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Chiral Atropisomeric-NHC Catechodithiolate Ruthenium Complexes for Z-Selective Asymmetric Ring-Opening Cross Metathesis of *Exo*-Norbornenes

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Abstract: A set of 16 chiral ruthenium complexes containing atropisomerically stable N-Heterocyclic Carbene (NHC) ligands was synthesized from prochiral NHC precursors. After a rapid screening in asymmetric ring-opening-cross metathesis (AROCM), the most effective chiral *atrop*BIAN-NHC Ru-catalyst (up

to 97:3 er) was then converted to a Z-selective catechodithiolate complex. The latter proved to be highly efficient in Z-selective AROCM of *exo*-norbornenes affording valuable *trans*-cyclopentanes with excellent Z-selectivity (>98%) and high enantioselectivity (up to 96.5:3.5 er).

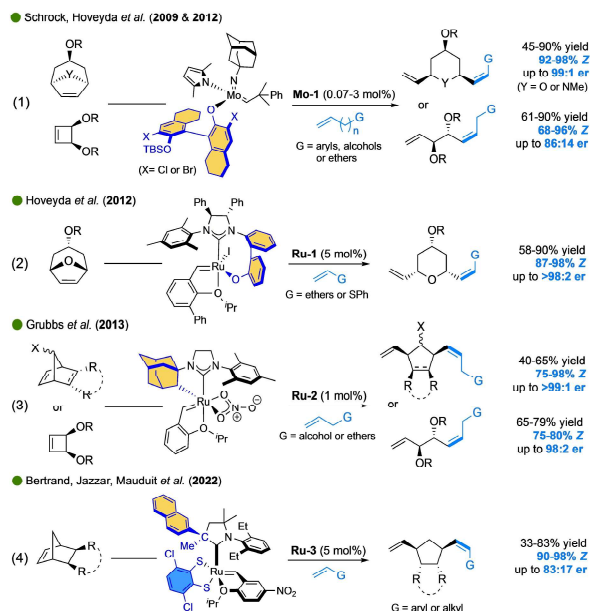
Introduction

Asymmetric olefin metathesis represents an efficient and versatile synthetic tool to produce highly valuable chiral building blocks with high enantiopurity.^[1,2] This seminal breakthrough arises from the synthesis of well-defined chiral molybdenum or ruthenium complexes that demonstrated high enantioselectivity (up to 99:1 er) in asymmetric ring-closing metathesis (ARCM)^[3] and ring-opening cross-metathesis (AROCM)^[4] but also a promising 52% ee in asymmetric cross-metathesis (ACM).^[5] Merging the Z-selectivity^[6,7] and the enantioselectivity of metathetic transformations represents a challenging way for producing relevant chiral molecules featuring a Z-alkene moiety.^[8] However, as depicted in Figure 1, only few examples were described in Z-selective AROCM.^[9] Schrock, Hoveyda and coworkers reported in 2009 the first chiral Mo-complex **Mo-1** containing a monodentate BINOL-type ligand, which gave high enantioinductions in various asymmetric ring-opening cross-metathesis (AROCM) combined with a remarkable degree of Z-selectivity [Figure 1, Equation (1)].^[9a,b] Hoveyda and coworkers then developed the chiral-at-ruthenium complex **Ru-1** containing a chiral bidentate aryloxy N-heterocyclic Carbene (NHC) ligand that efficiently promoted the

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A. State of the art in Z-selective AROCM



B. First chiral catechodithiolate NHC-containing ruthenium complex (this work)

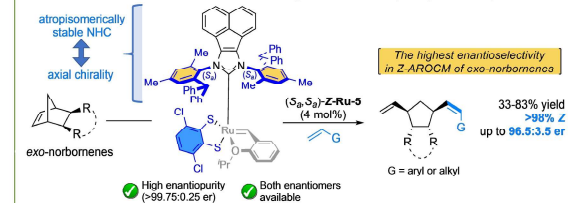


Figure 1. (A) Previously described Z-selective AROCM. (B) Synthesis of the first chiral NHC–Ru complex for Z-selective AROCM of *exo*-norbornenes (this work).

AROCM of oxabicyclic alkenes furnishing tetrahydropyran products with excellent enantioselectivities (up to >98:2 er) and good to excellent Z selectivity [87–98%; Figure 1, Equation (2)].^[9c]

The chiral cyclometalated Ru-catalyst **Ru-2** designed by Grubbs and coworkers has also proved to be highly efficient in Z-AROCM of *endo*-norbornenes and cyclobutenes, affording various Z-alkenes with high ees [Figure 1, Equation (3)].^[9d,e] Very recently, we reported the first synthesis of chiral **Ru-3** complex,^[10] which combines a chiral cyclic(alkyl)(amino)carbene (CAAC) ligand^[11] and a catechodithiolate moiety [Figure 1, Equation (4)].^[7f–k] **Ru-3** demonstrated good catalytic performances in Z-AROCM of *exo*-norbornenes leading to valuable chiral *trans*-cyclopentanes with excellent Z-selectivity (90–98%) and promising enantioselectivities (up to 83:17 er). In order to improve the efficiency of readily accessible Z-enantioselective catechodithiolate catalysts, we wished to develop their NHC-based congeners (Figure 1, B). In this context, we focused our attention on chiral atropisomeric NHC ligands recently developed in our groups, which capitalize an expedient access from simple prochiral imidazolium salts.^[12]

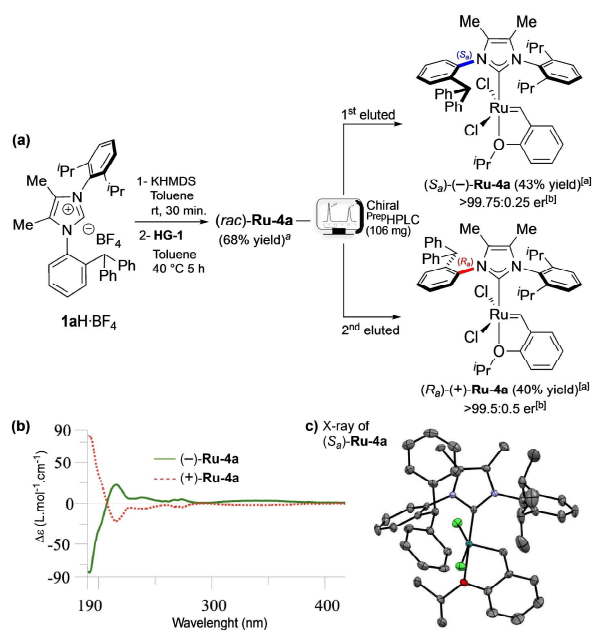
Results and Discussion

Our study was initiated by the synthesis of C_1 -symmetric Ru-complex **Ru-4a** from the prochiral NHC precursor **1aH**·BF₄ (Scheme 1, a).^[12] The latter was deprotonated by KHMDS and

the resulting free carbene was then reacted with commercially available first generation Hoveyda complex **HG-1**. The expected NHC-based Ru-complex **Ru-4a** was isolated in 68% yield after silica gel purification. To our delight, a racemic mixture of stable atropisomers was confirmed by chiral-stationary phase HPLC analysis and both enantiomers were efficiently isolated in good yields (40–43% over theoretically 50%) and excellent enantiopurities (>99.5:0.5 to >99.75:0.25 er) by preparative chiral HPLC on a Chiralpak IG column (see Supporting Information for details).

The chiroptical properties of **Ru-4a** were obtained through Electronic Circular Dichroism (ECD) that showed expected mirror-image spectra for the enantiomers (Scheme 1, b). Importantly, no racemization occurred for (–)-**Ru-4a** in 1,2-dichlorobenzene after 12 h at 180 °C, implying a rotation barrier value higher than 170 kJ·mol^{–1}. This impressive atropisomeric robustness was also confirmed by DFT calculations (Figure 2; 190.0 and 209.2 kJ·mol^{–1}; see Supporting Information for details). Noteworthy, this stability is maintained even at 80 °C with half-life times up to 20 000 years (see Supporting Information, P19).

Following this efficient methodology, we were able to synthesize other Ru-complexes containing various C_1 - and C_2 -symmetric atropisomeric ^{atrop}NHC ligands that featured various *ortho*-substituents as well as a bis(imino)acenaphthene (BIAN)^[13] backbone (Scheme 2, for more details about the synthesis of NHC precursors **1b–g**, see Supporting Information). We were pleased to observe that in all cases, highly stable atropisomeric Ru-complexes were formed. Moreover, each enantiomer was successfully isolated in moderate to excellent yield (38 to 49%) and high enantiopurity (>99:1 to >99.75:0.25 er). However, C_2 -symmetric ^{atrop}BIAN-NHC also led to the formation of the corresponding achiral *meso*-complex, which alters the yield of the desired homochiral counterpart. Fortunately, an efficient separation by silica gel chromatography and/or HPLC at preparative scale was possible and expected C_2 -symmetric homochiral **Ru-4g–h** complexes were isolated in moderate 38–45% overall yields and excellent enantiomeric purities (>99.75:0.25 er). Furthermore, the absolute configuration of each complex was attributed via X-ray diffraction analysis (Figure 3),^[14] excepted for complexes **Ru-4d, f** and **Ru-4h** for which the configuration of enantiomers was attributed by ECD spectra comparison.



Scheme 1. Proof of concept: (a) synthesis of C_1 -symmetric ^{atrop}NHC-**Ru-4a** and its preparative HPLC resolution. (b) ECD spectra. (c) Solid-state structure of complex (S_a)-(–)-**Ru-4a** from single crystal X-ray diffraction. Displacement ellipsoids are drawn at 50% probability. Hydrogen atoms have been omitted for clarity. [a] Isolated yield. [b] Determined by chiral-stationary phase HPLC analysis.

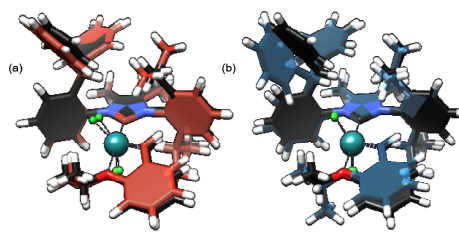
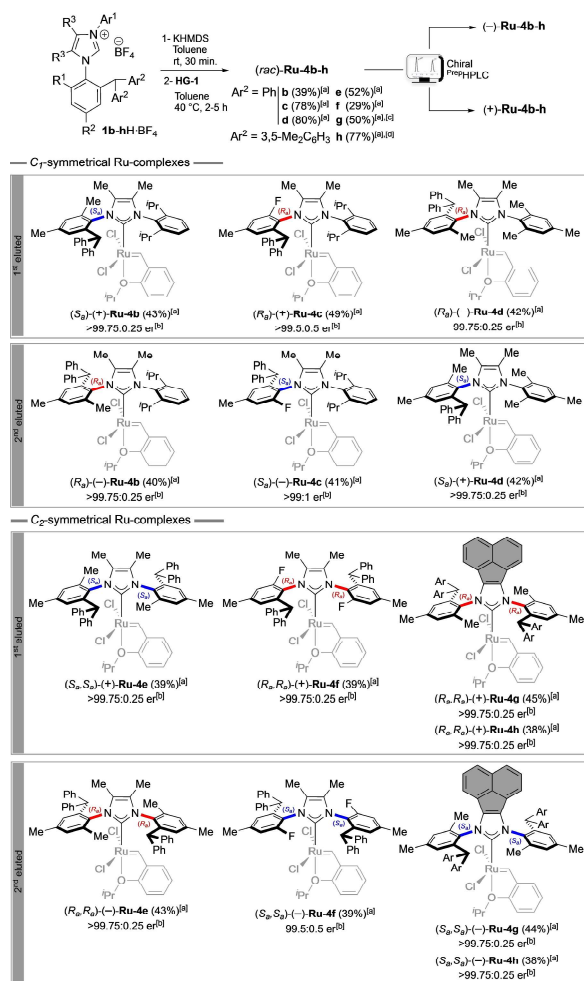


Figure 2. Comparison between the experimental (Xray) geometry of complex **4a** (in black) and DFT calculated structures. (a) structure optimised from the Xray's coordinates (in red) and (b) best minimum structure (in blue).



Scheme 2. Library of enantiomerically pure C₁- and C₂-symmetric *atrop*NHC-Ru-4b-h complexes. [a] Isolated yield. [b] Determined by chiral-stationary phase HPLC analysis. [c] 27% of *meso*-complex was also formed (see Supporting Information for details). [d] An inseparable mixture of C₂/*meso* (1.3/1) complexes was isolated.

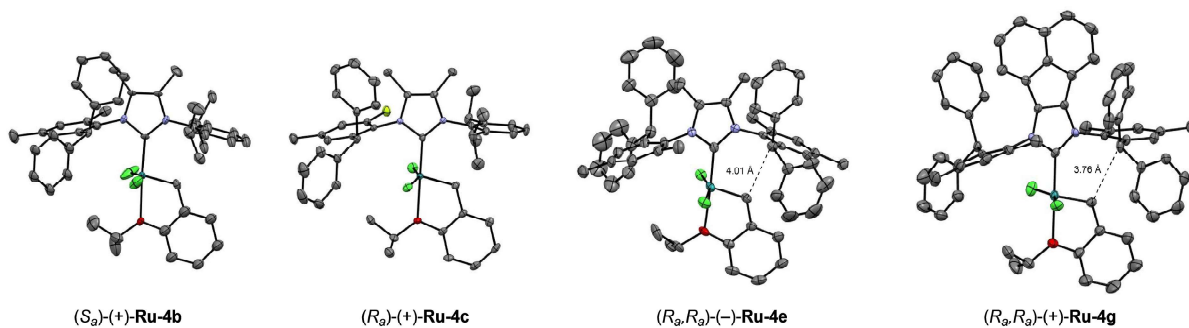


Figure 3. Solid-state structures of C₁-symmetric *atrop*NHC-Ru-4b, c and C₂-symmetric *atrop*NHC-Ru-4e, g from single crystal X-ray diffraction. Displacement ellipsoids are drawn at 50% probability. Hydrogen atoms have been omitted for clarity.

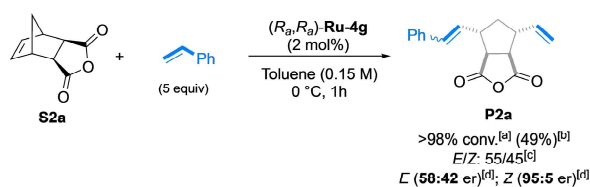
Having this small library of enantiomerically pure C₁- and C₂-symmetric *atrop*NHC-ruthenium complexes in hand, we next investigated their catalytic performances in the AROCM of *meso*-norbornene derivative **51** (Table 1). First, the reaction was conducted in toluene^[15] at room temperature using 1 or 2 mol% of ruthenium in presence of styrene (5 equiv.). C₁-symmetric complexes afforded moderate enantioselectivities, reaching a maximum of 78.5:21.5 er with (R_a)-Ru-4c that contains a fluorine ortho-substituent (entries 1–4). Of note, usual *E*:*Z* ratios were observed with the *E*-stereoisomer formed as the major product (80:20 to 90:10). Interestingly, C₂-symmetric counterparts showed higher reactivity completing the reaction within 30 min at 1 mol% catalytic loading with excellent enantioselectivities (entries 5–7). The highest enantiomeric ratio was reached with (R_aR_a)-Ru-4g complex (96:4 er, entry 7), thanks to the BIAN-skeleton that brings a more favourable spatial arrangement of benzhydryl fragments, closer to the reactive site (3.76 Å, Figure 3). Performing the AROCM at 0 °C enabled to slightly increase the enantio-induction as well as the isolated yield (97:3 er, 75%; entry 9). However, BIAN (R_aR_a)-Ru-4h featuring a 3,5-dimethylphenyl moiety at the quaternary center would seem too sterically congested, as a slight decrease of enantioinduction was observed (93.5:6.5; entry 10). At last, the bis-iodo analog (S_aS_a)-(-)-Ru-4i was also synthesized as the replacement of chlorines by bulkier iodides usually gave higher enantioselectivities.^[16] Unfortunately, no improvement of enantioselectivity was observed under the established reaction conditions (92.5:7.5 er, see Supporting Information table S4.3).

We further investigated the AROCM with *exo*-norbornene derivatives **S2a** and styrene that led to valuable *trans*-cyclopentanes **P2a** (Scheme 3).^[17] It is worth noticing that AROCM with *exo*-norbornenes are very scarce and have been reported to give significant lower enantioselectivities than *endo*-substrates.^[18] Despite a full conversion reached after one hour and a moderate 49% isolated yield, we observed a noticeable drop of the *E*/*Z* ratio (55/45) in comparison with *endo*-norbornenes **51**. Unexpectedly, a sharp contrast about the enantioselectivity of *E*- and *Z*-isomers between was observed, with as a low 58:42 er for the former while an excellent 95:5 er was reached for the latter.

Table 1. Evaluation of enantiomerically pure C_2 - and C_2 -symmetric $atrop$ -NHC-Ru-4 a-h complexes in catalytic AROCM of *meso*-norbornene **S1**.

Entry	catalyst [mol%]	Time [h]	Conv. [%] ^[a] (yield) ^[b,c]	E/Z ratio ^[d]	er (E)-P1 ^[e]
1	(<i>S_a</i>)-Ru-4 a (2)	1.5	99 (58)	90/10	71.5:28.5
2	(<i>S_a</i>)-Ru-4 b (2)	1.5	99 (63)	80/20	78:22
3	(<i>R_a</i>)-Ru-4 c (2)	1.5	99 (54)	85/15	78.5:21.5
4	(<i>R_a</i>)-Ru-4 d (2)	1.5	99 (54)	90/10	67:34 ^{ent}
5	(<i>S_aS_a</i>)-Ru-4 e (1)	0.5	99 (58)	85/15	91.5:8.5
6	(<i>R_aR_a</i>)-Ru-4 f (1)	0.5	99 (69)	90/10	92:8
7	(<i>R_aR_a</i>)-Ru-4 g (1)	0.5	99 (65)	80/20	96:4 ^{ent}
8 ^[f]	(<i>R_aR_a</i>)-Ru-4 g (1)	22	99 (66)	85/15	96.5:3.5 ^{ent}
9 ^[f]	(<i>R_aR_a</i>)-Ru-4 g (2)	3.5	99 (75)	85/15	97:3 ^{ent}
10 ^[f]	(<i>S_aS_a</i>)-Ru-4 h (2)	6	99 (54)	75/25	93.5:6.5

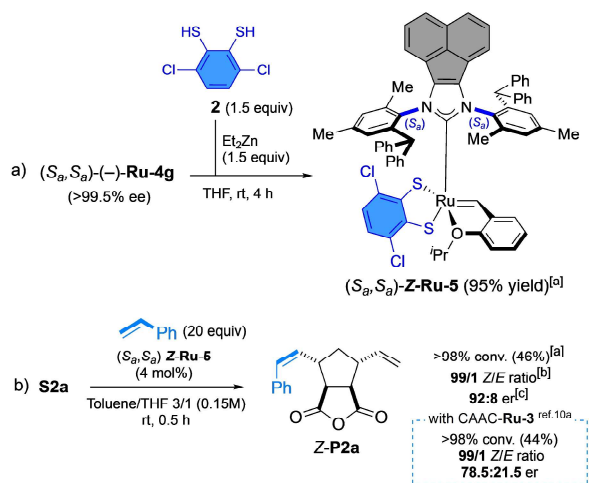
[a] Conversions were determined by ¹H NMR spectroscopy using 1,3,5-trimethoxybenzene as internal standard. [b] Isolated yield. [c] 4 to 15% of over metathesis product P1' were also formed (see Supporting Information for details). [d] Determined by SFC on the crude mixture. [e] Determined by SFC on a chiral phase. Absolute configuration determined in accordance with literature (see Ref. [10a]). [f] Reaction performed at 0 °C. *ent* = opposite enantiomer.



Scheme 3. AROCM of *exo*-norbornene **S2a** catalysed by enantiomerically pure C_2 -symmetric $atrop$ -NHC (R_a,R_a)-Ru-4 g. [a] Conversion was determined by ¹H NMR spectroscopy using 1,3,5-trimethoxybenzene as internal standard. [b] Isolated yield. [c] Determined by GC analysis. [d] Determined by HPLC or GC analysis on chiral phase.

This last result encouraged us to develop a Z-selective version of chiral BIAN-Ru-4 g, which would afford the exclusive formation of Z-*trans* cyclopentanes with high enantioselectivity. Taking into consideration their straightforward access (one step) and the excellent Z-selectivity gained in various cross-metathesis transformations, we focused our attention to the class of Z-selective catechodithiolate Ru-catalysts previously developed by Hoveyda and coworkers.^[7f-k]

Following a modified synthetic protocol,^[19] catechodithiolate (S_a,S_a)-Z-Ru-5 was synthesized in 95% isolated yield by reacting (S_a,S_a)-Ru-4 g and 3,6-dichlorocatechodithiol **2** in presence of diethylzinc (Scheme 4, a). To our delight, (S_a,S_a)-Z-Ru-5 efficiently promoted the AROCM between *exo*-norbornene **S2a** and styrene at ambient temperature within 30 min (Scheme 4, b).^[20] The *trans*-cyclopentane Z-P2a was isolated in moderate 46% yield and an excellent >98% Z-selectivity. As expected, a good 92:8 enantiomeric ratio was reached, outperforming the enantioselectivity recently reached with chiral CAAC Ru-3 (Figure 1; 78.5:21.5 er; see Ref. [10a]). Before extending the scope of *exo*-norbornenes, we decided to confirm that (S_a,S_a)-Z-



Scheme 4. Synthesis of enantiomerically pure catechodithiolate (S_a,S_a)-Z-Ru-5 and its catalytic evaluation in Z-selective AROCM. [a] Isolated yield. [b] Determined by GC analysis. [c] Determined by GC analysis on chiral phase.

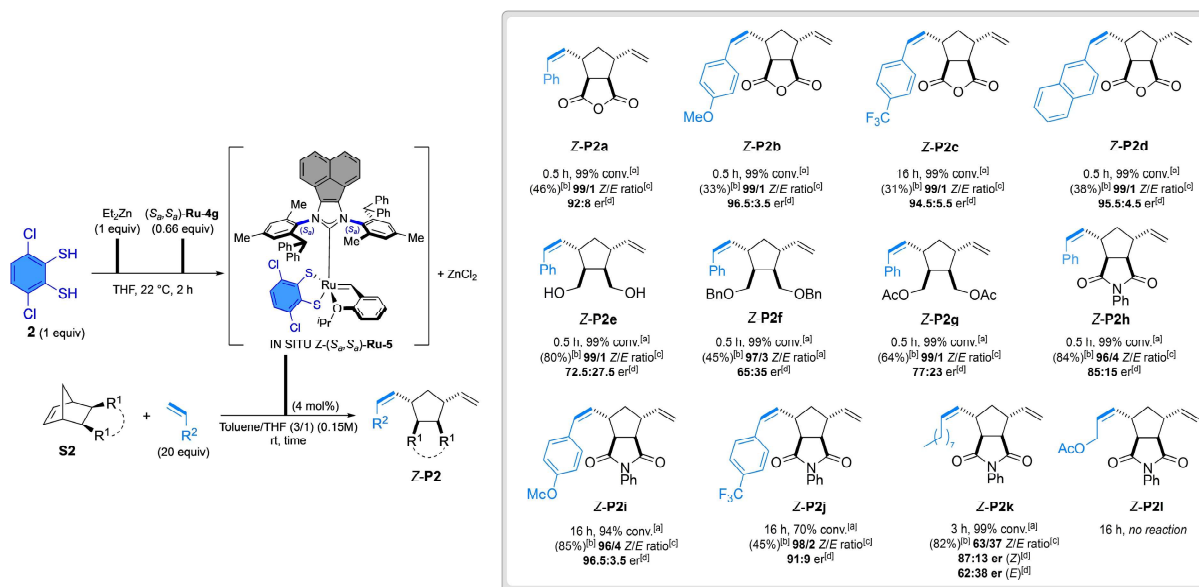
Ru-5 catalyst could be generated in situ (IS) following a robust protocol recently developed in our group preventing the use of a glove-box.^[19] As disclosed in Scheme 5, we were delighted to observe that Z-P2a was formed in similar 46% yield with the same high levels of Z-selectivity and enantio-induction.

A range of *exo*-norbornene derivatives and functionalized styrenes were then studied using this more user-friendly protocol (Scheme 5). Resulting AROCM products were isolated with moderate to good isolated yields (31–85%)^[21] and excellent Z/E ratios (96/4 to 99/1).

Trans-cyclopentanes Z-P2 b,c,d and Z-P2 h,i,j containing respectively an anhydride or a succinimide function provided good to excellent enantiomeric ratios (from 85:15 to 96.5:3.5 er, the best reported so far^[18]) while the chiral induction slightly decreased for diol Z-P2 e and its protected congeners Z-P2 f,g (65:35 to 77:23 er). However, AROCM with 1-decene yielded Z-P2 k in 82% with a good 87:13 er but the Z-selectivity dropped to 63/37 and no reaction was observed with allyl acetate.

Conclusion

In summary, 16 chiral ruthenium complexes containing various atropisomerically stable NHCs were synthesized in good yields with excellent enantiomeric purities (up > 99.75:0.25 er), thanks to a preparative HPLC resolution on a chiral stationary phase. The chiral BIAN-based Ru-complex Ru-4 g was the most efficient to catalyse the asymmetric ring-opening-cross metathesis of *endo*- and *exo*-norbornenes (up to 97:3 er). Successfully converted into its corresponding Z-selective catechodithiolate complex Z-Ru-5 (95% isolated yield or in situ generated), the latter demonstrated high efficiency in Z-selective AROCM of *exo*-norbornenes affording valuable *trans*-cyclopentanes in



Scheme 5. Scope of Z-selective AROCM catalysed by in situ (IS) generated enantiomerically pure catechodithiolate ($S_{or}S_{or}$)-Z-Ru-5. [a] Conversions were determined by ^1H NMR spectroscopy using 1,3,5-trimethoxybenzene as internal standard. [b] Isolated yield after column chromatography (Note that Z-P2a–d, f are prone to rapidly decompose during the purification). [c] Determined by GC analysis. [d] Determined by GC analysis on chiral phase.

>98% Z-selectivity and the highest enantioselectivities reported so far (up to 96.5:3.5 er).

Experimental Section

All experimental and crystallographic data associated with this work are available in the Supporting Information.

General procedure for AROCM: In a flame dried 10-mL Schlenk under Ar, were placed the desired substrate (0.2 mmol, 1.0 equiv) and the desired cross partner (1.0 mmol, 5.0 equiv). Toluene was added (1.33 mL) and the reaction mixture was placed at the desired temperature (using isopropanol bath thermostated via a cryostat if cooling was necessary). A freshly prepared solution under Ar of the desired catalyst was added. The mixture was stirred at the desired temperature until completion. Reaction was quenched with ethyl vinyl ether. Volatiles were removed under vacuum. The crude mixture was analysed to determine E/Z ratio (by GC or ^1H NMR). Product was purified by silica gel column chromatography. Enantiomeric excesses (ees) were determined on chiral stationary phase by HPLC, GC or SFC. See detailed procedure for each substrate and data characterization in the Supporting Information.

General procedure for Z-AROCM with in-situ generated ($S_{or}S_{or}$)-Z-Ru-5: Out of the glove box, in a flame-dried 4-mL vial under Ar, 1,4-dichlorocatechol dithiolate **2** (8 mg, 0.038 mmol, 1.5 equiv) and diethyl zinc solution (1 M in hexanes, 38 μL , 0.038 mmol, 1.5 equiv) were dissolved in THF (2.5 mL). ($S_{or}S_{or}$)-Ru-4g (0.025 mmol, 1.0 equiv) was added. The green mixture was stirred 4 h at room temperature. This freshly prepared solution of catalyst ($S_{or}S_{or}$)-Ru-5 was used without further purification. In a flame-dried 10-mL Schlenk under Ar, the desired substrate (0.2 mmol, 1.0 equiv) and the desired cross partner (4.0 mmol, 20.0 equiv) were diluted in Toluene (1.0 mL). The previously prepared solution of Ru-5 (0.33 mL, 0.008 mmol, 4 mol%) was added. The mixture was stirred until completion at

room temperature. The reaction was quenched with ethyl vinyl ether. Volatiles were removed under vacuum. The crude mixture was analysed to determine E/Z ratio (by GC or ^1H NMR). Product was purified by silica gel column chromatography. Ees were determined on chiral stationary phase by HPLC. See detailed procedure for each substrate and data characterization in the Supporting Information.

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Conflict of Interest

The authors declare no conflict of interest.

Keywords: atropisomers · enantioselectivity · NHC · olefin metathesis · Z-selectivity

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- [15] A rapid screening of other solvents was performed but similar levels of enantioselectivity were observed (see Supporting Information, table S4.3 for details).
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