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Chiral Phosphate in Rhodium-Catalyzed Asymmetric [2+2+2] Cycloaddition: Ligand, Counterion, or Both?

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Abstract: Investigations based on NMR spectroscopy, mass spectrometry, and DFT calculations shed light on the metallic species generated in the rhodium-catalyzed asymmetric [2+2+2] cycloaddition reaction between diynes and isocyanates with the chiral phosphate TRIP. The catalytic mixture comprising [{Rh(cod)Cl}$_2$], 1,4-diphenylphosphinobutane (dppb), and Ag(*S*)-TRIP actually gives rise to two species, both having an effect on the stereoselectivity. One is a rhodium(I) complex in which TRIP is a weakly coordinating counterion, whereas the other is a bimetallic Rh/Ag complex in which TRIP is a strongly coordinating X-type ligand.

Introduction

Enantioselective metal-catalyzed transformations are a cornerstone of modern synthetic organic chemistry.[1,2] Over the last decade, the limits of this discipline have been pushed even further, notably through the design of original ligands[3] or the use of multiple stereodifferentiation approaches.[4] Recent years have also witnessed the rise of the asymmetric counterion-directed catalysis (ACDC) approach, whereby the counterion of a catalytically active cationic metal species is employed as vehicle for the transfer of stereochemical information to the reaction products.[5] Disclosed in 2000 by Arndtsen and coworkers for a copper-catalyzed borate-assisted styrene aziridination,[6] ACDC has been subject to intense interest following the reports by the groups of Krische, List, and Toste in 2006 and 2007.[7,8] The use of the BINOL-derived hindered phosphate [TRIP]$^-$ as the chirality carrier[9] constituted a real breakthrough, as high enantioselectivities could be achieved for a variety of transformations.[5,10] However, the exact nature of the phosphate chirality carrier, that is, X-type ligand or counterion, is often a source of controversy. If it remains bound to the metal during the stereochemistry-determining step, then its mode of action is not very different from a classical L-type monodentate ligand. If it is well separated from the metal center (loose ion pair), then the transfer of stereochemical information would require an anchoring of the counterion on the ligands or on the substrate itself.[11] In this case, the induction models should be completely distinct. To date, no report has brought firm evidence on this issue. The strong dependence of the *ee* on solvent polarity suggests that a large interionic distance is deleterious to the chirality transfer but does not disclose the actual location of the phosphate.[12] X-ray structure analyses generally reveal short metal–oxygen bonds, in agreement with strong covalent bonding.[13] However, this does not mean that such bonds remain covalent or undergo solvation during catalysis. For instance, although the phosphate–gold complexes **A** and **B** were proved to be covalent in CD_2Cl_2 (Figure 1),[13b,14] the phosphate moiety is believed to be a "true" counterion in catalysis due to the linear geometry of the [(R_3P)Au(substrate)]$^+$ complex **C**, which imposes the phosphate keeping off the coordination sphere of the metal to allow substrate activation.[8] This reasoning based on geometrical constraints cannot be so obviously applied with metal ions of Ir, Pd, Cu, Ru, or Rh.[15] In these cases, DFT studies have been helpful to support a counterion role of the phosphate on the Ir complex **D**,[10c] and on the palladium complex **E** (Figure 1).[16] However, to date, no physical evidence on the counterion or ligand nature of the phosphate has been reported.

We describe herein a study aimed at shedding light on the issue of the ligand or counterion nature of a chiral phosphate on catalytically active square planar Rh$^+$ complexes. We recently reported the first case of chiral phosphate-directed

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*Supporting information for this article, containing full NMR and ESI characterizations for complexes **[I]**$^+$[(S)-TRIP]$^-$, **II** and **III**, experimental procedures, HPLC traces; kinetic studies, and coordinates and energy of the calculated species, is available on the WWW under http://dx.doi.org/10.1002/chem.201601188.*

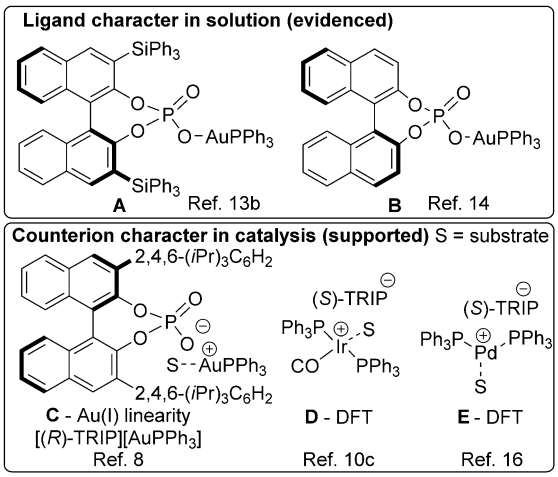
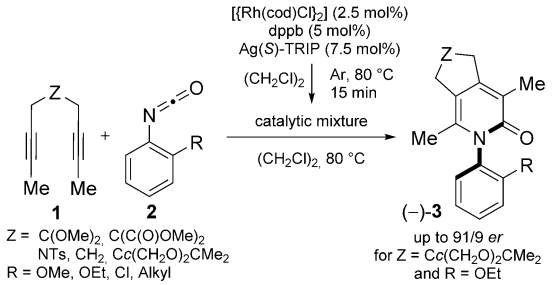


Figure 1. Ligand vs. counterion character of chiral phosphates in transition metal complexes.

asymmetric [2+2+2] cycloaddition (Scheme 1).[10b] We have shown that diynes **1** and isocyanates **2** lead to enantiomerically enriched pyridones **3** in up to 91:9 e.r., in the presence of the phosphate $[(S)\text{-TRIP}]^-$ (Figure 2) as the sole chirality source of a catalytic mixture comprising $[\{Rh(cod)Cl\}_2]$ (cod = 1,5-cyclooctadiene), 1,4-diphenylphosphinobutane (dppb), and Ag(*S*)-TRIP. A likely component of this mixture would be [Rh(cod)(dppb){(*S*)-TRIP}] formed after chloride abstraction by



Scheme 1. Asymmetric counterion-directed Rh-catalyzed [2+2+2] cycloaddition.[10b]

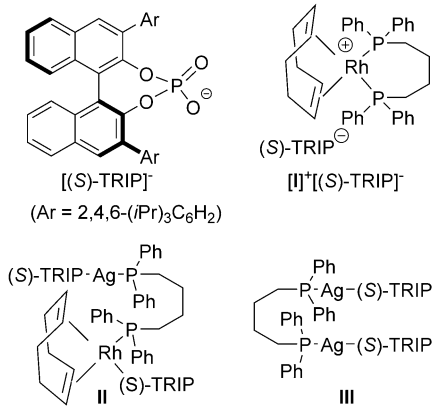


Figure 2. Species involved in this study.

the silver salt. Such a complex could adopt various coordination modes. Even though the square planar geometry should be always favored, the phosphate could be an X-type ligand if cod or dppb acts as a monodentate ligand. On the other hand, if both cod and dppb allow an η^2,η^2-Rh complex, then the phosphate should be a counterion as in $[\mathbf{I}]^+[(S)\text{-TRIP}]^-$ (Figure 2) and the complex could be either a tight or a loose ion pair. Under the optimized conditions, Ag(*S*)-TRIP is used in a 1.5-fold excess compared to Rh. If the anion metathesis is complete, 2.5 mol% of Ag(*S*)-TRIP should still be present. Since the silver complex is not catalytically active, the impact of the presence of this salt on the stereoselectivity is puzzling. Thus, we decided to study carefully the species contained in this catalytic mixture,[17] focusing on the nature, ligand or counterion, of the chiral phosphate.

Results and Discussion

We first examined the species formed by mixing $[\{Rh(cod)Cl\}_2]$ (0.5 equiv), dppb (1 equiv) and Ag(*S*)-TRIP (1 equiv) in $(CH_2Cl)_2$ at 80 °C under argon for 15 min (sealed NMR tube), which corresponds to the premix conditions for the cycloaddition reaction shown in Scheme 1. 1D and 2D NMR experiments were in agreement with the proposed structure $[\mathbf{I}]^+[(S)\text{-TRIP}]^-$ (Figure 2; see the Supporting Information, sections 2.1 to 2.3). The formation of this species at room temperature in CD_2Cl_2 was also ascertained by NMR spectroscopy.[18] In particular, the ^{31}P spectrum shows two signals, one accounting for the dppb ligand [$\delta = 24.6$ ppm, d, $J(^{103}Rh,^{31}P) = 144$ Hz] and the other for the phosphate (broad s, $\delta = 4.8$ ppm).[18] The ^1H–^{103}Rh HMQC spectrum shows a triplet at $\delta = -8466$ ppm.[19,20a] This is consistent with a $[Rh(P)_2(alkene)_n]$-type complex.[21] ESI mass spectrometry experiments carried out on the mixture also confirmed this hypothesis, as both cation $[\mathbf{I}]^+$ (positive mode, *m/z* 637, Figure 3) and anion $[(S)\text{-TRIP}]^-$ (negative mode, *m/z* 751) were detected (see the Supporting Information, section 2.4).

The question of the interaction between $[\mathbf{I}]^+$ and $[(S)\text{-TRIP}]^-$ remained to be answered. In addition to conductivity measurements and IR and 1D NMR spectroscopy,[6,13b] a powerful tool

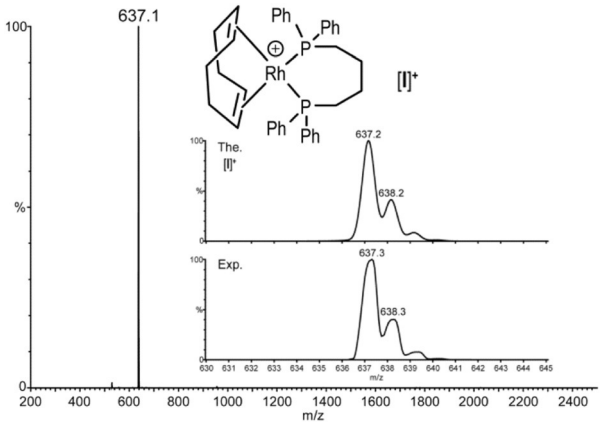


Figure 3. Simulated and experimental ESI-MS (positive mode) of species $[\mathbf{I}]^+[(S)\text{-TRIP}]^-$.

to evidence ion pairing is diffusion ordered spectroscopy (DOSY). This technique has been extensively used by the groups of Pregosin and Macchioni to study cationic organometallic species.[22] To date, application of this method to complexes relevant to ACDC is limited to a single example:[23] for [Rh(cod)(BINAP)][B(BINOL)$_2$], Brown and co-workers observed the same diffusion coefficients for [Rh(cod)(BINAP)] and [B(BINOL)$_2$]. They therefore concluded that this complex is the tight ion pair [Rh(cod)(BINAP)]$^+$[B(BINOL)$_2$]$^-$ in solution, the assembly of the two ionic entities being achieved through noncovalent interactions. To definitively settle the ligand or counterion character of (*S*)-TRIP in [**I**][(*S*)-TRIP], we carried out three NMR experiments: i) 1D HMQC ^{31}P–^{103}Rh to detect long-range couplings between the phosphate and the rhodium nucleus; ii) 2D NOESY and ROESY to detect any noncovalent interactions between the phosphate and the ligands; iii) DOSY (Figure 4).

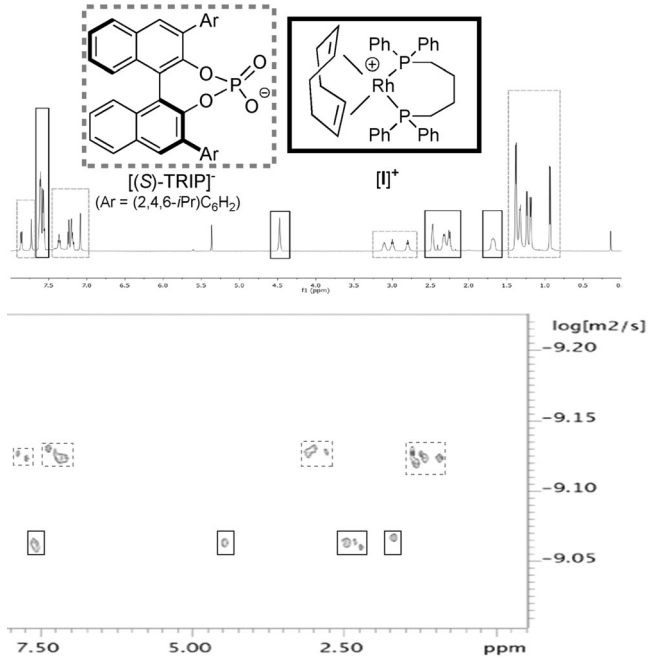
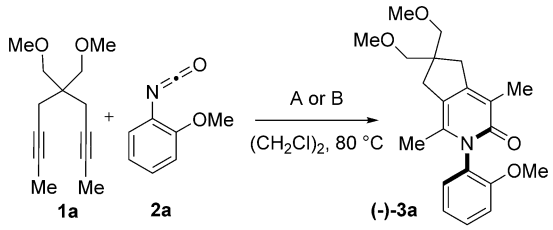


Figure 4. DOSY experiment (CD_2Cl_2, 600 MHz, 300 K).

The first two experiments showed no phosphate–^{103}Rh correlation signal (see the Supporting Information, section 2.2) or phosphate–ligand interaction (see the Supporting Information, section 2.6). From DOSY, we derived the following diffusions coefficients: $D_{[TRIP]} = 7.5\,E^{-10}\ m^2\,s^{-1}$ (i.e., a hydrodynamic radius of $r_H = 7.2$ Å); $D_{[I]} = 8.7\,E^{-10}\ m^2\,s^{-1}$ (i.e., $r_H = 6.2$ Å; see the Supporting Information, section 2.6).[24,25,26] Since the two fragments have different diffusion coefficients, it is clear that they move independently. On the basis of these three experiments, it can be concluded that [(*S*)-TRIP]$^-$ can be qualified as a counterion and that complex [**I**]$^+$[(*S*)-TRIP]$^-$ behaves as a loose ion pair in solution.

[**I**]$^+$[(*S*)-TRIP]$^-$ was independently synthesized to evaluate its catalytic activity and stereoselectivity. This isolated complex, the NMR data of which fit with those of the in situ-generated



Cond. A: *i)* [Rh(COD)Cl]$_2$ (2.5 mol%), dppb (5 mol%), Ag(S)-TRIP (7.5 mol%), $(CH_2Cl)_2$, 80 °C, 15 min — 77%, 85/15 er

ii) reagents

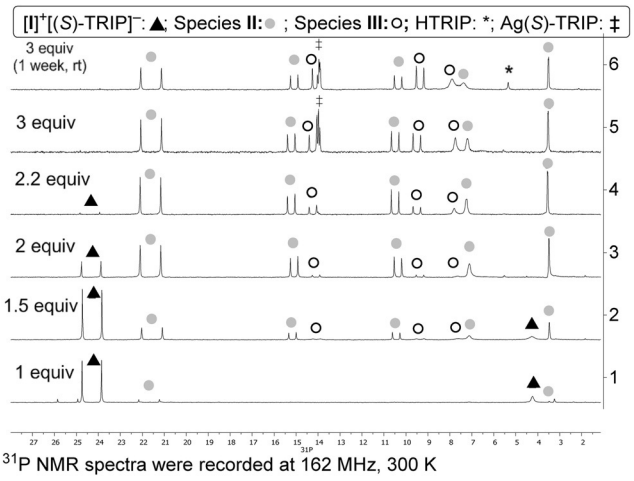
Cond. B: [**I**]$^+$[(S)-TRIP]$^-$ (5 mol%) and reagents — 79%, 75/25 er

Scheme 2. Evaluation of [**I**]$^+$[(*S*)-TRIP]$^-$ in enantioselective [2+2+2] cycloaddition.

species discussed above, was tested in a [2+2+2] cycloaddition between diyne **1a** and isocyanate **2a** and led to the desired pyridone (−)-**3a** in 79% yield (Scheme 2, conditions B). Surprisingly, a decrease of the enantiomeric ratio from 85:15 in the ACDC-optimized conditions (Scheme 2, conditions A) to 75:25 was observed. The results of conditions A and B were reproducible (see the Supporting Information, section 2.5).

The influence of the amount of Ag(*S*)-TRIP on the rhodium complexes was then assessed by ^{31}P NMR spectroscopy. When 1 equivalent of Ag(*S*)-TRIP vs. Rh was used (0.5 equiv [{Rh(cod)Cl}$_2$], 1 equiv dppb, 1 equiv Ag(*S*)-TRIP), the major product was [**I**]$^+$[(*S*)-TRIP]$^-$, as discussed above (Figure 5, spectrum 1). When adding more Ag(*S*)-TRIP, the latter does not accumulate in the reaction mixture but generates two new species **II** and **III**. Their proportions grow with increasing amounts of Ag(*S*)-TRIP (Figure 5, spectra 2–6). Disappearance of [**I**]$^+$[(*S*)-TRIP]$^-$ is virtually achieved with 2.2 equivalents of Ag(*S*)-TRIP (spectrum 4).

Species **II** shows four different sets of signals, at $\delta = 21.6$ [d, $^1J(^{103}Rh,^{31}P) = 152$ Hz], 12.8 [d, $^1J(^{109}Ag,^{31}P) = 820$ Hz; d, $^1J(^{107}Ag,^{31}P) = 710$ Hz], 7.1 [br s, P(O)OAg], and 3.5 ppm [s, P(O)]. It is a highly dissymmetric complex, bearing one excep-



^{31}P NMR spectra were recorded at 162 MHz, 300 K

Figure 5. ^{31}P NMR monitoring of the metallic species as a function of Ag(*S*)-TRIP equivalents.[18]

tionally shielded cod double bond [^{1}H NMR: $\delta = 2.80$ (1H), 2.63 ppm (1H); ^{13}C NMR: $\delta = 70.5$, 68.0 ppm]. Its ^{103}Rh NMR signal splits as a doublet (rather than a triplet as in species [**I**]$^+$[(*S*)-TRIP]$^-$) and shifts 993 ppm downfield, from $\delta = -8644$ ppm (species [**I**]$^+$[(*S*)-TRIP]$^-$) to $\delta = -7651$ ppm.[19,20b] Both represent the replacement of one of the phosphane by an oxygen ligand.[21] The latter downfield shift would probably arise from decoordination of one end of the dppb ligand by excess Ag(*S*)-TRIP and concomitant coordination of the phosphate. Indeed, ^{31}P–^{109}Ag HMQC revealed a doublet at $\delta = 426$ ppm [$^1J(^{31}P,^{109}Ag = 820$ Hz)], consistent with a two-coordinate linear silver complex.[27] The postulated [Rh(cod)(dppb){(*S*)-TRIP}{Ag(*S*)-TRIP}] structure **II** (Figure 2) matches 1D and 2D experiments (see the Supporting Information, sections 3.1 to 3.3). The ^{31}P–^{103}Rh 1D HMQC experiment confirmed that, in this case, the phosphate is an X-type ligand (see the Supporting Information, spectrum SI-16).[28] Moreover, the bulky cationic structure [**II**-(*S*)-TRIP]$^+$ was detected by ESI(+) analysis (see the Supporting Information, section 3.5). Note that only traces of the latter were detected, which is consistent with the low ionic character of the Rh-TRIP bound in this complex. This cation is pretty stable, as increasing the energy does not lead to subsequent fragmentation. In particular, cation [**I**]$^+$ (*m/z* 637) was not detected by MS/MS analysis.

The NMR data of species **III** reveal a symmetric structure with two phosphorus patterns at $\delta = 11.8$ [d, $J(^{109}Ag,^{31}P) = 820$ Hz and d, $J(^{107}Ag,^{31}P) = 710$ Hz], and 7.7 ppm [br s, P(O)OAg]. The postulated bis-silver structure [(dppb)(Ag(*S*)-TRIP)$_2$] for this complex was corroborated by 1D and 2D experiments, as well as ESI(+)-MS which revealed ion peaks for [**III** + Ag]$^+$ at *m/z* 2253.9 and [**III** − TRIP]$^+$ at *m/z* 1393.5 (see the Supporting Information, section 4). The same NMR features were recorded for a mixture of dppb with 2 equivalents of Ag(*S*)-TRIP in CD_2Cl_2 at RT. Notably, this independently synthesized complex is catalytically inactive.

We then monitored the evolution of the species in conditions close to those of the reaction, in the presence of the diyne and isocyanate reagents [(CD_2Cl)$_2$, 70 °C] with 2 equivalents of Ag(*S*)-TRIP (10 mol%) vs. Rh, starting from a [**I**]$^+$[(*S*)-TRIP]$^-$/**II**/**III** ratio of 1:3.5:1 (Figure 6). A 2:1.4:1 ratio was reached after 4.5 h. It is worth underlining that during this study, no reaction intermediate or other catalytic species could be detected by ^{31}P or ^{1}H NMR spectroscopy

^{1}H exchange spectroscopy (EXSY) showed that species [**I**]$^+$[(*S*)-TRIP]$^-$ and **II** are indeed in equilibrium in the reaction mixture, that is, coordination/decoordination of silver phosphate occurs with exchange rate constants $k_1 = 0.012 \pm 0.001$ s^{-1} and $k_{-1} = 0.049 \pm 0.01$ s^{-1} at 300 K (Scheme 3). A conformational equilibrium was also revealed by the observation of the NMR signals of the cod protons which exchange in pairs. Since the dppb protons do not exchange, this equilibrium can be explained by the flip of the Rh–dppb–Ag(*S*)-TRIP side chain, above and below the rhodium atom. This second equilibrium occurs with an exchange rate constant of $k' = 0.034 \pm 0.005$ s^{-1} (see the Supporting Information, section 5).[29]

The free energy of the Rh/Ag transmetallation of one phosphane moiety was estimated by DFT computations using

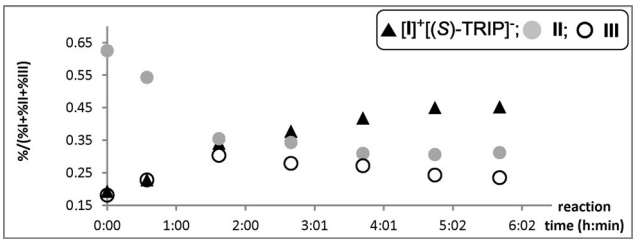
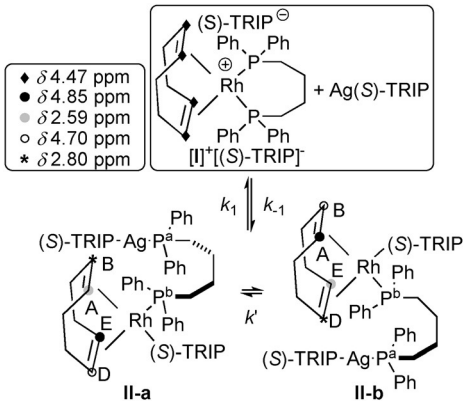


Figure 6. Evolution of the species in the reaction mixture [^{31}P NMR, (CD_2Cl)$_2$, 201 MHz, 343 K, $c = 0.005$ M].



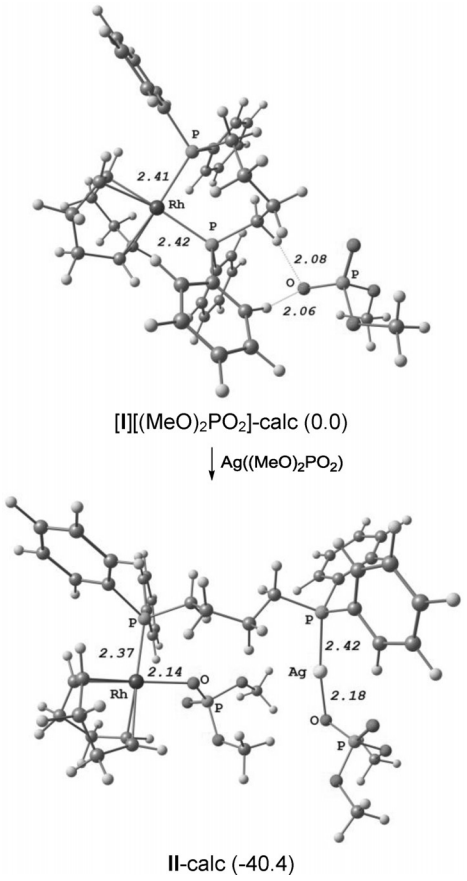
Scheme 3. ^{1}H EXSY study of the equilibrium between species [**I**]$^+$[(*S*)-TRIP]$^-$/Ag(*S*)-TRIP and **II** (300 K).

[$(MeO)_2PO_2$]$^-$ as model phosphate (Scheme 4). The calculations were carried out at the M06/SDD(Rh,Ag)6-31 + G(d,p)//B3LYP/LANL2DZ(Rh,Ag)6-31Gd) level using the Gaussian 09 software package (see the Supporting Information, section 6).

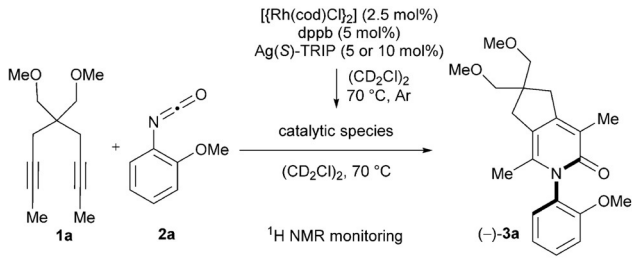
As shown by the quite long CH–O distances of 2.06 and 2.08 Å, respectively, in the calculated [**I**][$(MeO)_2PO_2$] ([**I**][$(MeO)_2PO_2$]-calc), the binding of the phosphate to [**I**]$^+$ is achieved through weak hydrogen bonds in the gas phase. One phenyl moiety and one CH_2 unit of dppb serve as hydrogen bond donors. Notably, another isomer in which the cod ligand plays the role of hydrogen bond donor was also computed but it was found to be less stable than [**I**][$(MeO)_2PO_2$]-calc by 3 kcal mol^{-1}. The computed ΔG_{298} for [**I**][$(MeO)_2PO_2$]-calc + Ag$(MeO)_2PO_2$ → **II**-calc is of −40.4 kcal mol^{-1}. This large exergonicity supports the proposed phosphane exchange.

We then evaluated these rhodium species in the [2+2+2] cycloaddition reaction of diyne **1a** with isocyanate **2a** under the conditions defined in Figure 7. As shown above, with 5 mol% of Ag(*S*)-TRIP, the catalytic mixture is mostly composed of [**I**]$^+$[(*S*)-TRIP]$^-$. With 10 mol% of Ag(*S*)-TRIP, it is enriched in species **II**. Both catalytic systems led to full conversion in about 1 h at 70 °C. However, the initial rate was higher with 5 mol% Ag(*S*)-TRIP.

We then analyzed the enantiomeric excess of the resulting pyridone **3a** as a function of the Ag(*S*)-TRIP/[Rh] ratio (Table 1). With a 0.5:1 ratio, a low e.r. of 55:45 was measured (Table 1, entry 1). A significant increase of the e.r. to 77:23 was observed with a 0.9:1 ratio (entry 2). An excess of silver compared to rhodium further raised the e.r. (Table 1, entries 3–5). When



Scheme 4. Computed Rh/Ag transmetallation (kcal mol^{-1}, distances in Å).



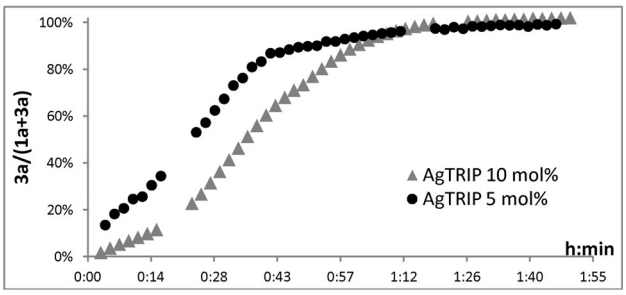
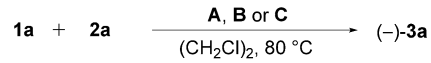


Figure 7. ^{1}H NMR monitoring of the reaction [600 MHz, $(CD_2Cl)_2$, 343 K].

a larger excess of Ag(*S*)-TRIP was introduced (3:1 ratio), species **III** accumulated but the e.r. remained similar (83:17; Table 1, entry 6). These results suggest that species **II** has a positive effect on the stereoselectivity. To probe this hypothesis, we compared the use of the isolated complex [**I**]$^+$[(*S*)-TRIP]$^-$ (5 mol%) without or with addition of Ag(*S*)-TRIP (2.5 mol%), which should generate the [**I**]$^+$[(*S*)-TRIP]$^-$/**II** mixture in solution. Whereas, as noted in Scheme 2, the isolated complex [**I**]$^+$[(*S*)-TRIP]$^-$ alone led to a 75:25 e.r. (Table 1, entry 7), pyridone **3a** was obtained in an improved e.r. of 88:12 when additional Ag(*S*)-TRIP was used (Table 1, entry 8). This finding supports the beneficial role of species **II** in the enantioselectivity of the cycloaddition. However, as [**I**]$^+$[(*S*)-TRIP]$^-$ and **II** are in equilibrium, we cannot exclude that **II** is catalytically inactive and that **I** is the only active species. The boost in enantioselectivity in the presence of **II** may therefore result from the excess Ag(*S*)-TRIP in the reaction mixture.

Table 1. Influence of Ag(*S*)-TRIP/[Rh] ratio on the e.r.



Conditions A: i) [{Rh(cod)Cl}$_2$] (2.5 mol%), dppb (5 mol%), Ag(*S*)-TRIP (*x* mol%), $(CH_2Cl)_2$, 80 °C, 15 min ii) reagents

Conditions B: [**I**]$^+$[(*S*)-TRIP]$^-$ (5 mol%) and reagents

Conditions C: i) [**I**]$^+$[(*S*)-TRIP]$^-$ (5 mol%), Ag(*S*)-TRIP (*x* mol%) $(CH_2Cl)_2$, 80 °C, 15 min ii) reagents

Entry	Conditions	*x* [mol%]	Ag(*S*)-TRIP/[Rh]	Yield [%]	e.r.[a]
1	A	2.5	0.5:1	87	55:45
2	A	4.5	0.9:1	91	77:23
3	A	6.5	1.3:1	91	84:16
4	A	7.5	1.5:1	93	84:16
5	A	10	2:1	93	85:15
6	A	15	3:1	76	83:17
7	B	0	1:1	79	75:25
8	C	2.5	1.5:1	70	88:12

[a] Derived from HPLC (see the Supporting Information, section 3.4).

Conclusion

For the first time, some physical evidences of the counterionic character of the TRIP anion in an organometallic species have been established. By using NMR spectroscopy, mass spectrometry, and DFT calculations, we studied the organometallic species involved in phosphate-directed Rh-catalyzed [2+2+2] cycloaddition of diynes to isocyanates. The use of Ag(*S*)-TRIP, in slight excess compared to the rhodium complex, gives rise to various species in equilibrium. The major one, [**I**]$^+$[(*S*)-TRIP]$^-$, leads to the desired pyridone in 75:25 e.r., even in the absence of excess of silver salt. It is a loose ion pair and the counterionic character of the phosphate in this complex has been ascertained by DOSY and other NMR experiments. With an excess of silver salt, a second species appears in equilibrium with the first. It is the bimetallic [Rh(cod)(dppb){(*S*)-TRIP}{Ag(*S*)-TRIP}] species **II**, the presence of which boosts the reaction enantioselectivity. In this species, the ^{31}P–^{103}Rh 1D HMQC experiment

showed that the phosphate is coordinated to the metal. Clearly the question as to whether a phosphate is a ligand or a counterion in the organometallic species involved in ACDC cannot be answered simply. Our work suggests that the two options may coexist.

Acknowledgements

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Keywords: chirality · cycloaddition · homogeneous catalysis · ligand effects · rhodium

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