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Rhodium-Catalyzed Pauson–Khand Reaction Using a Small-Bite-Angle *P*-Stereogenic C_1-Diphosphine Ligand

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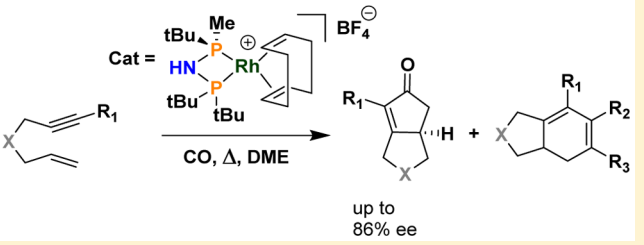
Supporting Information

ABSTRACT: The asymmetric Pauson–Khand reaction catalyzed by [Rh(COD)(MaxPHOS)]BF_4 is described. Several 1,6-enynes have been chosen as model substrates affording moderate yields and selectivities of up to 86% ee. Besides binap-type ligands, we have demonstrated that the *P*-stereogenic C_1-symmetry small-bite-angle ligand MaxPHOS is a viable ligand in this process. The formation of [2+2+2] cycloaddition compounds has shown to be a competitive process. A mechanism is proposed to account for the observed results. The intermediate rhodium dicarbonyl complex **6** was synthesized, and its solid-state structure was elucidated by X-ray crystallography.

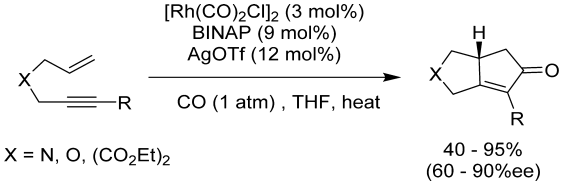


INTRODUCTION

The Pauson–Khand reaction (PKR) is one of the most efficient methods for the construction of cyclopentanic compounds.[1,2] Both the intra- and the intermolecular version of this process have been utilized in the synthesis of natural products and bioactive molecules.[3,4] A great deal of effort has been devoted to the development of enantioselective versions of the PKR using cobalt,[5] titanium,[6] rhodium,[7] and iridium.[8,9] In 2000 Jeong and co-workers published the first catalyzed enantioselective intermolecular PKR under a CO atmosphere in the presence of a rhodium source and the chiral atropoisomeric ligand BINAP (Scheme 1).[7] Since this early report, mostly C_2-symmetric 1,1-binaphthyl diphosphines have been used in Rh-catalyzed intermolecular PKR.[7,10−17] Ratovelomanana-Vidal has shown that electronic and steric effects of the diphosphine ligands are crucial to achieve good conversions and high enantioselectivity.[10,11,13] Interestingly, other C_2-diphosphines such as DIOP, CHIRAPHOS, or Me-DuPHOS have not shown catalytic activity in this reaction.[7] To the best of our knowledge, no examples of electron-rich diphosphines bearing a stereogenic phosphorus atom have been applied in the PKR.

Our group has a long-standing experience in the development of asymmetric approaches for the intermolecular PKR using chiral auxiliaries and ligands.[3,4,18−21] We have recently developed novel methodologies for the synthesis of *P*-stereogenic phosphine ligands. In this field, we have prepared the small-bite-angle MaxPHOS ligand (Scheme 2).[22−24] We have shown that the MaxPHOS-Rh complex **2** is a highly active and efficient catalyst in asymmetric hydrogenation.[25] Due to NH/PH tautomerism, protonation of MaxPHOS leads to the

Scheme 1. Initial Report on the Rh(I)-Catalyzed Asymmetric PKR



Scheme 2. Synthesis of MaxPHOS-Rh Complex 2

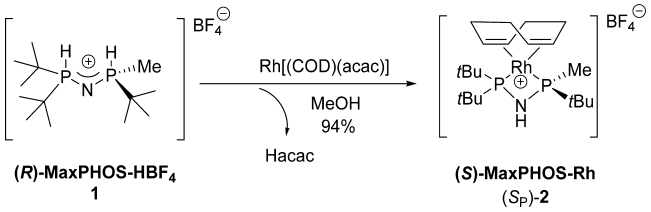


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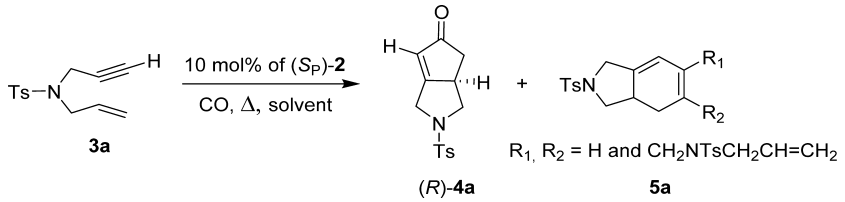
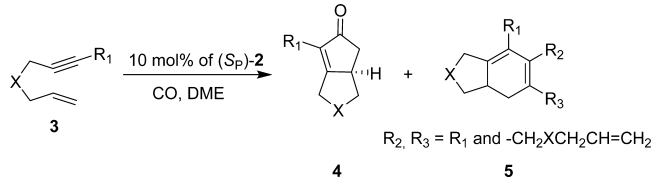
Table 1. Pauson–Khand Reaction of Enyne 3a Catalyzed by Complex 2



entry[a]	CO (barg)[b]	solvent	temp (°C)	yield **4a** (%)[c]	yield **5a** (%)[d]	ee 4a (%)[e]
1	1	THF	100	11	nd	74
2	1	toluene	100	48	nd	64
3	1	DME	100	50	nd	72
4	1	dioxane	100	19	nd	71
5	1	DME	120	52	nd	72
6	2	DME	120	50	nd	71
7	0	DME	120	30	32	86
8	1	DME	85	8	31	84

[a]Ts = *p*-toluensulfonyl. [b]Gauge pressure measured in bar. 0 barg denotes the atmospheric pressure of CO (balloon). [c]Reaction time 24 h. Isolated yields of **4a** after flash column chromatography. [d]Isolated yield of **5a**. Compound **5a** was obtained as 1:1 mixture of regioisomers. [e]Enantiomeric excess was determined by chiral HPLC.

Table 2. Pauson–Khand Reaction of Enynes 3b–f Catalyzed by Complex 2



entry	X	R_1	SM	CO (barg)[a]	temp (°C)	yield **4** (%)[b]	yield **5** (%)[c]	ee 4 (%)[d]	product
1	NTs	Ph	**3b**	1	100	trace		n.d.	**4b**
2	NTs	Ph	**3b**	1	120	62		82	**4b**
3	NTs	Ph	**3b**	0	120	2	40	n.d.	**4b**
4	NTs	Ph	**3b**		80		36		**4b**
5	NTs	Me	**3c**	1	120	55		81	**4c**
6	O	Ph	**3d**	1	120	35		67	**4d**
7	$C(CO_2Et)_2$	H	**3e**	1	120	39	8	79	**4e**
8	$C(CO_2Et)_2$	Me	**3f**	1	120	16	22	72	**4f**

[a]Gauge pressure measured in bar. 0 barg denotes atmospheric pressure of CO (balloon). [b]Reaction time 24 h. Isolated yields of **4b–f** after purification by flash column chromatography. [c]Isolated yield of **5b–f**. Compounds **5b–f** were obtained as a 1:1 mixture of regioisomers at the R_2/R_3 positions. [d]Enantiomeric excess was determined by chiral HPLC.

stable PH form of the ligand, in which the overall positive charge is distributed on both P centers. The MaxPHOS·HBF_4 salt is an air-stable compound both in the solid state and in solution, and it is also a convenient precursor for the preparation of rhodium(I) complexes by direct ligand exchange with the complex [Rh(acac)(COD)]. With the aim of further exploring the potential of complex **2** in asymmetric catalysis, we present a study on its use as a catalyst precursor in the intramolecular PKR. Herein, we describe the first successful asymmetric Pauson–Khand reaction with a small-bite-angle *P*-stereogenic C_1 ligand with bulky groups at phosphorus.[26,27]

RESULTS AND DISCUSSION

We first looked for the best reaction conditions using the nitrogen-tethered substrate **3a** and 10 mol % of catalyst (Table 1). The reactions were first carried out at 1 barg of carbon monoxide. Employing THF as solvent and heating the reaction to 100 °C provided the desired compound **4a** with 11% yield and 74% ee (Table 1, entry 1). Using (S_P)-MaxPHOS the absolute configuration of the cyclization product was *R*. The use of toluene provided a remarkable increase in yield to 48% with a slight decline in selectivity (Table 1, entry 2). The optimal compromise between yield and selectivity was found using 1,2-dimethoxyethane (DME) as solvent. Using DME, cyclopentenone **4a** was obtained in 50% yield and 72% enantiomeric excess (Table 1, entry 3). At this stage, increasing the reaction temperature to 120 °C or the CO pressure to 2 barg had no effect, and the yield and selectivity remained the same (Table 1, entries 5 and 6).

On the other hand, lowering the CO pressure to atmospheric pressure with a balloon of CO (0 barg) had a major impact on the outcome of the reaction. In this case, the yield of compound **4a** reached only 30%, although the enantiomeric excess increased to 86% (Table 1 entry 7). After column chromatography, a 32% yield of compound **5a** was isolated and identified by ^{1}H NMR and HPLC-mass spectroscopy as a mixture of regioisomers with a 1:1 ratio. Compound **5a** arises from the [2+2+2] cycloaddition between two molecules of **3a**.[23,28−31] Finally, cycloaddition reaction at 1 barg and 85 °C produces an even lower amount of enone **4a**, while the yield of

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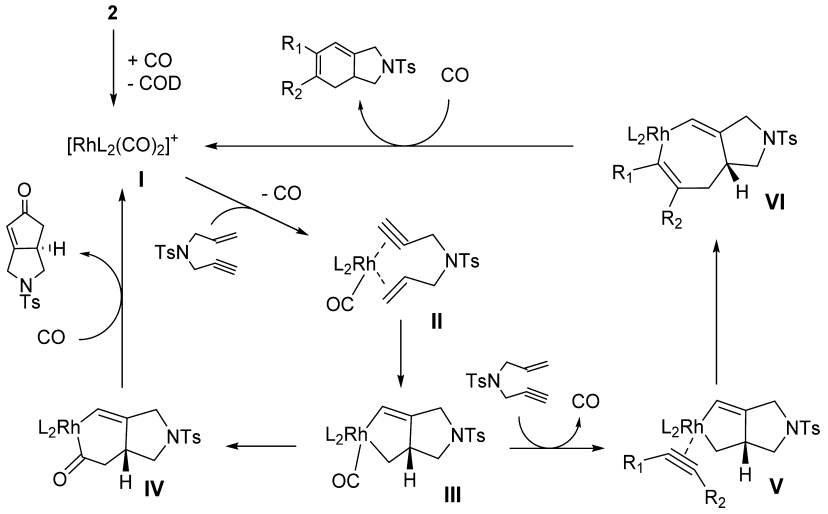
Scheme 3. Mechanistic Hypothesis for the Cycloaddition of Enynes Catalyzed by Complex 2 (L_2 = MaxPHOS)



the [2+2+2] cycloaddition remains unaffected at 31% (Table 1 entry 8). Thus, we concluded that low CO pressures and low temperatures favor the [2+2+2] cycloaddition reaction.

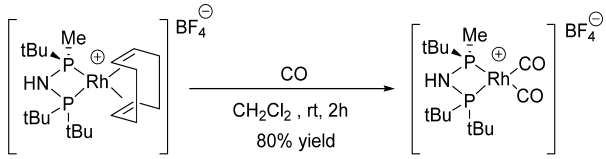
In order to assess the scope of the reaction, the cyclization of several enyne substrates was next studied (Table 2). When substrate **3b** with a phenyl substituent in the alkyne moiety was heated at 100 °C at 1 barg of CO, only traces the cyclization product could be isolated (Table 2, entry 1). We reasoned that such poor reactivity was due to the steric hindrance of the extra phenyl group. However, increasing the reaction temperature to 120 °C was enough to obtain the expected enone (*R*)-**4b** in 62% yield and 82% ee (Table 2 entry 2). This result is quite remarkable since enyne **3b** is considered a challenging substrate in the intramolecular PKR and most BINAP-Rh catalysts fail to catalyze the reaction with high enantioselectivity.[13] When **3b** was cyclized at low CO pressure (balloon of CO), the [2+2+2] cycloaddition product was obtained almost exclusively (Table 2, entry 3). The [2+2+2] cycloaddition reaction can also be run in the absence of carbon monoxide. Reaction of **3b** at 80 °C for 24 h under a nitrogen atmosphere provided a 36% yield of compound **5b** as a 1:1 mixture of regioisomers as determined by HPLC-mass spectroscopy analysis.

The reaction of enyne **3c**, bearing a methyl substituent at the triple bond, was carried out under the optimized conditions of 1 barg and 120 °C to afford **4c** in 55% yield and 81% enantiomeric excess (Table 2, entry 5). The reaction efficiency was next examined for the oxygen- and malonate-tethered substrates **3d**–**f**. The optimized conditions were applied for the substrate **3d** at 1 barg of CO, obtaining a moderate conversion (35% yield) and high selectivity (67% ee, Table 2, entry 6). Compounds **3e** and **3f** offered in general lower conversions but higher enantiomeric excesses. Under the standard conditions compound **4e** was obtained in moderate yield (39%) and high selectivity (79% ee). In this case, 8% yield of the [2+2+2] cycloaddition compound was isolated once again as a 1:1 mixture of regioisomers. In the same reaction conditions substrate **3f** gave rise to the PKR adduct in 16% yield and 72% ee. The [2+2+2] product **5f** was isolated in 22% yield as a mixture of regioisomers.

A feasible mechanistic hypothesis that would rationalize the observed experimental results is depicted in Scheme 3. Common intermediate **III** accounts for both the PKR product and the [2+2+2] cycloaddition. From **III**, carbon monoxide migratory insertion and reductive elimination should produce the cyclopentenone and regenerate the Rh-carbonyl complex **I**. Also from **III**, CO-alkyne ligand exchange provides intermediate **V**, which through migratory insertion of the alkyne unit and reductive elimination will eventually give rise to the [2+2+2] cycloaddition compound. The present mechanistic scheme is consistent with the fact that low CO pressures (or the absence of CO) favor the formation of the cyclotrimer.

A key common intermediate in the proposed mechanism is the rhodium dicarbonyl complex **I** (Scheme 3). To further confirm the role of **I** as intermediate in the catalytic cycle, we sought to isolate the dicarbonyl complex derived from **2** (Scheme 4). Thus, a dichloromethane solution of complex **2**

Scheme 4. Synthesis of Dicarbonyl Complex 6



was bubbled with CO gas. A rapid color change from orange to yellow was observed. The solution was brought to dryness, and the resulting solid residue was crystallized from a CH_2Cl_2/Et_2O mixture to yield a yellow crystalline solid.

Suitable single crystals for X-ray analysis were obtained by layering diethyl ether on top of a solution of the R_P enantiomer of **6** in dichloromethane. The resulting solid-state structure of (R_P)-**6** is depicted in Figure 1. As expected, the rhodium center shows a distorted square planar geometry with the chelating PNP ligand forming an almost planar diamond-like shape. The complex **6** shows a P–N–P angle of 104.1° and a bite angle of 69.7°. The bite angle is even smaller than the one reported for the precursor complex **2**, which is 70.0°.[22] This is mostly due to the slightly larger P–Rh distances (2.33 and 2.33 Å) and shorter P–N distances (1.69 and 1.69 Å) in complex **6**, in comparison with the cyclooctadienyl complex **2**.

To assess whether the dicarbonyl complex **6** was a catalytically active intermediate, it was tested in the PKR of **3b** (Scheme 5). Reaction of **3b** under 1 barg of carbon monoxide at 120 °C using dicarbonyl complex **6** as a catalyst

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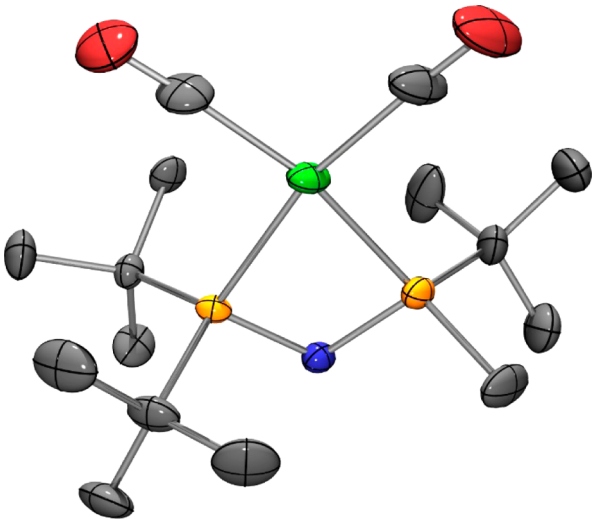
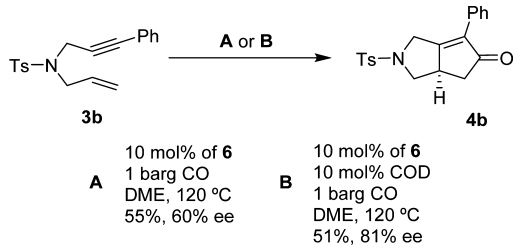


Figure 1. X-ray structure of (*R*)-[Rh(MaxPHOS)$(CO)_2$]BF_4 complex **6**. ORTEP representation drawn with 50% probability ellipsoids. The BF_4 counterion was omitted for clarity. Selected bond distances (Å) and angles (deg): P(1)−N(1), 1.688; P(2)−N(1), 1.691; P(1)−Rh, 2.327; P(2)−Rh, 2.337; P(1)−N(1)−P(2), 104.13; and P(1)−Rh−N(1), 69.70.

Scheme 5. Pauson−Khand Reaction Using 6 as Catalyst



provided the Pauson−Khand product in similar yield (55%) but lower enantiomeric excess (60%, conditions A). Alternatively, when the reaction was performed in the presence of added 1,5-cyclooctadiene (conditions B), the enantiomeric excess increased back to 81%, a similar selectivity to the one obtained when complex **2** was used as catalyst. These experiments confirm that **6** is a plausible intermediate in the catalytic Pauson−Khand reaction catalyzed by complex **2** and highlight that the presence of COD in the reaction mixture has a beneficial impact on selectivity. This observation suggests that along the reaction pathway the COD ligand behaves as a transient labile ligand and that as a consequence has an influence on the enantioselectivity.

CONCLUSIONS

We have shown that the small-bite-angle C_1-symmetric *P*-stereogenic ligand MaxPHOS is active in the rhodium-catalyzed asymmetric Pauson−Khand reaction of several 1,6-enynes, affording selectivities up to 86% enantiomeric excess. The [2+2+2] cycloaddition between the enyne and the triple bond of another enyne has been disclosed as a competitive process. Low CO pressures favor the formation of the [2+2+2] cycloaddition compound. As disclosed in the proposed mechanism, this behavior may be explained by a competitive ligand exchange process on intermediate **III**. Finally, the putative intermediate rhodium dicarbonyl complex **6** has been synthesized, and its structure has been elucidated by X-ray analysis. The use of the dicarbonyl complex as a catalyst has shown that **6** is a catalytically active intermediate and has disclosed that the presence of the COD ligand in the reaction mixture is important to attain high selectivity. The COD complex **2** is, therefore, the most convenient precatalyst for the Pauson−Khand reaction. Overall, the present results indicate that, besides binap-type ligands, other ligand scaffolds are competent in the rhodium-catalyzed Pauson−Khand reaction.

EXPERIMENTAL SECTION

[Rh(*S*-MaxPHOS)$(CO)_2$]BF_4, 6. Complex [Rh(MaxPHOS)(COD)]BF_4 (56.1 mg, 0.1 mmol) was dissolved in 5 mL of CH_2Cl_2, and CO was bubbled for a minute to saturate the solution. An immediate color change from orange to bright yellow was observed. The solution was left stirring under a CO atmosphere for 1 h. The mixture was brought to dryness under vacuum, and the crude product was recrystallized in CH_2Cl_2/Et_2O. Yield: 40.9 mg (80%). $[\alpha]_D$: −35.4 (*c* 0.28, CH_2Cl_2). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 1.30 (d, *J* = 18.0 Hz, 9H), 1.39 (d, *J* = 16.4 Hz, 9H), 1.44 (d, *J* = 16.8 Hz, 9H), 1.88 (dd, *J* = 1.1 y 8.8 Hz, 3H), 5.95 (s, br, 1H) ppm. ^{13}C NMR ($CDCl_3$, 400 MHz): δ 13.6 (d, *J* = 26.4 Hz, CH_3), 26.0 (d, *J* = 5.9 Hz, CH_3), 28.4 (d, *J* = 5.5 Hz, CH_3), 28.6 (d, *J* = 5.9 Hz, CH_3), 35.9 (dt, *J* = 1.0 y 35.6 Hz, CH), 38.7 (dt, *J* = 1.0. 18.8 Hz, CH), 39.6 (dd, *J* = 1.2, 18.2 Hz, CH) ppm. IR (film): ν_{max} 3250, 2969, 2092, 2042, 1983, 1479 cm^{-1}. ^{31}P NMR ($CDCl_3$, 161 MHz): δ 46.9 (dd, *J* = 49.4, 104.0 Hz), 73.5 (dd, *J* = 49.4. 102.9 Hz) ppm. ^{19}F NMR ($CDCl_3$, 376 MHz): δ −150.04 (s), −149.99 (s) ppm. Anal. Calcd for $C_{15}H_{31}BF_4NO_2P_2Rh$: C 35.39, H 6.14, N 2.75. Found: C 35.32, H 6.57, N 2.73.

General Procedure for the Catalytic Pauson−Khand Reaction. The catalyst and substrate were weighed and placed in an Ace glass pressure tube equipped with a pressure gauge and valve. The system was purged with three cycles of vacuum-nitrogen, and then the solvent was added. The equipment was connected to a carbon monoxide manifold, and the system was flushed with three cycles of vacuum-carbon monoxide pressure. At this point the working carbon monoxide pressure was set and the reaction was heated to the desired temperature and time. The reaction crude was purified by column chromatography with a mixture of hexane/ethyl acetate from 95:5 to 5:95 to yield the corresponding compounds. All the compounds were spectroscopically identical to the ones described in the literature.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.organomet.5b00576.

Figures and tables giving X-ray crystal data with atomic distances and angles for complex **6**. General experimental methods, characterization, and analysis data for Pauson−Khand reaction products (PDF)

Crystallographic data (CIF)

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Notes

The authors declare no competing financial interest.

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