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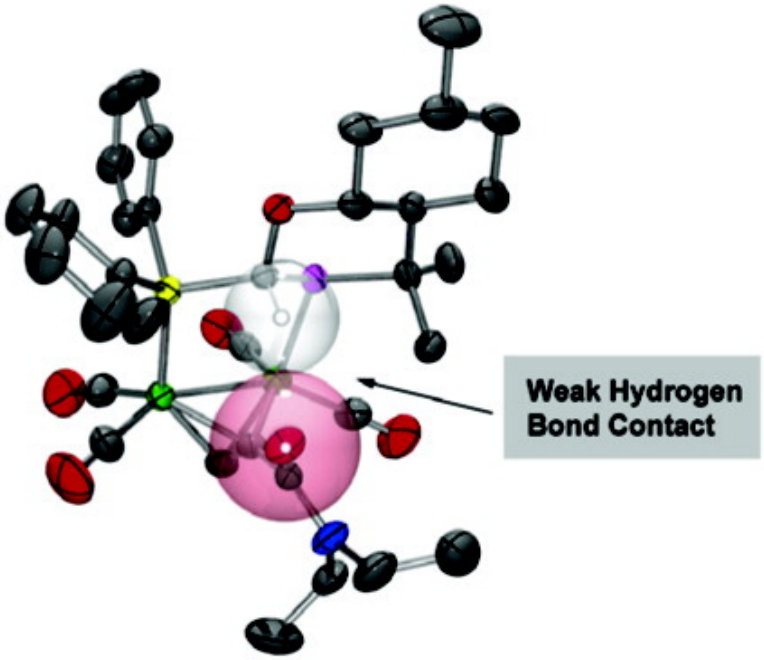
J. Am. Chem. Soc., **2005**, 127 (39), 13629-13633• DOI: 10.1021/ja053653u • Publication Date (Web): 08 September 2005



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Published on Web 09/08/2005

Phosphine−Substrate Recognition through the C−H···O Hydrogen Bond: Application to the Asymmetric Pauson−Khand Reaction

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Abstract: A unique methine moiety attached to three heteroatoms (O, P, S) and contained in the PuPHOS and CamPHOS ligands serves as a strong hydrogen-bond donor. Nonclassical hydrogen bonding of this methine with an amido-carbonyl acceptor provides a completely diastereoselective ligand exchange process between an alkyne dicobalthexacarbonyl complex and a phosphine ligand. This weak contact has been studied by means of X-ray analysis, ^{1}H NMR, and quantum mechanical calculations and revealed that the present interaction falls in the range of strong C−H···O═C bonds. The hydrogen-bond bias obtained in the ligand exchange process has been exploited in the asymmetric intermolecular Pauson−Khand reaction to yield the corresponding cyclization adducts in up to 94% ee.

Introduction

Weak C−H···X hydrogen bonds were first found and identified in the solid state and have been demonstrated to be of crucial importance in crystal formation and crystal packing.[1] During the past decade, interest in nonclassical hydrogen bonding has increased exponentially since it has been attributed to play a major role in structural biology. Numerous studies have highlighted its importance in protein folding,[2] membrane structure,[3] and drug binding processes.[4] In contrast, these stabilizing interactions have scarcely been exploited in asymmetric synthesis.[5] For example, phosphine ligands, one of the most ubiquitous ligands in asymmetric catalysis, have mostly relied on steric repulsive interactions to achieve a good asymmetric recognition between substrate and ligand.[6] Here, we report on the use of weak C−H···O bonding to enhance the chiral recognition event between a bidentate H-bond donor P,S ligand and its substrate and its application in the asymmetric intermolecular Pauson−Khand reaction.

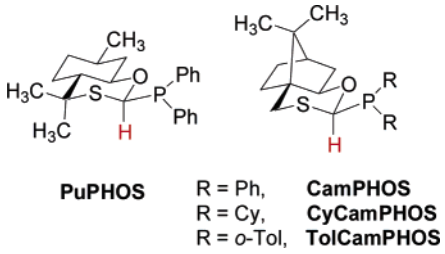

Figure 1. Chiral P,S ligands used in the asymmetric Pauson−Khand reaction.

Over the past few years, our group has developed bidentate P,S ligands for the asymmetric Pauson−Khand reaction (Figure 1).[7] When coordinated to a terminal alkyne complex, these ligands provide two (**I**, **II**) bridged diastereomeric complexes (Scheme 1). Upon reaction with norbornadiene, each diastereomer provides the corresponding Pauson−Khand product in high optical purity.[8] To obtain high yields of the desired chiral cyclopentenone, a single bridged isomer is required. It is therefore of great importance to control selectivity in the ligand exchange process. Purely steric repulsive interactions provide low selectivities. For instance, ligand exchange of the *tert*-

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(5) The use of a formyl as a hydrogen-bond donor moiety has been elegantly exploited by Corey and co-workers in asymmetric synthesis and catalysis, see: (a) Corey, E. J. *Angew. Chem., Int. Ed.* **2002**, *41*, 1650−1667. (b) Corey, E. J.; Barnes-Seeman, D.; Lee, T. W. *Tetrahedron Lett.* **1997**, *38*, 4351−4354.
(6) Jacobsen, E. N.; Pfaltz, A.; Yamamoto, H. *Comprehensive Asymmetric Catalysis*; Springer: Berlin, 1999.
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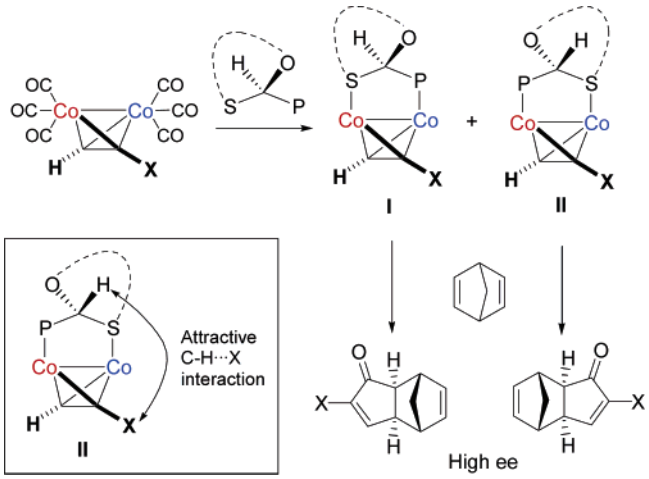
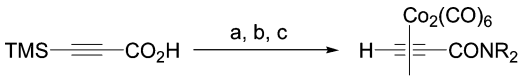
(8) Norbornadiene derived chiral cyclopentenones have found valuable synthetic applications, see: Iqbal, M.; Evans, P.; Lledo, A.; Verdaguer, X.; Pericas, M. A.; Riera, A.; Loeffler, C.; Sinha, A. K.; Mueller, M. J. *ChemBioChem* **2005**, *6*, 276−280.

Scheme 1. Diastereomeric Bridged P,S Complexes[a]



[a] Carbonyl groups, phosphine substituents, and ligand backbone are omitted for clarity. Just one of the two ligand alignments grants a contact within the acceptor (X) and the methine group on the ligand.

Scheme 2 [a]



1, R = Et, 78 %
2, R = *i*-Pr 75 %
3, R = -$(CH_2)_5$- 62%

[a] Reagents: (a) HOBt, DCC, HNR_2; (b) $Co_2(CO)_8$, hexane; (c) $KHCO_3$/K_2CO_3 aq, MeOH.

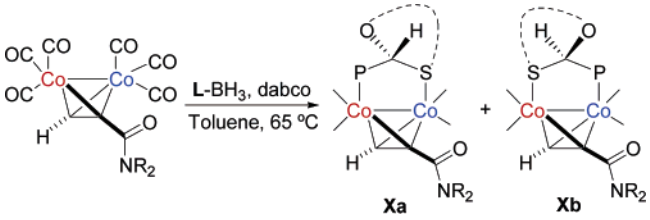
butylethyne dicobalt complex with the reported CamPHOS and PuPHOS ligands yields 33% and 50% de, respectively.[7b,c] Examination of the structural features of these ligands showed a unique methine group attached to three heteroatoms (O, P, and S), which could serve as a hydrogen-bond donor moiety (Figure 1).[9] We hypothesized that coordination to an alkyne substrate bearing an appropriate hydrogen-bond acceptor would yield an efficient recognition event because only one of the two possible diastereomers (**II**) would produce the speculative stabilizing C−H···X interaction (Scheme 1).

Results and Discussion

To verify this supposition, we synthesized terminal alkyne dicobalt complexes with a properly placed hydrogen-bond acceptor. We chose amides because of their capacity to form hydrogen bonds in comparison with other carbonyl functionalities.[10] The synthesis of three distinct amido complexes derived from propynoic acid is described in Scheme 2. Starting from the TMS protected alkyne, amide formation, complexation with $Co_2(CO)_8$, and deprotection of the alkyne terminal position led to excellent overall yields of the corresponding dicobalt hexacarbonyl complexes **1**−**3**.

Initial experiments showed that the thermal ligand exchange reaction was highly selective. Reaction of the diethylamido complex **1** with PuPHOS provided tetracarbonyl complexes **4a**/**4b** in 94% de and 68% yield (Table 1, entry 1). This result was encouraging, because exchange experiments with alkyne com-

Table 1. Ligand Exchange Reaction for Bidentate P,S Ligands[a]



entry	R	L	yield (%)[b]	Xa/Xb	de (%)[c]
1	Et	PuPHOS	68	**4a**/**4b**	94
2	*i*-Pr	PuPHOS	70	**5a**/**5b**	90
3	−$(CH_2)_5$−	PuPHOS	74	**6a**/**6b**	76
4	Et	CamPHOS	74	**7a**/**7b**	96
5	*i*-Pr	CamPHOS	89	**8a**/**8b**	99
6	*i*-Pr	CamPHOS	90	**8a**/**8b**	80[d]
7	−$(CH_2)_5$−	CamPHOS	73	**10a**/**10b**	99
8	Et	TolCamPHOS	85	**9a**/**9b**	99
9	Et	CyCamPHOS	66	**11a**/**11b**	51

[a] During the reaction, removal of CO was effected by vacuum and argon refilling. [b] Yields refer to the sum of purified diastereomeric complexes by flash chromatography. [c] Diastereomeric excess was determined by weight ratio of the corresponding complexes. [d] Reaction was run in THF (65 °C, 16 h) instead of toluene.

plexes that cannot form a hydrogen bond (HC≡CTMS and HC≡CBu^t) yield only up to 50% de.[7b,c] Increased diastereomeric ratios were also observed for diisopropyl and piperidino amides (Table 1, entries 2 and 3). CamPHOS ligand showed an increased selectivity versus PuPHOS, because complete selectivities were observed for diisopropyl (99% de) and piperidino (99% de) complexes (Table 1, entries 5 and 6). Again, the novel TolCamPHOS showed total selectivity (99% de, Table 1, entry 8). In contrast, exchange reaction with the CyCamPHOS ligand, bearing a phosphine-dicyclohexyl moiety, provided lower selectivity (Table 1, entry 9). The right choice of solvent was important to attain high selectivities. Usually reactions were conducted in toluene. When a more polar solvent was employed (THF), diastereoselectivity decreased to 80% de (Table 1, entry 6). Most conveniently, diastereomeric mixtures were readily separated by flash chromatography because they show an extraordinary large polarity difference ($\Delta R_f \approx 0.5$).[11] Once isolated by chromatography, diastereomeric complexes are configurationally stable and no isomerization is detected at room temperature or below.

In the present set of experiments (Table 1), ligand exchange behavior is consistent with the coordination pathway observed for PuPHOS and CamPHOS with alkynes that cannot form a hydrogen-bond interaction.[7b] Phosphorus coordination to one of the cobalt centers occurs in the first place with low or no selectivity as it can be monitored by either ^{1}H NMR or TLC. In a second stage, sulfur coordination provides the final thermodynamic equilibration mixtures for **Xa**/**Xb**. Thus, the relative energies of **Xa** and **Xb** will determine the final diastereomeric ratio observed. Equilibration for hemilabile P,S ligands is likely to occur at the monodentate-phosphine stage. Thus, phosphines with aromatic substituents tend to isomerize more readily that the corresponding aliphatic equivalents. That could explain why CyCamPHOS (Table 1, entry 9) bearing a dicyclohexyl phosphane moiety provided lower selectivity.

(9) The methylene moiety of dppm has been reported to act as a hydrogen-bond donor, see: Hong, F.-E.; Ho, Y.-I.; Chang, Y.-C.; Lai, Y.-C. *Tetrahedron* **2004**, *60*, 2639−2645.
(10) Hunter, C. A. *Angew. Chem., Int. Ed.* **2004**, *43*, 5310−5324.
(11) The complex bearing two P,S ligands acting as monodentate phosphines could be isolated as byproduct in some cases.

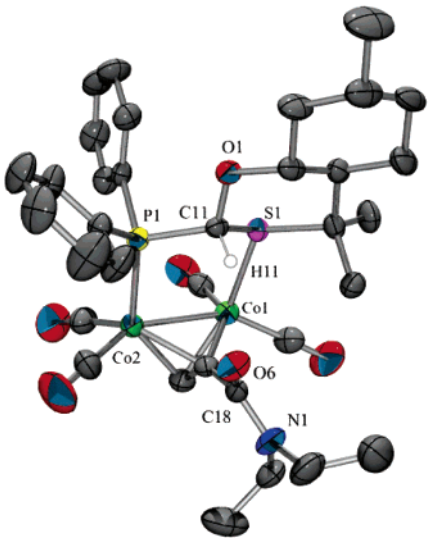
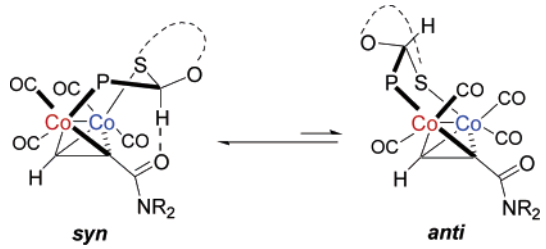


Figure 2. ORTEP drawing of **4a** with 50% probability ellipsoids. Only the hydrogen providing the weak hydrogen bond is depicted.

Scheme 3. Possible Fluxional Conformers Syn/Anti for Major Complexes **Xa**



To verify whether the postulated C−H···O hydrogen bond was responsible for the selectivities observed, a solid-state study was undertaken. Suitable single crystals of major diastereomer **4a** were grown from hexane mixtures. X-ray analysis of **4a** (Figure 2) confirmed that a nonclassical hydrogen bond is established between the methine (C11, H11) and the carbonyl group (O6) of the amide. The distances C(11)−O(6) and H(11)−O(6) are 3.27(1) and 2.35(1) Å, respectively, and the angles θ (C−H···O) = 155.7(5)° and ϕ (H···O−C) = 103.3(5)°. These values are in agreement with similar C−O···H bonds reported in the literature.[1] In this case, the hydrogen bond lies slightly above the plane formed by the oxygen lone pairs, 34(1)°, but in fairly good alignment with one of these.

Bridged ligands show fluxional behavior around the Co−Co axis.[12] Thus, dicobalt complexes of terminal alkynes bearing a bridged ligand may exist in two different fluxional conformations, anti and syn, depending on the relative position of the alkyne substituent and the bidentate ligand. Major diastereomer **4a** could exist in either one of these two conformations or alternatively an equilibrium mixture between them (Scheme 3). It is important to point out that in only one of these conformations (syn) the stabilizing hydrogen-bond contact can occur. For most reported X-ray structures, repulsive steric interactions force the ligand to adopt an anti conformation away from the alkyne substituent.[13] Most remarkably, in the present example, the X-ray structure of **4a** demonstrates that in the solid sate the bonding interaction forces the bidentate ligand and the amido group in the alkyne moiety to adopt a syn conformation.

To check whether the stabilizing weak C−O···H interaction was also in operation in solution as in the solid state, isolated major diastereomeric complexes **Xa** were investigated via ^{1}H NMR. For all major complexes **4a**−**11a**, a remarkable downfield shift for the methine (H11) resonance in C_6D_6 solution was observed with respect to complexes with alkynes that cannot form a hydrogen-bond interaction. This was indicative that in solution the hydrogen bond was also taking place and that it forced the bidentate ligand to adopt a syn conformation. In the case of diasteromeric complexes **11a**/**11b**, the absence of aromatic resonances allowed an excellent comparison of the corresponding methine resonances for both diastereomers (Figure 3). Resonances for Ha (H11, according to numbering shown in Figure 2) for each diastereomer were assigned by means of (^{1}H, ^{13}C) two-dimensional heteronuclear single quantum correlation (HSQC) experiments. Resonances for Ha were correlated with the adjacent (88.7 and 94.0 ppm) carbon resonances. Thus, minor complex **11b** showed a singlet for Ha at 4.5 ppm, while major **11a** displayed the same resonance at 6.6 ppm. This represents a downfield shift of more than 2.0 ppm for Ha, while the formerly acetylenic proton Hb remains practically unaffected. Similar downfield shifts were observed for **11a** in CD_3OD and DMSO-d_6, indicating that intramolecular hydrogen bonding occurred in solution even in polar, hydrogen bond-accepting solvents.

The average computed interaction energies for organic C−H···X bonded dimers in the gas phase range from 0.5 to 3.8 kcal/mol, which is approximately one-half the energy associated with a classical hydrogen bond (O−H···O).[14] On the other hand, exceptionally high interaction energies between 9 and 18 kcal/mol have been computed for $^+$N−CH$_3$····O bonds.[15] Such strong interactions remain stabilizing even in polar solvents and are postulated to be involved in several recognition processes.[16] In an attempt to estimate the interaction energy of the present C−H···O bond, a quantum mechanical calculation was made on the basis of the solid-state structure. An intermolecular model **12** was constructed from the X-ray structure. For computing purposes, the metal cluster was removed and the amide was transformed into a dimethylformamide (DMF) fragment (Figure 4). Single point calculations for model **12** yielded an interaction energy in the gas phase of 5.4 kcal/mol (MP2/6311+G(2d,p)).[17] Corrections for the basis set superposition error (BSSE) were included and had been determined through the counterpoise method described by Boys and Bernardi.[18] Although a rough estimate, the present MP2 value is higher than the computed C$^\alpha$−H···O═C bond energy for a DMF complex and falls in the range of a classical hydrogen

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(17) Quantum chemical calculations have been done using the Gaussian 03 program package: Frisch, M. J.; et al. *Gaussian 03*, revision C.02; Gaussian, Inc.: Wallingford, CT, 2004.
(18) Boys, S. F.; Bernardi, F. *Mol. Phys.* **1970**, *19*, 553−556.

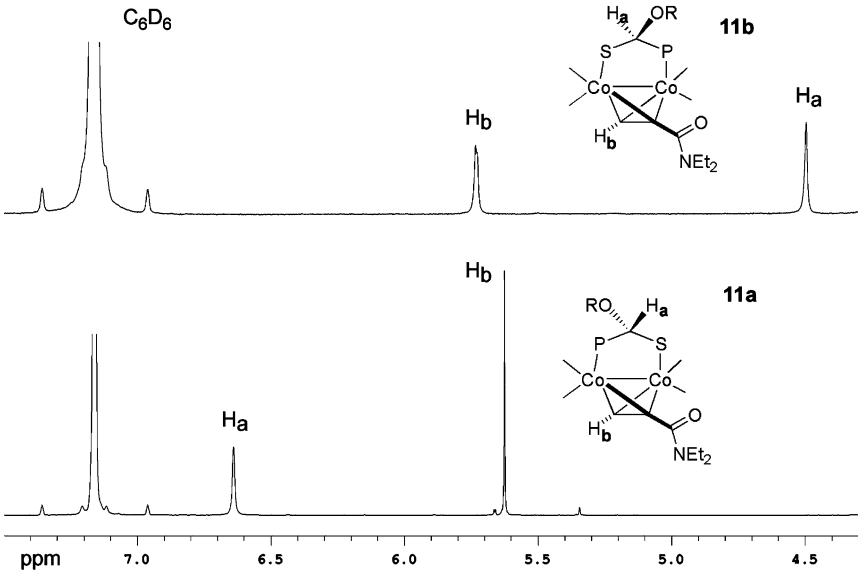


Figure 3. Comparison of ^{1}H resonances for major and minor complexes **11a/11b**.

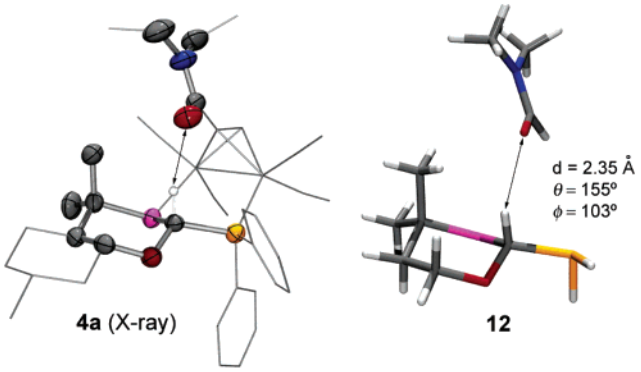


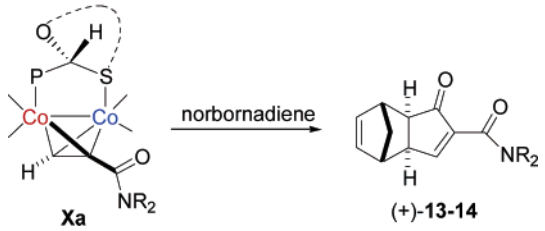
Figure 4. Original X-ray structure for **4a** and simplified model **12**. Weak C−H···O═C contact is depicted with a double-ended arrow for both structures.

bond (X−H···X), indicating that this is a strong C−H···O interaction.[19,20]

Finally, to demonstrate the significance of the present approach in asymmetric synthesis, major diastereomeric complexes were subjected to an intermolecular Pauson−Khand reaction with norbornadiene (Table 2).[21] Thermal activation of the PuPHOS complex **4a** at 70 °C for 18 h yielded the corresponding levorotatory *exo*-cyclopentenone in excellent 90% ee, albeit in a moderate 33% yield (Table 1, entry 1). Alternatively, activation with *N*-methylmorpholine *N*-oxide (NMO) afforded better yields but decreased selectivities with respect to thermal reactions (Table 1, entries 2 and 5).[22] CamPHOS amidocomplexes provided improved yields and selectivities (Table 1, entries 3, 4, and 6). A single crystallization of the product amide **14** (91% ee) provided virtually optically pure material (99% ee), thus allowing, for the first time, access to optically pure 2-carboxyamido Pauson−Khand adducts. Absolute configuration of **13** and **14** was established by optical rotation and analogy with known chiral Pauson−Khand adducts.[7b,23]

In summary, a unique methine moiety attached to three heteroatoms (O, P, S) and contained in the PuPHOS and CamPHOS ligands serves as a strong hydrogen-bond donor, which, upon interaction with an amide, provides a nonclassical C−H···O bond. Due to the ligand chirality, this contact can be established in just one of two possible diastereomeric dicobalt complexes. This allows for an efficient recognition between the ligand and the substrate and a completely selective ligand

Table 2. Intermolecular Pauson−Khand Reaction of Major Diastereomers



entry	complex	R	L	conditions[a]	yield (%)	ee (%)[c]	product
1	**4a**	Et	PuPHOS	thermal	33	90	**13**
2	**4a**	Et	PuPHOS	NMO	81	73	**13**
3	**7a**	Et	CamPHOS	thermal	47	94	**13**
4	**7a**	Et	CamPHOS	thermal[b]	68	92	**13**
5	**7a**	Et	CamPHOS	NMO	81	80	**13**
6	**8a**	*i*-Pr	CamPHOS	thermal	91	91	**14**
7	**8a**	*i*-Pr	CamPHOS	NMO	72	79	**14**
8	**9a**	Et	TolCamPHOS	thermal	47	93	**13**
9	**11a**	Et	CyCamPHOS	thermal	81	87	**13**

[a] Thermal conditions: norbornadiene (10 equiv), toluene, 65 °C under nitrogen (6−24 h). NMO conditions: norbornadiene (10 equiv), *N*-methylmorpholine *N*-oxide (6 equiv), CH_2Cl_2, room temperature, (24−48 h). [b] Toluene, 70 °C, DMSO (10 equiv), 4 h. [c] Enantiomeric excess was determined by chiral HPLC (Chiralcel-OD-H, hexane/IPA).

(19) Vargas, R.; Garza, J.; Dixon, D. A.; Hay, B. P. *J. Am. Chem. Soc.* **2000**, *122*, 4750−4755.
(20) Calculated ^{1}H NMR chemical shifts at the B3LYP/ level (GIAO) predict a downfield shift of 1.0 ppm for H(11) in **12**. Deviation from the experimentally observed value for **11a** (2.0 ppm) may be partly attributable to a deficient description of such weak contacts by DFT theory, see: Cosp, A.; Larrosa, I.; Anglada, J. M.; Bofill, J. M.; Romea, P.; Urpí, F. *Org. Lett.* **2003**, *5*, 2809−2812.
(21) For reviews and recent examples of intermolecular Pauson−Khand reaction, see: (a) Gibson, S. E.; Stevenazzi, A. *Angew. Chem., Int. Ed.* **2003**, *42*, 1800−1810. (b) Geis, O.; Schmalz, H.-G. *Angew. Chem., Int. Ed.* **1998**, *37*, 911−914. (c) Rivero, M. R.; Rosa, J. C. d. l.; Carretero, J. C. *J. Am. Chem. Soc.* **2003**, *125*, 14992−14993.
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exchange reaction. X-ray analysis, ^{1}H NMR studies, and quantum mechanical calculations indicate that the present interaction falls in the range of strong C−H···O═C bonds. Finally, our results demonstrate that phosphine ligands provide a valuable hydrogen bond-based recognition event that can be exploited in the intermolecular asymmetric Pauson−Khand reaction. This new approach to substrate−ligand recognition is complementary to steric repulsion and should be useful in other phosphine-based asymmetric synthesis and catalysis.

Experimental Section

Dicobalt Hexacarbonyl Complex of Propynoic Acid Diisopropylamide, 2. To a solution of 3-trimethylsilyl propynoic acid (250 mg, 1.76 mmol) in dry dichloromethane (25 mL) under nitrogen were added 1-hydroxybenzotriazole hydrate (HOBt) (260 mg, 1.92 mmol) and *N*,*N*′-dicyclohexylcarbodiimide (DCC) (400 mg, 1.93 mmol) sequentially. After 2 h of stirring at room temperature, 0.38 mL (2.64 mmol) of diisopropylamine was added via a syringe. The mixture was stirred overnight at room temperature and cooled to 0 °C. The precipitated *N*,*N*′-dicyclohexylurea was filtered through Celite and washed with dichloromethane (25 mL). The filtrates were washed with HCl 0.1 N (2 × 10 mL) and with a saturated $NaHCO_3$ solution (2 × 10 mL). The organic extracts were dried over magnesium sulfate, filtered, and the solvent was removed under reduced pressure. The crude residue was redissolved in hexanes (20 mL), and solid dicobaltoctacarbonyl (600 mg, 1.76 mmol) was added under nitrogen. The reaction mixture was stirred at room temperature until CO evolution ceased. The solvent was removed in vacuo, and the resulting red residue was filtered through a path of silica and eluted with a hexane/ethyl acetate 90/10 mixture. The red colored fraction was taken, and the solvent was eliminated under reduced pressure. The red oily residue was then dissolved in methanol (15 mL), and 10 mL of a $KHCO_3/K_2CO_3$ aqueous buffer solution (6.2×10^{-3} M) was added. The mixture was stirred at 40 °C until no intermediate complex could be detected bviaTLC (16 h). At this stage, 20 mL of water was added, and the reaction mixture was filtered over a path of Celite. The filtrate was rejected, and the solid complex was recovered by eluting with CH_2Cl_2. The solvent was dried ($MgSO_4$) and removed in vacuo to yield 580 mg (1.32 mmol, 75%) of the desired complex as a red oil. IR (film): ν_{max} = 3053, 2097, 2050, 2007, 1606, 1524 cm^{-1}. ^{1}H NMR (400 MHz, C_6D_6): δ 0.96 (broad s, 6H), 1.54 (broad s, 6H), 3.13 (broad s, 1H), 4.30 (broad s, 1H), 5.48 (broad s, 1H) ppm. ^{13}C NMR (100 MHz, C_6D_6): δ 20.5 (CH_3), 46.7 (CH), 49.6 (CH), 72.9 (CH), 83.5 (C), 163.9 (C), 199.2 (C) ppm. MS (FAB, NBA) *m*/*e* = 440 ([M + 1]$^+$, 65%), 412 ([M + H − CO]$^+$, 63%), 355 ([M − 4CO]$^+$, 100%). HRMS (FAB-NBA): calcd for $C_{15}H_{15}Co_2NO_7$ + 2H, 440.9669; found, 440.9676.

$Co_2(\mu$-^{i}Pr$_2$NCOC$_2$H)(CO)$_4(\mu$-C$_{23}$H$_{27}$OPS), 8a. Dicobalt hexacarbonyl complex **2** (300 mg, 0.68 mmol), CamPHOS-borane complex (265 mg, 0.67 mmol), DABCO (114 mg, 1.02 mmol), and toluene (5 mL) were charged in a Schlenk flask under argon. The reaction mixture was heated at 65 °C, and the CO was periodically removed by means of vacuum and argon refilling. Ligand exchange was monitored via TLC. Upon 9 h of reaction, solvent was removed in vacuo. The residue was then purified by flash chromatography on SiO_2 (hexane/AcOEt, 9/1) to yield 456 mg (0.42 mmol, 89%) of **8a**.

IR (film): ν_{max} = 2030, 1999, 1917 cm^{-1}. ^{1}H NMR (400 MHz, C_6D_6): δ 0.50 (s, 3H), 0.50−0.72 (m, 2H), 0.82 (d, *J* = 6 Hz, 3H), 0.87 (s, 3H), 0.97 (d, *J* = 6 Hz, 3H), 0.87−1.05 (m, 1H), 1.16−140 (m, 3H), 1.55−1.58 (m, 1H), 1.60 (d, *J* = 6 Hz, 3H), 1.62 (d, *J* = 6 Hz, 3H), 2.84 (dd, *J* = 6 Hz, *J* = 13 Hz, 1H), 3.17 (h, *J* = 6 Hz, 1H), 3.65 (d, *J* = 13 Hz, 1H), 3.79 (dd, *J* = 3 Hz, *J* = 8 Hz, 1H), 4.43 (h, *J* = 6 Hz, 1H), 5.65 (s, 1H), 6.96−7.22 (m, 7H), 7.63 (m, 2H), 7.94 (m, 2H) ppm. ^{13}C NMR (100 MHz, C_6D_6): δ 20.1 (CH_3), 20.7 (CH_3), 21.00 (CH_3), 21.05 (CH_3), 21.08 (CH_3), 22.7 (CH_3), 27.1 (CH_2), 33.9 (CH_2), 37.3 (CH_2), 39.8 (d, J_P = 7 Hz, CH_2), 44.8 (C), 45.9 (C), 46.4 (CH), 46.7 (C), 49.8 (CH), 77.0 (CH), 87.2 (d, J_P = 3 Hz, CH), 89.4 (d, J_P = 26 Hz, CH), 128.7 (d, J_P = 9 Hz, CH), 129.6 (CH), 130.7 (CH), 131.4 (d, J_P = 27 Hz, C), 131.9 (d, J_P = 11 Hz, C), 135.0 (d, J_P = 13 Hz, C), 136.0 (d, J_P = 38 Hz, C), 171.2 (C) ppm. ^{31}P NMR (121 MHz, C_6D_6): δ 53.4 ppm. MS (FAB, NBA) *m*/*e* = 766 ([M]$^+$, 4%), 710 ([M − 2CO]$^+$, 46%), 682 ([M − 3CO]$^+$, 13%), 682 ([M − H − 4CO]$^+$, 100%). HRMS (FAB-NBA): calcd for $C_{36}H_{42}Co_2NO_6PS$ + H, 766.1213; found, 766.1219.

$Co_2(\mu$-^{i}Pr$_2$NCOC$_2$H)(CO)$_4(\mu$-C$_{23}$H$_{27}$OPS), 8b. Minor complex **8b** was obtained in 9% yield when THF was employed as solvent. IR-(film): ν_{max}= 2064, 2027, 1998, 1968 cm^{-1}. ^{1}H NMR (400 MHz, C_6D_6): δ 0.35−0.45 (m, 2H), 0.45 (s, 3H), 0.58 (m, 2H), 0.81 (s, 3H), 0.92 (m, 1H), 1.13−1.23 (m, 3H), 1.19 (s, 3H), 1.23−1.36 (m, 1H), 1.50 (m, 1H), 1.65 (m, 6H), 2.58 (d, *J* = 14 Hz, 1H), 2.76 (dd, *J* = 14 Hz, *J* = 6 Hz, 1H), 3.06 (m, 1H), 3.19 (h, *J* = 6 Hz, 1H), 4.89 (s, 1H), 5.37 (h, *J* = 6 Hz, 1H), 5.90 (d, *J* = 8 Hz, 1H), 7.00−7.20 (m, 6 Hz), 7.60 (m, 2H), 7.73 (m, 2H). ^{31}P NMR (121 MHz, C_6D_6): δ 53.2 ppm.

(+)-(1*S*,2*S*,6*S*,7*R*)-Tricyclo[5.2.1.0^{2,6}]-4,8-decadien-3-one-4-carboxylic Acid Diisopropylamide 14. Thermal Conditions. A solution of $Co_2(\mu$-^{i}Pr$_2$NCOC$_2$H)(CO)$_4(\mu$-C$_{23}$H$_{27}$OPS), **8a** (100 mg, 0.13 mmol), and norbornadiene (132 μL, 1.3 mmol) in toluene (2.5 mL) was heated under nitrogen at 70 °C for 16 h. Solvent removal in vacuo and purification by column chromatography (SiO_2, hexane/AcOEt, 20%) afforded 32 mg (91%) of the desired product as a white solid in 91% ee (HPLC).

NMO Promoted Conditions. To a solution of $Co_2(\mu$-^{i}Pr$_2$NCOC$_2$H)-(CO)$_4(\mu$-C$_{23}$H$_{27}$OPS) were added **8a** (430 mg, 0.56 mmol) in dry dichloromethane (7 mL), norbornadiene (0.68 mL, 6.72 mmol), and *N*-methylmorpholine *N*-oxide (400 mg, 3.41 mmol). The mixture was stirred at room temperature for 48 h. Solvent removal in vacuo and purification by column chromatography (SiO_2, hexane/AcOEt, 20%) afforded 110 mg (72%) of (+)-**14** as a white solid in 79% ee (HPLC). Recrystallization of **14** in hot hexanes provided optically pure product (99% ee) as determined by HPLC. $[\alpha]_D$ = +54.3 (*c* = 0.5, $CHCl_3$). Mp = 97−98 °C. IR (film): 2971, 2936, 1705, 1632, 1441, 1370, 1339 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): 1.17 (d, *J* = 9 Hz, 6H), 1.34 (d, *J* = 13 Hz, 2H), 1.47 (d, *J* = 9 Hz, 6H), 2.37 (dt, *J* = 2 Hz, *J* = 7 Hz, 1H), 2.79 (m, 1H), 2.85 (m, 1H), 2.98 (m, 1H), 3.50 (h, *J* = 9 Hz, 1H), 3.70 (h, *J* = 9 Hz, 1H), 6.24 (dd, *J* = 4 Hz, *J* = 8 Hz, 1H), 6.32 (dd, *J* = 4 Hz, *J* = 8 Hz, 1H), 7.52 (d, *J* = 4 Hz, 1H). ^{13}C NMR (100 MHz, C_6Cl_3): 20.6 (CH_3), 21.0 (CH_3), 41.7 (CH_2), 43.4 (CH), 44.2 (CH), 46.0 (CH), 48.8 (CH), 51.2 (CH), 52.9 (CH), 137.5 (CH), 138.8 (CH), 148.3 (C), 161.7 (CH), 164.0 (C), 205.1 (C). MS (CI-NH_3): 274 ([M + 1]$^+$, 100%).

HRMS (EI+): calcd for $C_{17}H_{23}NO_2$, 273.1729; found, 273.1723. HPLC: Daicel Chiracel OD-H. Hexane/*i*-PrOH 95:5, 0.5 mL/min, λ = 254 nm. t_R (−) = 19.4 min. t_R (+) = 25.2 min.

Acknowledgment. This work was supported by DGI-MYCT (BQU2002-02459) and DURSI (2001SGR50). X.V. thanks the DURSI for "Distinció per a la Promoció de la Recerca Universitatria". J.S. thanks the DURSI and Universitat de Barcelona for a fellowship. We thank S. Olivella for helpful advice on quantum mechanics calculations.

Note Added after ASAP Publication. After this paper was published ASAP on September 8, 2005, a typographical error in the first sentence of paragraph 7 in the Results and Discussion section was corrected. The corrected version was published ASAP on September 9, 2005.

Supporting Information Available: Complete ref 17, and general methods, experimental procedures, and characterization data for alkyne complexes and Pauson−Khand adducts. X-ray crystal data, complete numbering scheme, atomic distances, and angles for **4a**. This material is available free of charge via the Internet at http://pubs.acs.org.

JA053653U