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[(Indenyl)Ru(biphop-F)]$^+$: A Lewis Acid Catalyst That Controls both the Diene and the Dienophile Facial Selectivity in Diels – Alder Reactions**

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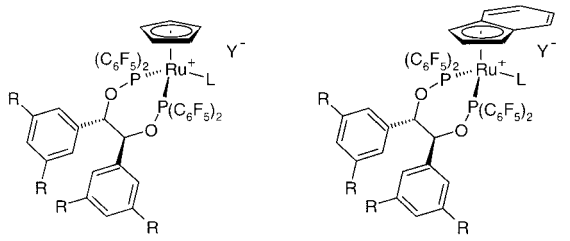
Cationic arene and cyclopentadienyl complexes of iron and ruthenium incorporating chiral bidentate ligands have been shown to be efficient Lewis acid catalysts for the asymmetric Diels – Alder reaction between enals and dienes.[1–5] Our research in this area has focused on cyclopentadienyliron and -ruthenium complexes, the former giving higher rates and enantiomeric excesses and the latter being more stable and easily recycled.[2] Enantioselectivity in the Ru complexes was strongly increased on changing the aryl groups in the ligand backbone, that is by using **3** rather than **2** as precatalysts.[2a]

The structurally characterized complex [CpRu(biphop-F)-(methacrolein)][SbF_6] (**1d**; biphop-F = 1,2-bis[bis(pentafluoro-



1 R = H, L = $CH_2C(Me)CHO$
2 R = H, L = Me_2CO
3 R = Me, L = Me_2CO

4 R = H, L = $CH_2C(Me)CHO$
5 R = H, L = Me_2CO
6 R = Me, L = Me_2CO

Y = OTf (**a**), BF_4 (**b**), PF_6 (**c**), SbF_6 (**d**), TFPB (**e**)

phenyl)phosphanyloxy]-1,2-diphenylethane)has provided a detailed picture of the catalyst/substrate interaction and of the influence of the anion on the rate of catalysis.[2b] Evidence from the solid-state structure of **1d** and from F/H NMR correlation spectra in solutions of the BF_4^- and the PF_6^- analogues (**1b** and **1c**, respectively) point to ion pairs in which the anion interacts with both the bound substrate and the cationic catalyst.[2a, b] We concluded that the anion slows down product/substrate exchange at the catalyst site. Consequently, complex **1e**, which incorporates the tetrakis[3,5-bis(trifluoromethyl)phenyl] borate anion (TFPB) whose bulk renders this proximity impossible, showed the highest activity. Another way to bring about a larger separation of the anion from the enal group in the catalyst site is to increase the size of the catalyst's capping ligand, for example by changing from the cyclopentadienyl to the indenyl complexes. With an indenyl ligand the question of preferred rotamers arises. Moreover, the propensity of the indenyl ligand to undergo a slip/fold rearrangement[6] risks the occurrence of a different mode of enal binding and reactivity than the desired single coordination site Lewis acid.

The results described herein provide answers to these questions. The properties of the indenyl complexes are indeed significantly altered from those of the cyclopentadienyl analogues, and diastereoselectivities not previously encountered in the Diels – Alder reaction of enals with dienes are realized. We also note that despite the detailed attention that indenyl complexes of Group 8 metals have received, asymmetric catalytic reactions with this family of compounds have not been reported.[7]

Given that the reaction of [$Ru_3(CO)_{12}$] with indene affords a low yield of the resultant complex,[8] we opted for the thermal substitution of the two PPh_3 ligands in [IndRu-(PPh_3)$_2$Cl][9](**7**) by the bidentate biphop-F[2c, 10](**8**) and Me_4biphop-F (**9**)[2a] ligands to give the Ru complexes **10** and **11** respectively (Scheme 1).

This reaction was complete in 1.5 h, whereas with the cyclopentadienyl analogue the reaction with the very similar ligand 1,2-bis[bis(pentafluorophenyl)phosphanyloxy]cyclopentane (cyclop-F)[2d] took one week to complete. In analogy to the mechanism established in reactions of [$IndRh(CO)_2$], the higher reactivity of the indenyl complex could be ascribed to a reversible η^5/η^3 slippage of the ligand in an associative mechanism (indenyl effect).[11] However, phosphane substitu-

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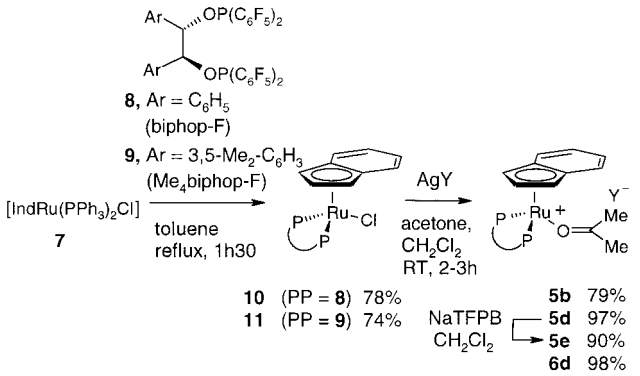
[**] This work was supported by the Swiss National Science Foundation (FNS grant 20-59374.99) and The Ministère des Affaires Etrangères from France (Lavoisier grant to V.A.). biphop-F = 1,2-bis[bis(pentafluorophenyl)phosphanyloxy]-1,2-diphenylethane.



Scheme 1. Synthesis of indenyl (Ind) complexes.

tion in the Ru complex **7** has been shown to be dissociative, and rate enhancement in going from the cyclopentadienyl to the indenyl complex in this reaction has been attributed to the indenyl moiety acting as an electron reservoir toward the metal fragment thus favoring Ru–P bond cleavage and/or stabilization of the 16-electron intermediate.[12] The X-ray crystal structure of (*S*,*S*)-**10** (Figure 1)[13] shows an arrangement of the [IndRu((*S*,*S*)-biphop-F)] core that closely matches

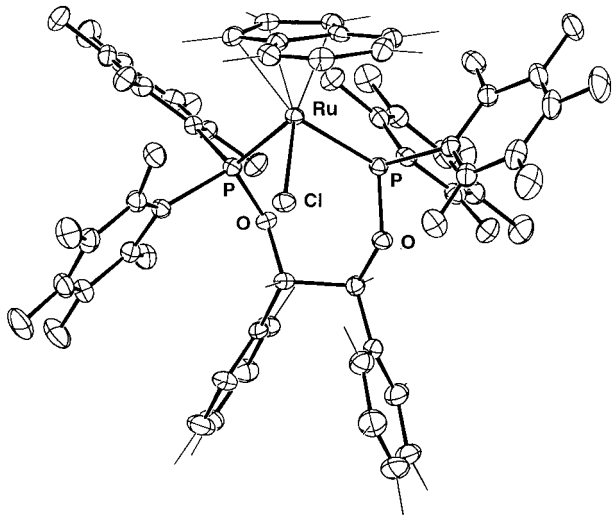


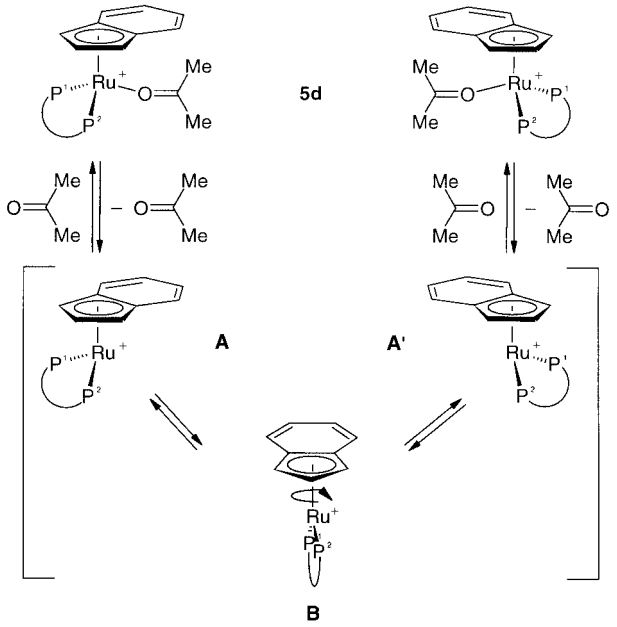
Figure 1. X-ray crystal structure of (*S*,*S*)-**10** (ORTEP view; ellipsoids are represented at the 40% probability level).

that of complex (*S*,*S*)-**1d**[2b] except for the extension of the η^5 ligand. The indenyl ligand in **10** is η^5-coordinated in the solid state[14] and, according to ^{13}C NMR data, also in solution.[15] Rotation of the indenyl ligand should be sterically impeded by the pentafluorophenyl groups. The structure also shows that the indenyl arene ring occupies the same space as the SbF_6 anion in the [CpRu((*S*,*S*)-biphop-F)(methacrolein)][SbF_6] complex (*S*,*S*)-**1d**.[2b] The consequence of this structural change will become apparent when discussing the results of Diels–Alder reactions.

Reaction of a solution of **10** or **11** in acetone with the appropriate silver salt generated the air-stable cationic complexes **5b, d**[16] and **6d** (see Scheme 1). Complex **5e** was obtained from **5d** by anion metathesis[17] with sodium tetrakis[3,5-bis(*m*-trifluoromethyl)phenyl]borate (NaTFPB).[18]

Like their cyclopentadienyl analogues, the indenyl complexes **5** and **6** are stable in solution at room temperature. In CH_2Cl_2, methacrolein readily displaced the coordinated acetone in **5d** to give complex **4d**. The ^{1}H NMR spectrum of **4d** in CD_2Cl_2 was of particular interest because it showed coordinated ($\delta =$ 8.66) and free methacrolein ($\delta = 9.52$). This unusual formyl proton downfield shift (in **1d**, $\delta = 9.74$[2b]) is attributed to the magnetic anisotropy of the indenyl ring.[19] The ^{31}P NMR spectrum of **5d** in [D_6]acetone at room temperature was different from that of the cyclopentadienyl analogue in that it showed a singlet for the two diastereotopic P nuclei of the bidentate ligand. The possibility of coincidental overlap was excluded by the observation of the usual AB quartet at $-80\,^\circ$C.

While we cannot rule out at this stage a Ru–P bond breaking/bond making process, we favor the alternative mechanism shown in Scheme 2. Dissociation of acetone in **5d** leads to the 16-electron intermediate **A**. In the singlet state,



Scheme 2. Proposed pathway for phosphorus site exchange.

A should be pyramidal at the metal center because of the σ-donor and π-acceptor properties of the bidentate ligand biphop-F.[20–22] Inversion of the pyramidal geometry at the metal center through a pendulum movement of the bidentate ligand then gives **A′**. This is accompanied by rotation of the indenyl ligand at point **B**. The process is completed by coordination of acetone. Because of the C_2 symmetry of the ligand, **A** and **A′** are identical.[23] The ^{31}P NMR singlet indicates that at room temperature this process occurs rapidly on the NMR time scale, thus rendering the two phosphorus atoms equivalent.[24] In view of the use of **5d** in catalysis, we note that ligand exchange occurs more rapidly with the indenyl complexes than with the cyclopentadienyl analogues. With regards to asymmetric induction, the pendulum movement of the biphop-F ligand in **5d** is not expected to lead to an erosion of product enantioselectivity because an identical

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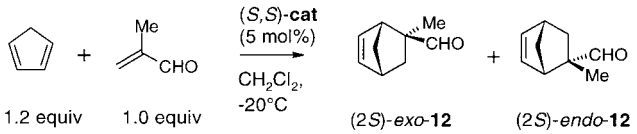
stereochemical environment exists in the catalyst–substrate complex at all times.

Diels–Alder reaction of methacrolein with cyclopentadiene catalyzed by (*S*,*S*)-**5d** (5 mol%, CH_2Cl_2, −20 °C) gave the corresponding cycloadduct (*S*)-**12** in 85% yield (see Figure 2) with a diastereomeric ratio of 99.7:0.3 (*exo*:*endo*) and an enantioselectivity of 88% *ee* (*exo*). The chiral cyclopentadienyl and the indenyl complexes afforded the products



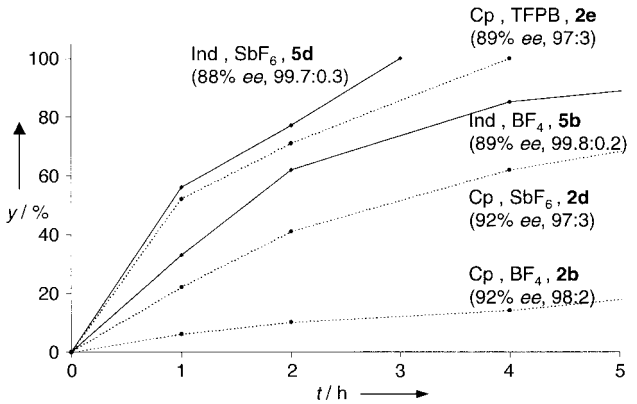


Figure 2. Plot of GC yield (y) as a function of reaction time (t) for the reaction of methacrolein with cyclopentadiene in the presence of (*S*,*S*)-**2b, d, e** (••••) or (*S*,*S*)-**5b, d** (——). In parentheses: *ee* value of the *exo*-cycloadduct **12**, *exo*:*endo* ratio.

with the same sense of asymmetric induction and we take this as an indication that the reaction occurs through an identical diene approach.[2b] Diels–Alder reactions with the indenyl catalysts were faster than with the cyclopentadienyl analogues (Table 1, compare entries 4 and 2 or 5 and 3). Fine-tuning of the ligand backbone by switching from biphop-F (**8**) to Me_4biphop-F (**9**) results in higher asymmetric induction as previously found for cyclopentadienyl complexes (Table 1, entries 4 and 5).

Selected results for the Diels–Alder reaction of methacrolein with cyclopentadiene catalyzed with indenyl (Ind) complexes **5** and analogous cyclopentadienyl (Cp) complexes **2** are presented in Figure 2. The same trend is observed in both cases, that is the rate of Diels–Alder reaction varies with the catalyst counteranion and it increases in the order $BF_4 < SbF_6 <$ TFPB (for clarity, we have omitted the curve for **5e** (TFPB), which is very close to that of **5d**). However the range of rate variations in the indenyl complexes is significantly reduced compared to that for the cyclopentadienyl complexes, and the large change in reactivity found with the TFPB anion in the cyclopentadienyl complex is not observed with the indenyl catalyst.

In the cyclopentadienyl complexes, the anion effect is due to competition between the anion and the aldehyde substrate for the Lewis acid coordination site (with OTf^-), and cooperative binding of the anion to both the aldehyde product and the catalyst (with BF_4^-, PF_6^-, SbF_6^-). The latter modifies the rate of product release and thereby affects the turnover frequency.[2a,b] In the indenyl complexes the anion is further away from the coordination site because of the indenyl arene ring and both phenomena are reduced. A further consequence of the higher efficiency of product/substrate exchange is a switch in the rate-determining step. In contrast to the cyclopentadienyl analogue, changing the ratio of diene:dienophile from 1.2:1 to 5:1 resulted in a faster reaction with indenyl complex **5d** (reaction of methacrolein and cyclopentadiene with 5 mol% of **5d** was completed in 1 h instead of 2.5 h). We take this as an indication that cycloaddition has become the rate-determining step with the indenyl catalyst, whereas it was the product/substrate exchange in the cyclopentadienyl complexes.

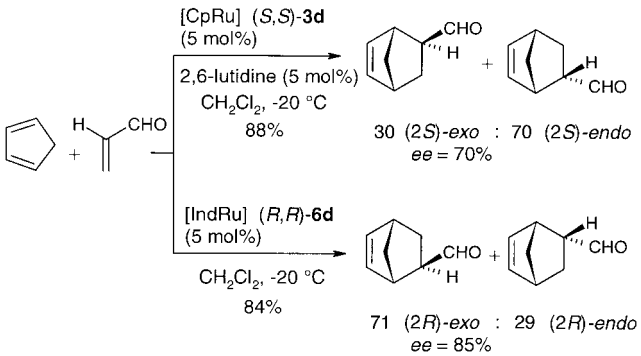
The most remarkable feature of the indenyl catalyst, however, is the increased diastereoselectivity that favors the *exo* cycloadduct by an order of magnitude over that of the cyclopentadienyl catalyst (Table 1, entries 4 and 5). We selected the Diels–Alder reaction of acrolein with cyclopentadiene to further investigate this characteristic. This reaction is known to always give the *endo* cycloadduct as the major product.[26] With **6d** as catalyst, the reaction afforded the *exo* cycloadduct as major product with an *exo*:*endo* ratio of 71:29—a complete inversion of the diastereoselectivity compared to that obtained with the cyclopentadienyl catalyst **3d** (Scheme 3).

To our knowledge, this is the first Diels–Alder reaction of acrolein with cyclopentadiene that favors the *exo* cycloadduct.

Table 1. Reaction of methacrolein with cyclopentadiene.[a]

Entry	Catalyst	Reaction time [h]	Yield [b] [%]	*exo*:*endo*	*ee* [c] [%]	ref.
1	[CpFe((*R*,*R*)-biphop-F)][SbF_6][d]	1	85	98:2	97 (*R*)	[2a]
2	(*S*,*S*)-**2d**	22	91	97:3	92 (*S*)	[2b]
3	(*S*,*S*)-**3d**	22	87	97:3	97 (*S*)	[2a]
4	(*S*,*S*)-**5d**	2.5	85	99.7:0.3	88 (*S*)	
5	(*S*,*S*)-**6d**	4	80	99.8:0.2	95 (*S*)	

[a] Reactions were carried out with 1 mmol methacrolein, 1.2 mmol cyclopentadiene and 5 mol% catalyst in dichloromethane (1 mL) at −20 °C. [b] Yield of cycloadduct isolated. [c] The enantiomeric excess of the *exo* cycloadduct was determined by GC analysis of the diastereomeric acetals obtained by reaction with (2*R*,4*R*)-pentanediol.[25] [d] Reaction was carried out with 1 mmol methacrolein, 5 mmol cyclopentadiene, 5 mol% catalyst, and 5 mol% 2,6-lutidine in dichloromethane (1 mL) at −20 °C.



Scheme 3. Diels–Alder reaction of acrolein with cyclopentadiene catalyzed by (*S*,*S*)-**3d** and (*R*,*R*)-**6d**, respectively: inversion of diastereoselectivity.

As shown in Figure 3, we ascribe the selectivity to an unfavorable *endo* approach of the cyclopentadiene. The cause is the indenyl arene ring that interferes with C(2)–H and C(3)–H of the approaching cyclopentadiene. In the *exo* approach, the envelope shape of the diene places the methylene group further away from this catalyst site capping ligand and this is therefore the favored pathway.

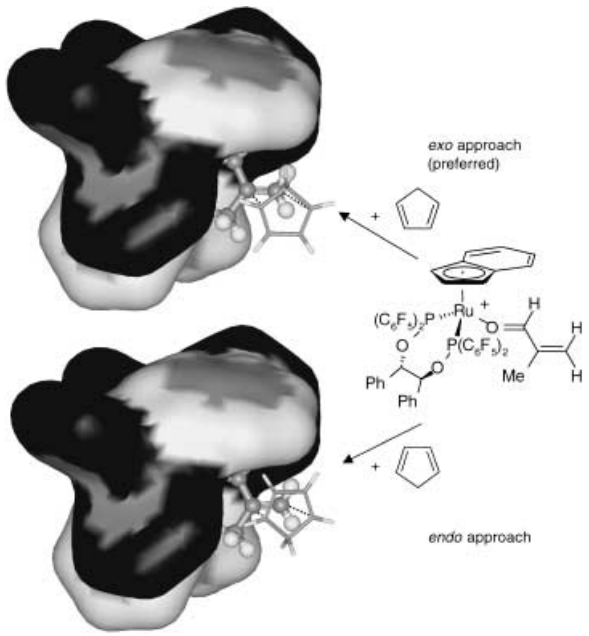


Figure 3. Model of the transition state for the Diels–Alder reaction of methacrolein and cyclopentadiene catalyzed by (*S*,*S*)-**5d**. Top: cyclopentadiene *exo* approach to the methacrolein C_α-*Re* face. Bottom: cyclopentadiene *endo* approach to the methacrolein C_α-*Re* face.

In conclusion, we have synthesized new chiral indenyl ruthenium complexes and have shown their efficiency as Lewis acids in Diels–Alder reactions. They exhibit unprecedented levels of *exo* selectivity, and reach the rates of the usually more active Fe catalysts. The room-temperature stable catalysts can be recovered in high yield.

Experimental Section

(*S*,*S*)-**10**: An orange solution of $[IndRu(PPh_3)_2Cl]$[9] (1.16 g, 1.50 mmol) and (*S*,*S*)-biphop-F (**8**)[2c] (1.42 g, 1.50 mmol) in dry and N_2 saturated toluene (120 mL) was refluxed under N_2 for 1.5 h. After evaporation of the solvent under vacuum, the crude product was purified by flash chromatography on silica gel (pentane:CH_2Cl_2 2:1 to 1:2). Recrystallization from CH_2Cl_2/MeOH afforded compound (*S*,*S*)-**10** as dark red crystals (1.41 g, 78%). ^{1}H NMR (400 MHz, CD_2Cl_2, 20 °C, TMS): $\delta = 7.41-7.34$ (m, 2H; H_{ind}), 7.15–7.00 (m, 7H; 1 H_{ind} + 6 H_{ar}), 6.97 (m, 2H; H_{ar}), 6.63 (bs, 2H; H_{ar}), 6.60 (d, ^3J(H,H) = 8.3 Hz, 1H; H_{ind}), 6.26 (dd, ^3J(H,P) = 14.3 Hz, ^3J(H,H) = 8.5 Hz, 1H; CH-O-P), 5.19 (s, 1H; H_{ind}), 4.90 (dd, ^3J(H,P) = 5.6 Hz, ^3J(H,H) = 8.5 Hz,1H; CH-O-P), 4.81 (s, 1H; H_{ind}), 4.36 (s, 1H; H_{ind}); ^{13}C NMR (100.6 MHz, CD_2Cl_2, 20 °C, TMS): $\delta = 136.1$ (d, J(C,P) = 7.5 Hz, 1C; *i*C (C_6H_5)), 135.6 (s, 1C; *i*C (C_6H_5)), 130.3 (s, 1(CH); $C(5,6)_{Ind}$), 128.9 (s, 1(CH); C_6H_5), 128.8 (s, 1(CH); C_6H_5), 128.3 (s, 4(CH); C_6H_5), 128.2 (s, 2(CH); C_6H_5), 128.0 (s, 1(CH); $C(5,6)_{Ind}$), 127.6 (s, 2(CH); C_6H_5), 124.4 (s, 1(CH); $C(4,7)_{Ind}$), 123.7 (s, 1(CH); $C(4,7)_{Ind}$), 115.8 (d, J(C,P) = 3.3 Hz, 1C; $C(3a,7a)_{Ind}$), 108.0 (d, J(C,P) = 7.5 Hz, 1C; $C(3a,7a)_{Ind}$), 85.7 (dd, J(C,P) = 10.0, 3.3 Hz, 1(CH); CH-O-P), 85.2 (s, 1(CH); $C(2)_{Ind}$), 83.7 (d, J(C,P) = 4.1 Hz, 1(CH); CH-O-P), 74.4 (d, J(C,P) = 10.0 Hz, 1(CH); $C(1,3)_{Ind}$), 72.6 (d, J(C,P) = 6.6 Hz, 1(CH); $C(1,3)_{Ind}$); ^{31}P NMR (202.5 MHz, CD_2Cl_2, 20 °C, H_3PO_4): $\delta = 127.6$ (d, ^2J(P,P) = 65 Hz), 121.2 (d, ^2J(P,P) = 65 Hz).

(*S*,*S*)-**5d**: A solution of $AgSbF_6$ (168 mg, 0.49 mmol) in dried CH_2Cl_2 (4.9 mL) was added to (*S*,*S*)-**10** (478 mg, 0.40 mmol) in dried acetone (6 mL). The mixture was stirred at room temperature for 3 h. After evaporation of the solvent under vacuum, the residue was filtered through celite with acetone. After evaporation of volatiles under vacuum, the product was purified by dissolution in acetone and precipitation by addition of Et_2O to give compound (*S*,*S*)-**5d** as an orange solid (564 mg, 97%). ^{1}H NMR (400 MHz, [D_6]acetone, 20 °C, TMS): $\delta = 7.78$ (d, ^3J(H,H) = 8.6 Hz, 1H; H_{ind}), 7.64 (t, ^3J(H,H) = 7.6 Hz, 1H; H_{ind}), 7.51–7.44 (m, 2H; H_{ind}), 7.14–7.07 (m, 4H; H_{ar}), 7.04–6.96 (m, 4H; H_{ar}), 6.87 (d, ^3J(H,H) = 7.0 Hz, 2H; H_{ar}), 5.63–5.57 (m, 1H; CH-O-P), 5.48 (s, 1H; H_{ind}), 5.32 (dd, ^3J(H,P) = 14.0 Hz, ^3J(H,H) = 7.5 Hz, 1H; CH-O-P), 5.22 (s, 1H; H_{ind}), 4.89 (s, 1H; H_{ind}); ^{13}C NMR (100.6 MHz, [D_6]acetone, 20 °C, TMS): $\delta = 135.5$ (t, J(C,P) = 4.1 Hz, 1C; *i*C (C_6H_5)), 135.2 (s, 1C; *i*C (C_6H_5)), 133.7 (s, 1(CH); $C(5,6)_{Ind}$), 131.0 (s, 1(CH); $C(5,6)_{Ind}$), 129.8 (s, 2(CH); C_6H_5), 129.1 (s, 2(CH); C_6H_5), 128.9 (s, 2(CH); C_6H_5), 128.6–128.4 (m, 1(CH); $C(4,7)_{Ind}$), 128.36 (s, 2(CH); C_6H_5), 128.3 (s, 2(CH); C_6H_5), 123.4 (s, 1(CH); $C(4,7)_{Ind}$), 119.6 (s, 1C; $C(3a,7a)_{Ind}$), 110.9 (s, 1C; $C(3a,7a)_{Ind}$), 86.6 (s, 1(CH); CH-O-P), 86.2 (s, 1(CH); CH-O-P), 83.6 (s, 1(CH); $C(2)_{Ind}$), 70.3 (t, J(C,P) = 7.0 Hz, 1(CH); $C(1,3)_{Ind}$), 68.6 (s, 1(CH); $C(1,3)_{Ind}$); ^{31}P NMR (162 MHz, [D_6]acetone, 20 °C, H_3PO_4): $\delta = 131.0$ (s); ^{31}P NMR (162 MHz, [D_6]acetone, −100 °C, H_3PO_4): $\delta = 129.9$ ($q_{A,B}$, $\Delta\tilde{\nu}_{A,B} = 510$ Hz, $J_{A,B} = 77$ Hz).

12: Methacrolein (0.082 mL, 1.00 mmol) and cyclopentadiene (0.100 mL, 1.22 mmol) were successively added to (*S*,*S*)-**5d** (72 mg, 0.05 mmol) in dried CH_2Cl_2 (1 mL) at −20 °C. After the mixture had been stirred at −20 °C for 2.5 h, acetone (0.4 mL) and water (0.1 mL) were added and the mixture was stirred for 5 min at room temperature. The solution was partially concentrated. Hexane (10 mL) was then added and the mixture filtered through celite. Chromatography on silica gel (pentane/CH_2Cl_2 8:1) gave cycloadduct (*S*)-**12** as a deliquescent white solid (116 mg, 85%) with an *exo*:*endo* ratio of 99.7:0.3 (determined before chromatography) and 88% *ee* (*exo*). Catalyst recovery: the precipitate was eluted from the celite with acetone and the solvent was evaporated under vacuum. After three cycles of dissolution in dried acetone and evaporation under vacuum, the acetone complex (*S*,*S*)-**5d** was recovered quantitatively.

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[13] Crystal structure determination of (*S*,*S*)-**10**: $[(C_9H_7)(C_{38}H_{12}O_2F_{20}P_2)\text{-RuCl}]\cdot(CH_4O)_2$; $M_r = 1258.2$; $\mu = 0.58\ mm^{-1}$, $\rho_{calcd} = 1.76\ g\,cm^{-3}$, monoclinic, $P2_1$, $Z = 2$, $a = 10.7173(6)$, $b = 12.4521(8)$, $c = 17.7987(10)$ Å, $\beta = 94.465(7)^\circ$, $V = 2368.1(2)$ Å^3, from 7998 reflections ($4.4^\circ < 2\Theta < 51.9^\circ$), red prism $0.14 \times 0.15 \times 0.15$ mm mounted on a quartz fiber with RS3000 oil to prevent degradation. Cell dimensions and intensities were measured at 170 K on a STOE IPDS diffractometer with graphite-monochromated $Mo_{K\alpha}$ radiation ($\lambda = 0.71069$ Å). $-13 < h < 13$; $-15 < k < 15$; $-21 < l < 21$; 29958 measured reflections, 9236 unique reflections of which 8264 were observable ($|F_o| > 4\sigma(F_o)$); R_{int} for equivalent reflections 0.027. Data were corrected for absorption (T_{min}, $T_{max} = 0.9119$, 0.9408). The structure was solved by direct methods using hte program MULTAN 87,[27] all other calculations used the XTAL[28] system and ORTEP[29] programs. Full-matrix least-squares refinement based on F using weight of $1/[\sigma^2(F_o) + 0.0002(F_o)^2]$ gave final values $R = 0.026$, $wR = 0.029$ and $S = 1.87(2)$ for 700 variables and 8264 contributing reflections. Flack parameter $x = -0.01(2)$. Hydrogen atoms were placed in calculated positions except those of the hydroxy groups that were observed and refined with a fixed value of isotropic displacement parameters ($U = 0.05$ Å^2). The final $\Delta\rho$ showed a maximum of $+0.50$ and a minimum of $-0.29\ e\,Å^{-3}$. Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-167480 ((*S*,*S*)-**10**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

[14] For the comparison of solid-state structures the distortion parameters used by Taylor and Marder have been chosen: 1) the slip parameter (Δ) defined as the difference in the average bond lengths of the metal to the ring junction carbons C(3a), C(7a), and of the metal to adjacent carbon atoms of the five-membered ring, C(1), C(3); 2) the hinge angle (HA) defined as the angle between the planes defined by C(1), C(2), and C(3) and C(1), C(3), C(3a), and C(7a). a) S. A. Westcott, A. K. Kakkar, G. Stringer, N. J. Taylor, T. B. Marder, *J. Organomet. Chem.* **1990**, *394*, 777–794; b) A. K. Kakkar, S. F. Jones, N. J. Taylor, S. Collins, T. B. Marder, *J. Chem. Soc. Chem. Commun.* **1989**, 1454–1456. For (*S*,*S*)-**10**, the HA values of 3.5° and the Δ value of 0.12 Å clearly indicate a η^5 coordination of the indenyl ligand.

[15] The parameter $\Delta\delta$ (C3a,7a) = δ(C3a,7a; η^x-indenyl complex) – δ(C3a,7a; sodium indenyl) has been proposed as a measure of the indenyl distortion. Values in the range -20 to -40 ppm are typical for a planar η^5-indenyl ligand, -10 to -20 ppm for a partially slipped η^5-coordination mode and $+5$ to $+30$ ppm for a η^3-coordination mode: R. T. Baker, T. H. Tulip, *Organometallics* **1986**, *5*, 839–845. The $\Delta\delta$ (C3a,7a) value of -18.8 ppm in (*S*,*S*)-**10**, indicates a weak distortion of the indenyl ligand.

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CH ··· O Hydrogen Bonding Influences π-Facial Stereoselective Epoxidations**

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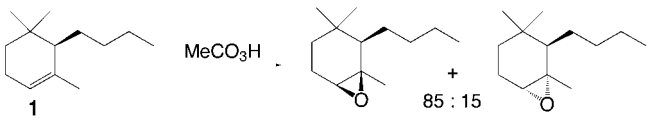
Epoxidations of α-cyclogeranyl systems,[1] such as **1** [Eq. (1)], occur *syn* to the alkyl group at C3, contrary to expectation based upon steric effects. To determine the origin and scope of



(1)

this effect, transition structures have been located for oxygen transfer from peracetic acid to several substituted cyclohexenes (**2**–**4**) with quantum-mechanical methods. An explanation of the anomalous stereoselectivity of epoxidations of **1** was obtained and predictions were made about the

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