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Double-Stereodifferentiation in Rhodium-Catalyzed [2 + 2 + 2] Cycloaddition: Chiral Ligand/Chiral Counterion Matched Pair

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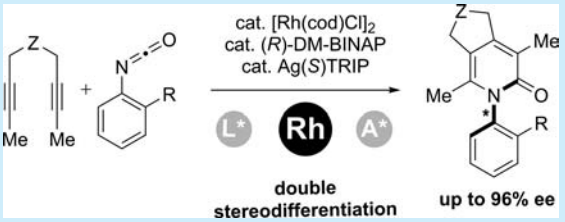
Supporting Information

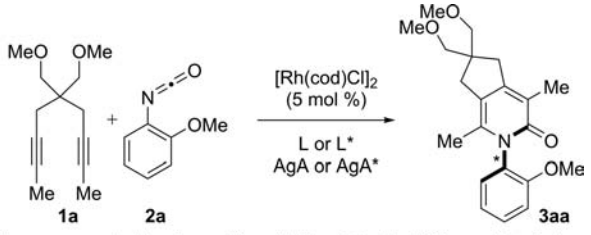
ABSTRACT: The first enantioselective metal-catalyzed [2 + 2 + 2] cycloaddition involving a double asymmetric induction has been devised. It relies on the use of an in situ generated chiral cationic rhodium(I) catalyst with a matched chiral ligand/chiral counterion pair. Careful optimization of the catalytic system, as well as of the reaction conditions, led to atroposelective [2 + 2 + 2] pyridone cycloadducts with high ee's up to 96%. This strategy outperformed those previously described involving a chiral ligand only or a chiral counterion only.



Chirality control is a major challenge for synthetic chemists, especially given the importance of optically active drugs.[1] Although several methods exist to control the enantioselectivity, such as chirality transfer from a nonracemic substrate or reagent and asymmetric organo- and organometallic catalysis, optical purities of the corresponding products are sometimes not satisfying enough. In such cases, combining the sources of stereoselectivity should result in better control.[2] Particularly double stereodifferentiation which involves two chiral inducers acting in cooperation may offer an attractive strategy to improve the stereoselectivity, provided that a *matched* pair is selected. For instance, chiral substrate/chiral auxiliary or chiral substrate/chiral ligand pairings are commonly used in synthesis.[3] In contrast, examples of double-asymmetric induction from different chiral catalytic sources remain scarce.[4] Among those, only a few cases of copper, gold, and iridium catalysis[4b−j] have involved a chiral ligand and a chiral counterion.[5] We decided to test this emerging strategy in the field of rhodium catalysis.[6] We show herein how the enantioselectivity in [2 + 2 + 2] cycloaddition between a diyne and an isocyanate can be improved by using both a chiral ligand and a chiral counterion.[7−9] To the best of our knowledge, enantioselective [2 + 2 + 2] cycloadditions relying on double-stereodifferentiation are unprecedented.

Recently, we achieved the atroposelective cycloaddition of diyne **1a** with isocyanate **2a** in which the stereochemical information was located on the counterion **A*** of the cationic rhodium species (Scheme 1, eq 2).[7a] Despite the fact that the concept was unprecedented in [2 + 2 + 2] cycloaddition, no significant asymmetric induction improvement was made compared to the standard chiral ligand strategy (Scheme 1, eq 3).[9c] In both cases, the best enantiomeric excess reached about 70%. We thus aimed at developing a second generation catalytic system, including a chiral counterion **A*** and a chiral ligand **L***, in anticipation of a double-stereodifferentiation (Scheme 1, eq 1).

Scheme 1. Asymmetric Synthesis of Pyridone 3aa



(eq 1)	double stereodifferentiation (L* + AgA*)?	this study
(eq 2)	chiral counterion strategy (dppb + Ag(*S*)-TRIP)[7a]	71% ee (−)
(eq 3)	chiral ligand strategy ((*R*)-BINAP + $AgBF_4$)[9c,7a]	67% ee (+)

We showed previously that the treatment of diyne **1a** and isocyanate **2a** in the presence of a prestirred solution of $[Rh(cod)Cl]_2$, bis(diphenylphosphino)butane (dppb), and Ag(*S*)-TRIP (**Ag-4**) as the sole source of chirality led to pyridone (−)-**3aa** in 77% yield and 71% ee (Table 1, entry 1).[7a] We then decided to use a chiral bidentate ligand instead of dppb. *rac*-2,2′-Bis(di-*p*-tolylphosphino)-1,1′-binaphthyl (TolBINAP) was first selected to assess reactivity and induction. Under the same reaction conditions (dichloroethane, 80 °C), pyridone (+)-**3aa** was obtained in a poor 7% ee (entry 2). Hypothesizing a *match* and a *mismatch* pairing, (*R*)- and (*S*)-TolBINAP were successively tested (entries 3 and 4, respectively). Unfortunately, no chiral amplification was observed, and similar but opposite ee were obtained (45% (+) and 44% (−), respectively). The counterion thus seems to play a spectator role under these conditions.

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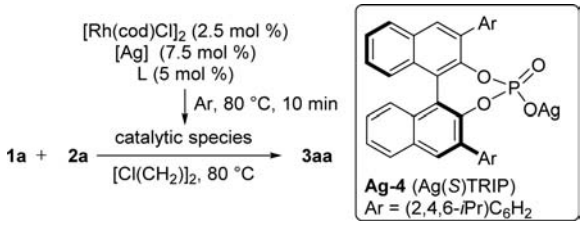
Table 1. Joint Use of a Chiral Ligand and a Chiral Counterion at 80 °C[7a]

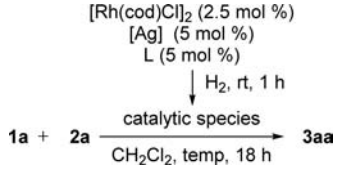


entry	L[a]	[Ag]	yield (%)	ee (%)
1	dppb	**Ag-4**	77	71 (−)
2	*rac*-TolBINAP	**Ag-4**	85	7 (+)
3	(*R*)-TolBINAP	**Ag-4**	96	45 (+)
4	(*S*)-TolBINAP	**Ag-4**	91	44 (−)

[a]dppb: bis(diphenylphosphino)butane. TolBINAP: 2,2′-bis(di-*p*-tolylphosphino)-1,1′-binaphthyl.

We assumed that the high temperature (80 °C) might be responsible for the absence of counterion effect in this reaction. However, when both the prestirring and the addition of the substrates were carried out at room temperature, no reaction took place. Since the heating is presumably required to displace the cyclooctadiene (cod) ligand from the metal,[7a] we reasoned that the use of H_2 to reduce the cod may favor the formation of active species at ambient temperature. Thus, the precatalytic species was hydrogenated under standard conditions (1 h, rt) and then tested on the cycloaddition reaction at rt. Combining *rac*-TolBINAP as the ligand and the TRIP phosphate **4** as the counterion, the desired pyridone (−)-**3aa** was isolated in 34% yield, and a moderate but improved 19% ee in favor this time of the levorotary enantiomer (Table 2, entry 1 vs Table 1, entry 2).

Table 2. Joint Use of a Chiral Ligand and a Chiral Counterion under Mild Conditions



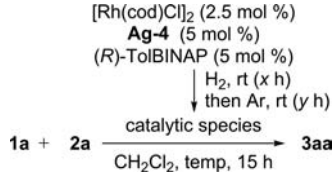
	L	[Ag]	temp (°C)	yield (%)	ee (%)
1	*rac*-TolBINAP	**Ag-4**	rt	34	19 (−)
2[a]	*rac*-TolBINAP	**Ag-4**	−20	41	16 (−)
3	(*R*)-TolBINAP	**Ag-4**	rt	39	22 (+)
4	(*S*)-TolBINAP	**Ag-4**	rt	16	9 (−)
5[b]	(*R*)-TolBINAP	$AgBF_4$	rt	81	59 (+)
6	(*R*)-TolBINAP	**Ag-4** (5 mol %) + $AgBF_4$ (5 mol %)	rt	92	54 (+)

[a]Catalyst prestirring: 3 h. [b]5.5 mol % of $AgBF_4$ was used.

Decreasing the reaction temperature to −20 °C slightly altered the selectivity (16% ee, entry 2). Switching to (*R*)- and (*S*)-TolBINAP led to low yields and poor enantioselectivities (22% and 9% ee, respectively, entries 3 and 4). Nevertheless, it is noteworthy that there was a counterion effect since these ee's were significantly lower than those obtained only with the chiral ligand and an achiral counterion (BF_4^-) (59% ee, entry 5). We supposed that the high steric hindrance brought about by the phosphate might prevent complete ion-pair formation under these mild prestirring conditions (H_2, 1 h, rt). To verify this hypothesis, we added $AgBF_4$ as additional chloride scavenger, as it easily abstracts chloride atom from $[Rh(cod)Cl]_2$ dimer. A consecutive borate/phosphate metathesis driven by the lower solubility of the inorganic silver salt $AgBF_4$ might then generate the desired chiral ion pair. However, no change in the enantiomeric excess was observed (59% vs 54% ee, entries 5 and 6).[10]

To encourage the anion metathesis, the prestirring time was probed next. When the hydrogenation was carried out for 7 h instead of 1 h, both the yield and the selectivity increased (54% yield and 80% ee; Table 3, entry 1 vs Table 2, entry 3).

Table 3. Influence of the Prestirring Time



	H_2 (*x* h)	Ar (*y* h)	temp (°C)	yield (%)	ee (%)
1	7	0	rt	54	80 (−)
2	1	7	rt	67	77 (−)
3	1	15	rt	78	81 (−)
4[a]	1	15	−10	34	56 (−)
5[b]	1	7	80	73	64 (−)

[a]The reaction mixture was stirred for 48 h to improve conversion. [b]The reaction was run in 1,2-dichloroethane as the solvent.

Interestingly, increasing the prestirring time favored the levorotary pyridone (−)-**3aa**. This finding corroborated our hypothesis that the ion-pair formation was previously incomplete. This would explain why the selectivity was controlled by the chiral ligand rather than the chiral ligand/chiral counterion combination. The reaction yield could then be improved without loss of enantioselectivity by performing a sequential H_2/Ar prestirring, leading to pyridone (−)-**3aa** in up to 78% yield and 81% ee (entries 2 and 3).[11] Finally, we showed that modifying the reaction temperature to −10 or 80 °C decreased the selectivity (entries 4 and 5, 56% and 64% ee, respectively).

Having set up the proper conditions to generate the active catalytic species, we then screened chiral bidentate ligands (Table 4). We first observed a mismatch pairing between (*S*)-TolBINAP and Ag(*S*)-TRIP **Ag-4** as this combination led to a decrease of the ee to 53% (entry 2). (*R*)-H_8-BINAP, (*R*)-SYNPHOS, and (*R*)-SEGPHOS showed almost no reactivity (not displayed in Table 4). (*R*)-DM-MeO-BIPHEP afforded pyridone (−)-**3aa** in a low 18% yield and a moderate 45% ee (entry 3). When (*R*)-BINAP was used, a slight decrease of the selectivity was observed compared to (*R*)-TolBINAP (entry 4, 60% ee). On the contrary, the use of the bulkier and more electron-rich (*R*)-DM-BINAP improved the ee to 88% (entry 5). However, when the more hindered (*R*)-DTBOMe-BINAP was used, lower conversion and selectivity were observed (entry 7). Increasing the prestirring time to 48 h did not improve this result (entry 8). The mismatch pairing was ascertained by using the enantiomer (*S*)-DM-BINAP in the presence of Ag(*S*)-TRIP **Ag-4**. A reversal of selectivity was observed, as well as a drop of yield and enantioselectivity (50%, ee = 79% (+), entry 6), in spite of extended reaction time.

Scope and limitations were then investigated. Use of isocyanate **2b**, bearing an ethoxy substituent at the 2-position, led to (−)-**3ab** in an excellent 96% ee (Table 5, entry 2, right

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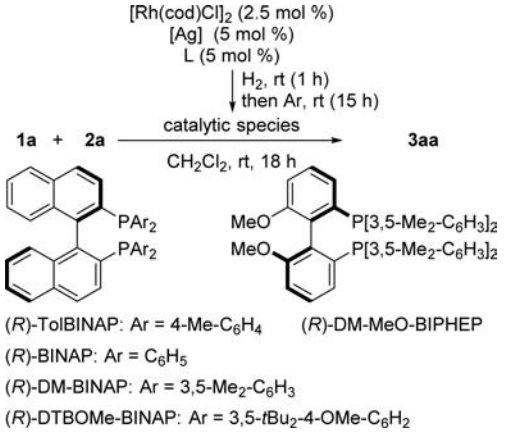
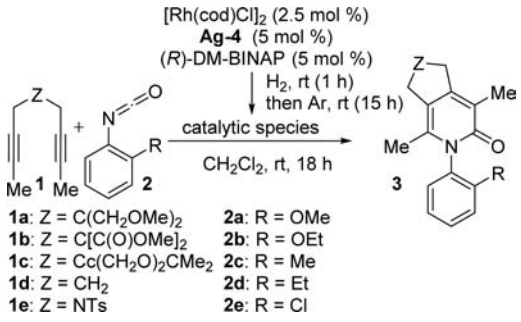
Table 4. Ligand Screening



	L	[Ag]	yield (%)	ee (%)
1	(*R*)-TolBINAP	**Ag-4**	78	81 (−)
2	(*S*)-TolBINAP	**Ag-4**	89	53 (+)
3	(*R*)-DM-MeO-BIPHEP	**Ag-4**	18	45 (−)
4	(*R*)-BINAP	**Ag-4**	84	60 (−)
5	**(*R*)-DM-BINAP**	**Ag-4**	**70**	**88 (−)**
6[a]	(*S*)-DM-BINAP	**Ag-4**	50	79 (+)
7	(*R*)-DTBOMe-BINAP	**Ag-4**	57	30 (−)
8[a]	(*R*)-DTBOMe-BINAP	**Ag-4**	68	34 (−)

[a]The reaction was run for 48 h.

Table 5. Scope and Chiral Induction Comparison



	1	2	3	yield (%)	L + AgA* ee[a] (%)	L* + $AgBF_4$ ee[b] (%)	L* + AgA* ee (%)
1	1a	2a	3aa	70	71 (−)	68 (−)	**88 (−)**
2[c]	1a	2b	3ab	91	81 (−)	88 (−)	**96 (−)**
3	1a	2c	3ac	72	29 (−)		**3 (+)**
4	1a	2d	3ad	67	32 (−)	4 (−)[d]	**9 (+)**
5	1a	2e	3ae	69	36 (−)	62 (+)[d]	**41 (−)**
6	1b	2a	3ba	88	77 (−)	80 (−)	**92 (−)**
7	1c	2a	3ca	96	74 (−)	73 (−)	**86 (−)**
8	1d	2a	3da	66	58 (−)	80 (−)	**86 (−)**
9	1e	2a	3ea	52	72 (−)	95 (−)	**94 (−)**

[a]Reference7a: $[Rh(cod)Cl]_2$/dppb/**Ag-4**, $(CH_2Cl)_2$, 80 °C (catalyst prestirring: 15 min at 80 °C). [b]$[Rh(cod)Cl]_2$/(*R*)-DM-BINAP/$AgBF_4$ (5 mol %, catalyst prestirring: 1 h under H_2 then 15 h under Ar). [c]The (*S*)-DM-BINAP/**Ag-4** pairing (48 h) led to (+)-**3ab** in 31% yield and 91% ee. [d]The (*S*)-DM-BINAP was used as the ligand.

column). Double stereodifferenciation significantly improved the results obtained with the chiral counterion or the chiral ligand (ee's of 81% and 88%, respectively, entry 2) only.[12] It is noteworthy that when (*S*)-DM-BINAP was used, a drop of reactivity (31% yield, in spite of extended reaction time) and selectivity (91% ee (+)) was observed as for test isocyanate **2a** (Table 5, footnote c). In contrast, isocyanate with alkyl substituents at the 2-position turned out to be poor substrates as they led to a quasiracemic mixture of products: pyridones (+)-**3ac** and (+)-**3ad** were isolated in 3% and 9% ee, respectively (entries 3 and 4). Likewise, when a chlorine atom is introduced at this position, a modest 41% ee is obtained (entry 5). An ether substituent in 2-position is thus essential for high chiral induction.

We then screened the diyne linker with 2-methoxyphenyl isocyanate **1a** (entries 6−9). We observed that the optimized double-stereodifferentiating conditions almost always outperformed chiral ligand or chiral counterion strategies (entries 1, 2, and 6−9), whatever the diyne used. It is noteworthy that a *gem*-dialkyl effect is not required, as 2,7-nonediyne **1d** led to pyridone (−)-**3da** in 86% ee (entry 8).

In conclusion, we have achieved the first enantioselective rhodium-catalyzed reaction in which the chirality is located both on the ligand and the counterion of a cationic rhodium active species. When ether-substituted isocyanates are used, the double-stereodifferentiation conditions outperform the selectivity of simple ones, i.e., when the chirality is introduced on the ligand or on the anion only. This work enriches the small collection of previously reported examples of double-asymmetric induction in which the two cooperative stereochemical pieces of information are introduced in a catalytic manner. It also represents one of the very few cases of the joint use of a chiral ligand and a chiral counterion. Lastly, it constitutes a proof of concept for double-asymmetric induction in [2 + 2 + 2] cycloadditions.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.orglett.5b01738.

NMR and HPLC data for pyridones **3** (PDF)

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Notes

The authors declare no competing financial interest.

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(10) A similar 59% (+) ee was obtained when $AgSbF_6$ was used as the silver salt. On the other hand, a lower 45% (+) ee was obtained with AgOTf.

(11) NMR analysis of the reaction mixture did not allow us to formally identify the catalytic species involved.

(12) We thank one of the reviewers for suggesting we compare double-stereodifferentiation data with Table 5, column 7, i.e., $[Rh(cod)Cl]_2$/(*R*)-DM-BINAP/$AgBF_4$ (5 mol %), catalyst prestirring, 1 h under H_2 then 15 h under Ar; instead of the previously described chiral ligand conditions ((*R*)-BINAP, 5 mol %, catalyst prestirring, 1 h under H_2; see refs 7a and 9c).

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