Chiral Cyclopentadienyl-Iron and -Ruthenium Lewis Acids Containing the Electron-Poor BIPHOP-F Ligand: a Comparison as Catalysts in an Asymmetric Diels–Alder Reaction

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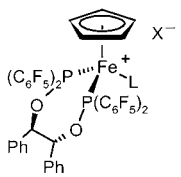
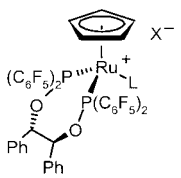
Received June 6, 2000; Accepted August 14, 2000

Keywords: asymmetric catalysis; cycloadditions; iron; Lewis acids; ruthenium

Lewis acids play a key role as catalysts in organic synthesis and applications advance at a rapid pace.[1] Transition metal Lewis acid catalysts show high promise because of increased stability, structural definition, and resistance to hydrolysis.[2] Our target is the development of stable chiral transition metal Lewis acids that activate substrates by single point coordination and that efficiently induce asymmetry in the reaction products. In previous reports we have shown that the readily prepared Fe and Ru Lewis acids $[CpFe(BIPHOP\text{-}F)]^+$ (**1**) and $[CpRu(BIPHOP\text{-}F)]^+$ (**2**) (BIPHOP-F = 1,2-bis-[bis(pentafluorophenyl)phosphanyloxy]-1,2-diphenylethane) give high induction in the Diels-Alder reaction of dienes with enals.[3] In this communication we relate new data and synthetic procedures for this family of catalysts. We also compare the behavior of the isoelectronic and isostructural Fe(II) complexes (*R*,*R*)-**1 a–e** and Ru(II) complexes (*S*,*S*)-**2 a–e** in their characteristics as catalysts for the asymmetric Diels–Alder reaction of methacrolein and cyclopentadiene.[4]



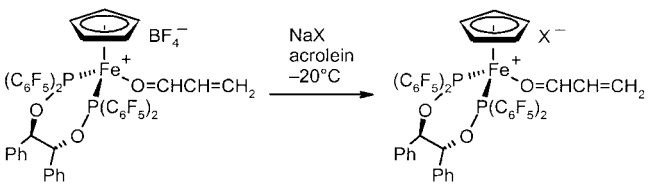
(*R*,*R*)-**1a** (L = CH_2CHCHO, X = BF_4)
(*R*,*R*)-**1b** (L = CH_2CHCHO, X = OTf)
(*R*,*R*)-**1c** (L = CH_2CHCHO, X = PF_6)
(*R*,*R*)-**1d** (L = CH_2CHCHO, X = SbF_6)
(*R*,*R*)-**1e** (L = CH_2CHCHO, X = TFPB)



(*S*,*S*)-**2a** (L = $(CH_3)_2CO$, X = BF_4)
(*S*,*S*)-**2b** (L = $(CH_3)_2CO$, X = OTf)
(*S*,*S*)-**2c** (L = $(CH_3)_2CO$, X = PF_6)
(*S*,*S*)-**2d** (L = $(CH_3)_2CO$, X = SbF_6)
(*S*,*S*)-**2e** (L = $(CH_3)_2CO$, X = TFPB)
(*S*,*S*)-**3a** (L = H_2O, X = BF_4)
(*S*,*S*)-**3d** (L = H_2O, X = SbF_6)
(*S*,*S*)-**4a** (L = $CH_2C(CH_3)CHO$, X = BF_4)
(*S*,*S*)-**4d** (L = $CH_2C(CH_3)CHO$, X = SbF_6)

Complex Synthesis

With the Ru catalysts **2**, the rate of Diels–Alder reactions depends strongly on the catalyst counteranion. This raises the question of whether the same effect would be observed in the Fe catalyst series **1**. As reported, the Ru catalysts (*S*,*S*)-**2 a–d** are readily generated by iodide abstraction in [CpRu(BIPHOP-F)I] with the appropriate silver salt[3b] and, for (*S*,*S*)-**2 e**, by metathesis of the SbF_6^- anion in (*S*,*S*)-**2 d** with sodium tetrakis[3,5-bis(trifluoromethyl)phenyl]borate (NaTFPB)[5] in CH_2Cl_2.[6] Anion variation in the Fe catalyst is less straightforward: whereas protonation of [CpFe(BIPHOP-F)Me] with commercially available $HBF_4 \cdot Et_2O$ in CH_2Cl_2 followed by addition of acrolein affords cleanly the complex (*R*,*R*)-**1 a**,[3a] other acids are either not readily available (in pure form or as solutions in aprotic solvents) or are difficult to handle ($HSbF_6$). Iodide abstraction in [CpFe(BIPHOP-F)I][7] by $AgSbF_6$ in CH_2Cl_2 followed by addition of acrolein is partially successful but purification of the cationic Fe species is hampered by the low thermal stability of the complex. Anion metathesis in (*R*,*R*)-**1 a** in acetone[6b] using an excess of the appropriate sodium salt



(*R*,*R*)-**1a**

(*R*,*R*)-**1b** (X = OTf) 75%
(*R*,*R*)-**1c** (X = PF_6) 77%
(*R*,*R*)-**1d** (X = SbF_6) 95%
(*R*,*R*)-**1e** (X = TFPB) 85%

Scheme 1. Synthesis of (*R*,*R*)-**1 b–e** by anion metathesis on (*R*,*R*)-**1 a**.

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has not been successful in our hands. After much experimentation we found that when this reaction is carried out in neat acrolein, the complexes (*R*,*R*)-**1 b–e** are obtained in good yields (Scheme 1). This efficient route is an important step forward in the Fe Lewis acid catalyst synthesis.

Properties

The additional step of anion metathesis in the synthesis of (*R*,*R*)-**1 b–e** provides cleaner Fe catalysts and this makes the addition of 2,6-lutidine or 2,6-di-*t*-butyl-pyridine to scavenge achiral acid impurities redundant.[6a] With (*R*,*R*)-**1d** the enantiomeric excess in the Diels–Alder reaction[8] of methacrolein with cyclopentadiene decreases only slightly (from 97% ee to 95% ee) without added base. This parallels our findings with the corresponding Ru complexes.[5b]

Complexes (*R*,*R*)-**1 b–e** decompose in CH_2Cl_2 above –20 °C and thus have analogous stability as (*R*,*R*)-**1 a**.[5a] Addition of D_2O to a solution of (*R*,*R*)-**1 d** in [D_8]THF at –20 °C also results in rapid complex degradation. This contrasts with the room temperature stable solutions of the analogous Ru complex (*S*,*S*)-**2 d**, and with the formation of the stable aquo complex (*S*,*S*)-**3 d** upon addition of water. The aquo complex is labile and provides another entry to the catalyst: results obtained in the Diels–Alder reaction[8] of methacrolein with cyclopentadiene are very similar in terms of reactivity and selectivity (21 h reaction time, 96% yield, 89% ee) to those with the acetone complex (*S*,*S*)-**2d** (22h reaction time, 91% yield, 92% ee).

Rate of Diels-Alder Reactions

As mentioned, with the Ru catalysts (*S*,*S*)-**2 a–e** the rate of the Diels–Alder reaction[8] of methacrolein and cyclopentadiene strongly varies with the catalyst counteranion and it increases in the order $TfO^- < BF_4^- < PF_6^- < SbF_6^- < TFPB^-$.[5b] With the Fe complexes (*R*,*R*)-**1 a–e** the same trend is observed except that no further rate increase is found on going from (*R*,*R*)-**1 d** (SbF_6) to (*R*,*R*)-**1 e** (TFPB). Selected results are shown in Fig. 1. For clarity we have omitted the curves for (*R*,*R*)-**1 c** (PF_6) and (*R*,*R*)-**1 e** (TFPB). With the former the reaction is complete after 2 h (97% ee) and the curve of the latter is almost superimposable with that of (*R*,*R*)-**1 d**.

Two interpretations have been advanced to explain the effect of the anion on the rate: competition of the anion and the aldehyde substrate for the Lewis acid coordination site of the catalyst[9] and decrease of rate of product release due to cooperative binding of the anion to both the aldehyde product and the catalyst. This second hypothesis is based on the observation

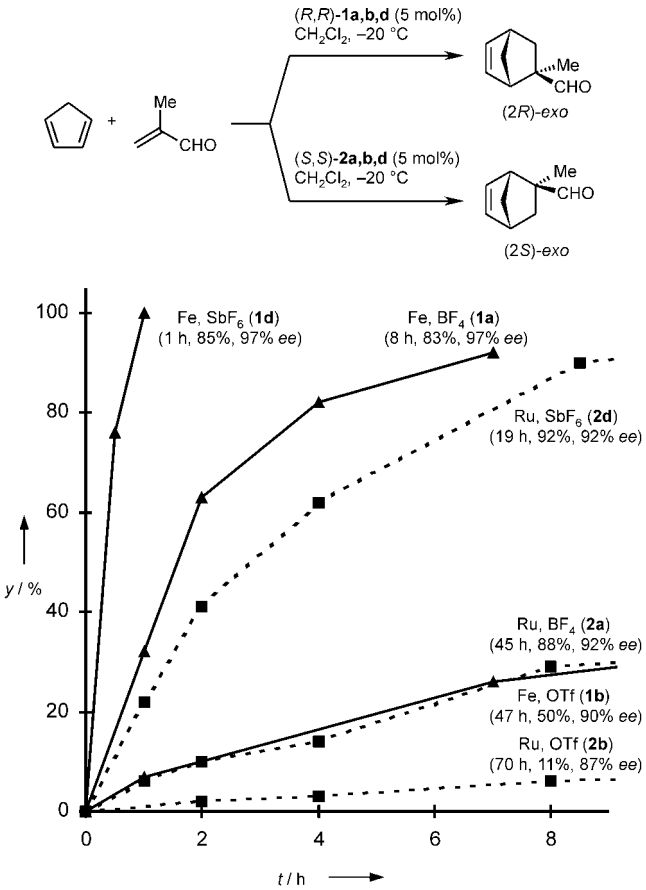

Fig. 1. Plot of GC yield (*y*) as a function of reaction time (*t*) for the reaction of methacrolein with cyclopentadiene in the presence of (*R*,*R*)-**1 a, b, d** or (*S*,*S*)-**2 a, b, d**. In parentheses: total reaction time, yield of isolated product and *ee* value of the *exo*-cycloadduct. Reactions with catalysts **1** (plot lines ___) were carried out with excess diene (5 equiv), those with catalysts **2** (plot lines .....) with 1 equiv diene (excess diene has an effect only on the rate of reaction with catalysts **1** but not **2**, see text). The difference in chemical yield with the low activity-catalysts **1 b** and **2 a** likely reflects degradation of the less stable catalyst **1 b** over the long time period during which the reaction was run.

of H···F interactions between F atoms of SbF_6^- and cyclopentadienyl H and formyl H of the coordinated methacrolein in the solid state structure of the SbF_6 methacrolein Ru complex (*S*,*S*)-**4 d**.[5b] Though weak, these interactions must be highly sensitive to the nature of the anion. The existence of close ion-pairs in CD_2Cl_2 solution in our Ru catalyst system has now been demonstrated using the ^1H-^{19}F HOESY NMR experiment.[10] The magnetic characteristics of the Sb isotope nuclei preclude this measurement with the SbF_6^- anion. With the BF_4 methacrolein Ru complex (*S*,*S*)-**4 a** in CD_2Cl_2 at room temperature, the observed cross-peaks indicate clearly interactions between the formyl H and the cyclopentadienyl H with F atoms of the BF_4^- anion (Fig. 2). Analogous data have been obtained with the PF_6 complex.

This, of course, does not rule out the hypothesis of competition between aldehyde and anion for the Lewis acid coordination site and a ^{1}H NMR experiment indeed confirms coordination of the TfO^- anion to the Ru catalyst: addition of successive portions of nBu$_4$NOTf to the SbF_6 acetone Ru complex (*S*,*S*)-**2 d** in CD_2Cl_2 at room temperature results in displacement of the coordinated acetone by TfO^- and formation of the neutral complex [CpRu(BIPHOP-F)(OTf)] as indicated by ^{1}H, ^{19}F and ^{31}P NMR data.[11] Interestingly, a similar experiment with nBu$_4$NBF$_4$ shows no evidence for coordination of BF_4^- anion.

In the case of a dienophile/anion or dienophile/cycloadduct competition for the coordination site, an increase of the dienophile concentration should result in a higher rate of catalysis. This effect is indeed observed for the reaction catalyzed by the BF_4 Fe complex (*R*,*R*)-**1 a** and the BF_4 Ru complex (*S*,*S*)-**2 a**

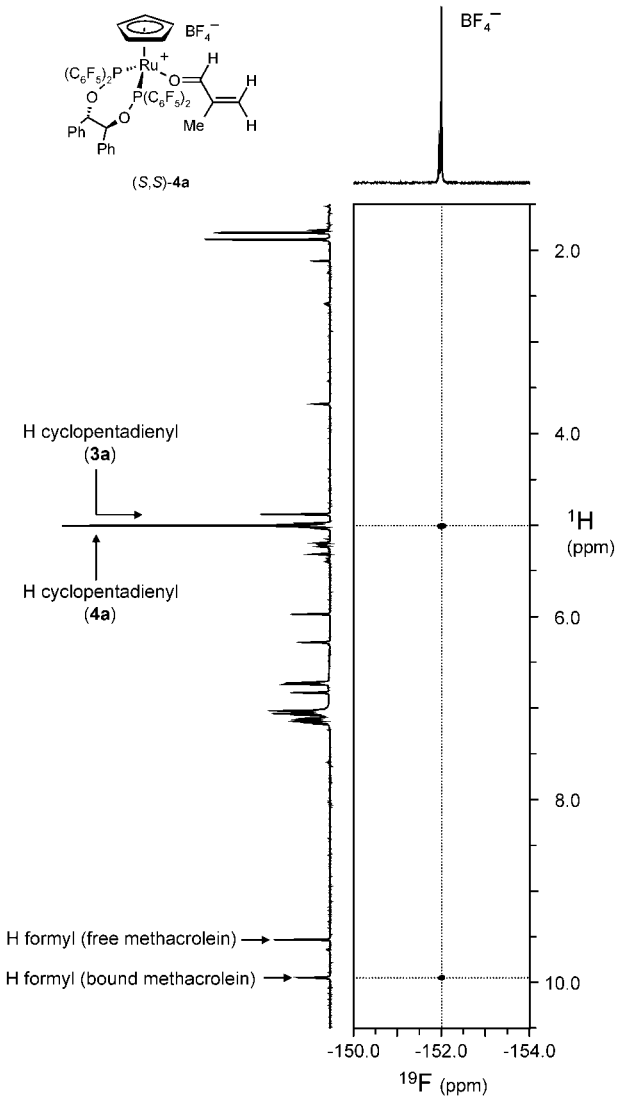

Fig. 2. ^{1}H-^{19}F HOESY NMR spectrum of the complex [CpRu(BIPHOP-F)(methacrolein)][BF_4] (*S*,*S*)-**4 a**.

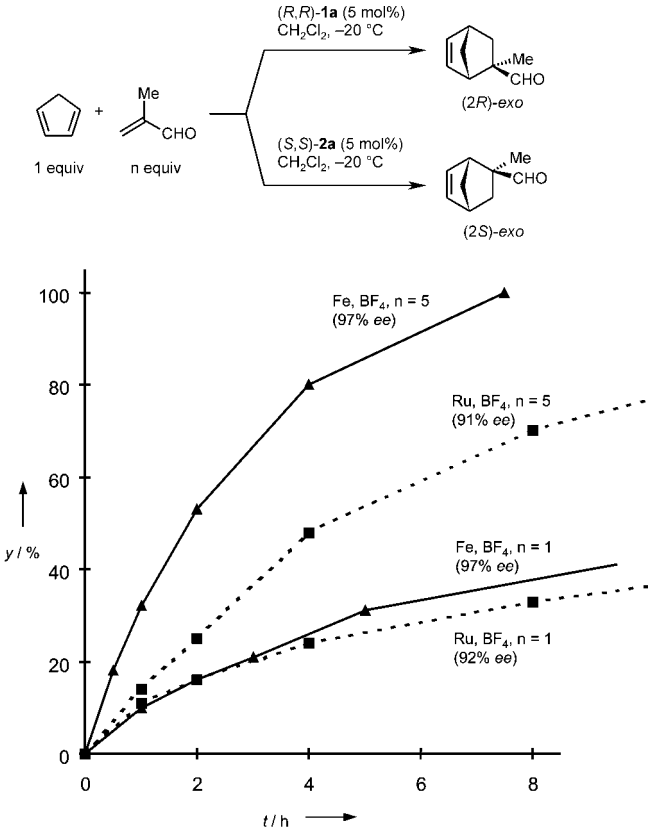

Fig. 3. Plot of GC yield (y) as a function of reaction time (t) for the catalyzed reaction of methacrolein (1 or 5 equiv) with cyclopentadiene (1 equiv) in presence of (*R*,*R*)-**1 a** or (*S*,*S*)-**2 a**. In parentheses: ee value of *exo*-cycloadduct.

Table 1. Comparison of (*R*,*R*)-**1 d** and (*S*,*S*)-**2 d** as catalysts for the reaction of methacrolein with cyclopentadiene in CH_2Cl_2 at –20 °C

(*R*,*R*)-**1 d** [mol%]	(*S*,*S*)-**2 d** [mol%]	n[a]	GC yield after 1 h [%]	ee[b] [%]	r[c]
5	0	1	50	97	–
5	0	5	100	97	–
0	5	1	19	–92	–
0	5	5	18	–92	–
2.5	2.5	1	40	50	3.0
2.5	2.5	5	56	74	7.1

[a] n = ratio cyclopentadiene:methacrolein.
[b] Determined by GC analysis of the diastereomeric acetals obtained by reaction with (2*R*,4*R*)-pentanediol.[12]
[c] $r = ([R]_{Fe} + [S]_{Fe})/([R]_{Ru} + [S]_{Ru}) = (ee_{Ru} - ee_{mix})/(ee_{mix} - ee_{Fe})$.[13]

(Fig. 3). On the other hand, an increase in dienophile concentration has no effect when the SbF_6 Fe complex (*R*,*R*)-**1d** or the SbF_6 Ru complex (*S*,*S*)-**2 d** is used. A competition between the dienophile and the anion for the Lewis acid coordination site, may be inferred for BF_4^- but not for SbF_6^-.

Diels–Alder reactions[8] with the Fe catalysts (*R*,*R*)-**1 a-e** are faster than with the Ru analogues (*S*,*S*)-**2 a–e**. A direct reactivity comparison of the two cata-

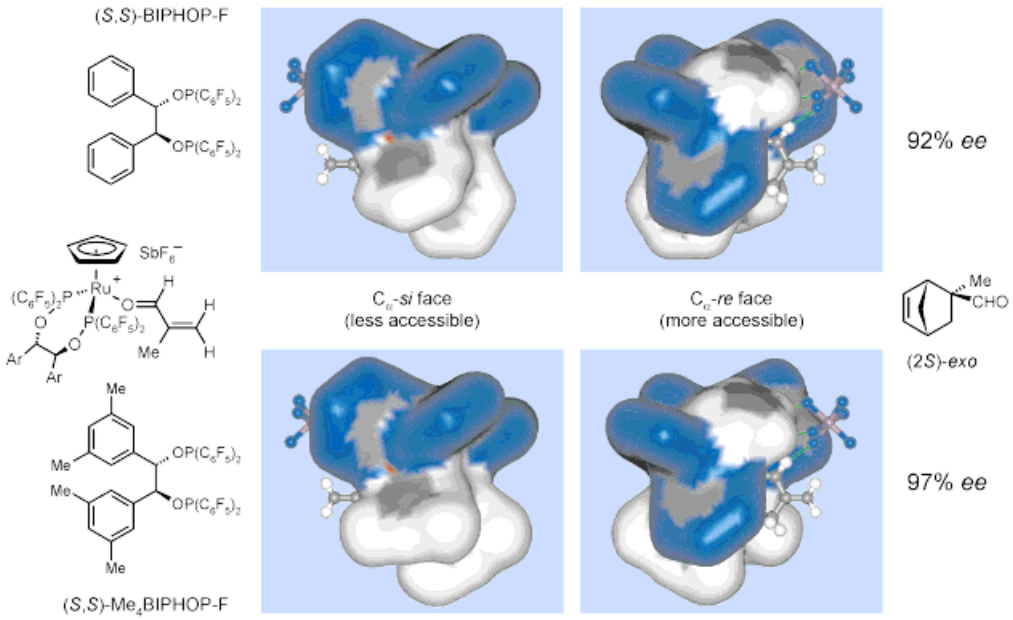

Fig. 4. *Top:* Projection onto the methacrolein C_α-*si* and the C_α-*re* face in the solid state structure of the complex [CpRu-(BIPHOP-F)(methacrolein)][SbF_6], (*S*,*S*)-**4 d**, and asymmetric induction in the Diels-Alder reaction of cyclopentadiene and methacrolein. *Bottom:* Same as above but modified with the new ligand (*S*,*S*)-Me_4BIPHOP-F.

lysts has been realized in a competition experiment. Carrying out the Diels–Alder reaction (CH_2Cl_2, –20 °C) with a 1 : 1 mixture of Fe and Ru complexes of opposite chirality [2.5 mol% (*R*,*R*)-**1 d** and 2.5 mol% (*S*,*S*)-**2 d**] with a 1 : 1 ratio of diene:dienophile shows that the Fe complex is 3 times more active than the analogous Ru complex. Changing the ratio of diene:dienophile to 5 : 1 the balance is even more shifted towards the Fe catalyzed reaction (7 times more active) (Table 1). In the Fe catalyzed reaction, the observation of a rate dependence on diene concentration may indicate that aldehyde exchange is rapid, that the cycloaddition is the rate limiting step, and that the effect of the different anions in the ion paired catalyst consists in attenuating or increasing catalyst activity. With the slower Ru catalysts, diene concentration has no effect on rate and we presume that the rate limiting step here is the cycloadduct release.

Catalyst Recovery

Low thermal stability precludes recovery of the Fe catalysts (*R*,*R*)-**1 a–e** at the end of the Diels–Alder reaction. The high stability of the Ru complex (*S*,*S*)-**2 d** renders recycling via the iodo complex [CpRu-(BIPHOP-F)I] straightforward.[3b] Direct and near quantitative (95%) catalyst recovery in the form of the directly reusable acetone complex (*S*,*S*)-**2 d** has now evolved as an even shorter process (see Experimental Section).

Ru Catalyst: Higher Selectivity with a New Ligand

A comparison of the data shows that while the Ru catalysts are readily recovered, they provide the product with lower enantioselectivity. Thus, the Diels–Alder reaction[8] with the Ru complexes (*S*,*S*)-**2 a, c–d** gives the cycloadduct in 97 : 3 *exo* : *endo* ratio with 92% ee for the *exo*-product. With the Fe complexes (*R*,*R*)-**1a, c–e** the corresponding data are 98 : 2 *exo* : *endo*, 97% ee. The issue of chiral induction has led us to the following analysis and catalyst improvement. Fig. 4 shows a projection onto the methacrolein C_α-*re* and the C_α-*si* face in the solid state structure of the methacrolein Ru complex (*S*,*S*)-**4 d**.[3b] The view onto the less accessible C_α-*si* alkene face suggests that ligand modification at the *meta* position of the ligand backbone phenyl rings may be beneficial and more efficiently block the access to this enantioface.[14] Consequently, the new ligand (*S*,*S*)-Me_4BIPHOP-F[15] was synthesized and incorporated in the Ru catalyst. Our hypothesis of improved selectivity has been realized as shown by an increase of the enantioselectivity of the Diels–Alder reaction[8] of methacrolein and cyclopentadiene from 92% ee to 97% ee.

Conclusion

Synthetic and mechanistic studies give a detailed picture of the Fe and Ru transition metal Lewis acid catalyzed Diels–Alder reaction of dienes with enals. With

improved, stable and fully recoverable transition metal catalysts, selectivities equal to those of the widely used chiral main group catalysts are now reality.[1,17] Chiral transition metal Lewis acids show high promise and their further development and applications will be actively pursued.

Experimental Section

Synthesis of (*R*,*R*)-1 d; Typical Procedure

(*R*,*R*)-**1 a** (205 mg, 0.17 mmol) was added in one portion to a solution of $NaSbF_6$ (440 mg, 1.7 mmol) in acrolein (5 mL, flash-distilled over $CaSO_4$) at –20 °C. This temperature was maintained in all subsequent manipulations. The deep red solution was stirred for 30 min and volatiles were then removed under vacuum. The orange residue was dissolved in CH_2Cl_2 (10 mL) and the suspension was filtered over celite. The resulting red solution was concentrated to *ca.* 2 mL. Addition of hexane (20 mL) at –60 °C precipitated a red solid. Isolation by decantation after one night at –40 °C and drying under vacuum afforded (*R*,*R*)-**1 d** as a red solid (220 mg, 95% yield).

The complexes (*R*,*R*)-**1 b–c, e** were synthesized following the same procedure in respectively 75%, 77% and 85% yield.

GC-Analysis of the Diels–Alder Reaction

Procedures for the Diels-Alder reactions catalyzed with (*R*,*R*)-**1 a** and (*S*,*S*)-**2 d** were detailed previously.[3] The course of the reaction was monitored using *n*-decane as an internal standard. Samples of the reaction mixture were rapidly removed by pipette, quenched in acetonitrile and analysed by GC [column Optima-1701-0.25 μm (25 m × 0.32 mm), helium 2 mL min^{-1}, 80 °C, 5 min, 5 °C min^{-1}: 2.99 min (*n*-decane), 5.13 min (*exo*-cycloadduct), 5.87 min (*endo*-cycloadduct)].

Recovery of the Ru Catalyst (*S*,*S*)-2 d

At the end of the Diels-Alder reaction [methacrolein (1 mmol), cyclopentadiene (1.2 mmol), CH_2Cl_2 (1 mL)], acetone:water (4 : 1, 0.5 mL) and then hexane (10 mL) were added and the solvent was partially evaporated. The yellow suspension obtained was filtered through celite and the pad was washed with hexane (10 mL). This first filtrate contained the cycloadduct, which was subsequently purified by chromatography. The catalyst was then eluted from the celite pad with acetone. This was followed by three cycles of evaporation to dryness and dissolution in dry acetone (5 mL portions) to transform the aquo-complex (*S*,*S*)-**3 d** into the acetone complex (*S*,*S*)-**2 d**. Catalyst (*S*,*S*)-**2 d** was recovered as a yellow solid in 95% yield.

Acknowledgments

We thank the Swiss National Science Foundation for support (grant 20-59374.99).

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[7] [CpFe(BIPHOP-F)I] was synthesized via sequential treatment of a CH_2Cl_2 solution of [CpFe(BIPHOP-F)-Me] by HBF_4 (–78 °C) and $MePh_3PI$ (–78 °C → –20 °C).

[8] Conditions: 5 mol% catalyst, CH_2Cl_2, –20 °C.

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[11] On addition of nBu_4NOTf, the signals assigned to the SbF_6 acetone Ru complex (*S*,*S*)-**2 d** [^{1}H NMR (500 MHz, CD_2Cl_2, 20 °C, TMS): δ = 4.93 (Cp), 2.56 (coordinated acetone); ^{31}P NMR (202.5 MHz, CD_2Cl_2, 20 °C, H_3PO_4): δ = 127.6 (br. d_{AB}, ^2J(P,P) = 67 Hz), 122.4 (br. d_{AB}, ^2J(P,P) = 67 Hz)] gradually decreased and signals that are assigned to free acetone and the triflate complex appeared: free acetone [^{1}H NMR (500 MHz, CD_2Cl_2, 20 °C, TMS): δ = 2.13]; free TfO^- [^{19}F NMR (471 MHz, CD_2Cl_2, 20 °C, C_6F_6): δ = 84.7]; [CpRu(BIPHOP-F)(OTf)] [^{1}H NMR (500 MHz, CD_2Cl_2, 20 °C, TMS): δ = 4.89 (Cp); ^{19}F NMR (471 MHz, CD_2Cl_2, 20 °C, C_6F_6): δ = 86.3 (coordinated TfO^-); ^{31}P NMR (202.5 MHz, CD_2Cl_2, 20 °C, H_3PO_4): δ = 125.2 (br. d_{AB}, ^2J(P,P) = 69 Hz), 121.3 (br. d_{AB}, ^2J(P,P) = 69 Hz)].

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[13] ee_{Fe} and ee_{Ru} are the enantiomeric excess of (2*R*)-*exo*-product obtained with Fe catalyst (*R*,*R*)-**1 d** and Ru catalyst (*S*,*S*)-**2 d**:
$ee_{Fe} = ([R]_{Fe} - [S]_{Fe})/([R]_{Fe} + [S]_{Fe}) = 0.97$
$ee_{Ru} = ([R]_{Ru} - [S]_{Ru})/([R]_{Ru} + [S]_{Ru}) = -0.92$
ee_{mix} is the enantiomeric excess of (2*R*)-*exo*-product

obtained with a 1 : 1 mixture of catalysts (*R*,*R*)-**1 d** and (*S*,*S*)-**2 d**:
$ee_{mix} = (([R]_{Fe} + [R]_{Ru}) - ([S]_{Fe} + [S]_{Ru}))/(([R]_{Fe} + [R]_{Ru}) + ([S]_{Fe} + [S]_{Ru}))$
r is the ratio of *exo*-product formed by the Fe catalyst and the Ru catalyst:
$r = ([R]_{Fe} + [S]_{Fe})/([R]_{Ru} + [S]_{Ru}) = (ee_{Ru} - ee_{mix})/(ee_{mix} - ee_{Fe})$.

[14] From elegant studies, Albinati and Pregosin et al. have concluded that the ligand meta dialkyl effect results in a number of catalysts in a more rigid chiral pocket which in turn can lead to marked improvement of observed enantioselectivities; (a) G. Trabesinger, A. Albinati, N. Feiken, R. W. Kunz, P. S. Pregosin, A. Tschoerner, *J. Am. Chem. Soc.* **1997**, *119*, 6315–6323; (b) K. Selvakumar, A. Valentini, P. S. Pregosin, A. Albinati, F. Eisentraeger, *Organometallics*, **2000**, *19*, 1299–1307.

[15] Ligand (*S*,*S*)-Me_4BIPHOP-F was synthesized by reaction of (*S*,*S*)-1,2-bis(3,5-dimethylphenyl)ethane-1,2-diol[16] with $BrP(C_6F_5)_2$[17]. Data: mp 107–109 °C; $[\alpha]_D^{20}$: –84.3 (*c* 0.97, CH_2Cl_2); ^{1}H NMR (500 MHz, CD_2Cl_2, 20 °C, TMS): δ = 6.77 (s, 2 H; *p*-H_{ar}), 6.69 (s, 4 H; *o*-H_{ar}), 5.18 (m, 2 H; OCH), 2.12 (s, 12 H; CH_3); ^{13}C NMR (126 MHz, CD_2Cl_2, 20 °C, TMS): δ = 138.3 (s; *m*-C_{ar}), 136.2 (d, ^3J(C,P) = 2.3 Hz; *i*-C_{ar}), 130.6 (s; *p*-C_{ar}), 125.8 (s; *o*-C_{ar}), 88.1 (dd, ^2J(C,P) = 25.8 Hz, ^3J(C,P) = 7.5 Hz; OCH), 21.0 (s; CH_3); ^{19}F NMR (471 MHz, CD_2Cl_2, 20 °C, C_6F_6): δ = 31.5 (m, 4 F; *o*-F), 30.7 (m, 4 F; *o*-F), 13.8 (m, 2 F; *p*-F), 12.7 (m, 2 F; *p*-F), 1.9 (m, 8 F; *o*-F); ^{31}P NMR (202.5 MHz, CD_2Cl_2, 20 °C, H_3PO_4): δ = 83.44 (quint, ^3J(P,F) = 37 Hz); IR (CH_2Cl_2): $\tilde{\nu}$ = 1640, 1516, 1480, 1380, 1091, 1029, 980, 857 cm^{-1}.

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[18] For a highly enantioselective organocatalytic Diels–Alder reaction, see: K. Ahrendt, C. J. Borths, D. W. C. MacMillan, *J. Am. Chem. Soc.* **2000**, *122*, 4243–4244.