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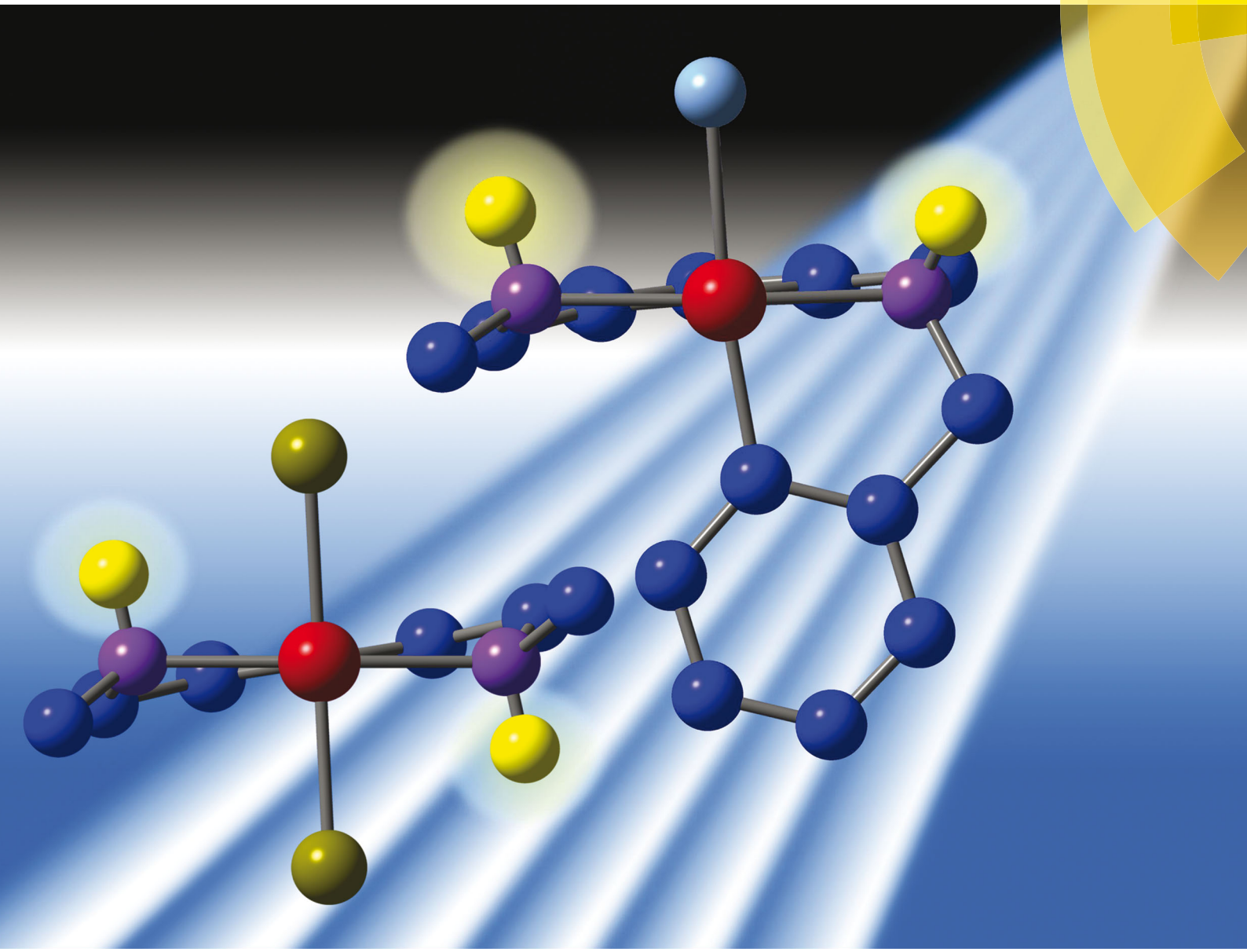

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Modulation of the coordination geometries of NCN and NCNC Rh complexes for ambidextrous chiral catalysts†

Jun-ichi Ito, *[a] Takahiro Ishihara,[b] Takaki Fukuoka,[b] Siti Rokiah Binti Mat Napi,[b] Hajime Kameo [c] and Hisao Nishiyama*[b]

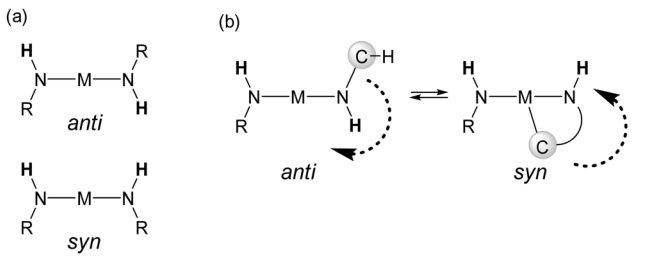
A chirality switch between novel NCN pincer Rh complexes and a related double cyclometalated NCNC Rh complex containing secondary amino groups is described. Their catalytic abilities were determined in asymmetric alkynylation of ethyl trifluoropyruvate, and the change in the coordination geometry of the Rh catalysts affected the stereochemistry of the products.

Artificial systems inspired by natural substances, such as allosteric proteins and metalloenzymes, have been studied to help fabricate switchable catalysts triggered by external stimuli, such as irradiation, pH changes, oxidation, and the addition of other substances.[1] Structural changes in the active site of a catalyst are critical to the switching function of the active and inactive forms.[2] Switchable catalysts are also an attractive tool for chirality control in asymmetric reactions.[3,4] This strategy enables the synthesis of both enantiomers through structural changes in catalysts containing a single chiral source. Recently, Feringa and co-workers demonstrated a photo- and thermo-responsive organocatalyst,[5] and Canary and co-workers described chiral switching in a redox responsive system involving a Cu atom.[6] In those systems, a structural change involving a hydrogen-bonding group, such as an N–H bond, was important for substrate recognition.

Transition-metal catalysts containing an N–H bond adjacent to a metal center are potential synergistic systems due to hydrogen bonding.[7,8] In systems with chiral ligands, multiple N–H bonds confer geometric diversity. For example, bis(amino) ligands containing two N–H bonds can form the *anti* and *syn* conformational isomers (Scheme 1a).[9] These isomers should possess different chiral recognition abilities. Therefore, structural interconversion between isomers might provide chiral switching functionality in asymmetric catalysis. However, bis(amino) ligands generally adopt one of the two conformations according to their structure (*i.e.*, acyclic or macrocyclic).[10,11] To induce the switching function, an additional coordinating group that governs interconversion and immobilization must be introduced. The present study examined metal–carbon covalent bonds as a trigger for structural changes (Scheme 1b). Cyclometalation results in an additional metal–carbon bond, which fixes the coordination geometry.[12] Therefore, the formation and cleavage of a metal–carbon bond were hypothesized to alter the coordination pattern upon interconversion of the *anti* and *syn* conformations of the N–H bonds.

Thus, the present study focused on an NCN pincer ligand with secondary amino tethers as the flexible coordination sites in the rigid pincer scaffold.[13] Construction of a double cyclometalated NCNC complex was also achieved by C–H bond activation of the NCN complex. The catalytic activities of the Rh complexes were evaluated in asymmetric alkynylation of a ketoester with an alkyne; the structures of the complexes significantly affected the absolute configurations of the products.

Ligand precursors **1a–c** were prepared by substitution of 1,5-bis(chloromethyl)-2,4-dimethylbenzene with the corresponding



Scheme 1 (a) Bisamino ligand systems with *anti* and *syn* conformations. (b) Interconversion of the *anti* and *syn* conformations by cyclometalation.

[a] *Department of Molecular and Macromolecular Chemistry, Graduate School of Engineering, Nagoya University, Furo-cho, Chikusa-ku, Nagoya 464-8603, Japan. E-mail: jito@chembio.nagoya-u.ac.jp*
[b] *Department of Applied Chemistry, Graduate School of Engineering, Nagoya University, Furo-cho, Chikusa-ku, Nagoya 464-8603, Japan. E-mail: hnishi@chembio.nagoya-u.ac.jp*
[c] *Department of Chemistry, Graduate School of Science, Osaka Prefecture University, 1-1 Gakuen-cho, Naka-ku, Sakai, Osaka 599-8531, Japan*

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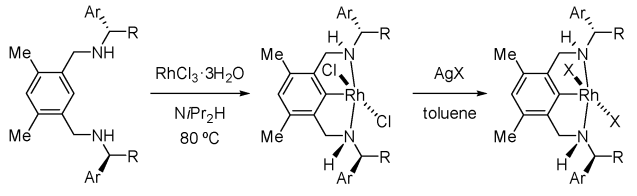
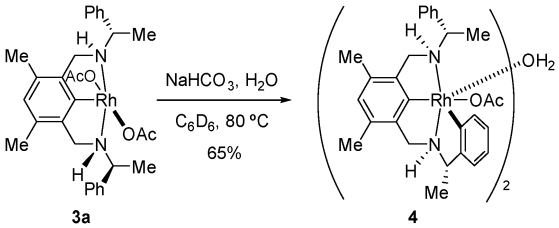


Scheme 2 Preparation of NCN-Rh complexes.



Scheme 3 Preparation of NCNC-Rh complex **4**.

chiral amines.[14] The desired NCN-Rh complexes **2a–c** were prepared by cyclometalation of **1a–c** with $RhCl_3{\cdot}3H_2O$ in diisopropylamine with heating (Scheme 2). The ^{1}H NMR spectra of **2a–c** indicated C_2-symmetric geometry in solution. An N–H signal was observed at δ 4.75–5.10 ppm. In the ^{13}C NMR spectra, the Rh–C signal appeared as a doublet at δ 145.7–147.2 ppm ($^1J_{RhC}$ = 30.8 Hz). Further reaction of **2a–c** with silver acetate or silver pivalate gave the corresponding carboxylate complexes **3a–c** in 75–90% yields. The N–H signals of **3a–c** appeared at δ 7.64–7.78 ppm in the ^{1}H NMR spectra, which were shifted downfield compared to those of **2a–c** due to hydrogen bonding with the acetate ligands.

X-ray analysis revealed that **2a** and **3a** possessed C_2-symmetry with *anti*-arrangement of the N–H moieties (Fig. 1). The sterically hindered phenyl groups were oriented outside toward the Rh center. The absolute configuration of the N atoms attached to the Rh center was determined to be *S*. In **3a**, the N1–O3 and N2–O4 distances (2.75 and 2.77 Å, respectively) as well as ^{1}H NMR data suggested the presence of hydrogen bonding between the acetate ligands and N–H groups.[15] Another structural feature was the square pyramidal geometry of Rh(III), in which the C1 atom of the phenyl fragment was located in the apical position.[16] This is in marked contrast to other NCN pincer Rh complexes, in which Rh centers adopt an octahedral geometry upon H_2O ligation.[17] The DFT calculations indicated that the unusual geometry of **2a** was due to the unexpectedly high LUMO level and high steric bulkiness of the nitrogen substituents.[14]

The aromatic rings at the flexible tethers of the amino groups were thought to undergo intramolecular C–H bond activation mediated by the acetate ligands.[18,19] Heating **3a** with $NaHCO_3$ in benzene resulted in the formation of double cyclometalated complex **4** in 65% yield (Scheme 3). The phenyl carbons of **4** attached to Rh at the pendant and center positions appeared at 128.7 ($^1J_{RhC}$ = 21.9 Hz) and 151.9 ppm ($^1J_{RhC}$ = 37.6 Hz), respectively, in the ^{13}C NMR spectrum. These types of double cyclometalated complexes are quite rare.[20]

The molecular structure of **4** was dinuclear with a bridging H_2O ligand (Fig. 2). Each Rh fragment possessed an octahedral geometry, with NCNC tetradentate coordination. A significant feature was the *syn* arrangement of the N–H bonds. Accordingly, the configurations of the N1 and N2 atoms were *R* and *S*, respectively. Thus, the stereochemistry at the N1 atom was inverted during cyclometalation. This result clearly indicates that NCN and NCNC complexes provided complementary reaction fields stemming from the *anti*- and *syn*-substitution patterns of the N–H bonds.

After establishing the geometric control of the ancillary ligands, the catalytic activities of the NCN and NCNC ligated Rh complexes were evaluated in the asymmetric alkynylation of ethyl trifluoropyruvate **6** with phenylacetylene **5a** as a model reaction (Table 1).[21] When NCN-Rh complex **3a** was used as a catalyst, (*R*)-propargyl alcohol (*R*)-**7a** was obtained in 72% yield with 63% ee (entry 1). Complex **3b** containing bulky substituents increased the enantioselectivity, while **3c** was inactive (entries 2 and 3). In contrast, **4** resulted in the inversion of enantioselectivity, affording the *S*-enantiomer (*S*)-**7a** in 81% yield with 36% ee (entry 4). The enantioselectivity improved upon a decrease in temperature (entry 5). These results confirm the concept of the

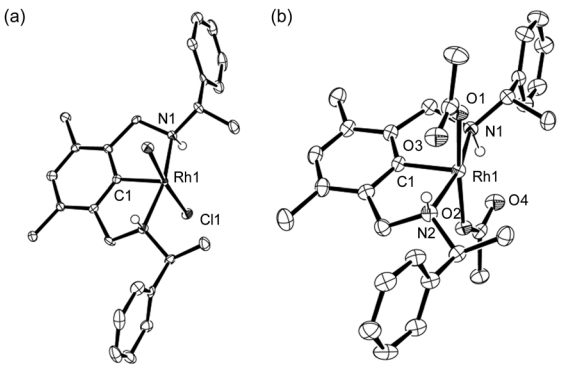


Fig. 1 ORTEP diagrams of (a) **2a** and (b) **3a** with 50% probability. Selected bond lengths (Å) of **2a**: Rh1–C1 1.909(8), Rh1–N1 2.076(4), Rh1–Cl1 2.3117(10), **3a**: Rh1–C1 1.904(3), Rh1–N1 2.085(3), Rh1–N2 2.072(3), Rh1–O1 2.037(2), Rh1–O3 2.030(2).

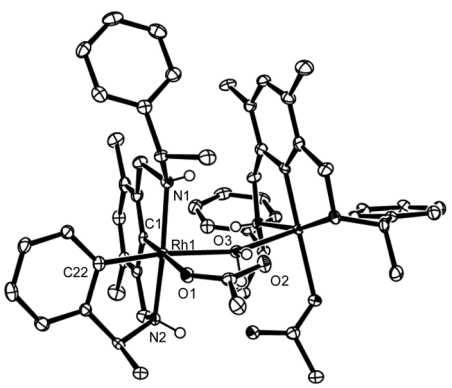
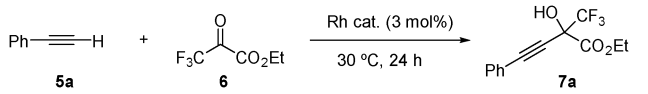


Fig. 2 ORTEP diagram of **4** with 50% probability. Selected bond lengths (Å): Rh1–C1 1.919(3), Rh1–C22 1.985(3), Rh1–N1 2.138(3), Rh1–N2 2.104(3), Rh1–O1 2.234(2), Rh1–O3 2.2807(6).

Table 1 Asymmetric alkynylation of **6** with **5a**[a]



Entry	Catalyst	Temp.	Yield (%)	ee[b] (%)
1	**3a**	30	72	63 (*R*)
2	**3b**	30	75	69 (*R*)
3	**3c**	30	3	40 (*R*)
4	**4**	30	81	36 (*S*)
5	**4**	0	57	66 (*S*)
6[c]	**4**	0	63	80 (*R*)

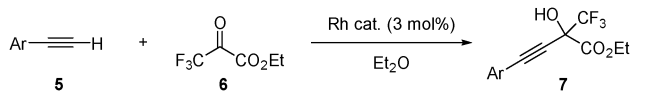
[a] Reaction conditions: **5a** (0.3 mmol), **6** (0.2 mmol), Rh catalyst (3 mol%), Et_2O (2 mL), 30 °C, 24 h. [b] Determined by HPLC. [c] Pretreatment of **4** with **5a** at room temperature for 1 h before addition of **6**.

catalyst design, as **3a** and **4** gave **7a** with opposite absolute configurations.

The experimental procedure also affected the chirality of the products. When **4** was treated with PhCCH at room temperature for 1 h prior to addition of **6**, the *R*-enantiomer (*R*)-**7a** was obtained with 80% ee (Table 1, entry 6). The stereochemistry of the product was comparable to that obtained with NCN Rh complex **3a**. Overall, this method provides a very simple way to control product chirality starting from **4**.

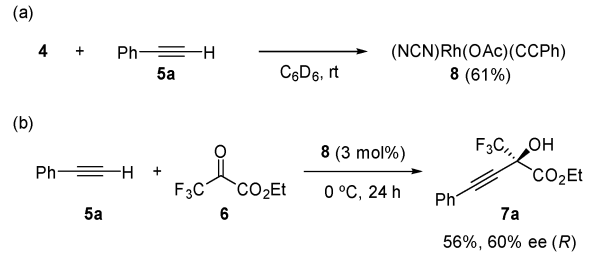
The chiral switching functions of **3a** and **4** in asymmetric alkynylation with different alkynes are illustrated in Table 2. The reaction of alkynes **5b** and **5c** in the presence of **3a** gave the corresponding alcohols in 85 and 79% ee, respectively (entries 1 and 3). In contrast, use of **4** provided the corresponding products with the inversion of stereochemistry in 46 and 79% ee (entries 2 and 4, respectively). 9-Ethynylphenanthrene **5d** showed a similar tendency (entries 5 and 6). The switching function of **4** triggered upon addition of an alkyne was also examined (entries 7–10). Catalysts generated by pretreating **4** with alkynes **5e** and **5f** gave the corresponding products in 66 and 75% ee, respectively. However, the use of **4** in the reaction afforded enantiomers in 69 and 57% ee, respectively.

Table 2 Asymmetric alkynylation of **6** with **5**[a]



Entry	Alkyne (Ar)	Catalyst	Yield (%)	ee[b] (%)
1	4-$CF_3C_6H_4$ (**5b**)	**3a**	58	85 (−)
2[c]	4-$CF_3C_6H_4$ (**5b**)	**4**	22	46 (+)
3	4-BrC_6H_4 (**5c**)	**3a**	72	79 (−)
4[c]	4-BrC_6H_4 (**5c**)	**4**	8	79 (+)
5	9-Phenanthrene (**5d**)	**3a**	67	68 (−)
6[c]	9-Phenanthrene (**5d**)	**4**	31	21 (+)
7[d,e]	4-$CH_3C_6H_4$ (**5e**)	**4**	54	66 (−)
8[f]	4-$CH_3C_6H_4$ (**5e**)	**4**	50	69 (+)
9[d,e]	4-$CH_3OC_6H_4$ (**5f**)	**4**	64	75 (−)
10[d]	4-$CH_3OC_6H_4$ (**5f**)	**4**	23	57 (+)

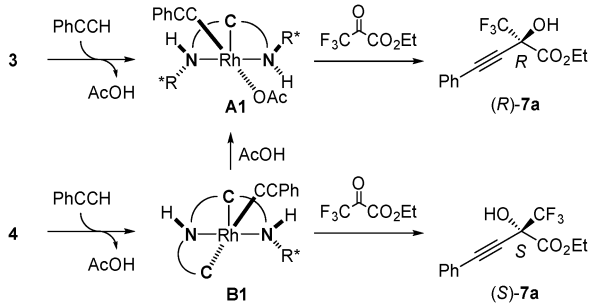
[a] Reaction conditions: **5** (0.3 mmol), **6** (0.2 mmol), Rh catalyst (3 mol%), Et_2O (2 mL), 30 °C, 24 h. [b] Determined by HPLC and polarimetry. [c] −20 °C, 48 h. [d] 0 °C, 24 h. [e] Pretreatment of **4** with **5** at room temperature for 12 h before addition of **6**. [f] 0 °C, 45 h.



Scheme 4 (a) Reaction of **4** with **5a**. (b) Catalytic reaction of **5a** with **6** by using **8** as a catalyst.

To obtain additional information about the catalytic reaction, the reactivity of **4** with alkyne **5a** was examined. The reaction proceeded smoothly at room temperature within 1 h to give NCN-Rh complex **8** in 61% yield (Scheme 4a). The ^{13}C NMR spectrum of **8** contained signals corresponding to the alkynyl ligand attached to the Rh center at δ 98.9 ($^1J_{RhC}$ = 58.1 Hz) and 105.2 ($^2J_{RhC}$ = 11.4 Hz) ppm. The signal for the *ipso* carbon in the NCN ligand was observed at 154.6 ppm ($^1J_{RhC}$ = 35.3 Hz). However, the signal of another *ipso* carbon observed at 128.7 ppm in **4** disappeared. Thus, **8** was identified as an alkynyl complex with NCN tridentate coordination. The catalytic reaction between **5a** and **6** using **8** as a catalyst similarly afforded *R*-enantiomer **7a** with 60% ee (Scheme 4b). This result implies that the NCN-Rh complexes act as catalysts for the formation of *R*-enantiomers.

A reaction pathway is proposed in Scheme 5. Based on the reactivity of the Rh acetate complex with alkynes,[21,22] an alkynyl intermediate, **A1**, is generated upon C–H activation of PhCCH (**5a**) with **4**. Subsequent insertion of a ketone into the Rh–C bond of the alkynyl ligand gives (*R*)-**7a** with a *R*-stereocenter. The NCNC-Rh system is thought to undergo the same mechanism *via* **B1**, giving (*S*)-**7a** as a major enantiomer. In this case, the NCNC tetradentate coordination could be maintained during the catalytic cycle. Although the details of the enantiomeric discrimination and turnover-limiting step are unknown,[23] the *anti* and *syn* configurations of the two N–H bonds determined by NCN and NCNC ligand systems could control product chirality. The NCNC-Rh complex **4** also served as a catalyst for the *R*-product when an alkyne was treated before addition of a ketone. **B1** is relatively unstable in the presence of a proton source, such as acetic acid, which is generated by C–H bond activation of an



Scheme 5 Proposed reaction pathway for catalytic reaction.

alkyne. Consequently, active species switched from **B1** to **A1** upon protonation of the Rh–C bond in the NCNC ligand.

In conclusion, new NCN pincer Rh complexes containing secondary amino groups as tethered coordinating groups were prepared. The molecular structures of NCN pincer complexes **2** and **3** included five-coordinated square planar geometries with the *anti* configuration of the N–H bonds and the *S* absolute configuration at the nitrogen atoms. Acetate complex **3** underwent intermolecular C–H bond activation to give double cyclometalated complex **4**, which contained unique NCNC tetradentate coordination with the *syn* configuration of the N–H bonds. In asymmetric alkynylation of terminal alkynes with β-ketoesters, the NCN and NCNC Rh complexes acted as chiral switchable catalysts for the formation of both enantiomers. This switching system based on the NCN and NCNC Rh complexes is not yet fully reversible and requires different reactions such as heating reaction and addition of an alkyne.

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Conflicts of interest

There are no conflicts to declare.

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