*C*), 82.5 (Co−*C*H), 36.6 [*C*(CH_3)$_3$], 32.8 [C(*C*H_3)$_3$]; ^{31}P NMR (81 MHz, $CDCl_3$) δ 48.5 (s, br), 36.5 (s, br); IR (KBr) 2009, 1978, 1950, 1933 cm^{-1}; UV (CH_3CN) λ_{max} (log ϵ) 196 (1.45) nm. Anal. Calcd for $Co_2C_{54}H_{42}O_4P_2$·$(C_2H_5)_2O$: C, 68.92; H, 5.19. Found: C, 69.20; H, 5.36.

X-ray crystal structure analysis of **6a**·2$C_4H_{10}O$: $C_{62}H_{62}$-$Co_2O_6P_2$, M_r = 1082.92, crystal size 0.31 × 0.14 × 0.09 mm, monoclinic, space group $P2_1$, a = 16.413(2) Å, b = 10.3967(14) Å, c = 17.101(2) Å, β = 106.770(5)°, V = 2794.0(7) Å^3, ρ_{calcd} = 1.287 Mg m^{-3}, T = 143(2) K, Z = 2, λ = 0.710 73 Å; Bruker SMART 1000 CCD diffractometer, 33 528 reflections collected to θ = 30°, 16 020 independent reflections, 650 refined parameters, R1 = 0.0346, wR2 = 0.0692; programs used, SHELXL-97. The structure contains two molecules of diethyl ether, one of which is disordered over two sites. For details see ref 14.

(3,3-Dimethylbutyne)(dppm)$Co_2(CO)_4$ (6b). Flash chromatography (hexanes/ethyl acetate 6:1) yielded a red-brown solid (560 mg, 80%): mp 150 °C dec; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56−7.06 (m, 20H, aryl CH), 5.50 (s, br, 1H, CH), 3.62 (s, br, 1H, PCH_2P), 3.11 (s, br, 1H, PCH_2P), 1.36 [s, 9H,

(21) Billington and Pauson reported a 5% yield of 1,3,3a,6a-tetrahydro-5-phenyl-4*H*-cyclopenta[*c*]furan-4-one upon thermal reaction of **7** with 2,5-dihydrofuran.[18]

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(23) Varadi, G.; Vizi-Orosz, A.; Vastag, A.; Palyi, G. *J. Organomet. Chem.* **1976**, *108*, 225−233.

(24) Aime, S.; Milone, L.; Rossetti, R.; Stanghellini, P. L. *Inorg. Chim. Acta* **1977**, *22*, 135−137.

$C(CH_3)_3$]; ^{13}C NMR (100 MHz, $CDCl_3$) δ 208.0 (CO), 204.4 (CO), 139.2 (dd, $J_{C,P}$ = 19.8/19.8 Hz, 2C), 136.8 (dd, $J_{C,P}$ = 19.4/19.5 Hz, 2C, aryl C_q), 132.1 (dd, $J_{C,P}$ = 6.3/6.3 Hz, 4C), 131.7 (dd, $J_{C,P}$ = 6.3/6.3 Hz, 4C), 129.5 (d, $J_{C,P}$ = 5.8 Hz, 4C), 128.3 (dd, $J_{C,P}$ = 4.6/4.7 Hz, 4C), 128.2 (dd, $J_{C,P}$ = 4.6/4.7 Hz, 4C, aryl CH), 119.3 (d, $J_{C,P}$ = 17.0 Hz, 1C, Co−C_q), 72.5 (Co−*C*H), 42.4 (dd, $J_{C,P}$ = 19.3/19.5 Hz, 1C, P*C*H_2P), 36.9 [*C*$(CH_3)_3$], 33.4 [C(*C*$H_3)_3$]; ^{31}P NMR (81 MHz, $CDCl_3$) δ 42.4 (s, br); IR (KBr) 2017, 1983, 1955 cm^{-1}; UV (CH_3CN) λ_{max} (log ϵ) 196 (1.49) nm; MS (EI) *m*/*z* 696 (M, 1), 668 (16), 640 (4), 612 (28), 584 (100), 528 (9), 502 (24), 443 (6), 424 (7), 348 (18), 321 (11), 302 (10), 251 (14), 243 (10), 183 (32), 152 (5), 108 (8), 78 (6). Anal. Calcd for $Co_2C_{35}H_{32}O_4P_2$: C, 60.36; H, 4.63. Found: C, 61.12; H, 5.08.

(3,3-Dimethylbutyne)(dppe)$Co_2(CO)_4$ (6c). Flash chromatography (hexanes/ethyl acetate 15:1) yielded a red-brown solid (280 mg, 39%): mp 150 °C dec; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67−7.01 (m, 20H, aryl CH), 5.41−5.28 (m, 1H, CH), 2.18−1.93 (m, 4H, PCH_2CH_2P), 1.35 [s, 9H, C$(CH_3)_3$]; ^{13}C NMR (100 MHz, $CDCl_3$) δ 207.1 (CO), 206.1 (CO), 139.2−138.8 (m), 137.8−137.5 (m, 4C, aryl C_q), 132.6−132.5 (m), 131.3−131.2 (m), 129.6−129.2 (m), 128.6−128.2 (m, 20C, arom. CH), 110.4 (Co−C_q), 73.1 (Co-*C*H), 36.2 [*C*$(CH_3)_3$], 33.6 [C(*C*$H_3)_3$], 24.9 (CH_2), 24.7 (CH_2); ^{31}P NMR (81 MHz, $CDCl_3$) δ 38.6 (s, br); IR (KBr) 2010, 1981, 1958, 1923 cm^{-1}; UV (CH_3CN) λ_{max} (log ϵ) 196 (1.76) nm; MS (CI) *m*/*z* 711 (M + 1, 0.2), 568 (4), 540 (2), 345 (12), 263 (100), 237 (34), 206 (76), 189 (46), 176 (13), 78 (10). Anal. Calcd for $Co_2C_{36}H_{34}O_4P_2$: C, 60.86; H, 4.82. Found: C, 60.45; H, 5.08.

(Phenylacetylene)(dppm)$Co_2(CO)_4$ (7). Flash chromatography (hexanes/ethyl acetate 6:1) yielded a red-brown solid (360 mg, 50%):[18] mp 120 °C dec; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63−7.23 (m, 25H, aryl CH), 5.78 (s, br, 1H, CH), 3.58 (s, br, 1H, PCH_2P), 3.08 (s, br, 1H, PCH_2P); ^{13}C NMR (100 MHz, $CDCl_3$) δ 207.0 (CO), 203.2 (CO), 136.8−135.2 (m, 4C, aryl C_q), 132.2−131.5 (m), 129.9−129.3 (m), 128.4−127.9 (m), 126.1 (s, 26C, aryl CH), 109.4 (Co−C_q), 73.5 (Co-*C*H), 41.4 (dd, $J_{C,P}$ = 15.3/15.5 Hz, 1C, P*C*H_2P); ^{31}P NMR (81 MHz, $CDCl_3$) δ 43.4 (s, br); IR (KBr) 2023, 1992, 1968 cm^{-1}; UV (CH_3CN) λ_{max} (log ϵ) 196 (1.64) nm; MS (CI) *m*/*z* 717 (M + 1, 1), 689 (5), 661 (1), 390 (2), 359 (6), 303 (7), 263 (100), 201 (57), 78 (7). Anal. Calcd for $Co_2C_{37}H_{28}O_4P_2$: C, 62.03; H, 3.94. Found: C, 62.05; H, 4.43.

X-ray crystal structure analysis of **7**·$^1/_2C_4H_{10}O$: $C_{39}H_{33}Co_2O_{4.5}P_2$, M_r = 753.45, crystal size 0.31 × 0.14 × 0.09 mm, monoclinic, space group *C*2/c, a = 39.765(4) Å, b = 12.232(2) Å, c = 14.6698(10) Å, β = 92.303(10)°, V = 7129.8(15) Å^3, ρ_{calcd} = 1.404 Mg m^{-3}, T = 143(2) K, Z = 8, λ = 0.710 73 Å; Bruker SMART 1000 CCD diffractometer, 40 338 reflections collected to θ = 29.5°, 9950 independent reflections, 430 refined parameters, R1 = 0.0294, wR2 = 0.0754; programs used, SHELXL-97. The structure contains one molecule of diethyl ether, disordered over an inversion center. For details see ref 14.

Pauson−Khand Reactions of Complexes 8a,b and Norbornene. Run 1. To a solution of **8a** (1.00 mmol) and anthracene (178 mg, 1.00 mmol, as internal standard) in toluene (20 mL) was added norbornene (141 mg, 1.50 mmol), and the reaction mixture was heated to 80 °C. Samples were taken after 2, 5, 10, 30, 60, 120, and 240 min, respectively, and analyzed by capillary GC.

Run 2. To a solution of **8a** (1.00 mmol) and anthracene (178 mg, 1.00 mmol, as internal standard) in CH_2Cl_2 (20 mL) were added norbornene (141 mg, 1.50 mmol) and NMO (703 mg, 6.00 mmol), and the reaction mixture was stirred at room temperature. Samples were taken and analyzed as described for run 1.

Run 3. To a solution of **8b** (1.00 mmol) and anthracene (178 mg, 1.00 mmol) in toluene (20 mL) was added norbornene (141 mg, 1.50 mmol), and the reaction mixture was heated to 80 °C. Samples were taken and analyzed as described for run 1.

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Supporting Information Available: Tables and figures giving X-ray crystal structure results for **6a** and **7**. This material is available free of charge via the Internet at http://pubs.acs.org.

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