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Synthesis, Coordination Study, and Catalytic Pauson–Khand Reactions of QuinoxP*(CO)$_4$-μ-Alkyne Dicobalt Complexes

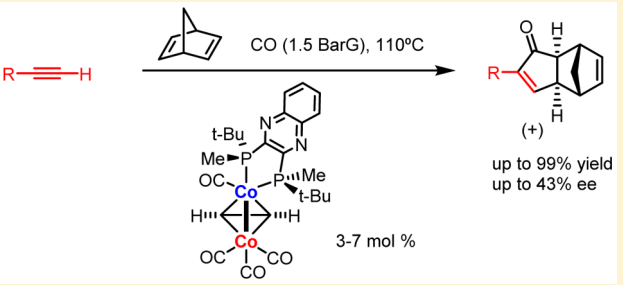
Martí Garçon,[†] Albert Cabré,[†] Xavier Verdaguer,*[,†,‡] and Antoni Riera*[,†,‡]

[†]Institute for Research in Biomedicine (IRB Barcelona), The Barcelona Institute of Science and Technology, Baldiri Reixac 10, Barcelona E-08028, Spain

[‡]Departament de Química Inorgànica i Orgànica, Secció Orgànica. Universitat de Barcelona, Martí i Franquès 1, Barcelona E-08028, Spain

Supporting Information

ABSTRACT: The coordination of the P-stereogenic and sterically demanding bisphosphine QuinoxP* to μ-alkyne dicobalt hexacarbonyl complexes was studied experimentally and computationally. Whereas the coordination occurred exclusively in a chelating fashion, the diastereoselectivity was highly substrate dependent. However, it could be explained from the computed structure and energies of the different coordination modes. The fluxional behavior of these complexes was also studied computationally. Their performance as catalysts for the Pauson–Khand reaction was explored, and outstanding reactivity was observed. Although the asymmetric induction was low to moderate, the stereochemical outcome could be mechanistically rationalized. This report provides promising results in terms of reactivity and mechanistic understanding for further developments of highly active chiral catalysts for intermolecular Pauson–Khand reactions.



INTRODUCTION

Dicobalt octacarbonyl is one of the most popular dinuclear complexes bearing a metal–metal bond, which has been used in a wide range of carbonylative[1] and noncarbonylative processes.[2] Particularly, μ-alkyne dicobalt hexacarbonyl complexes have found many uses, including applications in polymer science[3] and biomedicine.[4] Furthermore, they have become invaluable tools in organic synthesis, as alkyne protecting groups (or stabilizing groups for strained cycloalkynes),[5] or as key components in [2 + 2 + 2] cycloadditions,[6] Nicholas reactions,[7] and Pauson–Khand reactions (PKRs).[8,9]

Their structure consists of a tetrahedral core,[10] in which the alkyne coordinates to both cobalt atoms in a μ-η^2:η^2 fashion and the remaining CO ligands complete the coordination spheres, in such a way that these complexes belong to the C_{2v} symmetry point group, when the alkyne is symmetrically substituted. If the alkyne is not symmetrical, the C_2 axis is then lost and the two homotopic cobalt atoms become enantiotopic.

Several efforts have been devoted to the desymmetrization of these alkyne dicobalt clusters by using chiral ligands or reagents for applications in asymmetric synthesis.[11] Although the substitution of CO's by chiral ligands can give rise to multiple coordination modes, this number is normally reduced to one or two diastereomers due to fluxional processes which interconvert equatorial (eq) and axial (ax) positions within a cobalt atom (Figure 1).[12]

Bidentate ligands can bind to the same cobalt atom in a chelated (κ^2) fashion or to both cobalt atoms in a bridged (μ-κ^1:κ^1) fashion.[13] For unsymmetrical alkynes there could be up to 4 bridged and 12 chelated possible diastereomers that would be reduced to 2 bridged and 6 chelated isomers using C_2-symmetric ligands.[14] However, in most cases due to selectivity and fluxionality, the number of diastereomers is reduced to only 2.

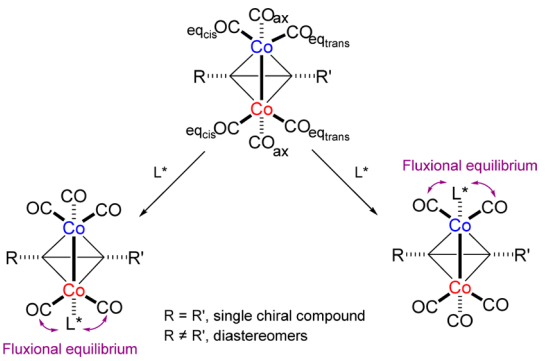


Figure 1. Nomenclature of the different CO positions (supposing that R has higher priority than R′) and formation of stereoisomeric alkyne dicobalt complexes when introducing a chiral monodentate ligand (L*).

The coordination mode of bidentate ligands is actually crucial in the reactivity of the complexes. Furthermore, their

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properties and stability can also vary significantly. An illustrative example are the BINAP-(μ-alkyne)dicobalt carbonyl complexes reported independently by Laschat[15] and Gibson.[16] From *tert*-butylacetylene only a bridged isomer was obtained, whereas for less hindered alkynes (such as acetylene, phenylacetylene, and methyl propiolate) and enynes chelated isomers are selectively formed. Remarkably, the reactivity of the bridged BINAP-(μ-^{t}BuCCH)-$Co_2(CO)_4$ complex in the Pauson–Khand reaction is practically nonexistent, whereas for the chelated examples the reaction occurs in moderate yields.

Although several efficient systems have been developed for the asymmetric intramolecular reaction,[14b,17] the intermolecular PKR has proven to be much more challenging. In general, the poor reactivity of bisphosphine complexes in the Pauson–Khand reaction is one of the principal reasons for the scarce presence of these complexes in the literature, with only few examples that show significant activity in the intermolecular PKR[14a,18] using electron-poor bisphosphines.

Our group has developed several chiral bidentate bridging hemilabile (P,S) ligands which gave outstanding results in terms of enantioselectivity in the intermolecular PKR.[19] However, the Co complexes of these ligands had to be used stoichiometrically, since they gave poor enantioselectivities in the catalytic version of the reaction.[20]

Very recently our group reported the first Co-catalyzed example with good yields and useful levels of enantioselectivity using the novel bisphosphine ThaxPHOS.[18] The range of alkynes, however, was limited to silylacetylenes. These inspiring results in terms of activity and enantioselectivity prompted us to study other bisphosphine cobalt complexes in order to deeply understand the behavior of these complexes. This would ultimately enable us to design proficient and more general chiral catalysts for the catalytic and intermolecular PKR.

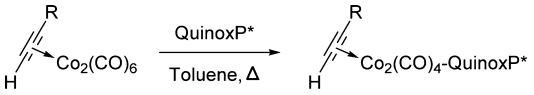
We decided to use the bulky *P*-stereogenic C_2-symmetric ligand QuinoxP*, developed by Imamoto and co-workers,[21] as it has been proved to provide excellent results in a wide range of asymmetric transformations.[22] Furthermore, the proximity of the chiral centers to the metal, the significant steric hindrance, and the relatively electron poor character given by the quinoxaline ring, made QuinoxP* a promising ligand to develop efficient PKR catalysts and an interesting case study to analyze all these effects in μ-alkyne dicobalt complexes, as well as to gain a deeper insight into these useful complexes. Hence, we describe herein the synthesis, coordination study, and catalytic activity of QuinoxP*$(CO)_4$-μ-alkyne dicobalt complexes.

RESULTS AND DISCUSSION

Synthesis and Stability of QuinoxP* Complexes. As a representative set of terminal alkynes, we selected acetylene (**1a**), 1-decyne (**1b**), phenylacetylene (**1c**), 2-methylbut-3-yn-2-ol (**1d**), and trimethylsilylacetylene (**1e**). The starting μ-alkyne dicobalt hexacarbonyl complexes **2** were prepared by mixing $Co_2(CO)_8$ with the corresponding alkynes in hexane. In the case of (μ-HCCH)-$Co_2(CO)_6$, acetylene gas was bubbled into a $Co_2(CO)_8$ solution. The complexes obtained can be purified by filtration through silica to remove the remaining unreactive cobalt decomposition to afford the pure desired complexes in excellent yields (see Table S1 in the Supporting Information).

Once the hexacarbonyl complexes were prepared, QuinoxP* complexes **3** were subsequently synthesized by ligand substitution of two carbonyl ligands. The initial yields obtained were low; therefore, a screening to find the optimal conditions was performed. No reaction was observed at room temperature; thus, higher temperatures were required. The optimal conditions found were heating at 70 °C for 5 h (in some substrates longer reaction times are not detrimental) and purging the system (with N_2 or vacuum cycles) every ca. 30 min, to avoid CO overpressure and facilitate the substitution. However, total elimination of the CO (i.e., under constant N_2 flow) destabilizes the complexes. Working on a small scale and filtering the starting hexacarbonyl complex through a silica plug immediately before the reaction usually provides the best yields (Table 1). These complexes are relatively unstable, producing small amounts of paramagnetic cobalt that hinder their characterization by NMR (see Figure S1 in the Supporting Information).

Table 1. Preparation (under Optimized Conditions) of QuinoxP*-μ-alkyne-$Co_2(CO)_4$ Complexes



2a-e **3a-e**

entry	starting complex	product, yield (%)	diastereomeric ratio[a]
1	**2a** (R = H)	**3a**, 36	
2	**2b** (R = *n*-octyl)	**3b**, 45	1.3:1
3	**2c** (R = Ph)	**3c**, 70	4:1
4	**2d** (R = $C(Me)_2OH$)	**3d**, 33	8:1
5	**2e** (R = TMS)	**3e**, 46	10:1

[a]Measured by ^{31}P NMR.

Characterization and Structural Analysis. All complexes **3** were fully characterized by conventional techniques (^1H, ^{31}P, and ^{13}C NMR, IR, and MS). In all cases, except for the symmetric **3a**, two diastereomers were observed by NMR (Figure 2). Remarkably, for complex **3e** or **3d** with a TMS or

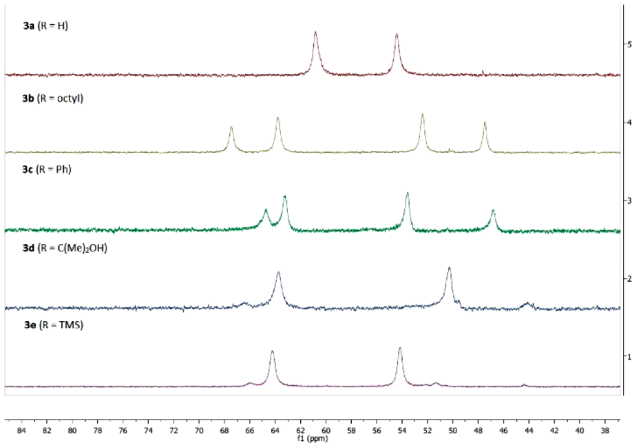


Figure 2. ^{31}P NMR of QuinoxP* complexes **3a–e**.

CMe_2OH substituent, one diastereomer was greatly favored. The selectivity decreased in the case of **3b** (*n*-octyl) and **3c** (Ph). Apparently, the bulky substituents on the alkyne increase the diastereoselectivity of the coordination.

Complex **3c** showed a distinctive equilibration behavior. When the reaction was performed with heating for 4 h, a ca. 1:1 mixture of diastereomers was obtained. However, if the mixture was heated for 6–7 h, equilibration between the two

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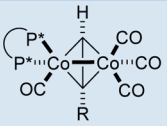
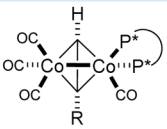
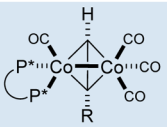
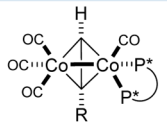
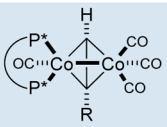
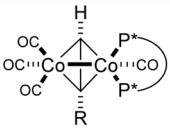
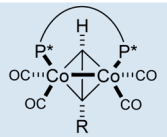
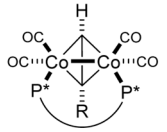
Table 2. Computed Energies (ΔG) of All Possible Coordination Modes of (*S*,*S*)-QuinoxP* Dicobalt Complexes of Different Alkynes (HCCR)[b]

Entry	Complexes	Structure	3a[a] (R=H)	3b' (R=propyl)	3c (R=Ph)	3d (R=C(Me)$_2$OH)	3e (R=TMS)
1	chelated_*pro-R* ax-eq$_{trans}$		0.0	0.1	0.0	0.0	0.0
2	chelated_*pro-S* ax-eq$_{trans}$		0.2	0.0	1.2	1.9	1.4
3	chelated_*pro-R* ax-eq$_{cis}$		-	1.5	3.2	5.1	4.5
4	chelated_*pro-S* ax-eq$_{cis}$		-	2.1	4.0	4.7	2.5
5	chelated_*pro-R* eq-eq		5.8	4.6	6.6	4.8	3.5
6	chelated_*pro-S* eq-eq		-	5.9	7.9	5.9	3.7
7	bridged_*trans*		-	8.6	9.7	8.6	6.0
8	bridged_*cis*		11.4	8.9	9.3	10.5	8.6

[a]Cobalt atoms in complex **2a** are homotopic. In this particular case, the *pro-S*/*pro-R* notation is inappropriate, but it was kept for the sake of generalization with the other substrates. Thus, for **3a**, chelated_*pro-R* (ax-eq$_{trans}$), chelated_*pro-S* (ax-eq$_{trans}$), and chelated_*pro-R* (eq-eq) are in fact conformers that can be interconverted through turnstile rotation. [b]Energies in kcal/mol are referenced to the most stable chelated *trans* diastereomer.

diastereomers occurred to afford a ca. 3:1 diastereomeric mixture. Heating overnight yields a ca. 4:1 mixture of diastereomers, in which the major diastereomer is the one whose X-ray structure was obtained (vide infra).

In order to discern the coordination mode (bridged, chelated, or a mixture of both), the NMR spectra gave little information. Nonetheless, the alkyne proton appeared as a doublet of doublets (dd) with coupling constants approximately in the range $^4J_{H-P}$ = 6.5−8.5 Hz and $^4J_{H-P}$ = 1.8−3.8 Hz, respectively. This fact would be consistent with the presence of chelated isomers, since the coupling constants with an axial and an equatorial phosphorus would be significantly different.

An FT-IR analysis was then performed, and we were pleased to see that for all cases the CO stretching bands were practically identical. The presence of a mixture of bridged and chelated isomers was then discarded. In the case of complexes **3c** and **3b**, the possibility of two bridged diastereomers was considered unlikely, since the fluxional processes would favor the *trans* over the *cis* form. For these reasons, we hypothesized that the coordination of QuinoxP* occurred exclusively via chelation.

In order to gain a deeper insight into these QuinoxP* complexes, molecular orbital calculations were performed. The geometries of the different bridged and chelated diastereomers of QuinoxP* dicobalt complexes were optimized using density functional theory (DFT) implemented in the Gaussian09 program package.[23] The calculations were done using the B3LYP functional and the standard 6-31+G(d,p) basis set. The energies of all possible diastereomers of the cobalt complexes **3a**−**e** are shown in Table 2.

For symmetrical alkynes such as acetylene, up to four stereoisomers (one bridged and three chelated) are possible. However, by fluxionality between the three chelated isomers bound to the same cobalt atom (ax-eq$_{cis}$, eq$_{cis}$-eq$_{trans}$, and ax-eq$_{trans}$) this number would be reduced to two: just one bridged and one chelated isomer. In the case of the acetylene cobalt

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complex **3a** only one set of signals was observed by NMR (see Figure 2). According to the calculations the most stable isomer is an axial−equatorial chelated complex which is 11.4 kcal/mol more stable than the bridged complex. Therefore, we assumed that those signals correspond to the chelated complex.

For terminal alkynes, two bridged and six chelated complexes were located. Gratifyingly, several trends could be observed. First, the chelated ax-eq$_{trans}$ diastereomers were always the most stable (6−11 kcal/mol lower than the bridged isomer). This can be explained taking into account the size of linker between both phosphorus atoms. The coordination mode (bridged or chelated) is crucially determined by this factor. For instance, for one-atom linkers the coordination is exclusively bridged, since a chelated coordination would afford a strained four-membered ring.[24] According to the present calculations, the linker with two (planar carbon) atoms affords the chelated coordination with the corresponding formation of a five-membered ring. The formation of the bridged isomers is not favored because this type of linker is too small to permit a geometrically unstrained six-membered ring. For bigger linkers, as in the case of BINAP, although the chelated isomer is normally favored, the linker also allows nonstrained bridged coordination modes. For this reason, for *tert*-butylacetylene complexes with BINAP the bridged isomer is obtained,[15] since this disposition minimizes the steric clash of the ligand with the bulky *tert*-butyl group.

The chelated equatorial−equatorial isomers were found to be 3.5−7.9 kcal/mol less stable than the most stable axial−equatorial stereoisomers. As could be expected for steric reasons, the chelated ax-eq$_{cis}$ complexes were 1.5−5.1 kcal/mol less stable than the *trans* species. Therefore, the two most stable stereoisomers were the ax-eq$_{trans}$ form chelated to either the *pro-R* or the *pro-S* cobalt atom (Figure 3).

In the case of **3b** a *n*-propyl chain was used as a model of the *n*-octyl chain to reduce the computational cost. In this case both ax-eq$_{trans}$ stereoisomers were nearly equal in energy. However, for **3c**−**e** the difference increased to 1.2, 1.9, and 1.4 kcal mol^{-1}, respectively, toward the complex with the *S,S* ligand chelated to the *pro-R* cobalt atom (Table 2 and Figure 3).

Most gratifyingly, the X-ray diffraction of the major diastereomer of complex **3c** (Figure 4) showed a *trans*-axial−equatorial chelated geometry in complete agreement with the most stable calculated geometry. Moreover, the employed level of theory accurately reproduced the experimental geometry, since the difference in the key geometric parameters (bond distances and angles) between the computed and the experimental structures (X-ray) was less than 1% (Table S1 in the Supporting Information).

In summary, the calculations nicely reproduce the experimental mixture of complexes observed by ^{31}P NMR. For complexes **3d**,**e**, the difference between the two diastereomers (ax-eq$_{trans}$ diastereomers) is around 1.4−1.9 kcal/mol, and one diastereomer is mainly observed. For **3c**, with a difference of around 1.2 kcal/mol, both diastereomers are formed, but equilibration between them occurs to afford an enriched mixture of the most stable diastereomer. Finally, for complex **3b** (in the calculations the octyl chain has been replaced by a propyl chain to avoid excessive computational cost) there is practically no energetic difference between diastereomers, and both are experimentally obtained and no equilibration is observed. We can then conclude that there is a thermodynamic control in the coordination of ligands to alkyne dicobalt complexes. The equilibration observed for complex **3c**, as well as many other reported examples of this behavior,[18−20] strongly support this conclusion, allowing DFT calculations to become a useful predictive tool for the diastereoselectivity of the coordination of chiral ligands to these complexes, by solely computing the energies of the products (alkyne-$Co_2(CO)_n$-L_n complexes). Nonetheless, it must be taken into account that in this case the computed energetic differences are rather small,

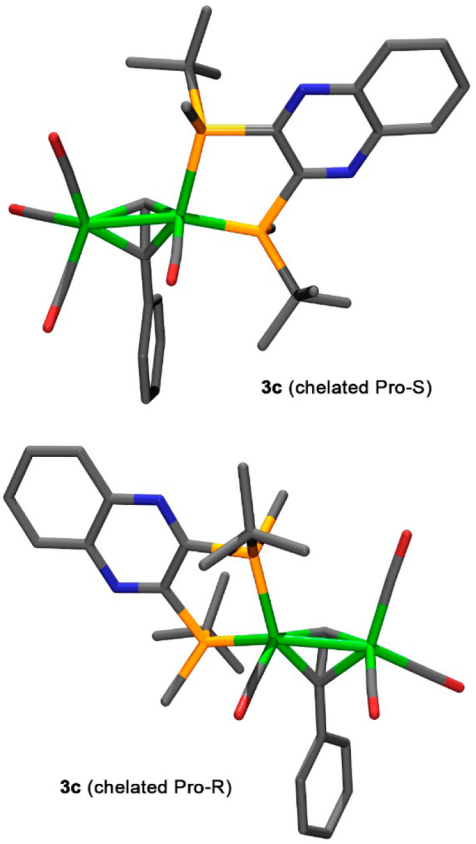

Figure 3. The two most stable computed structures for complex **3c** from (*S,S*)-QuinoxP*, corresponding to *pro-S* (1.2 kcal/mol) and *pro-R* (0.0 kcal/mol) axial−equatorial$_{trans}$ chelated diastereomers. Hydrogen atoms are omitted for clarity.

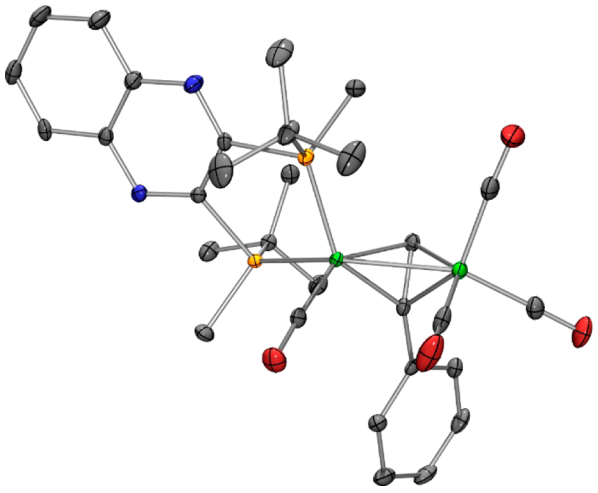

Figure 4. X-ray structure of the major diastereomer of complex **3c** from (*S,S*)-QuinoxP*: ORTEP drawing showing 50% probability ellipsoids. The elucidated structure corresponds to the *pro-R* ax-eq$_{trans}$ chelated isomer.

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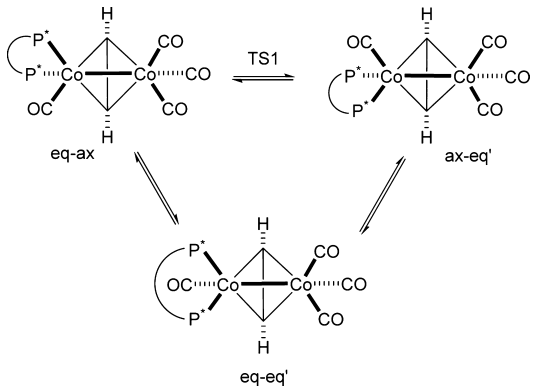
and although they are systematically consistent with the experimental results, cannot be used in quantitative trends.

Fluxionality of QuinoxP* around a Single Cobalt Center. For the symmetric complex **2a**, derived from acetylene, both cobalt centers are homotopic. Thus, coordination of (*S*,*S*)-QuinoxP* to either Co center provides a single stereoisomer. However, coordination of the bisphosphine ligand around the cobalt atom gives rise to three possible diastereomeric conformers (eq-ax/ax-eq′/eq-eq′, Scheme 1).

Scheme 1. Fluxional Behavior for Complex 3a[a]



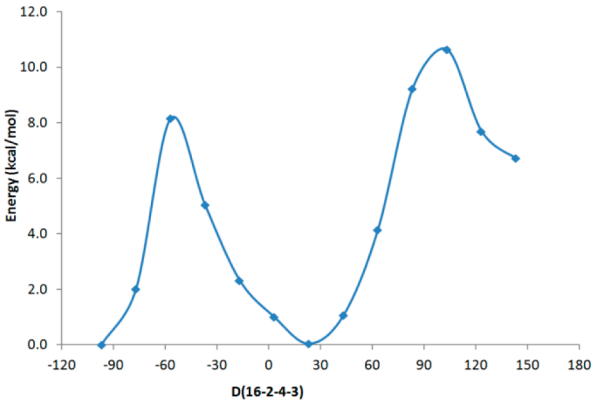
[a]Turnstile rotation interconverts three possible diastereomeric conformers.

While the ^{31}P NMR spectrum of complex **3a** showed a single set of signals corresponding to each diastereotopic phosphorus atom (see Supporting Information), calculations suggested that the eq-ax/ax-eq′ conformers were almost equal in energy (Table 2). These results implied that there had to be low-energy fluxional pathways which interconverted both conformers.

With the aim of studying more in detail the fluxional processes occurring in chelated bisphosphine-$(CO)_4$-μ-alkyne dicobalt complexes, we decided to perform a computational search for the barriers of turnstile rotation in complex **3a**. A scan of the potential energy surface of rotation was performed, and as expected, single barriers between conformers were observed. The barrier between the ax-eq′/eq-eq′ and eq-ax/eq-eq′ conformers was higher (around 11 kcal/mol) than the barrier between ax-eq′/eq-ax conformers. Thus, there is a low-energy pathway of direct interconversion between ax-eq′ and eq-ax diastereomeric conformers. Nevertheless, the longer interconversion pathway with two barriers going through the eq-eq′ intermediate is not excessively disfavored; therefore, at room temperature complete turnstile rotation should occur (Chart 1).

In order to better characterize the fluxional process, the lowest energy transition state (**TS1**) between eq-ax/ax-eq′ conformers was specifically computed, showing it to be 9.2 kcal/mol higher in energy than the lowest energy conformer. It should be highlighted that the computed potential energy is very similar to the value obtained for the dihedral angle scan. While for the three minima the cobalt atom bearing the bisphosphine ligand has a pseudo-octahedral geometry, for **TS1** it adopts a pseudo-trigonal-prismatic geometry (Figure 5). For the sake of comparison, the turnstile rotation of the three CO ligands attached to the other cobalt atom of complex **3a** was also examined. The potential energy barrier obtained (in the scan analysis) was just around 3 kcal/mol, which implies

Chart 1. Potential Energy Scan of the Turnstile Rotation of Complex 3a for the Interconversion of Conformers, with Respect to the Dihedral Angle (deg) P16−Co2−Co4−C3



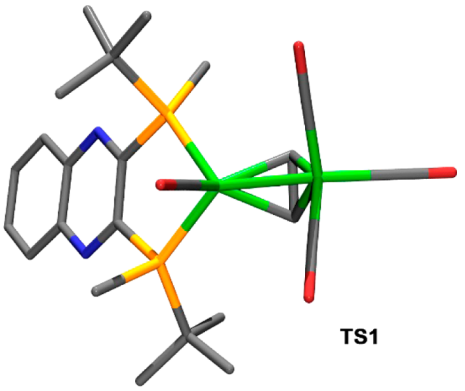


Figure 5. Computed structure for **TS1**, resulting from turnstile rotation of QuinoxP* in complex **3a**.

extremely fast rotation. Logically, the rotation of QuinoxP* is slower, but it is fast enough to experimentally observe a single set of signals for complex **3a**.

Catalytic Performance. Cobalt QuinoxP* complexes **3** were then evaluated as catalysts for the intermolecular Pauson−Khand reaction of alkynes **1b−j**. Since after the first catalytic cycle all catalysts should perform the same way, we used **3a**,**c** as catalysts for practical reasons. In this way, the yield obtained is truly from the catalytic reaction, since the first cycle affords a different adduct. The results are summarized in Table 3. Except for the more hindered alkynes (**1d**,**e**,**h**), we were delighted to observe that our catalysts were highly active PKR catalysts. In general, the desired products were obtained in excellent yields and purity with 3−7% mol catalyst loading. The lack of reactivity of more hindered alkynes could be attributed to excessive steric encumbrance of the ligand and the bulky TMS or $-C(Me)_2OH$ groups. In the case of propargyl acetate (see entry 6, Table 3) a remarkable 40% yield was obtained. It should be noted that this is a difficult substrate for PKR since the stoichiometric PKR under either thermal or NMO activation gives very poor yields. For the more demanding internal alkyne (see entry 9, Table 3), the reaction rate is slower but the yield after 16 h is also good. Thus, we can conclude that QuinoxP*-Co_2 complexes are highly active catalysts in the intermolecular Pauson−Khand reaction of nonbulky alkynes. The steric hindrance imparted by the ligand seems to boost the PKR yields, except for very hindered alkynes. In those cases, the excessive hindrance proved to be deleterious.

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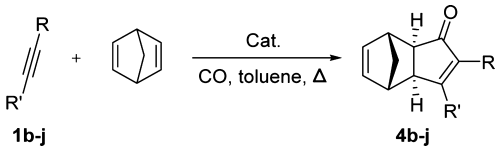
Table 3. Enantioselective Catalytic Pauson–Khand Reactions[a]



1b-j 4b-j

entry	alkyne	catalyst, catalyst loading (mol %)	chirality of the ligand	reaction conditions	product, yield (%)	ee (%)	$[\alpha]_D$
1	**1b** (R = *n*-octyl, R′ = H)	**3c**, 5	*S,S*	overnight at 95 °C	**4b**, 99	34–41	+
2	**1c** (R = Ph, R′ = H)	**3c**, 3	*S,S*	overnight at 100 °C	**4c**, 94	<5	
3	**1e** (R = TMS, R′ = H)	**3e**, 4	*S,S*	overnight at 120 °C	**4e**, 12	<5	
4	**1d** (R = $C(Me)_2OH$, *R′ = H)*	**3c**, 5	*S,S*	overnight at 110 °C	**4d**, 16	25	+
5	**1f** (R = CH_2OTBS, R′ = H)	**3a**, 7	*R,R*	6 h at 100 °C	**4f**, 86	8	
6	**1g** (R = CH_2OAc, R′ = H)	**3c**, 5	*S,S*	overnight at 100 °C	**4g**, 40	5	
7	**1h**, (R = CH(Me)OH, R′ = H)	**3c**, 7	*S,S*	overnight at 100 °C	**4h**, 22[b]	30	+
8	**1i** (R = cyclopropyl, R′ = H)	**3a**, 5	*S,S*	overnight at 110 °C	**4i**, 99	43	+
9	**1j** (R = Ph, R′ = Ph)	**3c**, 7	*S,S*	overnight at 120 °C	**4j**, 54[c]	15	+

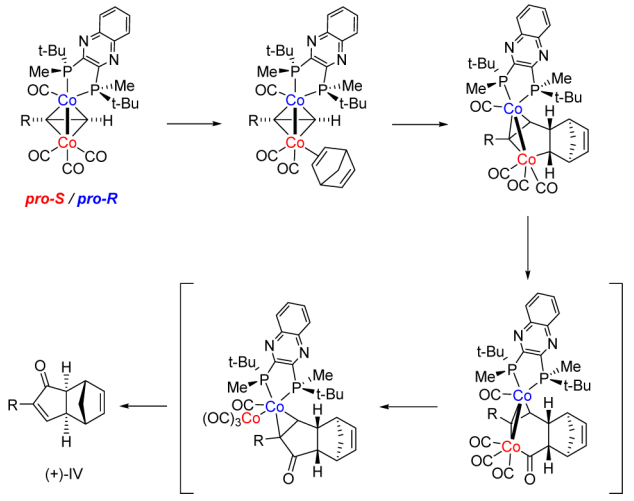
[a]The CO pressure was set to 1.5 barG. [b]Obtained as a ca. 2:1 mixture of diastereomers. [c]54% yield with 56% conversion.

The enantioselectivity of the reactions was then analyzed by chiral HPLC (Table 3). Although the enantiomeric excesses obtained were low to moderate, it is noteworthy that for 1-decyne (**1b**, entry 1, Table 3) and cyclopropylacetylene (**1i**, entry 8, Table 3) the asymmetric induction was significant, these results being the best enantioselectivities reported to date for substrates with alkyl chains.[18]

For all cases in which the induction was significant, the optical rotation was observed to be dextrorotatory (+) when (*S,S*)-QuinoxP* was employed. Since the substituent of the alkyne has little effect on the optical rotation of these PK adducts, we assigned the absolute configuration of these adducts to be (+)-(*S,S,S,R*)-**IV**, as shown in Scheme 2.[13]

The stereochemical outcome observed can be rationalized by taking into account the accepted mechanism for the intermolecular PKR,[25] as well as the stereochemical pathway that links the coordination of the olefin to the absolute configuration of the final adduct.[12] We needed to assume that *anti* cobaltacycles are significantly more stable than the *syn* species, which is supported by calculations.[26] According to this scheme, coordination of the olefin to the *pro-S* cobalt atom would lead to the (+)-**IV** adduct, whereas coordination to the *pro-R* atom would afford its enantiomer. According to our calculations (Table 2) starting from (*S,S*)-QuinoxP* the most stable diastereomer is that in which the ligand coordinates to the *pro-R* cobalt atom. Therefore, the olefin should coordinate to the *pro-S* Co leading to the dextrorotatory isomer (+)-**IV** as experimentally observed.

Scheme 2. Stereochemical Pathway from the Most Stable Diastereomer of (*S,S*)-QuinoxP* Complex to the Dextrorotatory PK Adduct[a]



[a]The stereochemically irrelevant steps of CO insertion and reductive elimination are included (in brackets) for mechanistic completeness and clarity.

CONCLUSIONS

Imamoto's P-stereogenic and bulky bisphosphine ligand QuinoxP* was employed successfully in the preparation of μ-alkyne-$Co_2(CO)_4$(QuinoxP*) complexes. Their chelated coordination mode was disclosed both experimentally and computationally, and its turnstile fluxionality has been studied by theoretical calculations. Their activity as PKR catalysts has also been investigated, and remarkable reactivity has been observed. Although the asymmetric induction is still not synthetically useful, the good reactivity and mechanistic insight of this report will help in the future development of new efficient chiral catalysts for the catalytic, intermolecular Pauson–Khand reaction.

EXPERIMENTAL SECTION

Computational Considerations. The geometries of the products were optimized using the B3LYP hybrid exchange-correlation functional with the Gaussian09 program suite. Stationary points were characterized depending on their imaginary frequencies (1 and 0 for TSs and minima, respectively). The split-valence 6-31+G(d,p) basis set was employed. The solvent effects were not taken into account, since the reactions were carried out in rather nonpolar solvents.

Experimental Procedures and Characterizations. *(R,R)-QuinoxP*-$Co_2(CO)_4$-(μ-HCCH) (**3a**).* Freshly filtered (through a silica plug) acetylene dicobalt hexacarbonyl complex **2a** (60 mg, 0.19 mmol, 1.1 equiv) was dissolved in anhydrous toluene (1.5 mL). A solution of (*R,R*)-QuinoxP* (60 mg, 0.18 mmol, 1 equiv) in anhydrous toluene (3 mL) was then added dropwise. The resulting mixture was stirred at 70 °C for 4 h. The system was purged with vacuum/N_2 cycles every 5 min for 30 min, then every 10 min for 1 h, and finally every 30 min for 2.5 h. The crude product was then filtered through an alumina plug, and

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the product was purified by column chromatography in neutral alumina using hexane/EtOAc (from 100/0 to 90/10) as the eluent to afford **3a** (38 mg, 36% yield) as a dark red oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 1.06 (d, $^3J_{H-P}$ = 14.3 Hz, 9H), 1.17 (d, $^3J_{H-P}$ = 14.6 Hz, 9H), 1.76 (d, $^2J_{H-P}$ = 7.6 Hz, 3H), 1.93 (d, $^2J_{H-P}$ = 7.0 Hz, 3H), 5.18−5.24 (m, 2H), 7.84−7.90 (m, 2H), 8.15−8.21 (m, 2H). ^{31}P{^{1}H} NMR (202 MHz, $CDCl_3$): δ (ppm) 54.41, 60.81. ^{13}C NMR (126 MHz, $CDCl_3$): δ (ppm) 11.3−12.2 (m, 2 × CH_3), 27.0 (s, 6 × CH_3), 34.1 (d, $^1J_{C-P}$ = 19.9 Hz, C), 35.2 (d, $^1J_{C-P}$ = 16.7 Hz, C), 70.2 (d, $^3J_{C-P}$ = 6.5 Hz, CH), 71.7 (d, $^2J_{C-P}$ = 9.5 Hz, CH), 130.2 (d, $^4J_{C-P}$ = 7.9 Hz, 2 × CH), 131.6 (d, $^5J_{C-P}$ = 6.1 Hz, 2 × CH), 140.9 (d, $^3J_{C-P}$ = 5.9 Hz, C), 141.2 (d, $^3J_{C-P}$ = 5.4 Hz, C), 160.5−162.5 (m, 2 × C), 204.9−207.0 (m, 3 × C), 208.1−209.7 (m, C). IR (ATR) ν (cm^{-1}): 2955, 2926, 2870, 2895, 2033, 1960, 1474, 886, 763. HRMS (ESI): calcd for $[C_{23}H_{30}Co_2N_2O_3P_2]^+$ 562.0390, found 562.0404 [M − CO]$^+$.

(S,S)-QuinoxP-$Co_2(CO)_4$-(μ-HCC$(CH_2)_7CH_3$) (**3b**).* 1-Decyne dicobalt hexacarbonyl complex **2b** (112 mg, 0.26 mmol, 1 equiv) was dissolved in anhydrous toluene (5 mL). A solution of (*S,S*)-QuinoxP* (90 mg, 0.26 mmol, 1 equiv) in anhydrous toluene (2 mL) was then added dropwise. The resulting mixture was stirred at 80 °C overnight with a gas outlet. The crude was filtered through an alumina plug and the product was purified by column chromatography in silica gel using hexane/EtOAc (from 100/0 to 90/10) as the eluent to afford **3b** (as a 1/1 mixture of diastereomers) (82 mg, 45% yield) as a dark red oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 0.85−0.91 (m, 6H), 0.94 (d, $^3J_{H-P}$ = 14.2 Hz, 9H), 1.01 (d, $^3J_{H-P}$ = 13.8 Hz, 9H), 1.13 (d, $^3J_{H-P}$ = 14.5 Hz, 9H), 1.13 (d, $^3J_{H-P}$ = 14.0 Hz, 9H), 1.21−1.42 (m, 20H), 1.44−1.51 (m, 2H), 1.69 (d, $^2J_{H-P}$ = 7.9 Hz, 3H), 1.71−1.77 (m, 1H), 1.80−1.86 (m, 6H), 1.87−1.96 (m, 1H), 2.01 (d, $^2J_{H-P}$ = 6.1 Hz, 3H), 2.67−2.85 (m, 2H), 2.86−3.02 (m, 2H), 5.20 (d, $^4J_{H-P}$ = 12.5 Hz, 1H), 5.32 (d, $^4J_{H-P}$ = 8.1 Hz, 1H), 7.80−7.92 (m, 4H), 8.12−8.25 (m, 4H). ^{31}P{^{1}H} NMR (202 MHz, $CDCl_3$): δ (ppm) 47.47, 52.40, 63.79, 67.46. ^{13}C NMR (126 MHz, $CDCl_3$): δ (ppm) 10.5 (d, $^1J_{C-P}$ = 16.5 Hz, CH_3), 10.9 (d, $^1J_{C-P}$ = 14.4 Hz, CH_3), 11.1 (d, $^1J_{C-P}$ = 6.5 Hz, CH_3), 11.8 (d, $^1J_{C-P}$ = 18.0 Hz, CH_3), 14.3 (s, CH_3), 22.8 (s, CH_2), 22.9 (s, CH_2), 26.6 (d, $^2J_{C-P}$ = 4.6 Hz, 3 × CH_3), 27.0 (d, $^2J_{C-P}$ = 4.9 Hz, 3 × CH_3), 27.1 (d, $^2J_{C-P}$ = 5.3 Hz, 3 × CH_3), 27.5 (d, $^2J_{C-P}$ = 5.9 Hz, 3 × CH_3), 29.5 (s, CH_2), 29.7 (s, CH_2), 29.8 (s, CH_2), 30.0 (s, CH_2), 32.0 (d, $^3J_{C-P}$ = 3.9 Hz, CH_2), 32.1 (s, CH_2), 34.1 (d, $^1J_{C-P}$ = 16.8 Hz, C), 34.8 (dd, $^1J_{C-P}$ = 22.6 Hz, $^3J'_{C-P}$ = 4.0 Hz, C), 35.2 (d, $^1J_{C-P}$ = 17.4 Hz, C), 36.1 (s, CH_2), 72.7 (s, CH), 78.7 (s, CH), 130.0−130.4 (m, 4 × CH), 131.3−131.7 (m, 4 × CH), 140.5 (s, C), 141.2 (s, C), 141.6 (s, C), 205 (s, 4 × C). IR (ATR) ν (cm^{-1}): 3050, 2958, 2923, 2860, 2026, 1958, 1540, 1505, 1473, 1195, 1144, 885, 761, 734. HRMS (ESI): calcd for $[C_{32}H_{46}Co_2N_2O_4P_2 + H^+]$ 703.1670, found 703.1642.

(S,S)-QuinoxP-$Co_2(CO)_4$-(μ-HCCPh) (**3c**).* Phenylacetylene dicobalt hexacarbonyl complex **2c** (64 mg, 0.16 mmol, 1 equiv) was dissolved in anhydrous toluene (2 mL). A solution of (*S,S*)-QuinoxP* (55 mg, 0.16 mmol, 1 equiv) in anhydrous toluene (2 mL) was then added dropwise. The resulting mixture was stirred at 70 °C for 7 h. The system was purged with a nitrogen flow every 30 min to remove the CO. The crude mixture was filtered through an alumina plug, and the product was purified by column chromatography in silica gel using hexane/EtOAc (from 100/0 to 90/10) as the eluent to afford **3c** (as a 3/1 mixture of diastereomers) (76 mg, 70% yield) as a dark red oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 0.71 (d, $^3J_{H-P}$ = 14.4 Hz, 9H), 0.82 (d, $^3J_{H-P}$ = 14.9 Hz, 9H*), 1.06 (d, $^3J_{H-P}$ = 13.8 Hz, 9H*), 1.17 (d, $^3J_{H-P}$ = 14.2 Hz, 9H), 1.52 (d, $^2J_{H-P}$ = 8.5 Hz, 3H*), 1.77 (d, $^2J_{H-P}$ = 8.3 Hz, 3H), 1.92 (d, $^2J_{H-P}$ = 6.7 Hz, 3H), 2.06 (d, $^2J_{H-P}$ = 6.2 Hz, 3H*), 5.51 (d, $^4J_{H-P}$ = 12.1 Hz, 1H*), 5.66 (dd, $^4J_{H-P}$ = 8.5 Hz, $^4J'_{H-P}$ = 1.8 Hz, 1H), 7.13−7.30 (m, 6H), 7.59−7.71 (m, 4H), 7.81−7.91 (m, 4H), 8.10−8.25 (m, 4H). ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$): δ (ppm) 46.83, 53.59, 63.24, 64.76. ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 10.7−11.4 (m, 2 × CH_3), 26.6 (d, $^2J_{C-P}$ = 4.8 Hz, 3 × CH_3), 27.5 (d, $^2J_{C-P}$ = 5.9 Hz, 3 × CH_3), 34.1 (d, $^1J_{C-P}$ = 17.7 Hz, C), 35.0 (d, $^1J_{C-P}$ = 17.7 Hz), 72.4 (s, CH), 125.9 (s, CH), 128.1 (d, $^4J_{C-P}$ = 9.0 Hz, 2 × CH), 129.8−131.0 (m, 4 × CH), 131.5 (d, $^5J_{C-P}$ = 3.3 Hz, 2 × CH), 140.6 (s, C), 141.6 (s, C), 143.3 (s, C), 203.8 (s, 4 × C). IR (ATR) ν (cm^{-1}): 3063, 3015, 2958, 2920, 2901, 2863, 2031, 1963, 1473, 1215, 883, 751. HRMS (ESI): calcd for $[C_{29}H_{34}Co_2N_2O_3P_2]^+$ 638.0703, found 638.0699 [M − CO]$^+$. Asterisks denote signals corresponding to a diastereomer.

(R,R)-QuinoxP-$Co_2(CO)_4$-(μ-HCCC(Me_2)OH) (**3d**).* 2-Methyl-3-butyn-2-ol dicobalt hexacarbonyl complex **2d** (98 mg, 0.26 mmol, 1 equiv) was dissolved in anhydrous toluene (5 mL). A solution of (*R,R*)-QuinoxP* (90 mg, 0.26 mmol, 1 equiv) in anhydrous toluene (2 mL) was then added dropwise. The resulting mixture was stirred at 80 °C overnight with a gas outlet. The crude mixture was filtered through an alumina plug, and the product was purified by column chromatography using hexane/EtOAc (from 100/0 to 50/50) as the eluent to afford **3d** (56 mg, 33% yield) as a dark red oil. ^{1}H NMR (400 MHz, CD_3CN): δ (ppm) 0.93 (d, $^3J_{H-P}$ = 14.3 Hz, 9H), 1.16 (d, $^3J_{H-P}$ = 14.1 Hz, 9H), 1.60 (s, 3H), 1.64 (s, 3H), 1.87 (d, $^2J_{H-P}$ = 7.7 Hz, 3H), 1.88 (d, $^2J_{H-P}$ = 7.6 Hz, 3H), 2.54 (s, 1H), 5.48 (dd, $^4J_{H-P}$ = 6.6 Hz, $^4J'_{H-P}$ = 3.8 Hz, 1H), 7.93−7.99 (m, 2H), 8.17−8.25 (m, 2H). ^{31}P{^{1}H} NMR (202 MHz, CD_3CN): δ (ppm) 50.32, 63.76. ^{13}C NMR (126 MHz, CD_3CN): δ (ppm) 11.4−12.1 (m, 2 × CH_3), 27.6 (s, 3 × CH_3), 27.9 (d, $^2J_{C-P}$ = 5.9 Hz, 3 × CH_3), 32.4 (s, CH_3), 34.8−34.9 (m, C), 35.0 (s, CH_3), 36.1 (d, $^1J_{C-P}$ = 17.3 Hz, C), 70.5 (s, CH), 72.6 (s, C), 80.9 (s, C), 130.7 (d, $^4J_{C-P}$ = 10.6 Hz, 2 × CH), 132.9 (d, $^5J_{C-P}$ = 15.8 Hz, 2 × CH), 141.4 (s, C), 141.9−143.1 (m, C), 163.0−164.3 (m, 2 × C), 204.9−205.9 (m, 4 × C). IR (ATR) ν (cm^{-1}): 3370, 2958, 2926, 2898, 2866, 2054, 2026, 1963, 1173, 889. HRMS (ESI): calcd for $[C_{27}H_{36}Co_2N_2O_5P_2 + H^+]$ 649.0836, found 649.0832.

(S,S)-QuinoxP-$Co_2(CO)_4$-(μ-HCCTMS) (**3e**).* Trimethylsilylacetylene dicobalt hexacarbonyl complex **2e** (101 mg, 0.26 mmol, 1 equiv) was dissolved in anhydrous toluene (5 mL). A solution of (*S,S*)-QuinoxP* (90 mg, 0.26 mmol, 1 equiv) in anhydrous toluene (2 mL) was then added dropwise. The resulting mixture was stirred at 70 °C with a gas outlet for 4 h until completion (TLC monitoring). The crude mixture was filtered through an alumina plug, and the product was purified by column chromatography in silica gel using hexane/EtOAc (from 100:0 to 80:20) as the eluent to afford **3e** (80.6 mg, 46% yield) as a dark red oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 0.35 (s, 9H), 0.92 (d, $^3J_{H-P}$ = 14.2 Hz, 9H), 1.13 (d, $^3J_{H-P}$ = 14.2 Hz, 9H), 1.86 (d, $^2J_{H-P}$ = 8.0 Hz, 3H), 1.93 (d, $^2J_{H-P}$ = 6.6 Hz, 3H), 5.72 (dd, $^4J_{H-P}$ = 7.2 Hz, $^4J'_{H-P}$ = 3.3 Hz, 1H), 7.90−7.83 (m, 2H), 8.23−8.14 (m, 2H). ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$): δ (ppm) 54.16, 64.22. ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 2.8 (d, $^4J_{C-P}$ = 1.9 Hz, 3 × CH_3), 11.9 (dd, $^1J_{C-P}$ = 21.5 Hz, $^3J'_{C-P}$ = 6.4 Hz, CH_3), 12.0 (d, $^1J_{C-P}$ = 15.4 Hz, CH_3), 27.1 (d, $^2J_{C-P}$ = 4.6 Hz, 3 × CH_3), 27.7 (d, $^2J_{C-P}$ = 5.8 Hz, 3 × CH_3), 34.3 (dd, $^1J_{C-P}$ = 19.3 Hz, $^3J'_{C-P}$ = 3.4 Hz, C), 35.3 (d, $^1J_{C-P}$ = 16.9 Hz, C), 85.9 (d, $^3J_{C-P}$ = 6.0 Hz, CH), 130.1 (d, $^4J_{C-P}$ = 2.6 Hz, 2 × CH), 131.5 (d, $^5J_{C-P}$ = 6.1 Hz, 2 × CH), 140.8 (d, $^3J_{C-P}$ = 7.0 Hz, C), 141.8 (d, $^3J_{C-P}$ = 5.7 Hz, C), 159.1 (dd, $^1J_{C-P}$ = 54.1 Hz, $^2J'_{C-P}$ = 45.6 Hz, C), 163.4 (dd, $^1J_{C-P}$ = 49.0 Hz, $^2J'_{C-P}$ = 35.0 Hz, C), 204.3−204.7 (m, 4 × C). IR (ATR) ν (cm^{-1}): 3012, 2954, 2914, 2901, 2852, 2029, 1961, 1480, 1454, 1214, 750. HRMS (ESI): calcd for $[C_{27}H_{38}Co_2N_2O_4P_2Si + H^+]$ 663.0813, found 663.0792.

General Procedure for the Pauson−Khand Reactions. In a pressure glass tube equipped with a manometer, the corresponding alkyne, norbornadiene, and the catalyst were dissolved in anhydrous toluene under a nitrogen atmosphere. The system was purged with nitrogen and then with carbon monoxide. Finally, the pressure of CO was set to 1.5 BarG and the reaction mixture was heated to the temperature indicated below for the appropriate time. The crude reaction mixture was then filtered through an alumina plug, the solvent was removed under reduced pressure, and the product was purified by flash column chromatography on silica gel to afford the desired compounds.

*2-Octyl-3a,4,7,7a-tetrahydro-1H-4,7-methanoinden-1-one (**4b**).* 1-Decyne (0.12 mL, 0.70 mmol, 1 equiv), norbornadiene (0.72 mL, 7 mmol, 10 equiv), and the catalyst **3c** (34 mg, 0.05 mmol, 0.07 equiv) were dissolved in anhydrous toluene (2.5 mL). The CO pressure was set to 1.5 barG, and the mixture was stirred at 120 °C overnight. The crude mixture was then filtered, and the product was purified by flash

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column chromatography on silica gel using hexane/EtOAc (from 100/0 to 90/10) as the eluent to afford **4b** (179 mg, 99% yield, 38% ee) as a reddish oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 0.88 (t, $^3J_{H-H}$ = 7.0 Hz, 3H), 1.18−1.23 (m, 1H), 1.23−1.33 (m, 10H), 1.37 (dt, $^2J_{H-H}$ = 9.3 Hz, $^3J'_{H-H}$ = 1.6 Hz, 1H), 1.41−1.51 (m, 2H), 2.15 (tdt, $^3J_{H-H}$ = 7.3 Hz, $^4J'_{H-H}$ = 2.8 Hz, $^4J''_{H-H}$ = 1.5 Hz, 2H), 2.28 (dt, $^3J_{H-H}$ = 5.0 Hz, $^3J'_{H-H}$ = 1.4 Hz, 1H), 2.64−2.67 (m, 1H), 2.68−2.72 (m, 1H), 2.88−2.92 (m, 1H), 6.20 (dd, $^3J_{H-H}$ = 5.6 Hz, $^3J'_{H-H}$ = 3.0 Hz, 1H), 6.28 (dd, $^3J_{H-H}$ = 5.6 Hz, $^3J'_{H-H}$ = 3.0 Hz, 1H), 7.15 (dt, $^3J_{H-H}$ = 2.7 Hz, $^4J'_{H-H}$ = 1.4 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 14.2 (CH_3), 22.8 (CH_2), 25.1 (CH_2), 27.9 (CH_2), 29.4 (CH_2), 29.5 (CH_2), 29.6 (CH_2), 32.0 (CH_2), 41.3 (CH_2), 43.1 (CH), 43.8 (CH), 47.8 (CH), 52.7 (CH), 137.2 (CH), 138.5 (CH), 151.0 (C), 158.8 (CH), 210.1 (C). IR (ATR) ν (cm^{-1}): 3017, 2926, 2855, 1690, 1458, 1215, 747. HRMS (ESI): calcd for [$C_{18}H_{26}O$ + H^+] 259.2056, found 259.2058. GC: β-DEX (30 m), 180 °C, 1 mL/min, He. $t_R(-)$ = 63.0 min, $t_R(+)$ = 63.3 min.

*2-Phenyl-3a,4,7,7a-tetrahydro-1H-4,7-methanoinden-1-one (**4c**).* Phenylacetylene (90 μL, 0.82 mmol, 1 equiv), norbornadiene (0.59 mL, 5.70 mmol, 7 equiv) and the catalyst **3c** (18 mg, 0.03 mmol, 0.03 equiv) were dissolved in anhydrous toluene (2 mL). The CO pressure was set to 1.5 barG, and the mixture was stirred at 100 °C overnight. The crude mixture was then filtered, and the product was purified by flash column chromatography on silica gel using hexane/EtOAc (from 100/0 to 80/20) as the eluent to afford **4c** (171 mg, 94% yield) as a pale brown solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 1.34 (dt, $^2J_{H-H}$ = 9.4 Hz, $^3J'_{H-H}$ = 1.5 Hz, 1H), 1.43 (dt, $^2J_{H-H}$ = 9.4 Hz, $^3J'_{H-H}$ = 1.6 Hz, 1H), 2.47 (dt, $^3J_{H-H}$ = 5.2 Hz, $^3J'_{H-H}$ = 1.4 Hz, 1H), 2.76−2.80 (m, 1H), 2.82−2.86 (m, 1H), 2.99−3.05 (m, 1H), 6.25 (dd, $^3J_{H-H}$ = 5.6 Hz, $^3J'_{H-H}$ = 3.0 Hz, 1H), 6.33 (dd, $^3J_{H-H}$ = 5.6 Hz, $^3J'_{H-H}$ = 3.1 Hz, 1H), 7.29−7.40 (m, 3H), 7.67−7.72 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 41.5 (CH_2), 43.5 (CH), 44.3 (CH), 47.3 (CH), 53.7 (CH), 127.2 (2 × CH), 128.5 (2 × CH), 128.6 (CH) 131.8 (C), 137.3 (CH), 138.7 (CH), 147.3 (C), 160.0 (CH), 207.8 (C). IR (ATR): ν (cm^{-1}) 3060, 3015, 2974, 2939, 2876, 1694, 1493, 1323, 1215, 1142, 751. HRMS (ESI): calcd for [$C_{16}H_{14}O$ + H^+] 223.1117, found 223.1122. HPLC: Chiralcel OD-H, heptane/IPA 98/2, 1.0 mL/min, λ 254 nm. $t_R(+)$ = 12.1 min, $t_R(-)$ = 15.8 min.

*2-(2-Hydroxypropan-2-yl)-3a,4,7,7a-tetrahydro-1H-4,7-methanoinden-1-one (**4d**).* 2-Methylbut-3-yn-2-ol (64 μL, 0.66 mmol, 1 equiv), norbornadiene (0.68 mL, 6.6 mmol, 10 equiv), and the catalyst **3c** (22 mg, 0.03 mmol, 0.05 equiv) were dissolved in anhydrous toluene (2 mL). The CO pressure was set to 1.5 barG, and the mixture was stirred at 110 °C overnight. The crude mixture was then filtered, and the product was purified by flash column chromatography on silica gel using hexane/EtOAc (from 100/0 to 40/60) as the eluent to afford **4d** (22 mg, 16% yield, 25% ee) as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 1.22−1.26 (m, 1H), 1.38−1.42 (m, 1H), 1.43 (s, 6H), 2.33 (d, $^3J_{H-H}$ = 5.1 Hz, 1H), 2.68−2.77 (m, 2H), 2.93 (s, 1H), 3.68 (br s, 1H), 6.22 (dd, $^3J_{H-H}$ = 5.6 Hz, $^3J'_{H-H}$ = 3.0 Hz, 1H), 6.31 (dd, $^3J_{H-H}$ = 5.6 Hz, $^3J'_{H-H}$ = 3.1 Hz, 1H), 7.25 (d, $^3J_{H-H}$ = 2.7 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 28.6 (CH_3), 29.1 (CH_3), 41.2 (CH_2), 43.1 (CH), 43.9 (CH), 47.2 (CH), 53.5 (CH), 69.9 (C), 137.2 (CH), 138.7 (CH), 155.3 (C), 157.2 (CH), 210.5 (C). IR (ATR): ν (cm^{-1}) 3446, 3060, 3009, 2978, 2939, 2870, 1682, 1315, 750. HRMS (ESI): calcd for [$C_{13}H_{16}O_2$ + H^+] 205.1223, found 205.1219. HPLC: Chiralcel OD-H, heptane/IPA 95/5, 1.0 mL/min, λ 220 nm. $t_R(-)$ = 8.6 min, $t_R(+)$ = 10.1 min.

*2-(Trimethylsilyl)-3a,4,7,7a-tetrahydro-1H-4,7-methanoinden-1-one (**4e**).* Trimethylsilylacetylene dicobalt hexacarbonyl complex **2e** (100 mg, 0.26 mmol, 1 equiv) was dissolved in anhydrous toluene (7 mL). Norbornadiene (0.27 mL, 2.6 mmol, 10 equiv) was then added, and the solution was stirred at 70 °C for 2 h. The crude mixture was then filtered, and the product was purified by flash column chromatography on silica gel using hexane/ethyl acetate (from 100/0 to 80/20) as the eluent to afford **4e** (14 mg, 25% yield) as a white solid.[27] ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 0.19 (s, 9H), 1.19 (d, $^2J_{H-H}$ = 9.3 Hz, 1H), 1.35−1.40 (m, 1H), 2.29 (dt, $^3J_{H-H}$ = 5.2 Hz, $^3J'_{H-H}$ = 1.4 Hz, 1H), 2.69 (br s, 1H), 2.82−2.86 (m, 1H), 2.91 (br s, 1H), 6.20 (dd, $^3J_{H-H}$ = 5.6 Hz, $^3J'_{H-H}$ = 3.0 Hz, 1H), 6.27 (dd, $^3J_{H-H}$ = 5.6 Hz, $^3J'_{H-H}$ = 3.0 Hz, 1H), 7.59 (d, $^3J_{H-H}$ = 2.6 Hz, 1H). GC: β-DEX (30 m), 160 °C, 1 mL/min, He. $t_R(-)$ = 18.0 min, $t_R(+)$ = 18.5 min.

*2-(((tert-Butyldimethylsilyl)oxy)methyl)-3a,4,7,7a-tetrahydro-1H-4,7-methanoinden-1-one (**4f**).* *tert*-Butyldimethyl(prop-2-yn-1-yloxy)silane (177 mg, 1.04 mmol, 1 equiv), norbornadiene (1.06 mL, 10.40 mmol, 10 equiv), and the catalyst **3a** (43 mg, 0.07 mmol, 0.07 equiv) were dissolved in anhydrous toluene (3.5 mL). The CO pressure was set to 1.5 barG, and the mixture was stirred at 100 °C for 6 h. The crude mixture was then filtered, and the product was purified by flash column chromatography on silica gel using hexane/EtOAc (from 100/0 to 90/10) as the eluent to afford **4f** (260 mg, 86% yield, 8% ee) as a reddish oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 0.06 (s, 6H), 0.90 (s, 9H), 1.21−1.26 (m, 1H), 1.38 (dt, $^2J_{H-H}$ = 9.3 Hz, $^3J'_{H-H}$ = 1.5 Hz, 1H), 2.32 (ddd, $^3J_{H-H}$ = 5.0 Hz, $^3J'_{H-H}$ = 1.6 Hz, $^4J''_{H-H}$ = 1.1 Hz, 1H), 2.67−2.71 (m, 1H), 2.72−2.77 (m, 1H), 2.83−2.96 (m, 1H), 4.31−4.35 (m, 2H), 6.18 (dd, $^3J_{H-H}$ = 5.6 Hz, $^3J'_{H-H}$ = 3.0 Hz, 1H), 6.27 (dd, $^3J_{H-H}$ = 5.6 Hz, $^3J'_{H-H}$ = 3.1 Hz, 1H), 7.35−7.38 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) −5.3 (2 × CH_3), 18.5 (C), 26.0 (3 × CH_3), 41.4 (CH_2), 43.1 (CH), 43.7 (CH), 48.1 (CH), 53.7 (CH), 58.2 (CH_2), 137.2 (CH), 138.6 (CH), 150.6 (C), 159.0 (CH), 208.7 (C). IR (ATR): ν (cm^{-1}) 3012, 2945, 2923, 2852, 1687, 1215, 749. HRMS (ESI): calcd for [$C_{17}H_{26}O_2Si$ + H^+] 291.1775, found 291.1779. HPLC: Chiralpak AS, heptane/IPA 98.5/1.5, 0.5 mL/min, λ 210 nm. $t_R(R^*)$ = 12.2 min, $t_R(S^*)$ = 17.2 min.

*1-Oxo-3a,4,7,7a-tetrahydro-1H-4,7-methanoinden-2-yl)methyl Acetate (**4g**).* Propargyl acetate (66 μL, 0.66 mmol, 1 equiv), norbornadiene (0.68 mL, 6.6 mmol, 10 equiv), and the catalyst **3c** (22 mg, 0.03 mmol, 0.05 equiv) were dissolved in anhydrous toluene (2 mL). The CO pressure was set to 1.5 barG, and the mixture was stirred at 100 °C overnight. The crude mixture was then filtered, and the product was purified by flash column chromatography on silica gel using hexane/EtOAc (from 100/0 to 70/30) as the eluent to afford **4g** (57 mg, 40% yield, 5% ee) as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 1.21−1.26 (m, 1H), 1.39−1.44 (m, 1H), 2.09 (s, 3H), 2.34−2.37 (m, 1H), 2.71−2.74 (m, 1H), 2.78−2.82 (m, 1H), 2.95 (s, 1H), 4.74 (s, 2H), 6.22 (dd, $^3J_{H-H}$ = 5.6 Hz, $^3J'_{H-H}$ = 3.0 Hz, 1H), 6.30 (dd, $^3J_{H-H}$ = 5.7 Hz, $^3J'_{H-H}$ = 3.2 Hz, 1H), 7.41−7.44 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 21.0 (CH_3), 41.4 (CH_2), 43.1 (CH), 43.9 (CH), 48.3 (CH), 53.1 (CH), 58.1 (CH_2), 137.3 (CH), 138.6 (CH), 145.2 (C), 162.0 (CH), 170.8 (C), 207.9 (C). IR (ATR): ν (cm^{-1}) 3056, 2974, 2939, 2876, 2848, 1742, 1698, 1367, 1227, 1027, 706. HRMS (ESI): calcd for [$C_{13}H_{14}O_3$ + H^+]: 219.1016, found 219.1020. GC: β-DEX (30 m), 150 °C, 1 mL/min, He. $t_R(R^*)$ = 37.5 min, $t_R(S^*)$ = 37.6 min.

*2-(1-Hydroxyethyl)-3a,4,7,7a-tetrahydro-1H-4,7-methanoinden-1-one (**4h**).* But-3-yn-2-ol (35 μL, 0.43 mmol, 1 equiv), norbornadiene (0.45 mL, 4.3 mmol, 10 equiv), and the catalyst **3c** (20 mg, 0.03 mmol, 0.07 equiv) were dissolved in anhydrous toluene (2 mL). The CO pressure was set to 1.5 barG, and the mixture was stirred at 100 °C overnight. The crude mixture was then filtered, and the product was purified by flash column chromatography on silica gel using hexane/EtOAc (from 100/0 to 20/80) as the eluent to afford **4h** (as a ca. 2/1 mixture of diastereomers) (18 mg, 22% yield, 30% ee) as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 1.25−1.29 (m, 1H), 1.40 (d, $^3J_{H-H}$ = 6.5 Hz, 3H), 1.39−1.43 (m, 1H), 2.34 (dt, $^3J_{H-H}$ = 4.9 Hz, $^3J'_{H-H}$ = 1.4 Hz, 1H), 2.69−2.73 (m, 1H), 2.75−2.79 (m, 1H), 2.93 (s, 2H), 4.60 (q, $^3J_{H-H}$ = 6.8 Hz, 1H), 6.22 (dd, $^3J_{H-H}$ = 5.6 Hz, $^3J'_{H-H}$ = 3.0 Hz, 1H), 6.31 (dd, $^3J_{H-H}$ = 5.6 Hz, $^3J'_{H-H}$ = 3.1 Hz, 1H), 7.29−7.33 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 21.72 ($CH_{3\,diast\,2}$), 21.80 ($CH_{3\,diast\,1}$), 41.24 ($CH_{2\,diast\,2}$), 41.27 ($CH_{2\,diast\,1}$), 43.02 ($CH_{diast\,2}$), 43.05 ($CH_{diast\,1}$), 43.76 ($CH_{diast\,2}$), 43.78 ($CH_{diast\,1}$), 47.85 ($CH_{diast\,2}$), 47.87 ($CH_{diast\,1}$), 53.44 ($CH_{diast\,2}$), 53.51 ($CH_{diast\,1}$), 63.77 ($CH_{diast\,2}$), 63.92 ($CH_{diast\,1}$), 137.19 ($CH_{diast\,2}$), 137.21 ($CH_{diast\,1}$), 138.65 ($CH_{diast\,2}$), 138.70 ($CH_{diast\,1}$), 152.97 ($C_{diast\,1}$), 153.07 ($C_{diast\,2}$), 158.22 ($CH_{diast\,1}$), 158.26 ($CH_{diast\,2}$), 210.13 ($C_{diast\,2}$), 210.26 ($C_{diast\,1}$). IR (ATR): ν (cm^{-1}) 3414, 3063, 2974, 2933, 2876, 1683, 1626, 1215, 749. HRMS (ESI): calcd for [$C_{12}H_{14}O_2$ + H^+] 191.1067, found 191.1066. HPLC: Chiralpak IA, heptane/EtOH 90/

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10, 1.0 mL/min, λ 210 nm. t_R(*R** diast 1) = 9.9 min, t_R(*R** diast 2) = 13.9 min, t_R(*S** diast 1) = 19.5, t_R(*S** diast 2) = 20.6 min.

*2-Cyclopropyl-3a,4,7,7a-tetrahydro-1H-4,7-methanoinden-1-one (**4i**).* Cyclopropylacetylene (72 μL, 0.85 mmol, 1 equiv), norbornadiene (0.88 mL, 8.5 mmol, 10 equiv), and the catalyst **3a** (25 mg, 0.04 mmol, 0.05 equiv) were dissolved in anhydrous toluene (2.5 mL). The CO pressure was set to 1.5 barG, and the mixture was stirred at 110 °C overnight. The crude mixture was then filtered, and the product was purified by flash column chromatography on silica gel using hexane/EtOAc (from 100/0 to 80/20) as the eluent to afford **4i** (157 mg, 99% yield, 43% ee) as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 0.58−0.64 (m, 2H), 0.80−0.86 (m, 2H), 1.20 (dt, $^2J_{H-H}$ = 9.3 Hz, $^3J'_{H-H}$ = 1.6 Hz, 1H), 1.36 (dt, $^2J_{H-H}$ = 9.3 Hz, $^3J'_{H-H}$ = 1.6 Hz, 1H), 1.53−1.61 (m, 1H), 2.30 (ddd, $^3J_{H-H}$ = 5.0 Hz, $^3J'_{H-H}$ = 1.6 Hz, $^4J''_{H-H}$ = 1.1 Hz, 1H), 2.60−2.64 (m, 1H), 2.64−2.68 (m, 1H), 2.91 (s, 1H), 6.19 (dd, $^3J_{H-H}$ = 5.6 Hz, $^3J'_{H-H}$ = 3.0 Hz, 1H), 6.26 (dd, $^3J_{H-H}$ = 5.7 Hz, $^3J'_{H-H}$ = 3.1 Hz, 1H), 6.86 (d, $^3J_{H-H}$ = 2.8 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 6.5 (CH), 7.6 (CH_2), 7.8 (CH_2), 41.3 (CH_2), 43.2 (CH), 43.8 (CH), 47.2 (CH), 53.2 (CH), 137.2 (CH), 138.5 (CH), 152.7 (C), 154.5 (CH), 209.4 (C). IR (ATR): ν (cm^{-1}) 3063, 3003, 2974, 2936, 2870, 1690, 1013, 749. HRMS (ESI): calcd for [$C_{13}H_{14}O$ + H^+] 187.1117, found 187.1118. GC: β-DEX (30 m), 160 °C, 1 mL/min, He. t_R(−) = 19.6 min, t_R(+) = 20.0 min.

*2,3-Diphenyl-3a,4,7,7a-tetrahydro-1H-4,7-methanoinden-1-one (**4j**).* Diphenylacetylene (84 mg, 0.47 mmol, 1 equiv), norbornadiene (0.49 mL, 4.70 mmol, 10 equiv), and the catalyst **3c** (22 mg, 0.03 mmol, 0.07 equiv) were dissolved in anhydrous toluene (1.5 mL). The CO pressure was set to 1.5 barG, and the mixture was stirred at 120 °C overnight. The crude mixture was then filtered, and the product was purified by flash column chromatography on silica gel using hexane/EtOAc (from 100/0 to 80/20) as the eluent to afford **4j** (77 mg, 54% yield, 56% conversion, 15% ee) as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 1.44−1.49 (m, 2H), 2.59−2.64 (m, 2H), 3.10−3.14 (m, 1H), 3.35 (d, $^3J_{H-H}$ = 5.4 Hz, 1H), 6.31 (t, $^3J_{H-H}$ = 1.8 Hz, 2H), 7.17−7.22 (m, 2H), 7.25−7.33 (m, 8H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 42.0 (CH_2), 43.4 (CH), 44.3 (CH), 50.4 (CH), 52.9 (CH), 127.9 (CH), 128.4 (2 × CH), 128.5 (2 × CH), 128.6 (2 × CH), 129.4 (2 × CH), 129.7 (CH), 132.1 (C), 135.1 (C), 138.0 (CH), 138.4 (CH), 143.8 (C), 170.0 (C), 207.3 (C). IR (ATR): ν (cm^{-1}) 3056, 3012, 2974, 2939, 2873, 1686, 1347, 1215, 748. HRMS (ESI): calcd for [$C_{22}H_{18}O$ + H^+] 299.1430, found 299.1434. HPLC: Chiralpak IA, heptane/IPA 90/10, 0.5 mL/min, λ / 254 nm. t_R(+) = 12.6 min, t_R(−) = 17.5 min.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.organomet.7b00018.

Crystallographic data (CIF)

Cartesian coordinates of the computed structures of cobalt complexes **3a**, **3b′**, **3c**−**e**, and **TS1** (XYZ)

Supplementary tables and figures, experimental procedures for the synthesis of cobalt complexes **2a**−**e**, and computational results (PDF)

■ AUTHOR INFORMATION

Corresponding Authors

*E-mail for X.V.: xavier.verdaguer@irbbarcelona.org.

*E-mail for A.R.: antoni.riera@irbbarcelona.org.

ORCID

Xavier Verdaguer: 0000-0002-9229-969X

Antoni Riera: 0000-0001-7142-7675

Notes

The authors declare no competing financial interest.

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