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## RESEARCH ARTICLE

## Highly Enantioselective Cobalt-Catalyzed (3 + 2) Cycloadditions of Alkynylidenecyclopropanes

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**Abstract:** Low-valent cobalt complexes equipped with chiral ligands can efficiently promote highly enantioselective (3+2) cycloadditions of alkyne-tethered alkylidenecyclopropanes. The annulation allows to assemble bicyclic systems containing five-membered rings in good yields and with excellent enantiomeric ratios. We also present a mechanistic discussion based on experimental and computational data, which support the involvement of Co(I)/Co(III) catalytic cycles.

Transition-metal-catalyzed (TMC) cycloadditions are among the most practical and versatile methods to construct polycyclic products from simple acyclic materials, in an atom economical manner.<sup>[1]</sup> A number of enantioselective variants have been disclosed throughout the last decades, most of which relying on the use of second- and third-row precious metal catalysts.<sup>[2,3]</sup>

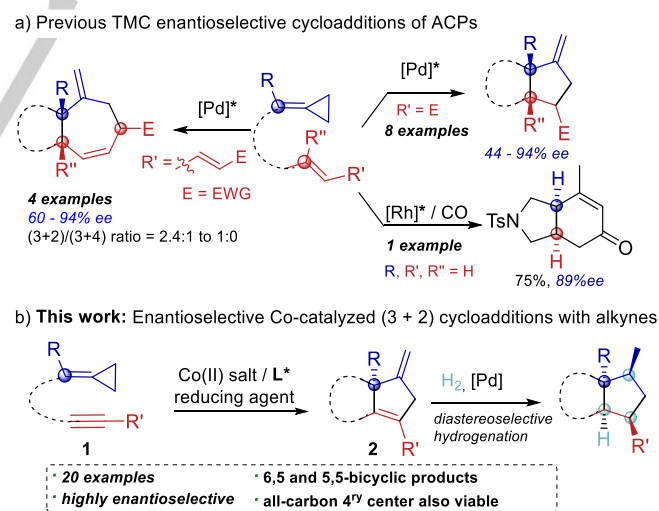
Among the different cycloaddition strategies developed so far, those involving the activation of C–C bonds of designed carbocyclic reactants are especially attractive.<sup>[4]</sup> In this context, we and others have shown that readily accessible alkylidenecyclopropanes (ACPs) can behave as versatile three-carbon components in a wide variety of synthetically powerful (3+n) and (3+n+m) annulations, promoted by Pd, Ni, Ru, or Rh catalysts.<sup>[5,6]</sup>

Curiously, despite the clear synthetic potential of these annulations, progress in the development of enantioselective variants has been extremely scarce and limited to an isolated case of a Rh-catalyzed (3+2+1) cycloaddition,<sup>[7]</sup> and to our recent report on Pd-catalyzed (3+2) and (3+4) cycloadditions between ACPs and tethered alkenes or 1,3-dienes (Scheme 1a).<sup>[8]</sup> Unfortunately, the success of these reactions is limited to substrates featuring electron-withdrawing groups at the terminal position of the alkene (or diene), and the enantiomeric ratios (er's) are strongly dependent on the nature of the connecting tether. Therefore, the development of new, efficient and versatile enantioselective annulations of ACPs remains a major goal in current synthetic chemistry.

In this context, we describe herein a highly enantioselective formal (3+2) intramolecular cycloaddition of alkynylidenecyclopropanes (Scheme 1b). The reaction, which is promoted by non-expensive cobalt catalysts featuring chiral bisphosphine ligands, represents the first enantioselective cycloaddition of ACPs catalyzed by an earth-abundant first-row metal complex, and the first (3+2) cycloaddition of ACPs promoted by cobalt.<sup>[9]</sup>

Moreover, it also constitutes one of the very few asymmetric (3+2) annulations promoted by cobalt reagents.<sup>[10]</sup>

The methodology provides a straightforward approach to five-membered fused bicyclic scaffolds (**2**) from simple, readily accessible ACP precursors (**1**, Scheme 1b).<sup>[11]</sup> Remarkably, we have found that the performance of the Co catalysts is much superior to that of Pd or Rh alternatives. We also demonstrate that a simple hydrogenation protocol allows the stereospecific transformation of the adducts into enantioenriched fused-bicyclic systems bearing up to four stereocenters. Importantly, we include experimental and computational results that allow us to propose a Co(I)/Co(III) catalytic cycle encompassing cobaltacyclopentene and  $\pi$ -allyl cobalt intermediates, and shed light into the origin of the enantioselectivity.



**Scheme 1.** Enantioselective cycloadditions of ACPs.

We started the study using alkynes as ACP cycloaddition partners considering that their well-known metal coordination properties could enable a more efficient enantiodiscriminating step.<sup>[12]</sup> Thus, we chose as substrates alkynyl-tethered ACPs of type **1**, which had never been explored in asymmetric reactions. We initially tested the reactivity of **1a** using our recently developed Pd-phosphoramidite chiral catalysts.<sup>[8]</sup> Heating **1a** in refluxing toluene for 3 h, in the presence of the catalyst generated *in situ*

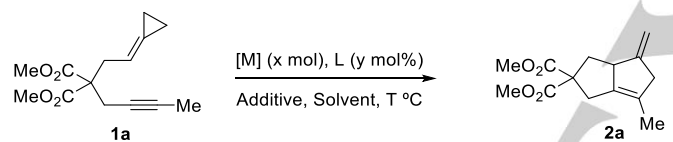
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from Pd<sub>2</sub>(dba)<sub>3</sub> and **L1**, afforded the desired adduct **2a** in moderate yield, and with a low 67:33 er (Table 1, entry 1). Related monodentate ligands like **L2**, or different Pd(0) sources, did not improve these values, whereas bidentate chiral ligands led to poor conversions (Table S1).<sup>[13]</sup> On the other hand, alternative Rh and Ni catalysts, which had previously been shown effective in a variety of ACP cycloadditions,<sup>[6]</sup> led to the recovery of **1a** (entries 3-6), thus precluding the exploration of chiral variants.

Considering the seminal work by Liebeskind and Jones,<sup>[14]</sup> as well as more recent studies by Dong and Yoshikai,<sup>[15]</sup> showing the potential of low-valent cobalt complexes for activating strained carbocyclic scaffolds, we were curious to explore their performance with our alkynyl-tethered ACPs. Cobalt catalysts are highly attractive from a sustainability standpoint, and also because of their rich coordination and redox properties, which might differ from those of their group IX congeners.<sup>[16]</sup>

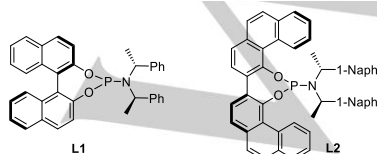
Gratifyingly, after a thorough screening, we found that the cobalt catalyst generated *in situ* from CoBr<sub>2</sub>, dppp, and a mixture of Zn and ZnI<sub>2</sub> promotes the cycloaddition of **1a** (in acetonitrile at 100 °C), delivering **2a** in a good 73% yield (entry 7). Curiously, related ligands such as dppe or Xantphos failed to promote the reaction (Table S2), whereas alternative cobalt(II) precursors such as CoCl<sub>2</sub>, CoI<sub>2</sub> and Co(acac)<sub>2</sub>, under otherwise identical conditions, provided incomplete conversions and lower yields of **2a** (34–70%, see Table S2).<sup>[13]</sup>

**Table 1.** Initial evaluation of suitable metal precursors for the development of an asymmetric cycloaddition of **1a**<sup>[a]</sup>



Entry	M (x mol%)	L (y mol%)	Additive	Solvent	t (h)	T (°C)	Yield (%)
1	Pd <sub>2</sub> (dba) <sub>3</sub> (6)	<b>L1</b> (13)	-	toluene	3	110	66 <sup>[b]</sup>
2	Pd <sub>2</sub> (dba) <sub>3</sub> (6)	<b>L2</b> (13)	-	toluene	16	110	12
3	Rh(COD)Cl] <sub>2</sub> (10)	P(OPh) <sub>3</sub> (12)	-	toluene	20	110	-
4	RhClO(PPH <sub>3</sub> ) <sub>2</sub> (10)	-	-	toluene	20	110	-
5	RhCl(PPh <sub>3</sub> ) <sub>3</sub> (10)	-	-	toluene	20	110	-
6	Ni(COD) <sub>2</sub> (10)	-	-	toluene	12	110	-
7	CoBr <sub>2</sub> (10)	dppp (12)	Zn / ZnI <sub>2</sub> <sup>[c]</sup>	CH <sub>3</sub> CN	3	100	73
8	CoBr <sub>2</sub> (10)	dppp (12)	Zn <sup>[d]</sup>	CH <sub>3</sub> CN	3	100	24
9	CoBr <sub>2</sub> (10)	dppp (12)	In <sup>[d]</sup>	CH <sub>3</sub> CN	3	100	82
10	CoBr <sub>2</sub> (10)	dppp (12)	In / InI <sub>3</sub> <sup>[e]</sup>	CH <sub>3</sub> CN	3	100	86

[a] Conditions: A solution of **1a**, [M] (x mol%), **L** (y mol%) and additive, in the corresponding solvent, was heated for 3–20 h at the indicated temperature. [b] Enantiomeric ratio = 67:33. [c] Carried out with Zn (50 mol%) and ZnI<sub>2</sub> (20 mol%). [d] Carried out with 50 mol% of the additive. [e] Carried out with In (50 mol%) and InI<sub>3</sub> (20 mol%).

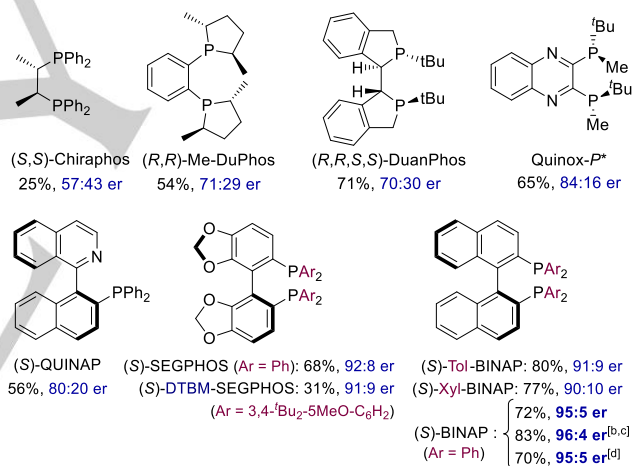


Likewise, in the absence of ZnI<sub>2</sub>, the efficiency of the reaction also decreased (entry 8). On the other hand, from all other reducing

agents tested (Table S3), only indium worked satisfactorily and, interestingly, it did not require the use of a Lewis acid additive to provide a good yield of **2a** (entry 9 vs 10).

Encouraged by these promising results, we analyzed the viability of a Co-catalyzed enantioselective variant. Asymmetric cobalt catalysis has received increasing attention in recent years;<sup>[17]</sup> however, most examples consist of addition processes such as hydrofunctionalizations of unsaturated bonds. Indeed, enantioselective Co-promoted annulations are rather scarce, and none of the reported cases involve the activation of C–C bonds of ACPs or related strained ring systems.<sup>[18]</sup>

After screening several bidentate chiral ligands in combination with CoBr<sub>2</sub> and Zn / ZnI<sub>2</sub>, we were glad to identify a number of ligands that allow the cycloaddition of **1a** to be performed with moderate to high enantioselectivity. As can be deduced from Figure 1 and Table S4, most of them are C<sub>2</sub>-symmetric bisphosphines, with the more common BINAP providing the best results. Using this ligand, the product **2a** was obtained in 73% yield, and an exciting 95:5 er (acetonitrile at 110 °C, 3 h). The reaction could also be carried out at lower temperatures but, curiously, it provides slightly lower er's (89:11 er at 90 °C, Table S5).<sup>[13]</sup> Finally, the use of 1,2-DCE, instead of acetonitrile, increased the reaction yield up to 83% (96:4 er), while with Indium reductants (In or In/InI<sub>3</sub>, instead of Zn/ZnI<sub>2</sub>) the reaction was similarly efficient (Figure 1).<sup>[19]</sup>



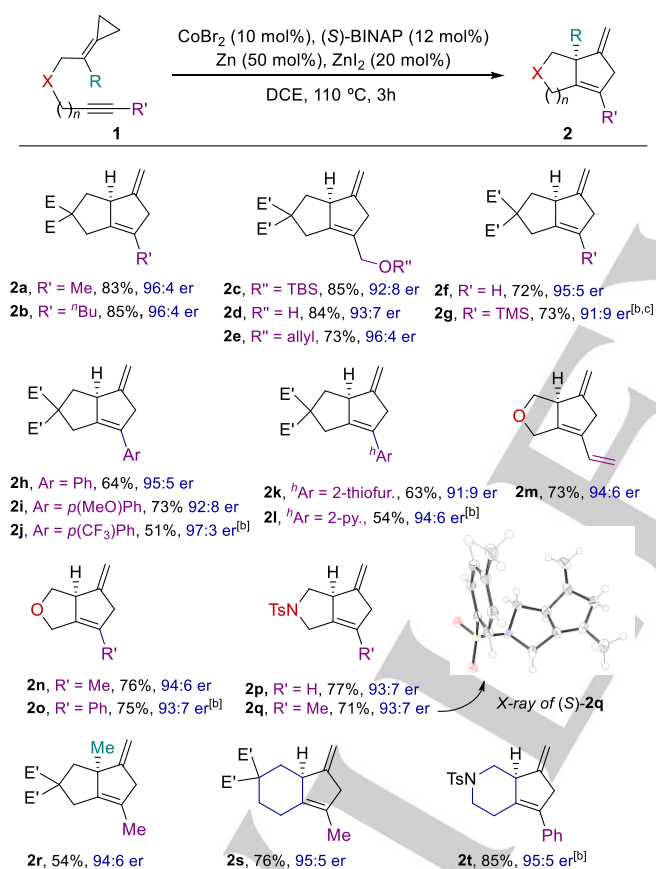
**Figure 1.** Ligands tested for the enantioselective cycloaddition of **1a**. Conditions: A solution of **1a** (1 equiv), CoBr<sub>2</sub> (10 mol%), ligand (12 mol%), Zn (50 mol%) and ZnI<sub>2</sub> (20 mol%) was heated in CH<sub>3</sub>CN at 110 °C for 3 h, unless otherwise noted. Yields determined by <sup>1</sup>H-NMR of the crude mixtures with an internal standard. [b] Carried out in 1,2-DCE as solvent. [c] Identical result obtained when using In (50 mol%) instead of Zn / ZnI<sub>2</sub>, in 1,2-DCE as solvent. [d] Carried out with In (50 mol%), / InI<sub>3</sub> (20 mol%), in 1,2-DCE.

With these optimized conditions in hand, we evaluated the scope of the method (Table 2). The presence of different alkyl groups at the terminal position of the alkyne was well tolerated (e.g. adducts **2a–2e**). The reaction proceeds well either with a bulky OTBS or with an unprotected hydroxyl moiety at the propargylic position, so that **2c** and **2d** are obtained in almost identical er's and yields. Likewise, the cycloaddition of precursor **1e**, bearing an O-allyl group, was also efficient and gave **2e** in 73% yield and 96:4 er. Notably, despite low-valent cobalt catalysts could insert into C<sub>sp</sub>–H bonds of alkynes,<sup>[20]</sup> the use of a terminal alkyne as a cycloaddition partner is also tolerated. Thus, precursor **1f** was efficiently transformed into its corresponding cycloadduct, **2f**, in 72% yield, and with an excellent 95:5 er. The reaction of precursor **1g**, bearing a TMS substituent, required the

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use of In / InI<sub>3</sub>, instead of Zn / ZnI<sub>2</sub>, to provide a good yield of the corresponding adduct (**2g**, 73% yield, 5 h at 130 °C). Despite the bulkiness of the TMS moiety, the er was not significantly eroded (91:9 er). Aromatic substituents with electron-neutral, donating or withdrawing groups (**1h–1j**), as well as heteroaromatic rings, such as an *ortho*-pyridine or a 2-thiofuryl group, are also well tolerated. Their corresponding products (**2h–2l**) were isolated with good yields and er's above 91:9, up to 97:3. Importantly, the presence of geminal diesters at the connecting tether is not essential; indeed, the cycloaddition also works with substrates that bear oxygen- or nitrogen-based groups, such as **1m–1q**. The expected 5,5-fused bicyclic systems **2m–2q** were obtained in yields above 70%, and with very good enantiomeric ratios (er's ≥ 93:7). Interestingly, enynes like in **1m**, which might engage in other side processes,<sup>[1bb]</sup> are also excellent partners, and exclusively provided the desired cycloadduct **2m** in good yield and 94:6 er. The absolute configuration of the *N*-tosyl derivate **2q** could be determined by X-ray crystallographic analysis (Table 2).<sup>[13]</sup>

**Table 2.** Scope of the Co-catalyzed enantioselective (3 + 2) cycloaddition<sup>[a]</sup>

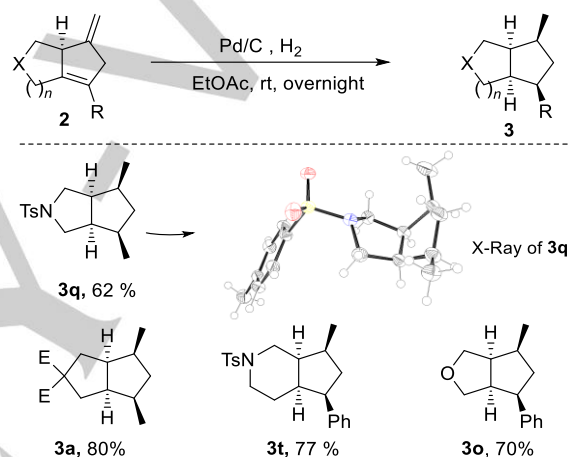


[a] Conditions: A solution of **1**, CoBr<sub>2</sub> (10%), (S)-BINAP (12%), Zn (50%) and ZnI<sub>2</sub> (20%) in 1,2-DCE were heated at 110 °C for 3 h, unless otherwise noted. Yields of isolated products after chromatography; er's determined by HPLC. E' = CO<sub>2</sub>Et; E = CO<sub>2</sub>Me.<sup>[13]</sup> [b] Carried out with In / InI<sub>3</sub>, instead of Zn / ZnI<sub>2</sub>. [c] Reaction heated at 130 °C for 5 h.

The robustness of the transformation was further demonstrated with a precursor that holds a methyl at the internal position of the ACP alkene (**1r**), which allowed to build a bicycle bearing a fully substituted quaternary carbon center at the ring fusion (**2r**, 94:6 er). Finally, the method could also be extended to the preparation of 6,5-fused bicyclic systems, just by elongating the connecting tether by one methylene unit. Thus, the reaction

of **1s** afforded the corresponding adduct (**2s**) in 76% yield and 95:5 er, whereas the reaction of the *N*-tosyl derivative **1t**, which was better when carried out using In / InI<sub>3</sub>, instead of Zn / ZnI<sub>2</sub>, provided **2t** in 85% yield, and a 95:5 er.

To further prove the synthetic potential of our methodology, we did a brief exploration on the elaboration possibilities of the cycloadducts. Therefore, azabicycle adduct **2q** was submitted to classical hydrogenation conditions using Pd/C. The reaction proceeded smoothly to provide the saturated bicycle **3q** as a single isomer in 62% yield (Scheme 2). The stereochemistry of this compound could be determined by X-ray diffraction analysis, which confirmed that the hydrogenation of both alkenes occurred through the same face. These reducing conditions can also be applied to other cycloadducts providing their respective saturated bicycles in good yields (Scheme 2). Overall, several enantioenriched 5,5- and 6,5-fused bicyclic skeletons, bearing up to four stereocenters, could be easily obtained in just two steps from simple acyclic precursors



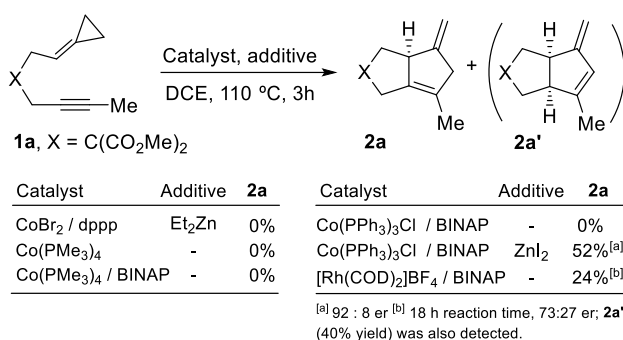
**Scheme 2.** Hydrogenation of the cycloadducts, [X = NTs, O or C(CO<sub>2</sub>Me)<sub>2</sub>, n = 1 or 2].

According to previous work on low-valent cobalt complexes generated *in situ* from Co(II) precursors,<sup>[16]</sup> the active catalyst might consist of a cationic bisphosphine-Co(I) species of type [(P–P)Co(L)<sub>2</sub>]<sup>+</sup> (L = solvent or substrate molecule, P–P = bisphosphine ligand). This species would be the result of a Zn–(or In–) promoted reduction of the initially formed Co(II) precursor [(P–P)CoBr<sub>2</sub>], followed by halide abstraction by ZnI<sub>2</sub> (or InI<sub>3</sub>). Nonetheless, the participation of a Co(0) precursor such as [(P–P)Co(0)L<sub>2</sub>]<sup>[21]</sup> cannot be ruled out, since the cycloaddition of **1a** also takes place to some extent just by adding Zn or In, without ZnI<sub>2</sub> or InI<sub>3</sub> salts (see Table 1, entries 8 and 9).<sup>[22]</sup> To shed some light onto the nature of the active catalyst, we screened different low-valent cobalt precursors, and other reducing agents, in the cycloaddition of **1a** (Scheme 3). Notably, the use of Et<sub>2</sub>Zn as reductant, which has been previously shown to deliver [(P–P)Co(0)] species from their respective Co(II) precursors [(P–P)CoX<sub>2</sub>]<sup>[22]</sup> led to the recovery of the starting material. Likewise, treatment of **1a** with Co(0) complexes such as Co(PMe<sub>3</sub>)<sub>4</sub> or Co(PMe<sub>3</sub>)<sub>4</sub>/BINAP, neither provided **2a** nor any other identifiable product. However, with the Co(I) precursor Co(PPh<sub>3</sub>)<sub>3</sub>Cl, in the presence of BINAP and ZnI<sub>2</sub>, we isolated a 52% yield of **2a** (92:8 er). Using identical conditions, but without ZnI<sub>2</sub>, the reaction did not proceed at all. Overall, these results strongly suggest the

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participation of a cationic Co(I) catalyst of the type [(P–P)Co(L)<sub>2</sub>]<sup>+</sup>.<sup>[23]</sup>

Since this type of square-planar d<sup>8</sup> reagents is well established with Rh(I), we analyzed the performance of [(BINAP)Rh(cod)]<sup>+</sup>, homologous to the above cobalt complex, in the cycloaddition of **1a**. The reaction took place sluggishly, requiring 18 h to achieve full conversion, and providing a mixture of the (3+2) adduct **2a** (24% yield), and the isomeric product **2a'** (40% yield). The enantiomeric ratio of **2a** turned out to be 73:27, significantly lower than that obtained with the cobalt catalyst. Therefore, the cobalt reagents clearly outperform the homologous Rh counterparts, both in terms of reaction efficiency and enantioselectivity.



**Scheme 3.** Results using different cobalt sources, and reaction with a cationic Rh(I) complex.

To gain more insight into the mechanism of this transformation, we carried out Density Functional Theory (DFT) calculations at the dispersion-corrected PCM(DCE)-B3LYP-D3/def2-SVP level.<sup>[13]</sup> We used the alkynylidenecyclopropane precursor **1a'** and the cationic Co(I) complex [(dppp)Co]<sup>+</sup> as model reactant and catalyst, respectively (Figure 2). Initially, we explored the viability of the insertion of the cobalt(I) catalyst into the distal bond of the ACP, in analogy to the routes previously identified for related Pd- or Rh-catalyzed processes.<sup>[24]</sup> We first found out a pathway involving a distal coordination and subsequent insertion of cationic cobalt complex, followed by alkyne-coordination leading to the five-coordinate 18-electron Co(III) trimethylenemethane (TMM) complex **INT1** (via **TS1**). This intermediate is easily converted into the  $\pi$ -allyl complex **INT2**, from which a C–C reductive elimination occurs with a very accessible barrier (12.7 kcal/mol, via **TS3**) to deliver the observed bicyclic product coordinated to the cobalt(I) catalyst. Finally, metal decoordination releases the observed cycloadduct and regenerates the active cobalt(I) catalyst (Figure 2).<sup>[13]</sup>

Notably, the oxidative addition step of this pathway, which directly yields the TMM metal complex, differs from that proposed for related processes involving Rh(I) or Pd(0) catalysts, which were found to generate metallacyclobutane intermediates.<sup>[24]</sup>

More remarkably, further computational scrutiny led us to discover two energetically more accessible pathways towards the intermediate **INT2**. In particular, we computationally located the intermediate **INT0'**, a highly stable Co(I)-complex in which both the alkene and the alkyne units of **1a'** are coordinated to [Co(dppp)]<sup>+</sup>. Our calculations indicate that this species can be transformed into the *exo*-methylene cobaltacyclobutane intermediate **INT1'**, via **TS1'**, with an energy barrier of ca. 31 kcal/mol in a highly endergonic process ( $\Delta G_R = 17.2$  kcal/mol). Should this intermediate **INT1'** be formed, it would readily evolve

to the significantly more stable Co(III)-TMM complex **INT1** through a barrierless ligand slippage process.<sup>[13]</sup>

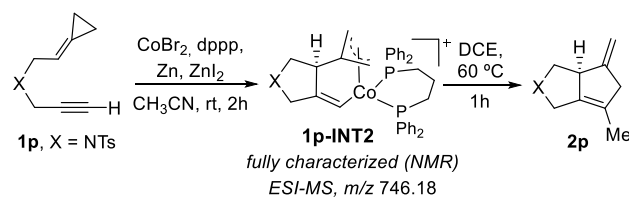
More importantly, besides this pathway, we additionally found that **INT0'** can alternatively undergo an oxidative cyclometallation to a cobaltacycle intermediate, **INT1''**, through **TS1''** with a significantly more accessible energy barrier of 14.1 kcal/mol. Interestingly, this spiro-metallacyclic intermediate (**INT1''**) can be transformed into the above-mentioned intermediate **INT2**, via a cyclopropyl to  $\pi$ -allyl rearrangement. This step is not a canonical  $\beta$ -carboelimination, but instead consists of a distal opening of the cyclopropyl ring (C···C bond distance of 2.10 Å in **TS2''**), a process reminiscent to that previously proposed for cyclopropyl Rh(III) complexes and other transition metal derivatives.<sup>[25]</sup>

Although the pathways proceeding through **TS1** and **TS1'** cannot be discarded, the high stability of **INT0'**, and especially, the low activation barriers associated with the subsequent steps, clearly favor the mechanism involving the cobaltacyclopentene **INT1''**.

Interestingly, the computational study showed that the cyclopropyl to  $\pi$ -allyl rearrangement is also viable using an homologous Rh(I) complex (difference in activation barriers of approx. 1 kcal/mol). However, the final reductive elimination step was much higher in the case of the Rh(I) counterpart (almost 9 kcal/mol more costly). This is consistent with the observed lower reactivity of Rh(I) catalysts (see above, Scheme 3), and might be partially ascribed to the stronger and less polarized nature of C–Rh compared to C–Co bonds.<sup>[26]</sup> Indeed, analysis of the Wiberg bond indexes (WBIs) on the corresponding intermediates (**INT2** and its Rh analog **INT2-Rh**), confirms that the two C–M bonds involved in the reductive elimination are significantly stronger for Rh (WBI's of 0.80 and 0.39) than for cobalt (WBI's of 0.65 and 0.32).<sup>[13]</sup>

With this information at hand, we pursued the experimental identification of some of the computationally located cobalt complex intermediates. Therefore, we mixed equimolar amounts of CoBr<sub>2</sub>, dppp, Zn, ZnI<sub>2</sub> and **2p**, at rt. After 2 h, we observed the formation of a novel cobalt-containing species, as deduced from the major molecular ion peak observed by ESI-MS at *m/z* 746.2. Gratifyingly, this species turned out to be rather stable, and could be analyzed by 1D- and 2D-NMR spectroscopy, confirming its identity as the  $\pi$ -allyl cobaltacyclic species **1p-INT2**, analogous to the theoretically calculated intermediate **INT2**.<sup>[27]</sup> As expected for an intermediate of the catalytic cycle, upon heating at 60 °C, the complex smoothly delivers the bicyclic product **2p** (Scheme 4).<sup>[13]</sup>

In consonance with the isolation of this diamagnetic intermediate, computational analysis of profiles involving cobalt triplet states (*S* = 1) revealed kinetically less favored pathways. In addition, the stationary points along the singlet hypersurface are more stable than their corresponding triplet analogs, and very much in particular in the case of **INT2**.<sup>[13]</sup> However, some eventual single-triplet crossovers along the pathway cannot be fully discarded.

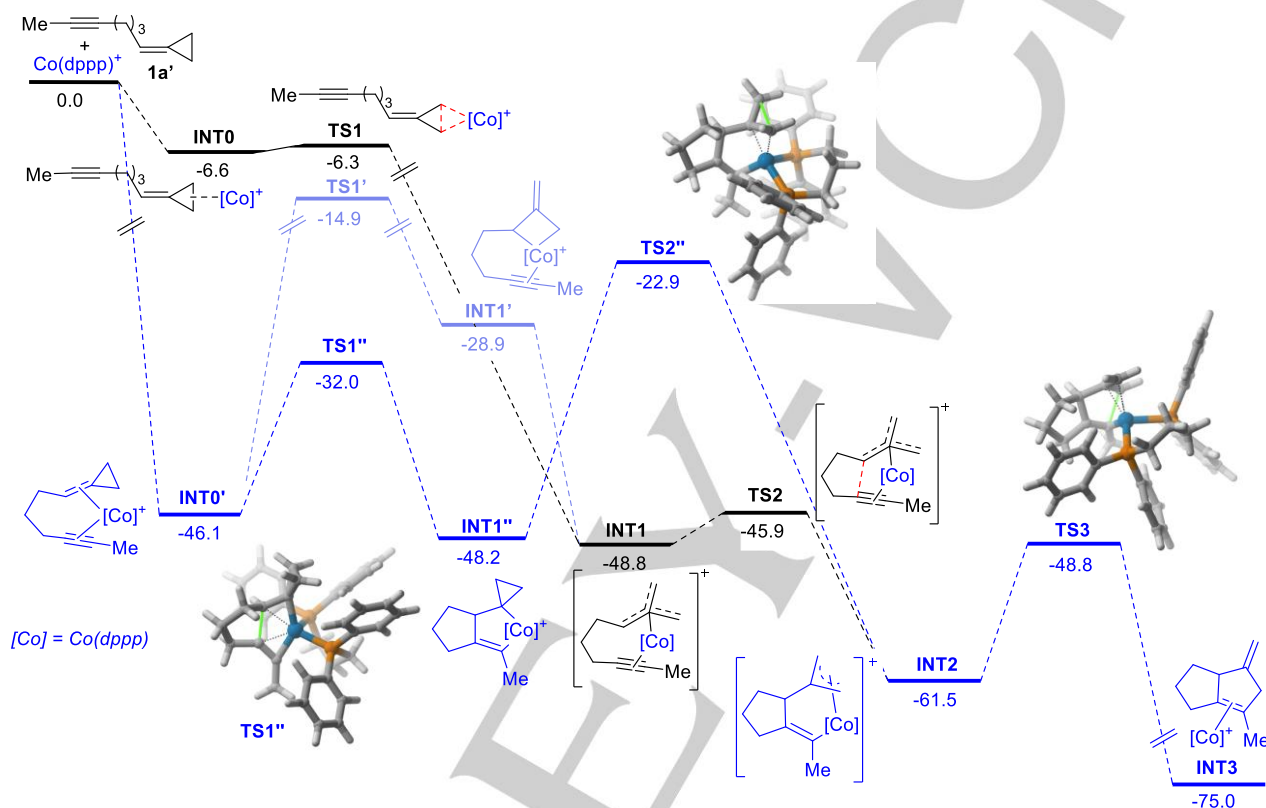


**Scheme 4.** Stoichiometric experiment: Isolation of  $\pi$ -allyl intermediate **1p-INT3**.

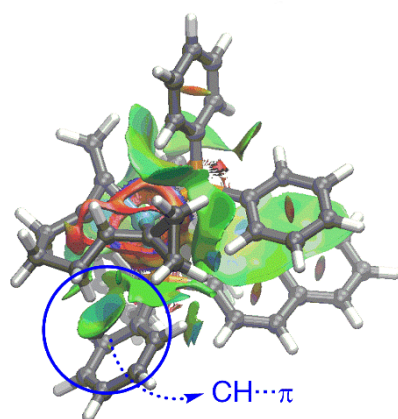
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Finally, to shed some light into the origin of the enantioinduction, we computationally analyzed the migratory insertion process leading to species **INT1''**, via **TS1''**, as it is the enantiodiscriminating step, using **1a'** and the chiral cobalt complex [(*S*)-BINAP-Co]<sup>+</sup>. Our preliminary calculations indicate that the transition state **TS1''(S,S)**, eventually leading to the observed (*S*)-product, lies 1.6 kcal/mol below its corresponding diastereomeric counterpart **TS1''(S,R)**, which is qualitatively consistent with the high enantioselectivity of the process. This energy difference may be in part ascribed to the presence of

stabilizing noncovalent C–H⋯π interactions in **TS1''(S,S)**, established between one of the phenyl groups of BINAP and a C–H bond adjacent to the reactive carbon atom (see green surfaces in Figure 3), interactions that are absent in **TS1''(S,R)**. Moreover, analysis of **TS2**, which is the enantiodetermining step in the alternative TMM mechanistic pathway, also indicates a strong preference for the *S,S*-diastereoisomeric transition state [**TS2(S,S)**], which also features a similar stabilizing C–H⋯π interaction.



**Figure 2.** Computed reaction profile for the reaction model ACP **1a'** and [Co(dppp)]<sup>+</sup>. Relative free energies ( $\Delta G$ , at 298 K) are given in kcal/mol. All data have been computed at the PCM(DCE)-B3LYP-D3/def2-SVP level.



**Figure 3.** Contour plots of the reduced density gradient isosurfaces (density cutoff of 0.03 a.u.) for **TS1''(S,S)**. The green surfaces indicate attractive non-covalent interactions.

In summary, we have developed the first enantioselective cycloaddition of alkylidenecyclopropanes (ACPs) promoted by

any type of earth-abundant metal complex, and the first (3+2) annulation of ACPs promoted by Co catalysts. Moreover, our results also represent the first asymmetric annulations of ACPs with alkynes. The reactions, promoted by a chiral low-valent Co(I) catalyst generated *in situ* from an air-stable Co(II) precursor, provide 5,5- and 6,5- fused bicyclic products in good yields and with excellent enantioselectivities. Mechanistic studies, supported by DFT calculations, allowed us to propose a pathway involving a bisphosphine cobalt(I) cationic complex as the active catalyst, and a key cobaltacycle intermediate (**INT1''**) that evolves via cyclopropane opening to a highly stable  $\pi$ -allyl cobaltacycle, which could even be isolated and characterized by spectroscopic methods. In addition to the novelty and synthetic significance of this method, our results pave the way for the development of novel enantioselective multicomponent cycloadditions based on earth-abundant, non-expensive cobalt catalysts.

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**Keywords:** Cycloaddition, cobalt, alkylidene cyclopropane, enantioselective, earth-abundant metal

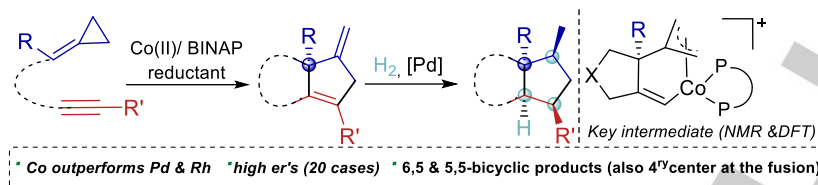
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The first enantioselective cycloaddition of alkyldenecyclopropanes (ACPs) promoted by any type of earth-abundant metal is described. In particular, a chiral low-valent Co(I) complex generated *in situ* from a Co(II) precursor, catalyzes an intramolecular (3+2) cycloaddition between ACPs and alkynes, to give fused bicyclic products in good yields and with excellent er's. Experimental data and DFT calculations shed light on the mechanistic details as well as on the reasons behind the superiority of Co over related Rh catalysts.

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