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Tetrahedron: *Asymmetry*

Synthesis of iridium complexes with new planar chiral chelating phosphinyl-imidazolylidene ligands and their application in asymmetric hydrogenation

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Abstract—The synthesis of planar chiral phosphinoimidazolium salts such as (R_p)-3-(4-diphenyl-phosphino[2.2]paracyclophan-12-ylmethyl)-1-(2,6-diisopropylphenyl)imidazolium bromide (R_p)-**11c** starting from enantiopure 4,12-dibromo[2.2]paracyclophane (R_p)-**6** is reported. After deprotonation of these salts and a subsequent reaction with $[Ir(COD)Cl]_2$, chelating iridium imidazolylidene complexes (R_p)-**5a**–**c** are obtained. These complexes catalyze the asymmetric hydrogenation of functionalized and simple alkenes with up to 89% ee.

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1. Introduction

N-Heterocyclic carbenes (NHC) and their use as ligands on metal complexes were reported as early as 1968 by Öfele[1a] and Wanzlick and Schönherr.[1b] The interest in this new ligand class increased significantly after Arduengo et al. described the first isolated free NHCs in 1991.[2] Since then, much progress has been made with respect to the synthesis and application of NHCs.[3,4] They now represent an attractive alternative to phosphine ligands in homogenous catalysis[5] since complexes bearing them often exhibit superior properties. A highly popular application for NHCs is olefin metathesis, where ruthenium–carbene complexes constitute the most active class of catalysts.[6]

Chiral NHCs have been applied in asymmetric catalysis.[7] The first example of a catalytic process involving an *N*-heterocyclic carbene was the use of a chiral thiazolium salt in the Stetter reaction by Sheenan and co-workers.[8] Later, triazolium salts were introduced by Enders and co-workers as organocatalysts in enantioselective benzoin condensations and Stetter reactions.[9] The use of metal complexes bearing chiral NHCs as ligands were first reported by Herrmann and co-workers and shortly afterwards by Enders and co-workers.[3d,10] Both applied chiral rhodium NHC complexes in enantioselective hydrosilylations. Recently, this process was improved by Shi and co-workers.[11] Grubbs and Hoveyda demonstrated the application of chiral ruthenium NHC complexes in asymmetric olefin metathesis.[12,13] Other examples include the use of silver NHC complexes in the conjugate addition of diethyl zinc to unsaturated ketones,[14] the synthesis of oxindoles by a palladium catalyzed, intramolecular α-arylation of amides[15] and the palladium-catalyzed allylic substitution.[16] Recently, [2.2]paracyclophane-based saturated imidazolium salts have been applied in the rhodium-catalyzed asymmetric conjugate addition of aryl boron reagents to enones.[17]

Most reactions mentioned so far involve the use of NHCs in C–C bond forming processes. However, transition metal NHC complexes have also been applied in alkene-to-alkane reductions and the transfer hydrogenation of ketones. For this purpose Nolan and co-workers prepared achiral iridium NHC complexes[18] similar to Crabtree's catalyst.[19] The synthesis and application of metal catalysts bearing chelating biscarbene ligands has been described by Crabtree and co-workers.[20] Asymmetric hydrogenations using unsaturated chiral iridium NHC complexes were reported by Burgess and co-workers.[21] They successfully applied iridium complex **1** bearing a chiral chelating imidazolylidene ligand as a catalyst in the hydrogenations of

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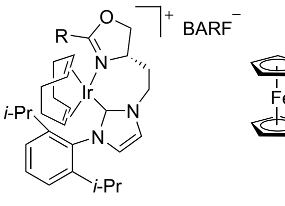

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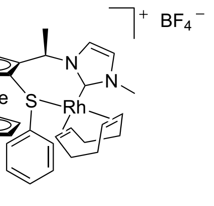

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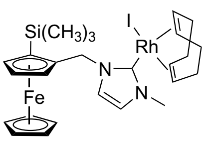

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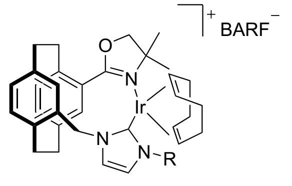

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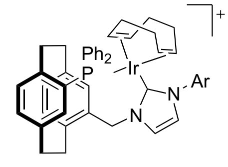


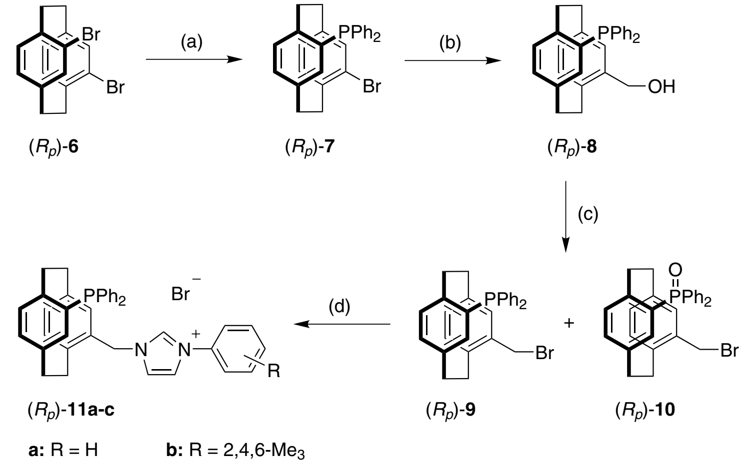
(R_p)-**5a**: Ar = Ph, X = BARF
(R_p)-**5b**: Ar = 2,4,6-Me_3Ph, X = BARF
(R_p)-**5c**: Ar = 2,6-*i*-Pr_2Ph, X = BARF
(R_p)-**5d**: Ar = 2,4,6-Me_3Ph, X = PF_6

unfunctionalized alkenes giving products with up to 99% ee in 98% yield. Chung and co-workers reported on the application of NHC metal complexes of type **2** having a planar chiral ferrocene backbone in the hydrogenation of dimethyl itaconate. The ee, however, was rather low (18%).[22a] Furthermore, ferrocene-based iridium and rhodium NHC complexes have been used in transfer hydrogenations of acetophenone derivatives giving enantioselectivities of up to 53% ee.[22b]

Recently, we reported on the synthesis of the first planar chiral carbene and its chromium and rhodium complexes **3**.[23] In this case, the planar chirality originated from the substitution pattern of the ferrocene backbone.[24] Then, planar chiral [2.2]paracyclophane-based imidazolium salts were described, in which the imidazolylidenyl and an oxazolinyl substituent were in pseudo-*ortho* positions of the [2.2]paracyclophane.[25,26] The corresponding iridium carbene complexes **4** were applied in asymmetric hydrogenations of alkenes giving enantioselectivities of up to 46% ee. We have now extended those studies and prepared [2.2]paracyclophanyl imidazolium salts having a phosphino substituent instead of the oxazoline moiety. Again, iridium complexes were prepared, and the applicability of **5** as catalysts in asymmetric hydrogenations of functionalized and simple olefines was tested.

2. Results and discussion

The syntheses of the planar chiral imidazolium salts started from enantiopure pseudo-*ortho*-dibromo-[2.2]paracyclophane **6**.[27,28] After treatment of (R_p)-**6** with 1 equiv of *n*-BuLi, the resulting carbanion was trapped with chlorodiphenylphosphine affording monophosphino paracyclophane (R_p)-**7** in 92% yield (Scheme 1). Alcohol (R_p)-**8** was then obtained by metallation of (R_p)-**7** with *n*-BuLi followed by reaction with CO_2 and subsequent reduction of the intermediate lithium carboxylate with $LiAlH_4$ (84% yield). Treatment of (R_p)-**8** with PBr_3 afforded methyl bromide (R_p)-**9** in 63%



Scheme 1. Reagents and conditions: (a) i. *n*-BuLi, THF, −78 °C; ii. PPh_2Cl, 92% yield; (b) i. *n*-BuLi, THF, −78 °C; ii. CO_2; iii. $LiAlH_4$, 84% yield; (c) PBr_3, THF, 63% (R_p)-**9** and 25% yield (R_p)-**10**; (d) imidazoles, toluene or DMF, 80–90 °C, 16–59% yield.

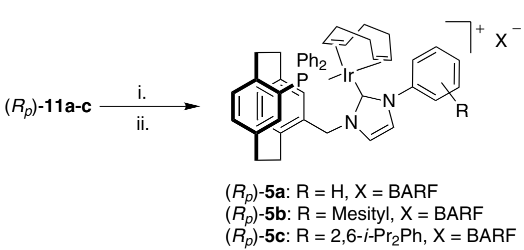
yield. However, even under careful exclusion of air small quantities (25% yield) of the corresponding phosphine oxide (R_p)-**10** were obtained. All attempts to avoid the formation of this side product by using other reagents failed. Presumably, (R_p)-**10** stems from an intramolecular activation of the benzylic hydroxyl group in (R_p)-**8** by the neighbouring phosphino moiety followed by an attack of the former by bromine. Thus the process would be similar to the bromination of alcohols with reagent combinations like PPh_3/Br_2.

Upon heating mixtures of methyl bromide (R_p)-**9** and 1-phenylimidazole, 1-mesitylimidazole[29] or 1-(2,6-diisopropylphenyl)imidazole[30] in toluene or DMF, the respective imidazolium salts (R_p)-**11a–c** were obtained in yields ranging from 16% to 59%. The experimental conditions had a significant impact on the outcome of the reaction. For example, treatment of (R_p)-**9** with 1-mesitylimidazole in DMF gave (R_p)-**11b** in 59% yield. The same reaction with (R_p)-**9** and 1-phenylimidazole in toluene afforded (R_p)-**11a** in only 16% yield. Presumably, the formation of phosphonium salts resulting from an intra- or intermolecular alkylation of the phosphino group limited the product yield.

In the attempt to improve the yields, an alternative synthesis of imidazolium salt **11c** was developed. In this sequence, [2.2]paracyclophane (S_p)-**8** [obtained from (S_p)-**6** according to Scheme 1] served as the starting material. Its phosphino group was first protected with sulfur, and subsequently, the hydroxymethyl of the resulting intermediate converted into a bromomethyl group to give (S_p)-**12** (Scheme 2). The yield of the bromination step (including the proceeding sulfur addition) increased to 85%. After reaction of methyl bromide (S_p)-**12** with 1-(2,6-diisopropylphenyl)imidazole, deprotection of the phosphine was achieved using freshly prepared Raney nickel to give imidazolium salt (S_p)-**11c** in 32% yield.[31]

All products were air stable, but nevertheless, for extended periods of time were stored under an inert atmosphere. The phosphino imidazolium salts were difficult to dry even under high vacuum at elevated temperatures and had the tendency to absorb moisture upon exposure to ambient atmosphere. This behaviour, however, did not influence the transformation of the imidazolium salts to their corresponding metal complexes.

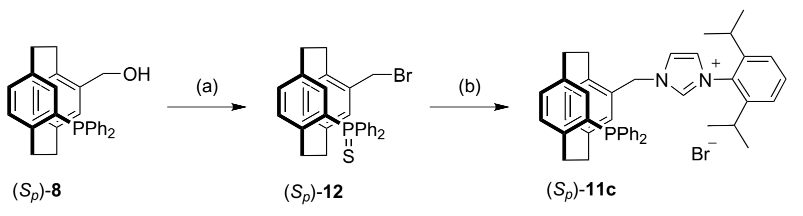
Next, we focused on the preparation of iridium complexes **5**. For their syntheses, imidazolium salts **11** were treated with LiO^{t}Bu or KO^{t}Bu in THF, and subsequent reaction of the in situ formed carbenes with $[Ir(COD)Cl]_2$ followed by anion exchange with NaBARF[32] in CH_2Cl_2/H_2O afforded complexes (R_p)-**5a–c** in yields of 54–91%. When the ion exchange was performed with KPF_6, (R_p)-**5d** was obtained from (R_p)-**11b** in 58% yield (Scheme 3).



Scheme 3. Reagents and conditions: (i) LiO^{t}Bu or KO^{t}Bu, $[Ir(COD)Cl]_2$, THF, 25 °C; (ii) NaBARF or KPF_6, CH_2Cl_2, H_2O, 54–91% yield.

Phosphino NHC iridium complexes **5a–d** are bright red, air-stable solids. The proposed chelation of the ligand is supported by NMR spectroscopy, where in the ^1H NMR spectra the two *ortho* protons relative to the functional groups at the [2.2]paracyclophane rings exhibit significant chemical shifts to lower and higher fields with δ values of 9.4–9.7 and 5.8–6.4 ppm, respectively. However, compared with the structurally related [2.2]paracyclophanyl-NHC-iridium complexes **4** bearing an oxazolinyl substituent, the high-field absorption is less pronounced.[25] In the ^{13}C NMR spectra, the carbene carbon absorbed at $\delta = 176.7–180.3$ ppm as a doublet with a coupling constant of $J_{PC} = 7.6–8.9$ Hz due to an interaction with the phosphino substituent opposite to the central iridium atom. The ^{31}P NMR absorptions of the phosphino moieties in the imidazolium salts were shifted downfield from $(\delta) = -4.2$ to -5.7 ppm to $\delta = 16.5–17.0$ ppm when coordinated to iridium.

Proof of the atom connectivity was finally obtained by X-ray crystal structure analysis of complex (R_p)-**5d** (Fig. 1). Unfortunately, all attempts to grow high-quality crystals from a solvent mixture of MeOH, EtOAc and CH_2Cl_2 failed. Although the collected diffraction data turned out to be sufficient enough to solve the structure, they did not allow a completely anisotropic refinement of the model on F or on F^2. Thus the structure shown in Figure 1 is the result of a refinement where only the Ir, the F and the P atoms have been treated anisotropically while the parameters of all the other nonhydrogen



Scheme 2. Reagents and conditions: (a) i. S_8, CH_2Cl_2; ii. PBr_3, CH_2Cl_2, 85% yield; (b) i. 1-(2,6-diisopropylphenyl)imidazole, DMF, 80 °C; ii. Ra-Ni, CH_3CN, 32% yield.

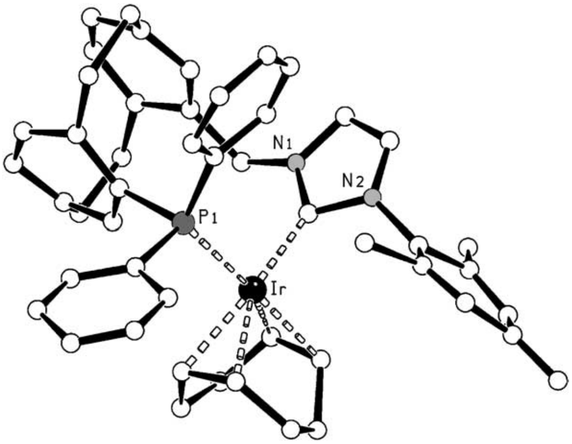


Figure 1. Representation (SCHAKAL plot) of the atom connectivity in the cationic fragment of (R_p)-**5d** (as determined by X-ray crystal structure analysis).

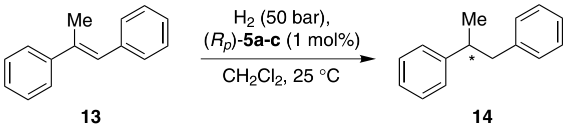
atoms have been optimized isotropically. While the obtained structure is sufficient to prove the connectivity of the atoms in the molecule, no discussion of the structural parameters is possible.

Next, iridium complexes **5a–d** were tested as chiral catalysts in the asymmetric hydrogenation of functionalized and simple alkenes.[33–35] (*E*)-1,2-Diphenyl-1-propene **13** was chosen as the first substrate (Table 1). All complexes exhibited low to good catalytic activity, with (R_p)-**5a** being the best leading to a 89% conversion of alkene **13**. The enantioselectivity in the formation of **14** reached 82% ee (Table 1, entry 3). Complexes (R_p)-**5b** and (R_p)-**5c** bearing sterically more demanding substituents on the carbene fragment afforded products with lower ee values (up to 29%; Table 1, entries 9 and 10, respectively). Interestingly, iridium complex (R_p)-**5a** gave **14** with an (*R*)-configuration, whereas (R_p)-**5b** and (R_p)-**5c** afforded (*S*)-configured products. Changing the solvent from dichloromethane to chloroform or toluene had only a marginal influence on the enantioselectivity. In toluene, however, the reaction rate seemed to decrease (Table 1, entry 5 vs 1). An important aspect appeared to be the purity of the solvent. Thus, we presume that traces of methanol or ethanol, which are often used for the stabilization of CH_2Cl_2 and $CHCl_3$, remained in the solvent even after purification and distillation and that they led to a decrease in catalytic activity in such solvents (Table 1, entries 1, 2 and 4). Evidence for this assumption stems from the observation that under otherwise identical reaction conditions a catalysis performed in amylene stabilized dichloromethane led to 89% substrate conversion (Table 1, entry 3).

The catalytic activity of complex (R_p)-**5a** was temperature dependent. Thus, when the temperature was increased from 25 to at 50 °C, the substrate conversion also increased from 42% to 99% (Table 1, entries 2 and 6). However, at the same time the enantioselectivity decreased from 81% to 73% ee. When the temperature was decreased to 0 and −20 °C the catalytic activity diminished with the ee of **14** being 78% and 67%, respectively (Table 1, entries 7 and 8).

The hydrogenation of the isomeric alkenes (*E*)-2-(4-methoxyphenyl)-2-butene **15**, (*Z*)-2-(4-methoxyphenyl)-2-butene **16** and 2-(4-methoxyphenyl)-1-butene **17** revealed an interesting dependence of the enantioselectivity in the formation of 2-(4-methoxyphenyl)butane **18** on the substrate structure. Regardless of the catalyst, hydrogenation of (*E*)-isomer **15** gave **18** with only 35–37% ee (Table 2, entries 1–3); the ee increased to 79% when (*Z*)-isomer **16** was the substrate and (R_p)-**5a** the catalyst (Table 2, entry 4). Complexes (R_p)-**5b** and (R_p)-**5c** catalyzed the formation of **18** with only 48% and 37% ee, respectively. Interestingly, the absolute configuration of the product was independent of the alkene stereo-

Table 1. Hydrogenation of (*E*)-1,2-diphenyl-1-propene **13** to give alkane **14** catalyzed by complexes (R_p)-**5a–c**[a]



Entry	Catalyst	Solvent	Temp. (°C)	Conversion (%)[b] (reaction time, h)	Ee (%)[c] (abs. config.)
1	(R_p)-**5a**	CH_2Cl_2	25	34 (2)	80 (*R*)
2	(R_p)-**5a**	CH_2Cl_2	25	42 (24)	81 (*R*)
3	(R_p)-**5a**	CH_2Cl_2[d]	25	89 (24)	82 (*R*)
4	(R_p)-**5a**	$CHCl_3$	25	64 (24)	80 (*R*)
5	(R_p)-**5a**	Toluene	25	16 (2)	78 (*R*)
6	(R_p)-**5a**	CH_2Cl_2	50	99 (24)	73 (*R*)
7	(R_p)-**5a**	CH_2Cl_2[d]	0	21 (24)	78 (*R*)
8	(R_p)-**5a**	CH_2Cl_2[d]	−20	3 (24)	67 (*R*)
9	(R_p)-**5b**	CH_2Cl_2	25	13 (24)	29 (*S*)
10	(R_p)-**5c**	CH_2Cl_2	25	41 (24)	22 (*S*)

[a] Reaction conditions: substrate (0.2–0.3 mmol), (R_p)-**5a–c** (1 mol%), solvent (1 mL), H_2 (50 bar); see experimental section for details.

[b] Determined by ^1H NMR.

[c] Determined by HPLC using a chiral column; the absolute configurations were revealed by comparison of the HPLC retention times with literature values.

[d] CH_2Cl_2 stabilized with amylene.

Table 2. Hydrogenations of (*E*)-2-(4-methoxyphenyl)-2-butene **15**, (*Z*)-2-(4-methoxyphenyl)-2-butene **16** and 2-(4-methoxyphenyl)-1-butene **17** to give 2-(4-methoxyphenyl)butane **18** catalyzed by complexes (R_p)-**5a**–**c**[a]

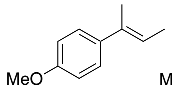
Entry	Substrate	Catalyst	H_2 pressure (bar)	Conversion (%)[b]	Ee (%)[c]
1	**15**	(R_p)-**5a**	50	100	37 (*R*)
2	**15**	(R_p)-**5b**	50	100	36 (*R*)
3	**15**	(R_p)-**5c**	50	100	35 (*R*)
4	**16**	(R_p)-**5a**	50	100	79 (*R*)
5	**16**	(R_p)-**5b**	50	99	48 (*R*)
6	**16**	(R_p)-**5c**	50	99	37 (*R*)
7	**17**	(R_p)-**5a**	50	100	37 (*S*)
8	**17**	(R_p)-**5a**	1	100	79 (*S*)
9	**17**	(R_p)-**5b**	50	100	32 (*R*)
10	**17**	(R_p)-**5b**	10	100	11 (*R*)
11	**17**	(R_p)-**5b**	1	100	37 (*S*)
12	**17**	(R_p)-**5c**	50	100	38 (*S*)
13	**17**	(R_p)-**5c**	10	100	39 (*S*)

[a] Reaction conditions: substrate (0.3 mmol), (R_p)-**5a**–**c** (1 mol %), solvent (1 mL), 25 °C, 24–48 h; see experimental section for details.

[b] Determined by ^1H NMR.

[c] Determined by HPLC using a chiral column; the absolute configurations were revealed by comparison of the HPLC retention times with literature values.

chemistry with hydrogenations of both isomers leading to (*R*)-**18**.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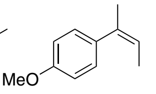
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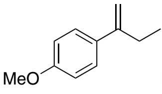
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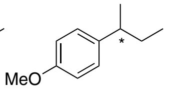
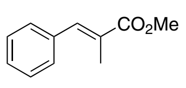

18

Hydrogenations of trisubstituted alkenes **15** and **16** were performed at a hydrogen pressure of 50 bar, since lowering the pressure to 1 bar led to low substrate conversions. In contrast, the hydrogenation of **17** went to completion even at 1 bar H_2 pressure. Using complex (R_p)-**5a** as catalyst, **18** was obtained with 79% under these conditions (Table 2, entry 8). Since the H_2 pressure was expected to have an effect on the enantioselectivity of the hydrogenations, the conversion of **17** with (R_p)-**5a** as catalyst was also performed at 50 bar H_2 with the result being the ee dropping to 37%. Most interesting was the pressure dependence of catalyses with (R_p)-**5b**. Here, the enantioselectivity in the formation of (*R*)-**18** decreased from 32% to 11% ee, when the H_2 pressure was lowered from 50 to 10 bar, respectively (Table 2, entries 9 and 10). At 1 bar of H_2 pressure the absolute configuration of the product changed, with the (*S*)-enantiomer of **18** being formed preferentially with an ee of 37%. Catalyses with complex (R_p)-**5c** (Table 2, entries 12 and 13) showed almost no pressure dependence.

The iridium complexes were also applied in hydrogenations of the functionalized alkenes methyl (*E*)-1-methylcinnamate **19**, dimethyl itaconate **20** and α-acetamidocinnamic acid **21**. Reactions of **19** led to enantioselectivities between 8% and 60% ee (Table 3, entries 1–6). While (R_p)-**5c** was the most selective catalyst (Table 3, entry 6), complexes (R_p)-**5a** and (R_p)-**5b** appeared to be more active than (R_p)-**5c**. In all cases, the (*R*)-configured product was formed in excess. As in the hydrogenation of the isomeric butenes, the enantioselectivity was pressure dependent. This effect was particularly pronounced in hydrogenations with catalyst (R_p)-**5a**. Whereas a hydrogen pressure of 50 bar led to (*R*)-**22** with 8% ee, the enantioselectivity was 53% ee in a catalysis at 1 bar of H_2 (Table 3, entries 1 and 2).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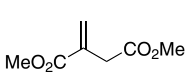
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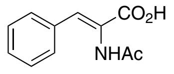
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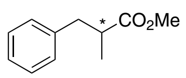
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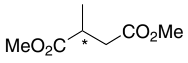
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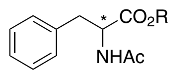
24: R = H; **25**: R = Me

The highest ee achieved was in the hydrogenation of the terminal alkene dimethyl itaconate **20**. Using complex (S_p)-**5c** as catalyst, (R_p)-**23** was obtained with an ee of 89% (Table 3, entry 12). When (R_p)-**5b**, having a sterically less bulky substituent at the carbene fragment of the ligand, was applied, the ee of **23** decreased to 68% (Table 3, entry 9). Remarkably, **23** had only 3% ee with (R_p)-**5a** as catalyst. In all cases (R_p)-configured catalysts yielded the (*S*)-enantiomer of **23** predominantly. Lowering the reaction temperature from 25 to 0 °C had no significant effect on the enantioselectivity (e.g., Table 3, entries 9 and 10).

As in the reactions of the butene and cinnamate derivatives, the conversion as well as the enantioselectivity in the hydrogenation of dimethyl itaconate **20** was dependent on the hydrogen pressure. Thus, in catalyses with (R_p)-**5a** and (R_p)-**5b** at 1 bar, the conversion of **20** was low, whereas full conversion was achieved at 50 bar of hydrogen pressure. Complex (R_p)-**5c** was more active, and with this catalyst 1 bar of H_2 was sufficient to lead to full conversion of **20**. With respect to the enantioselectivity, the situation was more complex. Thus, while in the hydrogenation of the butene and cinnamate derivatives, products with higher ee values were obtained at lower pressure, the opposite was observed in

Table 3. Hydrogenation of functionalized alkenes with iridium complexes **5a–c**[a]

Entry	Catalyst	Substrate	$p(H_2)$ (bar)	Conversion (%)[b]	Product	Ee (%)[c]
1	(R_p)-**5a**	**19**	50	100	**22**	8 (*R*)
2	(R_p)-**5a**	**19**	1	100	**22**	53 (*R*)
3	(R_p)-**5b**	**19**	50	93[d]	**22**	46 (*R*)
4	(R_p)-**5b**	**19**	1	87	**22**	53 (*R*)
5	(R_p)-**5c**	**19**	50	12[d]	**22**	35 (*R*)
6	(R_p)-**5c**	**19**	1	60	**22**	60 (*R*)
7	(R_p)-**5a**	**20**	50	100	**23**	3 (*S*)
8	(R_p)-**5a**	**20**	1	10	**23**	n.d.
9	(R_p)-**5b**	**20**	50	100[d]	**23**	68 (*S*)
10	(R_p)-**5b**	**20**	50	100[e]	**23**	70 (*S*)
11	(R_p)-**5b**	**20**	1	28	**23**	46 (*S*)
12	(S_p)-**5c**	**20**	50	100	**23**	89 (*R*)
13	(R_p)-**5c**[f]	**20**	50	100[e]	**23**	88 (*S*)
14	(R_p)-**5c**	**20**	1	100	**23**	35 (*S*)
15	(R_p)-**5b**	**21**	50	100	**24**[g]	6 (*S*)
16	(R_p)-**5c**	**21**	50	100	**24**[g]	71 (*S*)

[a] Reaction conditions: substrate (0.3 mmol for **19**, 0.2 mmol for **20** or 0.4 mmol for **21**), **5a–c** (1 mol %), solvent (1–2 mL; for entries 1–15 CH_2Cl_2, for entries 15, 16: CH_2Cl_2–MeOH, 1:1), 25 °C, 24 h; see experimental section for details.

[b] Determined by ^1H NMR.

[c] Determined by HPLC using a chiral column; the absolute configurations were established by comparison of the HPLC retention times with literature values.

[d] Reaction time: 2 h.

[e] Reaction temperature: 0 °C.

[f] Catalyst loading: 0.4 mol %.

[g] Ee analyzed as compound **25**.

the case of dimethyl itaconate. Here, the ee of **23** dropped from 70% to 46% [in a catalysis with (R_p)-**5b**], when the hydrogen pressure was decreased from 50 to 1 bar (Table 3, entries 10 and 11). With (R_p)-**5c** as catalyst, a decrease from 89% to 35% ee was found. Interestingly, a reversed pressure dependence was found in catalyses with the structurally similar [2.2]paracyclophanyl-NHC-iridium complexes **4** bearing an oxazolinyl substituent.[25]

Finally, catalysts (R_p)-**5b** and (R_p)-**5c** were tested in the hydrogenation of α-acetamidocinnamic acid **21**. Recently, Knochel applied iridium complexes with P, N-ligands in the hydrogenation of α-methyl acetamidocinnamate for the first time, thus achieving enantioselectivities of up to 97% ee in the formation of phenyl alanine derivatives.[35] We found that the application of (R_p)-**5b** in the reduction of **21** at a hydrogen pressure of 50 bar proceeded well and led to full conversion (Table 3, entry 15). The ee of the corresponding amino acid **24**, however, was only 6% (as determined at the ester stage after treatment of **24** with diazo methane to give **25**). The use of complex (R_p)-**5c** resulted in an improvement in the enantioselectivity, with **25** now obtained with 71% ee. In both cases, the (*S*)-enantiomer of the amino acid was formed in preference.

3. Conclusion

In summary, we have synthesized new iridium imidazolylidene complexes with a planar chiral [2.2]paracyclophane backbone. These complexes have been applied as catalysts in the asymmetric hydrogenations of simple and functionalized alkenes. Iridium complex (R_p)-**5a**, bearing a phenyl substituent at the imidazole ring, proved to be the most enantioselective catalyst in the hydrogenation of unfunctionalized alkenes such as (*E*)-1,2-diphenyl-1-propene **13** and the methoxyphenyl butene isomers **15–17**, giving products **14** and **18**, respectively, with up to 82% ee. In the hydrogenation of the functionalized substrates methyl (*E*)-1-methylcinnamate **19**, dimethyl itaconate **20** and α-acetamidocinnamic acid **21**, complex (R_p)- or (S_p)-**5c** was the best, yielding **22–24** with 60%, 89% and 71% ee, respectively. In this case, the imidazole ring of the carbene ligand was substituted with a highly sterically demanding 2,6-diisopropylphenyl group.

In general, the imidazole substituent appears to play a major role for the activity and selectivity of the iridium complexes. The mesityl and the 2,6-diisopropylphenyl group in complexes (R_p)-**5b** and (R_p)-**5c**, respectively, probably adopt an almost orthogonal arrangement with respect to the imidazole ring (as shown in Fig. 1), whereas the phenyl group in complex (R_p)-**5a** leads to a rather coplanar alignment with the heterocycle. Consequently, the steric properties of the imidazole substituent play an important role for the catalytic properties of the NHC complexes. This becomes particularly apparent in the hydrogenations of (*E*)-1,2-diphenylpropene and dimethyl itaconate. Whereas in the latter case the enantioselectivity is dramatically increased when the phenyl substituent at the imidazole ring of the ligand is changed to a mesityl or 2,6-diisopropylphenyl group (Table 3, entries 7, 9 and 13), the absolute configuration of the product changed from *R* to *S* in the hydrogenation of the stilbene derivative (Table 1, entries 3, 9 and 10). Although many differences in the structure/activity relationship exist, we note that similar trends have also been observed in the related iridium NHC complexes **4** based on the [2.2]paracyclophane skeleton bearing an oxazoline moiety.[25]

4. Experimental

4.1. General information

Pseudo-*ortho*-dibromo[2.2]paracyclophane **6**,[27,28] 1-mesitylimidazole,[29] 1-(2,6-diisopropylphenyl)imidazol[30] and NaBARF[32] were prepared according to published procedures. The following reagents and solvents are commercially available and were used as received: *n*-BuLi (1.6 M in *n*-hexane, Merck-Schuchardt), *t*-BuLi (1.48 M in pentane, Merck-Schuchardt), anhydrous DMF (Aldrich), chlorodiphenylphosphine (Aldrich), KO^{t}Bu (1 M, Aldrich), LiO^{t}Bu (Fluka), 1-phenylimidazole (Aldrich). $[\mathrm{Ir(COD)Cl}]_2$ was obtained as a gift from Umicore (formerly OMG). THF was distilled under nitrogen from sodium benzophenone ketyl and $\mathrm{CH_2Cl_2}$ from calcium hydride prior to use. All reactions were performed under an inert atmosphere of argon using standard Schlenk techniques. The NMR spectra were recorded on either a Varian Mercury 300 (^{1}H NMR at 300 MHz, ^{13}C NMR at 75 MHz, ^{31}P NMR at 121 MHz) or Varian Inova 400 (^{1}H NMR at 400 MHz, ^{13}C NMR at 100 MHz, ^{19}F NMR at 376 MHz, ^{31}P NMR at 162 MHz) spectrometer. Chemical shifts are given in ppm with internal referencing to TMS (^{1}H NMR), external $\mathrm{CFCl_3}$ (^{19}F NMR), external $\mathrm{H_3PO_4}$ (^{31}P NMR) or the solvent peaks (^{1}H NMR, ^{13}C NMR). Assignments are based on 2D NMR experiments. IR spectra were measured on a Perkin–Elmer 1760 FT spectrometer. Mass spectra were obtained by using a Varian MAT 212 (EI, ESI, APCI) and a Finnigan MAT 95 (SIMS-FAB) spectrometer. Only fragments containing the isotopes of the highest abundance are listed. Elemental analyses were carried out at the Institut für Organische Chemie der RWTH Aachen on a Heraeus CHNO-Rapid apparatus. Melting points were measured with a Büchi B-540 melting point determination apparatus. Optical rotations were measured on a Perkin–Elmer 241 polarimeter.

4.2. (+)-(R_p)-4-Bromo-12-diphenylphosphino[2.2]paracyclophane (R_p)-7

(R_p)-Pseudo-*ortho*-dibromo[2.2]paracyclophane (R_p)-**6** (8.5 g, 23.2 mmol) was placed in a Schlenk flask under an argon atmosphere and dissolved in anhydrous THF (100 mL). After cooling to −78 °C in a dry ice/acetone bath, a solution of *n*-BuLi in hexane (17.4 mL, 27.8 mmol) was added slowly. The reaction mixture was stirred at −78 °C for 1 h, after which chlorodiphenylphosphine (6.7 mL, 37.4 mmol) was added via syringe. The solution was then allowed to warm to room temperature overnight. After the addition of saturated $\mathrm{NH_4Cl}$ solution (50 mL), and phase separation and extraction of the aqueous layer with dichloromethane (3 × 50 mL), the combined organic phase was dried over $\mathrm{MgSO_4}$ and concentrated. The remaining residue was purified by column chromatography on silica gel (pentane–diethyl ether, 8:1 to 1:2) with degassed solvents to give 10.06 g of the title compound (92% yield) as a white solid. Mp 119–121 °C; $[\alpha]_D^{25} = +33$ (*c* 1.0, $\mathrm{CHCl_3}$); ^{1}H NMR (400 MHz, $\mathrm{CDCl_3}$) δ 2.60–2.71 (m, 2H, CH_2), 2.74–2.81 (m, 1H, CH_2), 2.86–2.95 (m, 2H, CH_2), 3.22–3.34 (m, 3H, CH_2), 6.24 (dd, 1H, $J = 7.9$, 1.6 Hz, *PCp*-C*H*), 6.40–6.51 (m, 4H, *PCp*-C*H*), 7.11 (br s, 1H, *PCp*-C*H*), 7.16–7.29 (m, 8H, *PPh*$_2$-C*H*), 7.40–7.45 (m, 2H, *PPh*$_2$-C*H*); ^{13}C NMR (100 MHz, $\mathrm{CDCl_3}$) δ 32.9, 33.4 (*C*$\mathrm{H_2}$), 35.7 (d, $J_{\mathrm{PC}} = 11.4$ Hz, *C*$\mathrm{H_2}$), 36.2 (*C*$\mathrm{H_2}$), 126.8 (q*C*), 128.4 (d, 2C, $J_{\mathrm{PC}} = 6.9$ Hz, *PPh*$_2$-*C*H), 128.5$_4$ (*PPh*$_2$-*C*H), 128.6 (2C, *PPh*$_2$-*C*H), 129.7 (*PPh*$_2$-*C*H), 131.7, 132.3 (*PCp*-*C*H), 133.2 (d, 2C, $J_{\mathrm{PC}} = 19.1$ Hz, *PPh*$_2$-*C*H), 133.7 (*PCp*-*C*H), 134.4 (d, $J_{\mathrm{PC}} = 5.4$ Hz, *PCp*-*C*H), 134.5 (d, $J_{\mathrm{PC}} = 4.6$ Hz, *PCp*-*C*H), 135.0 (*PCp*-*C*H), 136.0 (d, $J_{\mathrm{PC}} = 8.4$ Hz, q*C*), 136.6 (d, 2C, $J_{\mathrm{PC}} = 22.1$ Hz, *PPh*$_2$-*C*H), 137.3 (d, $J_{\mathrm{PC}} = 11.5$ Hz, q*C*), 138.5 (d, $J_{\mathrm{PC}} = 10.7$ Hz, q*C*), 139.0, 139.4, 141.9 (q*C*), 143.4 (d, $J_{\mathrm{PC}} = 19.8$ Hz, q*C*); ^{31}P NMR (162 MHz, $\mathrm{CDCl_3}$) δ −0.47 (s); IR (KBr): $\tilde{\nu} = 2954$, 2925, 2851, 1583, 1476, 1460, 1449, 1433, 1390, 1034, 907, 890, 862, 817, 741, 696, 668, 644, 501, 481 cm^{-1}; MS (EI, 70 eV) *m/z* (%) 473 (16), 472 (M$^+$, 73), 471 (14), 470 (M$^+$, 65), 289 (15), 288 (100), 209 (15), 178 (17). Anal. Calcd for $\mathrm{C_{28}H_{24}BrP}$: C, 71.35; H, 5.13. Found: C, 71.64; H, 5.09.

4.3. (+)-(R_p)-4-Diphenylphosphino-12-hydroxymethyl-[2.2]paracyclophane (R_p)-8

At −78 °C a solution of phosphine (R_p)-**7** (9.9 g, 21.0 mmol) in THF (180 mL) was treated slowly with a solution of *n*-BuLi in pentane (19.0 mL, 34.0 mmol). After stirring for 1 h at this temperature, carbon dioxide was bubbled through the reaction mixture for 30 min (at −78 °C). The reaction mixture was slowly warmed to room temperature, after which it was carefully degassed by means of a supersonic bath. Lithium aluminium hydride (1.2 g, 31.9 mmol) was added at 0 °C and the mixture stirred at room temperature overnight. It was then treated with aqueous HCl (5 M) until a pH of ~4–5 was reached. After phase separation, the aqueous layer was extracted with dichloromethane (3 × 50 mL). The combined organic phase was dried over $\mathrm{MgSO_4}$, concentrated, and the remaining residue purified by column chromatography on silica gel (degassed pentane–diethyl ether, 3:2) to give 7.46 g of (R_p)-**8** (84% yield) as a colourless oil, which crystallized upon treatment with pentane. Mp 126–128 °C; $[\alpha]_D^{25} = +8$ (*c* 1.0, $\mathrm{CHCl_3}$); ^{1}H NMR (400 MHz, $\mathrm{CDCl_3}$) δ 2.62 (ddd, 1H, $J = 13.1$, 10.0, 6.7 Hz, CH_2), 2.71–2.81 (m, 2H, CH_2), 2.99–3.10 (m, 2H, CH_2), 3.28 (ddd, 1H, $J = 13.3$, 10.0, 1.5 Hz, CH_2), 3.36–3.50 (m, 2H, CH_2), 3.97 (d, 1H, $J = 12.6$ Hz, CH_2OH), 4.27 (d, 1H, $J = 12.6$ Hz, CH_2OH), 5.87 (dd, 1H, $J = 8.2$, 1.6 Hz, *PCp*-C*H*), 6.49–6.52 (m, 3H, *PCp*-C*H*), 6.55 (dd, 1H, $J = 7.8$, 1.5 Hz, *PCp*-C*H*), 6.97 (br s, 1H, CH_2), 7.19–7.23 (m, 5H, *PPh*$_2$-C*H*), 7.37–7.41 (m, 3H, *PPh*$_2$-C*H*), 7.42–7.47 (m, 2H, *PPh*$_2$-C*H*); ^{13}C NMR (100 MHz, $\mathrm{CDCl_3}$) δ 33.3 (*C*$\mathrm{H_2}$), 33.9 (d, $J_{\mathrm{PC}} = 1.5$ Hz, *C*$\mathrm{H_2}$), 34.2 (*C*$\mathrm{H_2}$), 35.4 (d, $J_{\mathrm{PC}} = 13.0$ Hz, *C*$\mathrm{H_2}$), 64.4 (*C*$\mathrm{H_2}$OH), 128.5 (d, 2C, $J_{\mathrm{PC}} = 6.9$ Hz, *PPh*$_2$-*C*H), 128.6

(*PPh*$_2$-*C*H), 128.9 (d, 2C, $J_{\mathrm{PC}} = 8.4$ Hz, *PPh*$_2$-*C*H), 129.9 (*PPh*$_2$-*C*H), 130.4 (d, $J_{\mathrm{PC}} = 4.6$ Hz, *PCp*-*C*H), 132.4, 132.6 (*PCp*-*C*H), 133.1 (d, 2C, $J_{\mathrm{PC}} = 19.1$ Hz, *PPh*$_2$-*C*H), 133.9 (*PCp*-*C*H), 134.7 (d, $J_{\mathrm{PC}} = 5.4$ Hz, *PCp*-*C*H), 135.0 (*PCp*-*C*H), 136.1 (d, 2C, $J_{\mathrm{PC}} = 22.9$ Hz, *PPh*$_2$-*C*H), 136.4 (d, $J_{\mathrm{PC}} = 9.9$ Hz, q*C*), 136.9 (d, $J_{\mathrm{PC}} = 10.7$ Hz, q*C*), 137.8 (q*C*), 138.4 (d, $J_{\mathrm{PC}} = 9.2$ Hz, q*C*), 139.5, 139.6, 140.6 (q*C*), 144.0 (d, $J_{\mathrm{PC}} = 20.6$ Hz, q*C*); ^{31}P NMR (162 MHz, CDCl$_3$) δ −2.66 (s); IR (KBr) $\tilde{\nu}$ 3416, 2926, 1435, 1026, 863, 754, 745, 483 cm^{-1}; MS (EI, 70 eV) *m*/*z* (%) 423 (24), 422 (M$^+$, 91), 289 (28), 288 (100), 287 (26), 210 (15), 209 (26), 183 (11), 179 (14), 178 (30), 165 (15). Anal. Calcd for $C_{29}H_{27}OP$: C, 82.44; H, 6.44. Found: C, 82.24; H, 6.43.

4.4. (−)-(R_p)-12-Bromomethyl-4-diphenylphosphino[2.2]paracyclophane (R_p)-9

A solution of (R_p)-4-diphenylphosphino-12-hydroxymethyl[2.2]paracyclophane (R_p)-**8** (0.845 g, 2.0 mmol) in dichloromethane (10 mL) was treated with PBr$_3$ (80 μL, 0.84 mmol) at −20 °C. A white, cloudy precipitate immediately formed. The reaction mixture was stirred at room temperature overnight, diluted with CH$_2$Cl$_2$ (20 mL) and then washed with an ice-cold, saturated NaHCO$_3$ solution (10 mL). The organic phase was dried over MgSO$_4$, concentrated and the residue purified using a short silica gel column and degassed pentane–diethyl ether (6:1 to 1:1) as the eluent. Thus, 0.61 g (63% yield) of (R_p)-**9** was obtained as a white solid. As second fraction, 0.25 g (25% yield) of the corresponding phosphine oxide (R_p)-**10**, was isolated. (R_p)-**9**: Mp 315 °C (dec); $[\alpha]_D^{25} = -4$ (*c* 1.0, CHCl$_3$); ^{1}H NMR (400 MHz, CDCl$_3$) δ 2.55 (ddd, 1H, $J = 13.3$, 10.1, 6.9 Hz, C*H*$_2$), 2.67–2.77 (m, 2H, C*H*$_2$), 2.96–3.06 (m, 2H, C*H*$_2$), 3.22–3.28 (m, 1H, C*H*$_2$), 3.31 (ddd, 1H, $J = 12.9$, 10.0, 5.9 Hz, C*H*$_2$), 3.45 (ddd, 1H, $J = 13.2$, 10.2, 1.6 Hz, C*H*$_2$), 3.66 (d, 1H, $J = 10.2$ Hz, C*H*$_2$Br), 3.94 (d, 1H, $J = 10.1$ Hz, C*H*$_2$Br), 5.78 (d, 1H, $J = 7.7$ Hz, *PCp*-C*H*), 6.42–6.46 (m, 3H, *PCp*-C*H*), 6.49 (dd, 1H, $J = 8.0$, 1.6 Hz, *PCp*-C*H*), 6.83 (br s, 1H, *PCp*-C*H*), 7.08–7.18 (m, 5H, *PPh*$_2$-C*H*), 7.32–7.43 (m, 5H, *PPh*$_2$-C*H*); ^{13}C NMR (100 MHz, CDCl$_3$) δ 32.8 (*C*H$_2$Br), 33.5, 33.8, 34.1 (*C*H$_2$), 35.3 (d, $J_{\mathrm{PC}} = 13.7$ Hz, *C*H$_2$), 128.4 (d, 2C, $J_{\mathrm{PC}} = 6.9$ Hz, *PPh*$_2$-*C*H), 128.5 (*PPh*$_2$-*C*H), 129.0 (d, 2C, $J_{\mathrm{PC}} = 8.4$ Hz, *PPh*$_2$-*C*H), 130.1 (*PPh*$_2$-*C*H), 132.8 (d, $J_{\mathrm{PC}} = 6.1$ Hz, *PCp*-*C*H), 132.8$_7$ (d, 2C, $J_{\mathrm{PC}} = 19.0$ Hz, *PPh*$_2$-*C*H), 132.9, 133.6, 133.9 (*PCp*-*C*H), 135.0 (d, $J = 5.4$ Hz, *PCp*-*C*H), 135.5 (*PCp*-*C*H), 136.2 (d, 2C, $J_{\mathrm{PC}} = 22.8$ Hz, *PPh*$_2$-*C*H), 136.4 (d, $J_{\mathrm{PC}} = 10.7$ Hz, q*C*), 136.7 (q*C*), 136.8 (d, $J_{\mathrm{PC}} = 11.5$ Hz, q*C*), 138.1 (q*C*), 138.5 (d, $J_{\mathrm{PC}} = 9.9$ Hz, q*C*), 139.4, 140.8 (q*C*), 144.3 (d, $J_{\mathrm{PC}} = 21.4$ Hz, q*C*); ^{31}P NMR (162 MHz, CDCl$_3$) δ −3.47 (s); IR (KBr) $\tilde{\nu}$ 2926, 2855, 1477, 1433, 1206, 744, 722, 698, 588, 507, 479 cm^{-1}; MS (EI, 70 eV) *m*/*z* (%) 487 (29), 486 (M$^+$, 86), 485 (46), 484 (M$^+$, 100), 483 (19), 406 (20), 405 (62), 395 (10), 393 (12), 369 (12), 367 (13), 298 (11), 297 (45), 289 (21), 288 (90), 287 (32), 210 (18), 209 (32), 183 (13), 179 (18), 178 (36), 165 (19), 115 (12). Anal. Calcd for $C_{29}H_{26}BrP$: C, 71.76; H, 5.40. Found: C, 72.06; H, 5.56. Analytical data for phosphine oxide (R_p)-**10**: Mp 240 °C (dec); $[\alpha]_D^{25} = -51$ (*c* 0.9, CHCl$_3$); ^{1}H NMR (400 MHz, CDCl$_3$) δ 2.71–2.99 (m, 4H, C*H*$_2$), 3.11–3.17 (m 1H, C*H*$_2$), 3.36–3.45 (m, 3H, C*H*$_2$), 4.09 (d, 1H, $J = 10.1$ Hz, C*H*$_2$Br), 4.12 (d, 1H, $J = 9.9$ Hz, C*H*$_2$Br), 6.30 (dd, 1H, $J = 14.6$, 1.7 Hz, *PCp*-C*H*), 6.51 (d, 1H, $J = 7.7$ Hz, *PCp*-C*H*), 6.56–6.64 (m, 3H, *PCp*-C*H*), 7.05 (d, 1H, $J = 1.6$ Hz, *PCp*-C*H*), 7.34–7.38 (m, 2H, *P(O)Ph*$_2$-C*H*), 7.43–7.49 (m, 3H, *P(O)Ph*$_2$-C*H*), 7.51–7.59 (m, 3H, *P(O)Ph*$_2$-C*H*), 7.67–7.72 (m, 2H, *P(O)Ph*$_2$-C*H*); ^{13}C NMR (100 MHz, CDCl$_3$) δ 33.1 (*C*H$_2$), 33.4 (*C*H$_2$Br), 33.9, 35.0 (*C*H$_2$), 35.6 (d, $J_{\mathrm{PC}} = 4.6$ Hz, *C*H$_2$), 128.5$_6$ (d, 2C, $J_{\mathrm{PC}} = 11.5$ Hz, *P(O)Ph*$_2$-*C*H), 128.6 (d, 2C, $J_{\mathrm{PC}} = 11.5$ Hz, *P(O)Ph*$_2$-*C*H), 130.3 (d, $J_{\mathrm{PC}} = 105.3$ Hz, q*C*), 131.4 (d, 2C, $J_{\mathrm{PC}} = 9.9$ Hz, *P(O)Ph*$_2$-*C*H), 131.7 (d, $J_{\mathrm{PC}} = 3.0$ Hz, *P(O)Ph*$_2$-*C*H), 131.9 (d, $J_{\mathrm{PC}} = 2.3$ Hz, *P(O)Ph*$_2$-*C*H), 132.2 (d, 2C, $J_{\mathrm{PC}} = 9.1$ Hz, *P(O)Ph*$_2$-*C*H), 132.6 (d, $J_{\mathrm{PC}} = 103.0$ Hz, q*C*), 133.3 (*PCp*-*C*H), 133.5 (d, $J_{\mathrm{PC}} = 12.2$ Hz, *PCp*-*C*H), 134.6 (*PCp*-*C*H), 135.5 (d, $J_{\mathrm{PC}} = 103.8$ Hz, q*C*), 136.3$_6$ (*PCp*-*C*H), 136.4 (d, $J_{\mathrm{PC}} = 13.0$ Hz, *PCp*-*C*H), 136.8 (q*C*), 137.4 (d, $J_{\mathrm{PC}} = 2.3$ Hz, *PCp*-*C*H), 137.8 (q*C*), 139.2 (d, $J_{\mathrm{PC}} = 12.9$ Hz, q*C*), 140.9 (q*C*), 146.1 (d, $J_{\mathrm{PC}} = 7.7$ Hz, q*C*); ^{31}P NMR (162 MHz, CDCl$_3$) δ 26.82 (s); IR (KBr) $\tilde{\nu}$ 2927, 1436, 1178, 1134, 1118, 1104, 1069, 755, 748, 709, 697, 590, 560, 537, 515 cm^{-1}; MS (EI, 70 eV) *m*/*z* (%) 503 (10), 502 (M$^+$, 37), 501 (12), 500 (M$^+$, 38), 422 (10), 421 (37), 420 (16), 305 (24), 304 (100), 303 (46), 225 (13), 178 (13), 115 (11). Anal. Calcd for $C_{29}H_{26}BrOP$: C, 69.47; H, 5.23. Found: C, 69.32; H, 5.23.

4.5. (+)-(S_p)-12-Bromomethyl-4-diphenylthiophosphino-[2.2]paracyclophane (S_p)-12

To a solution of alcohol (S_p)-**8** (0.97 g, 2.3 mmol) in dichloromethane (20 mL) was added 0.1 g of sulfur (3.12 mmol). While stirring at room temperature for 2 h, the original yellow solution became colourless. PBr$_3$ (0.22 mL, 2.31 mmol) was added under cooling and the reaction mixture stirred overnight. After dilution with CH$_2$Cl$_2$ (20 mL), the organic phase was washed with an ice-cold, saturated NaHCO$_3$ solution (15 mL), dried over MgSO$_4$ and concentrated. The product was purified using a short silica gel column (pentane–diethyl ether, 4:1) to give 1.02 g of (S_p)-**12** (85% yield) as a white solid. Mp 231–232 °C; $[\alpha]_D^{25} = +57$ (*c* 1.1, CHCl$_3$); ^{1}H NMR (300 MHz, CDCl$_3$) δ 2.66–2.91 (m, 4H, C*H*$_2$), 3.09–3.17 (m, 1H, C*H*$_2$), 3.33–3.45 (m, 3H, C*H*$_2$), 4.10 (d, 1H, $J = 9.9$ Hz, C*H*$_2$Br), 4.34 (d, 1H, $J = 9.9$ Hz, C*H*$_2$Br), 6.18 (dd, 1H, $J = 15.6$, 1.7 Hz, *PCp*-C*H*), 6.47–6.60 (m, 4H, *PCp*-C*H*), 7.33–7.47 (m, 6H, *P(S)Ph*$_2$-C*H*), 7.57 (br s, 1H, *PCp*-C*H*), 7.72–7.83 (m, 4H, *P(S)Ph*$_2$-C*H*); ^{13}C NMR (75 MHz, CDCl$_3$) δ 32.4 (*C*H$_2$), 33.0 (*C*H$_2$Br), 33.2, 34.1 (*C*H$_2$), 34.4 (d, $J_{\mathrm{PC}} = 4.8$ Hz, *C*H$_2$), 128.2$_8$(d, $J_{\mathrm{PC}} = 88.0$ Hz, q*C*), 128.3 (d, 4C, $J_{\mathrm{PC}} = 12.5$ Hz, *P(S)Ph*$_2$-*C*H), 131.3 (d, $J_{\mathrm{PC}} = 3.6$ Hz, *P(S)Ph*$_2$-*C*H), 131.4 (d, $J_{\mathrm{PC}} = 2.9$ Hz, *P(S)Ph*$_2$-*C*H), 131.7 (d, 2C, $J_{\mathrm{PC}} = 10.2$ Hz, *P(S)Ph*$_2$-*C*H), 132.4 (d, 2C, $J_{\mathrm{PC}} = 10.1$ Hz, *P(S)Ph*$_2$-*C*H), 132.5$_6$ (d, $J_{\mathrm{PC}} = 83.8$ Hz, q*C*), 132.6 (d, $J_{\mathrm{PC}} = 10.8$ Hz, *PCp*-*C*H), 133.3, 133.9 (*PCp*-*C*H), 134.0 (*PCp*-*C*H), 134.7 (d, $J_{\mathrm{PC}} = 85.0$ Hz, q*C*), 136.4 (d, $J_{\mathrm{PC}} = 11.3$ Hz, *PCp*-*C*H), 136.8 (q*C*), 137.0 (d, $J_{\mathrm{PC}} = 3.6$ Hz, *PCp*-*C*H), 137.8

(q*C*), 138.8 (d, $J_{PC} = 13.1$ Hz, q*C*), 140.5 (q*C*), 145.4 (d, $J_{PC} = 8.4$ Hz, q*C*); ^{31}P NMR (121 MHz, CDCl$_3$) δ 38.43 (s); IR (KBr) $\tilde{\nu}$ 2926, 2856, 1477, 1435, 1097, 750, 699, 640, 616, 585, 541, 518, 501 cm^{-1}; MS (EI, 70 eV) *m*/*z* (%) 519 (13), 518 (M$^+$, 42), 517 (15), 516 (M$^+$, 39), 472 (17), 438 (19), 437 (45), 3211 (24), 320 (100), 319 (31), 209 (12), 183 (12). Anal. Calcd for $C_{29}H_{26}BrPS$: C, 67.31; H, 5.06. Found: C, 67.34; H, 5.18.

4.6. (−)-(R_p)-3-(4-Diphenylphosphino[2.2]paracyclophan-12-ylmethyl)-1-phenylimidazolium bromide (R_p)-11

A solution of methyl bromide (R_p)-**9** (1.94 g, 4.00 mmol) and 1-phenylimidazole (0.76 mL, 6.0 mmol) in degassed toluene (30 mL) was stirred at 80 °C for 72 h. After cooling to room temperature and reduction of the volume, the residue was purified by column chromatography on silica gel with degassed solvents (ethyl acetate–ethanol, 9:1 to 7:3). For the first fraction, 0.51 g (26%) of starting material (R_p)-**9** was recovered. For the second fraction, 0.41 g (0.65 mmol, 16% yield) of the title compound was isolated as a white solid. Mp 175 °C (dec); $[\alpha]_D^{25} = -134$ (*c* 1.0, CHCl$_3$); ^{1}H NMR (400 MHz, CDCl$_3$) δ 2.77–2.86 (m, 2H, C*H*$_2$), 3.01 (ddd, 1H, $J = 13.9$, 9.9, 7.1 Hz, C*H*$_2$), 3.09–3.18 (m, 2H, C*H*$_2$), 3.41 (ddd, 1H, $J = 12.9$, 9.9, 6.3 Hz, C*H*$_2$), 3.53–3.60 (m, 1H, C*H*$_2$), 3.69–3.75 (m, 1H, C*H*$_2$), 4.37 (d, 1H, $J = 14.0$ Hz, C*H*$_2$N), 5.53 (d, 1H, $J = 14.0$ Hz, C*H*$_2$N), 6.07 (dd, 1H, $J = 7.3$, $J = 1.5$ Hz, *PCp*-C*H*), 6.52–6.58 (m, 2H, *PCp*-C*H*), 6.60 (d, 1H, $J = 7.7$ Hz, *PCp*-C*H*), 6.68 (dd, 1H, $J = 8.0$, 1.7 Hz, *PCp*-C*H*), 7.04 (br s, 1H, *PCp*-C*H*), 7.06 (t, 1H, $J = 1.7$ Hz, NC*H*=CH), 7.16–7.24 (m, 5H, *PPh*$_2$-C*H*), 7.41–7.51 (m, 6H, *PPh*$_2$-C*H*, *NPh*-C*H*), 7.56–7.59 (m, 2H, *PPh*$_2$-C*H*), 7.69 (t, 1H, $J = 1.8$ Hz, NC*H*=CH), 7.79–7.81 (m, 2H, *NPh*-C*H*), 11.00 (t, 1H, $J = 1.4$ Hz, NC*H*N); ^{13}C NMR (100 MHz, CDCl$_3$) δ 33.8, 34.1, 34.6 (*C*H$_2$), 35.6 (d, $J_{PC} = 13.0$ Hz, *C*H$_2$), 52.0 (*C*H$_2$N), 120.7 (N*C*H=CH), 122.0 (2C, *NPh*-*C*H), 122.2 (N*C*H=CH), 128.5 (d, 2C, $J_{PC} = 6.9$ Hz, *PPh*$_2$-*C*H), 128.5$_2$ (*PPh*$_2$-*C*H), 129.5 (d, 2C, $J_{PC} = 8.4$ Hz, *PPh*$_2$-*C*H), 130.3 (*PPh*$_2$-*C*H), 130.5 (*NPh*-*C*H), 130.7 (3C, *NPh*-*C*H, q*C*), 131.4 (q*C*), 132.8 (d, 2C, $J_{PC} = 18.3$ Hz, *PPh*$_2$-*C*H), 133.6 (d, $J = 3.8$ Hz, *PCp*-*C*H), 133.7, 133.8 (*PCp*-*C*H), 134.6 (q*C*), 134.9 (*PCp*-*C*H), 135.0 (d, $J_{PC} = 5.3$ Hz, *PCp*-*C*H), 135.8 (N*C*HN), 136.2 (d, 2C, $J_{PC} = 21.4$ Hz, *PPh*$_2$-*C*H), 136.2$_1$ (d, $J = 11.4$ Hz, q*C*), 136.3 (*PCp*-*C*H), 139.5, 140.0, 141.5 (q*C*), 144.1 (d, $J_{PC} = 21.3$ Hz, q*C*); ^{31}P NMR (162 MHz, CDCl$_3$) δ −4.18 (s); IR (KBr) $\tilde{\nu}$ 3045, 2926, 1596, 1549, 1434, 1197, 1071, 756, 699, 506 cm^{-1}; MS (ESI, pos.) *m*/*z* (%) 550 (14), 549 (M$^+$, 41), 421 (23), 406 (30), 405 (100), 209 (10); MS (ESI, neg.) *m*/*z* (%) 81 (100), 79 (96). Anal. Calcd for $C_{38}H_{34}BrN_2P\cdot1.5H_2O$: C, 69.51; H, 5.68; N, 4.27. Found: C, 69.47; H, 5.71; N, 4.13.

4.7. (−)-(R_p)-3-(4-Diphenylphosphino[2.2]paracyclophan-12-ylmethyl)-1-(2,4,6-trimethylphenyl)imidazolium bromide (R_p)-11b

A solution of methyl bromide (R_p)-**9** (0.62 g, 1.28 mmol) and 1-mesitylimidazole (1.2 g, 6.44 mmol) in degassed DMF (5 mL) was stirred at 90 °C for 48 h. After cooling to room temperature and concentration of the volume, purification of the residue by column chromatography on silica gel (degassed ethyl acetate–ethanol, 1:0 to 4:2) yielded 0.51 g (59%) of (R_p)-**11b** as a white solid. Mp 274–275 °C; $[\alpha]_D^{25} = -90$ (*c* 0.85, CHCl$_3$); ^{1}H NMR (300 MHz, CDCl$_3$) δ 1.99 (s, 3H, C*H*$_3$), 2.05 (s, 3H, C*H*$_3$), 2.28 (s, 3H, C*H*$_3$), 2.74–2.85 (m, 2H, C*H*$_2$), 3.01–3.14 (m, 3H, C*H*$_2$), 3.35–3.46 (m, 2H, C*H*$_2$), 3.59 (ddd, 1H, $J = 13.4$, 10.1, 1.7 Hz, C*H*$_2$), 4.39 (d, 1H, $J = 14.3$ Hz, C*H*$_2$N), 5.55 (d, 1H, $J = 14.2$ Hz, C*H*$_2$N), 6.14 (dd, 1H, $J = 7.7$ Hz, $J = 1.3$ Hz, *PCp*-C*H*), 6.55–6.56 (m, 2H, *PCp*-C*H*), 6.61 (d, 1H, $J = 7.9$ Hz, *PCp*-C*H*), 6.69 (dd, 1H, $J = 7.8$, 1.6 Hz, *PCp*-C*H*), 6.95 (br s, 2H, *Mesityl*-C*H*), 7.00 (br s, 1H, *PCp*-C*H*), 7.13–7.23 (m, 6H, *PPh*$_2$-C*H*, NC*H*=CH), 7.28 (t, 1H, $J = 1.5$ Hz, NC*H*=CH), 7.42–7.58 (m, 5H, *PPh*$_2$-C*H*), 9.58 (t, 1H, $J = 1.5$ Hz, NC*H*N); ^{13}C NMR (75 MHz, CDCl$_3$) δ 18.3 (2C, *C*H$_3$), 21.3 (*C*H$_3$), 33.6, 33.8, 34.6 (*C*H$_2$), 35.5 (d, $J_{PC} = 13.8$ Hz, *C*H$_2$), 52.5 (*C*H$_2$N), 123.1, 123.4 (N*C*H=CH), 128.5 (d, 2C, $J_{PC} = 7.2$ Hz, *PPh*$_2$-*C*H), 128.5$_3$ (*PPh*$_2$-*C*H), 129.7 (d, 2C, $J_{PC} = 8.3$ Hz, *PPh*$_2$-*C*H), 130.1 (2C, *Mesityl*-*C*H), 130.5 (*PPh*$_2$-*C*H, q*C*), 130.7, 131.3 (q*C*), 132.8 (d, 2C, $J_{PC} = 19.2$ Hz, *PPh*$_2$-*C*H), 133.5 (d, $J_{PC} = 4.2$ Hz, *PCp*-*C*H), 133.7, 134.0 (*PCp*-*C*H), 134.5 (2C, q*C*), 134.9 (d, $J = 6.0$ Hz, *PCp*-*C*H), 135.1 (*PCp*-*C*H), 136.2 (d, 2C, $J_{PC} = 22.7$ Hz, *PPh*$_2$-*C*H), 136.3 (*PCp*-*C*H), 136.9 (N*C*HN), 137.0 (d, $J = 16.0$ Hz, q*C*), 138.6 (d, $J = 8.9$ Hz, q*C*), 139.4, 139.9, 141.5, 141.7 (q*C*), 144.3 (d, $J_{PC} = 21.6$ Hz, q*C*); ^{31}P NMR (121 MHz, CDCl$_3$) δ −4.83 (s); IR (KBr) $\tilde{\nu}$ 3057, 3007, 2918, 2856, 2809, 1545, 1477, 1432, 1204, 1157, 1069, 869, 756, 705, 507, 493 cm^{-1}; MS (ESI, pos.) *m*/*z* (%) 592 (24), 591 (M$^+$, 65), 406 (34), 405 (100). Anal. Calcd for $C_{41}H_{40}BrN_2P$: C, 73.32; H, 6.00; N, 4.17. Found: C, 73.02; H, 6.27; N, 3.99.

4.8. (−)-(R_p)/(+)-(S_p)-3-(4-Diphenylphosphino[2.2]paracyclophan-12-ylmethyl)-1-(2,6-diisopropylphenyl)imidazolium bromide (R_p)-11c and (S_p)-11c

Method A: The compound was prepared by the method described for the synthesis of (R_p)-**11b** using (R_p)-**9** (0.73 g, 1.5 mmol), 1-(2,6-diisopropylphenyl)imidazole (0.67 g, 2.93 mmol) and DMF (8 mL). After purification by column chromatography on silica gel (degassed ethyl acetate–ethanol, 1:0 to 6:1), 0.34 g (32% yield) of (R_p)-**11c** was isolated as a white solid.

Method B: A solution of the thiophosphine (S_p-**12**) (0.90 g, 1.74 mmol) and 1.30 g (6.44 mol) of 1-(2,6-diisopropylphenyl)imidazole in degassed DMF (2 mL) was heated to 100 °C for 48 h. After cooling to room temperature, diethyl ether was added. The precipitate was washed several times with diethyl ether, dried in vacuo and redissolved in degassed acetonitrile (20 mL). Freshly prepared Ra-Ni (from 16 g NiAl alloy) was added and the reaction mixture stirred overnight. Reaction control by ^{31}P NMR indicated full conversion of the thiophosphine. After filtration and concentration of the volume, the residue was purified by column chromatography on silica gel (degassed ethyl acetate–ethanol, 9:1). Thus, 0.4 g (32% yield) of (S_p-**11c**) was isolated as a white solid. Mp 150 °C (dec); for (R_p)-**11c**: $[\alpha]_D^{25} = -62$ (*c* 1.4, CHCl$_3$); (S_p)-**11c**: +64 (*c* 1.2, CHCl$_3$); ^{1}H NMR (400 MHz, CDCl$_3$) δ 1.07 (d, 3H, $J = 6.9$ Hz, CH(C*H*$_3$)$_2$), 1.12 (d, 6H, $J = 6.9$ Hz, CH(C*H*$_3$)$_2$), 1.19 (d, 3H, $J = 6.6$ Hz, CH(C*H*$_3$)$_2$), 2.11 (quin, 1H, $J = 6.8$ Hz, C*H* (CH$_3$)$_2$), 2.28 (quin, 1H, $J = 6.7$ Hz, C*H* (CH$_3$)$_2$), 2.73–2.85 (m, 2H, C*H*$_2$), 3.07–3.16 (m, 3H, C*H*$_2$), 3.36–3.46 (m, 1H, C*H*$_2$), 3.53–3.62 (m, 2H, C*H*$_2$), 4.41 (d, 1H, $J = 14.2$ Hz, C*H*$_2$N), 5.79 (d, 1H, $J = 14.3$ Hz, C*H*$_2$N), 6.14 (d, 1H, $J = 7.1$ Hz, *PCp*-C*H*), 6.52–6.57 (m, 2H, *PCp*-C*H*), 6.61 (d, 1H, $J = 7.7$ Hz, *PCp*-C*H*), 6.67 (br d, 1H, $J = 7.6$ Hz, *PCp*-C*H*), 7.02 (br s, 1H, *PCp*-C*H*), 7.17–7.27 (m, 8H, *PPh*$_2$-C*H*, NC*H*=CH, *^{i}Pr$_2$Ph*-C*H*), 7.42–7.59 (m, 7H, *PPh*$_2$-C*H*, NC*H*=CH, *^{i}Pr$_2$Ph*-C*H*), 9.97 (br s, 1H, NC*H*N); ^{13}C NMR (100 MHz, CDCl$_3$) δ 24.1, 24.4, 24.5, 24.6 (CH(*C*H$_3$)$_2$), 28.7$_7$, 28.8 (*C*H(CH$_3$)$_2$), 33.5, 33.6, 34.4 (*C*H$_2$), 35.4 (d, $J_{PC} = 13.0$ Hz, *C*H$_2$), 52.2 (*C*H$_2$N), 122.9, 124.2 (N*C*H=CH), 124.5$_8$, 124.6 (*^{i}Pr$_2$Ph*-*C*H), 128.2 (d, 2C, $J_{PC} = 6.9$ Hz, *PPh*$_2$-*C*H), 128.3 (*PPh*$_2$-*C*H), 129.3 (d, 2C, $J_{PC} = 8.4$ Hz, *PPh*$_2$-*C*H), 130.2 (2C, *PPh*$_2$-*C*H, q*C*), 131.6 (q*C*), 131.8 (*^{i}Pr$_2$Ph*-*C*H), 132.6 (d, 2C, $J_{PC} = 18.3$ Hz, *PPh*$_2$-*C*H), 133.1 (d, $J_{PC} = 3.1$ Hz, *PCp*-*C*H), 133.6 (2C, *PCp*-*C*H), 134.6$_9$ (d, $J_{PC} = 4.6$ Hz, *PCp*-*C*H), 134.7 (*PCp*-*C*H), 135.9 (d, 2C, $J_{PC} = 22.7$ Hz, *PPh*$_2$-*C*H), 136.0 (*PCp*-*C*H), 136.0 (q*C*), 136.9 (d, $J_{PC} = 11.4$ Hz, q*C*), 137.6 (N*C*HN), 138.3 (d, $J_{PC} = 8.4$ Hz, q*C*), 139.1, 139.8, 141.3 (q*C*), 143.8 (d, $J_{PC} = 21.4$ Hz, q*C*), 145.3 (2C, q*C*); ^{31}P NMR (162 MHz, CDCl$_3$) δ −5.36 (s); IR (KBr) $\tilde{\nu}$ 3010, 2962, 2927, 2867, 1667, 1542, 1462, 1434, 1180, 1095, 1068, 806, 747, 701, 506 cm^{-1}; MS (ESI, pos.) *m*/*z* (%) 634 (29), 633 (M$^+$, 78), 406 (33), 405 (100), 288 (18), 287 (15), 210 (11), 209 (47), 197 (13), 183 (11), 167 (10), 119 (11), 117 (45); MS (ESI, neg.) *m*/*z* (%) 81 (87), 79 (100). No correct elemental analysis could be obtained from this compound. Presumably, the presence of residual water, which could even not be removed after drying of the product under high vacuum at 60–80 °C, led to an unsatisfying result. Indirectly, the correct element composition was confirmed by the analysis of the corresponding Ir complex (S_p)-**11c**.

4.9. (+)-(R_p)-(η^4-1,5-Cyclooctadiene)(1-phenyl-3-(4-(diphenylphosphinyl)[2.2]paracyclophan-12-ylmethyl)imidazolin-2-ylidene)iridium(I) tetrakis(3,5-bis(trifluoromethyl)phenyl)borate (R_p)-5a

To a suspension of imidazolium salt (R_p)-**11a** (0.157 g, 0.25 mmol) and [Ir(COD)Cl]$_2$ (0.084 g, 0.125 mmol) in THF (10 mL) was added at room temperature a 1 M solution of KO^{t}Bu in THF (0.37 mL, 0.37 mmol) via syringe and the resulting mixture stirred at room temperature overnight. After removal of the volatiles in vacuo, NaBARF (0.332 g, 0.37 mmol), degassed water (10 mL) and dichloromethane (15 mL) were added and the mixture stirred vigorously for several hours. After phase separation, the aqueous layer was washed with CH$_2$Cl$_2$ (3 × 10 mL). The combined organic layers were dried over MgSO$_4$, evaporated and the residue purified by column chromatography using a short silica gel column and CH$_2$Cl$_2$–pentane (3:2) as the eluent. Complex (R_p)-**5a** was isolated as a bright red solid in 54% yield (0.233 g). Mp 190–191 °C; $[\alpha]_D^{25} = -0.8$ (*c* 2.2, CHCl$_3$); ^{1}H NMR (300 MHz, CDCl$_3$) δ 1.15–1.28 (m, 1H, *COD*-C*H*$_2$), 1.41–1.85 (m, 6H, C*H*$_2$, *COD*-C*H*$_2$), 1.98–2.18 (m, 2H, C*H*$_2$, *COD*-C*H*$_2$), 2.23–2.37 (m, 2H, C*H*$_2$, *COD*-C*H*$_2$), 2.42–2.50 (m, 1H, C*H*$_2$), 2.93–3.02 (m, 1H, C*H*$_2$), 3.11–3.28 (m, 5H, C*H*$_2$, *COD*-C*H*), 3.91–4.00 (m, 1H, *COD*-C*H*), 4.24–4.32 (m, 1H, *COD*-C*H*), 5.30 (d, 1H, $J = 16.8$ Hz, C*H*$_2$N), 5.71 (d, 1H, $J = 16.6$ Hz, C*H*$_2$N), 5.83 (s, 1H, *PCp*-C*H*), 6.46–6.52 (m, 4H, *PCp*-C*H*), 6.60–6.75 (br m, 2H, *PPh*$_2$-C*H*), 7.04 (d, 1H, $J = 2.2$ Hz, NC*H*=CH), 7.07–7.13 (m, 2H, *NPh*-C*H*, *PPh*$_2$-C*H*), 7.22–7.34 (m, 8H, *NPh*-C*H*, *PPh*$_2$-C*H*), 7.38–7.41 (m, 1H, *NPh*-C*H*, *PPh*$_2$-C*H*), 7.43 (br s, 4H, *BARF*-C*H*), 7.60 (d, 1H, $J = 2.0$ Hz, NC*H*=CH), 7.65 (t, 8H, $J = 2.4$ Hz, *BARF*-C*H*), 7.66–7.69 (m, 2H, *NPh*-C*H*, *PPh*$_2$-C*H*), 9.37 (dd, 1H, $J_{PH} = 20.0$ Hz, $J = 1.3$ Hz, *PCp*-C*H*); ^{13}C NMR (75 MHz, CDCl$_3$) δ 29.9 (d, $J_{PC} = 8.4$ Hz, *C*H$_2$), 30.3, 30.6, 31.5, 32.2, 32.7, 33.1, 34.6 (*C*H$_2$, *COD*-*C*H$_2$), 54.0 (*C*H$_2$N), 79.4 (*COD*-*C*H), 79.9 (d, $J_{PC} = 13.1$ Hz, *COD*-*C*H), 81.9 (d, $J_{PC} = 9.6$ Hz, *COD*-*C*H), 82.6 (*COD*-*C*H), 117.6 (m, 4C, *BARF*-*C*H), 122.9 (2C, N*C*H=CH, *Aryl*-*C*H), 123.3, 124.8 (*Aryl*-*C*H), 124.7 (q, $J_{FC} = 272.5$ Hz, *BARF*-*C*F$_3$), 127.3, 127.9 (q*C*), 128.2, 128.3 (*Aryl*-*C*H), 129.1 (q, $J_{FC} = 30.8$ Hz, *BARF*-*C*CF$_3$), 129.2, 129.4 (*Aryl*-*C*H), 129.8 (3C, N*C*H=CH, *Aryl*-*C*H), 130.3, 130.9 (q*C*), 131.3, 131.6, 132.8, 133.1, 133.2, 134.4 (*Aryl*-*C*H), 135.0 (br s, 8C, *BARF*-*C*H), 135.6 (d, $J_{PC} = 11.4$ Hz, *Aryl*-*C*H), 136.4 (q*C*), 138.1 (*Aryl*-*C*H), 138.3 (d, $J_{PC} = 21.8$ Hz, *Aryl*-*C*H), 138.5, 138.7 (*Aryl*-*C*H), 139.0 (q*C*), 139.1 (d, $J_{PC} = 15.0$ Hz, q*C*), 139.1$_4$ (*Aryl*-*C*H), 140.7, 144.6 (q*C*), 161.9 (q, $J_{CB} = 49.9$ Hz, B*C*), 176.7 (d, $J_{PC} = 8.9$ Hz, N*C*N); ^{19}F NMR (282 MHz, CDCl$_3$) δ −62.34 (s); ^{31}P NMR (121 MHz, CDCl$_3$) δ 17.02 (s); IR (KBr) $\tilde{\nu}$ 1355, 1279, 1128 cm^{-1}; MS (ESI, pos.) *m*/*z* (%) 850 (37), 849 (100, M$^+$), 848 (41), 847 (22), 740 (10), 739 (26), 738 (26), 737 (41), 736 (19), 735 (24); MS (ESI, neg.) *m*/*z* (%) 864 (38), 863 (100, M$^-$), 862 (19), 650 (23), 649 (14), 629 (11), 580 (24), 579 (11), 435 (24), 367 (13). Anal. Calcd for C$_{78}$H$_{57}$BF$_{24}$IrN$_2$P: C, 54.71; H, 3.36; N, 1.64. Found: C, 54.38; H, 3.63; N, 1.56.

4.10. (+)-(R_p)-(η^4-1,5-Cyclooctadiene)(1-(2,4,6-trimethylphenyl)-3-(4-(diphenylphosphinyl)[2.2]paracyclophan-12-ylmethyl)imidazolin-2-ylidene)iridium(I) tetrakis(3,5-bis(trifluoromethyl)phenyl)borate (R_p)-5b

This compound was prepared by the same procedure described for the synthesis of (R_p)-**5a** using imidazolium salt (R_p)-**11b** (0.202 g, 0.3 mmol), [Ir(COD)Cl]$_2$ (0.101 g, 0.15 mmol), KO^{t}Bu (0.4 mL, 0.4 mmol) and NaBARF (0.40 g, 0.45 mmol). After purification using a short silica gel column (CH$_2$Cl$_2$–pentane, 3:2), complex (R_p)-**5b** was obtained as a bright red solid (0.418 g, 79% yield). Mp 89–90 °C; $[\alpha]_D^{25} = +68$ (*c* 1.8, CHCl$_3$); ^{1}H NMR (400 MHz, CDCl$_3$) δ 1.05–1.14 (m, 1H, *COD*-C*H*$_2$), 1.28–1.42 (m, 2H, *COD*-C*H*$_2$), 1.68–1.77 (m, 3H, C*H*$_2$, *COD*-C*H*$_2$), 1.75 (s, 3H, *Mesityl*-C*H*$_3$), 1.83–1.91 (m, 2H, *COD*-C*H*$_2$), 2.04 (s, 3H, *Mesityl*-C*H*$_3$), 2.16–2.22 (m, 1H, *COD*-C*H*$_2$), 2.25 (s, 3H, *Mesityl*-C*H*$_3$), 2.35–

2.48 (m, 3H, CH_2, *COD*-CH_2), 2.90–3.01 (m, 2H, CH_2, *COD*-C*H*), 3.12–3.21 (m, 3H, CH_2), 3.23–3.30 (m, 1H, *COD*-C*H*), 4.04–4.08 (m, 1H, *COD*-C*H*), 4.78–4.83 (m, 1H, *COD*-C*H*), 5.32 (d, 1H, $J = 17.0$ Hz, CH_2N), 5.87 (d, 1H, $J = 17.0$ Hz, CH_2N), 6.24 (s, 1H, *PCp*-C*H*), 6.40–6.55 (m, 5H, *PCp*-C*H*, *PPh*$_2$-C*H*), 6.89 (s, 2H, *Mesityl*-C*H*), 7.05–7.36 (m, 8H, *PPh*$_2$-C*H*), 7.19 (d, 1H, $J = 2.2$ Hz, NC*H*=CH), 7.29 (d, 1H, $J = 1.9$ Hz, NC*H*=CH), 7.44 (s, 4H, *BARF*-C*H*), 7.44–7.48 (m, 1H, *PPh*$_2$-C*H*), 7.64 (t, 8H, $J = 2.2$ Hz, *BARF*-C*H*), 9.70 (d, 1H, $J_{PH} = 19.8$ Hz, *PCp*-C*H*); ^{13}C NMR (100 MHz, $CDCl_3$) δ 18.6, 20.9, (*Mesityl*-CH_3), 22.8 (d, $J_{PC} = 3.9$ Hz, *Mesityl*-CH_3), 27.7, 28.2, 31.2 (CH_2, *COD*-CH_2), 33.0 (2C, CH_2, *COD*-CH_2), 33.1 (d, $J = 3.9$ Hz, CH_2), 34.3, 35.1 (CH_2, *COD*-CH_2), 54.7 (CH_2N), 77.0, 77.6 (*COD*-CH), 81.7 (d, $J = 8.7$ Hz, *COD*-CH), 84.5 (*COD*-CH), 117.4 (m, 4C, *BARF*-CH), 122.8 (NCH=CH), 124.5 (q, $J_{FC} = 272.0$ Hz, *BARF*-CF_3), 127.4–130.6 (m, *Aryl*-CH, NCH=CH, *BARF*-CCF_3, Cq), 131.0 (2C, *Aryl*-CH), 131.4, 132.5, 134.3 (*Aryl*-CH), 134.8 (br s, 8C, *BARF*-CH), 135.1, 135.5, 135.9, 136.1 (q*C*), 138.0 (*Aryl*-CH), 138.1 (d, $J_{PC} = 6.9$ Hz, *Aryl*-CH), 138.5 (*Aryl*-CH), 138.7$_6$ (d, 2C, $J_{PC} = 16.9$ Hz, *Aryl*-CH), 138.7$_8$ (*Aryl*-CH), 140.0, 140.6, 144.7 (q*C*), 161.7 (q, $J_{CB} = 49.8$ Hz, *BARF*-BC), 179.8 (d, $J_{PC} = 8.1$ Hz, NCN); ^{19}F NMR (376 MHz, $CDCl_3$): δ −62.38 (s); ^{31}P NMR (162 MHz, $CDCl_3$) δ 16.61 (s); IR (KBr) $\tilde{\nu} = 1355, 1279, 1127$ cm^{-1}; MS (ESI, pos.) *m*/*z* (%) 893 (12), 892 (57), 891 (100, M$^+$), 890 (41), 889 (72), 829 (11), 823 (13), 822 (27), 820 (17), 782 (18), 781 (36), 779 (20), 120 (35); MS (ESI, neg.) *m*/*z* (%): 864 (29), 863 (100, M$^-$), 862 (14). Anal. Calcd for $C_{81}H_{63}BF_{24}IrN_2P$: C, 55.45; H, 3.62; N, 1.60. Found: C, 55.56; H, 3.95; N, 1.52.

4.11. (+)-(*R$_p$*)/(−)-(*S$_p$*)-(η^4-1,5-Cyclooctadiene)(1-(2,6-diisopropylphenyl)-3-(4-(diphenylphosphinyl)[2.2]paracyclophan-12-ylmethyl)imidazolin-2-ylidene)iridium(I) tetrakis-(3,5-bis(trifluoromethyl)phenyl)borate (*R$_p$*)-5c and (*S$_p$*)-5c

This compound was prepared by the method described for the synthesis of (*R$_p$*)-**10a** using imidazolium salt (*R$_p$*)- or (*S$_p$*)-**11c** (0.163 g, 0.23 mmol), [Ir(COD)Cl]$_2$ (0.077 g, 0.11 mmol), LiO^{t}Bu (0.027 g, 0.35 mmol) and NaBARF (0.266 g, 0.3 mmol). After column chromatography on silica gel (CH_2Cl_2–pentane, 3:3), the title compound was obtained as a bright red solid (0.374 g, 91% yield). Mp 79–80 °C; for (*R$_p$*)-**5c**: $[\alpha]_D = +68$ (*c* 1.1, $CHCl_3$); for (*S$_p$*)-**5c**: −71 (*c* 1.1, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.53 (d, 3H, $J = 6.7$ Hz, CH(CH_3)$_2$), 0.98 (d, 3H, $J = 7.0$ Hz, CH(CH_3)$_2$), 1.02–1.44 (m, 4H, *COD*-CH_2, C*H*(CH$_3$)$_3$), 1.08 (d, 3H, $J = 6.7$ Hz, CH(CH_3)$_2$), 1.09 (d, 3H, $J = 7.0$ Hz, CH(CH_3)$_2$), 1.62–1.94 (m, 5H, CH_2, *COD*-CH_2), 2.02–2.09 (m, 1H, *COD*-CH_2), 2.34–2.49 (m, 3H, CH_2, *COD*-CH_2), 2.91–3.04 (m, 3H, C*H*(CH$_3$)$_2$, CH_2, *COD*-C*H*), 3.09–3.22 (m, 3H, CH_2), 3.39–3.49 (m, 1H, *COD*-C*H*), 3.98–4.05 (m, 1H, *COD*-C*H*), 4.75–4.83 (m, 1H, *COD*-C*H*), 5.35 (d, 1H, $J = 17.4$ Hz, CH_2N), 5.96 (d, 1H, $J = 17.1$ Hz, CH_2N), 5.96–6.02 (m, 1H, *PPh*$_2$-C*H*), 6.35 (s, 1H, *PCp*-C*H*), 6.47–6.57 (m, 5H, *PCp*-C*H*, *PPh*$_2$-C*H*), 7.05–7.12 (m, 1H, *PPh*$_2$-C*H*), 7.14–7.42 (m, 11H, *PPh*$_2$-C*H*, NC*H*=CH, ^{i}*Pr*$_2$*Ph*-C*H*), 7.44 (s, 4H, *BARF*-C*H*), 7.46–7.53 (m, 1H, *PPh*$_2$-C*H*), 7.65 (br s, 8H, *BARF*-C*H*), 9.70 (d, 1H, $J = 19.8$ Hz, *PCp*-C*H*); ^{13}C NMR (100 MHz, $CDCl_3$) δ 23.4, 23.6 (^{i}*Pr*$_2$*Ph*-CH(CH_3)$_2$), 26.2 (^{i}*Pr*$_2$*Ph*-CH(CH_3)$_2$), 27.3 (^{i}*Pr*$_2$*Ph*-CH(CH_3)$_2$), 27.5, 27.7 (*COD*-CH_2), 29.0 (^{i}*Pr*$_2$*Ph*-CH(CH$_3$)$_2$), 29.4 (d, $J_{PC} = 4.6$ Hz, ^{i}*Pr*$_2$*Ph*-CH(CH$_3$)$_2$), 31.2, 31.9 (CH_2, *COD*-CH_2), 32.9 (d, $J_{PC} = 3.8$ Hz, CH_2), 33.1, 34.8, 35.3 (CH_2, *COD*-CH_2), 55.1 (CH_2N), 76.5 (d, $J_{PC} = 15.3$ Hz, *COD*-CH), 77.7 (*COD*-CH), 80.4 (d, $J_{PC} = 7.6$ Hz, *COD*-CH), 84.7 (*COD*-CH), 117.5 (m, 4C, *BARF*-CH), 122.6 (NCH=CH), 124.5$_6$ (*Aryl*-CH), 124.6 (q, $J_{FC} = 272.1$ Hz, *BARF*-CF_3), 124.7 (*Aryl*-CH), 125.9 (d, $J_{PC} = 11.4$ Hz, *Aryl*-CH), 127.3 (q*C*), 128.7 (d, $J_{PC} = 11.8$ Hz, *Aryl*-CH), 128.9 (q, $J_{FC} = 31.0$ Hz, *BARF*-CCF_3), 129.0 (d, $J_{PC} = 8.4$ Hz, *Aryl*-CH), 129.5 (*Aryl*-CH), 129.6 (q*C*), 129.9 (*Aryl*-CH), 130.0 (d, $J_{PC} = 3.9$ Hz, q*C*), 130.2 (NCH=CH), 130.3 (d, $J_{PC} = 6.9$ Hz, *Aryl*-CH), 131.0, 131.2, 131.4, 132.4 (*Aryl*-CH), 132.7 (d, $J_{PC} = 12.2$ Hz, *Aryl*-CH), 134.0 (d, $J_{PC} = 5.3$ Hz, *Aryl*-CH), 134.2 (*Aryl*-CH), 134.6 (q*C*), 134.9 (br s, 8C, *BARF*-CH), 135.2 (q*C*), 135.8 (d, $J_{PC} = 19.1$ Hz, *Aryl*-CH), 136.0 (q*C*), 138.0 (d, $J_{PC} = 23.6$ Hz, *Aryl*-CH), 138.2 (2C, *Aryl*-CH), 138.9 (d, $J_{PC} = 16.8$ Hz, q*C*), 140.7, 144.9, 145.6, 146.9 (q*C*), 161.7 (q, $J_{CB} = 49.6$ Hz, *BARF*-BC), 180.3 (d, $J_{PC} = 7.6$ Hz, NCN); ^{19}F NMR (376 MHz, $CDCl_3$) δ −62.33 (s); ^{31}P NMR (121 MHz, $CDCl_3$) δ 16.47 (s); IR (KBr) $\tilde{\nu}$ 1355, 1279, 1127 cm^{-1}; MS (ESI, pos.) *m*/*z* (%) 933 (9, M$^+$), 824 (21), 823 (83), 822 (64), 821 (70), 820 (90), 819 (100), 818 (33), 817 (15), 816 (19), 777 (11); MS (ESI, neg.) *m*/*z* (%) 864 (18), 863 (100, M$^-$), 862 (11), 650 (16), 580 (16), 435 (13). Anal. Calcd for $C_{84}H_{69}BF_{24}IrN_2P$: C, 56.16; H, 3.87; N, 1.56. Found: C 56.43; H, 4.10; N, 1.37.

4.12. (+)-(*R$_p$*)-(η^4-1,5-Cyclooctadiene)(1-(2,4,6-trimethylphenyl)-3-(4-(diphenylphosphinyl)[2.2]paracyclophan-12-ylmethyl)imidazolin-2-ylidene)iridium(I) hexafluorophosphate (*R$_p$*)-5d

This compound was prepared by the same procedure described for the synthesis of (*R$_p$*)-**5a** using imidazolium salt (*R$_p$*)-**11b** (0.269 g, 0.4 mmol), [Ir(COD)Cl]$_2$ (0.134 g, 0.2 mmol), KO^{t}Bu (0.6 mL, 0.6 mmol) and KPF_6 (0.147 g, 0.8 mmol). After purification using a short silica gel column (CH_2Cl_2–pentane, 7:3 to 1:0), complex (*R$_p$*)-**5d** was obtained as a bright red solid (0.242 g, 58%). Crystallization from a mixture of dichloromethane, ethyl acetate and methanol gave crystals, which in turn were used for the X-ray structural analysis. Mp 185–190 °C (dec); $[\alpha]_D^{25} = +95$ (*c* 1.1, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.08–1.20 (m, 1H, *COD*-CH_2), 1.34–1.46 (m, 2H, *COD*-CH_2), 1.68–1.81 (m, 3H, CH_2, *COD*-CH_2), 1.85–2.04 (m, 2H, *COD*-CH_2), 1.93 (s, 3H, *Mesityl*-CH_3), 2.13 (s, 3H, *Mesityl*-CH_3), 2.26–2.34 (m, 1H, *COD*-CH_2), 2.34 (s, 3H, *Mesityl*-CH_3), 2.38–2.60 (m, 3H, CH_2, *COD*-CH_2), 2.87–2.96 (m, 1H, *COD*-C*H*), 2.98–3.08 (m, 1H, CH_2), 3.27–3.32 (m, 2H, CH_2, *COD*-C*H*), 3.35–3.47 (m, 2H, CH_2), 4.02–4.08 (m, 1H, *COD*-C*H*), 5.15–5.22 (m, 1H, *COD*-C*H*), 5.62 (d, 1H,

$J = 17.5$ Hz, CH_2N), 5.87 (d, 1H, $J = 17.3$ Hz, CH_2N), 6.32 (s, 1H, *PCp*-C*H*), 6.53–6.65 (m, 5H, *PCp*-C*H*, *PPh*$_2$-C*H*), 6.96 (s, 2H, *Mesityl*-C*H*), 7.10–7.26 (br m, 3H, *PPh*$_2$-C*H*), 7.30 (d, 1H, $J = 1.9$ Hz, NC*H*=CH), 7.33–7.45 (m, 5H, *PPh*$_2$-C*H*), 7.41 (d, 1H, $J = 1.9$ Hz, NC*H*=CH), 7.53–7.58 (m, 1H, *PPh*$_2$-C*H*), 9.85 (d, 1H, $J_{\mathrm{PH}} = 20.1$ Hz, *PCp*-C*H*); ^{13}C NMR (75 MHz, CDCl$_3$) δ 18.7, 20.9 (*Mesityl*-CH$_3$), 22.9 (d, $J_{\mathrm{PC}} = 3.6$ Hz, *Mesityl*-*C*H$_3$), 27.8, 28.3, 31.2 (*C*H$_2$ *COD*-*C*H$_2$), 32.9 (d, $J_{\mathrm{PC}} = 3.0$ Hz, C*H*$_2$), 33.0 (2C, *C*H$_2$, *COD*-*C*H$_2$), 34.2, 35.0 (*C*H$_2$, *COD*-*C*H$_2$) 54.6 (*C*H$_2$N), 76.6, 77.7 (*COD*-*C*H), 83.2 (d, $J_{\mathrm{PC}} = 8.4$ Hz, *COD*-*C*H), 83.3 (*COD*-*C*H), 123.6 (N*C*H=CH), 128.1, 128.7 (*C*q), 129.0, 129.3 (*Aryl*-*C*H), 129.4 (*C*q), 129.9 (3C, *Aryl*-*C*H, N*C*H=CH), 130.0 (*C*q), 131.0 (2C, *Aryl*-*C*H), 131.9, 132.4 (*Aryl*-*C*H), 132.6–133.6 (m, 4C, *Aryl*-*C*H), 134.3 (*Aryl*-*C*H), 135.2, 135.8, 136.5 (*C*q), 136.6 (2C, *C*q), 138.0 (*Aryl*-*C*H), 138.1 (d, $J_{\mathrm{PC}} = 6.0$ Hz, *Aryl*-*C*H), 138.9, 139.3 (*Aryl*-*C*H), 139.4 (d, 2C, $J_{\mathrm{PC}} = 13.9$ Hz, *Aryl*-*C*H), 139.5, 140.2, 144.6 (q*C*), 178.5 (d, $J_{\mathrm{PC}} = 8.3$ Hz, N*C*N); ^{19}F NMR (282 MHz, CDCl$_3$) δ −73.08 (d, $J_{\mathrm{PF}} = 712.5$ Hz); ^{31}P NMR (121 MHz, CDCl$_3$) δ −144.25 (sep, $J_{\mathrm{PF}} = 713.0$ Hz, *P*F$_6$), 16.82 (s, *P*(Aryl)$_3$); IR (KBr) $\tilde{\nu}$ 842, 703, 557 cm^{-1}; MS (SIMS-FAB, pos.) *m*/*z* (%) 894 (10), 893 (20), 891 (11, M$^+$), 817 (15), 816 (21), 815 (22), 814 (20), 813 (13), 785 (16), 784 (42), 783 (78), 782 (56), 781 (100), 780 (35), 779 (46), 778 (13), 777 (12), 598 (11), 596 (11), 594 (12), 592 (13), 512 (10), 496 (16), 494 (12), 490 (10), 438 (15), 406 (14), 303 (11), 301 (17), 187 (34), 185 (25), 184 (18), 183 (23); MS (SIMS-FAB, neg.) *m*/*z* (%) 145 (100, M$^-$). Anal. Calcd for $C_{49}H_{51}F_6IrN_2P_2\cdot CH_3OH$: C, 56.22; H, 5.19; N, 2.62. Found: C, 56.12; H, 5.19; N, 2.58.

4.13. X-ray structure determination of (*R*$_p$)-5d

The compound {[$C_{49}H_{51}N_2PIr$][PF_6] M_r 1036.12} crystallizes in tetragonal space group $P4_32_12$ (No. 96) with cell dimensions $a = 12.190(8)$ and $c = 62.65(6)$ Å. A cell volume of $V = 9310(14)$ Å^3 and $Z = 8$ result in a calculated density of $\delta_{\mathrm{calcd}} = 1.478\,\mathrm{g\,cm^{-3}}$, 265,942 reflections have been collected at $T = 298$ K on a Bruker Smart Apex CCD diffractometer employing MoK$_\alpha$ radiation ($\lambda = 0.71073$ Å). Data collection covered the range $-14 \leqslant h \leqslant 14$, $-14 \leqslant k \leqslant 14$ and $-74 \leqslant l \leqslant 74$ up to $\Theta_{\max} = 25.14°$, $\mu = 2.996\,\mathrm{mm^{-1}}$, absorption correction with SADABS (max: 1.0000, min: 0.7988). The structure has been solved by direct methods as implemented in the Xtal3.7 suite of crystallographic routines[36] where GENSIN has been used to generate the structure invariant relationships and GENTAN for the general tangent phasing procedure. Due to the low crystal quality the structure could not be refined completely anisotropical (see text), 7931 observed reflections ($I > 2\sigma(I)$) have been included in the final refinement on F involving 286 parameters and converging at $R(R_w) = 0.113(0.103, w = 1/[\sigma^2(F) + 0.0004 \cdot F^2])$, $S = 4.994$ and a residual electron density of $-5.7/3.4\,\mathrm{e\,Å^{-3}}$. The hydrogen positions have been calculated in idealized positions. Their *U*s have been fixed at 1.5 times *U* of the relevant heavy atom, and no hydrogen parameters have been refined.

4.14. Procedure for the alkene hydrogenation and analysis of the products

The substrate, iridium complex **5a–c** and dichloromethane (1 mL) were added to a small tube containing a magnetic stirring bar, which was then placed in 100 mL autoclave. The autoclave was sealed and pressurized to 10–50 bar of hydrogen. One sequence of experiments was carried out at 50 °C using a heating mantle. Reactions at lower temperatures were performed using a cryostate and a cooling bath. Hydrogenations at ambient pressure were carried out in a Schlenk tube using a balloon and 2 mL of solvent. The tube containing the catalyst and the substrate was evacuated and refilled with hydrogen gas several times before adding the solvent. After stirring for the indicated time (see tables) at the appropriate temperature, the reaction vessel was vented. If necessary, it was cooled to room temperature before venting. Reaction times were not optimized. The reaction mixture was diluted with pentane and passed through a short silica gel plug using hexane–ethyl acetate (3:1) as the eluent. After evaporation of the solvents, the conversions and ees were determined by ^{1}H NMR and HPLC using a chiral column, respectively. In the case of α-acetamidocinnamic acid **21**, product **24** was converted to methyl ester **25** by use of an ethereal CH_2N_2 solution after hydrogenation and ethyl ether was used as the eluent when passing through silica gel. HPLC analysis: 1,2-diphenylpropane **14**: Daicel Chiralcel OJ column, 254 nm, 20 °C, 0.5 mL min^{-1}, *n*-heptane–2-propanol, 99:1, retention times (in min) = 15.5 (*R*), 25.7 (*S*), 29.5 (starting material).[33a] 2-(4-Methoxyphenyl)butane **18**: Daicel Chiralcel OD-H column, 254 nm, 20 °C, 0.5 mL min^{-1}, *n*-heptane, retention times (in min) = 15.5 (*S*), 17.4 (*R*).[34b] 2-Methyl-3-phenyl-propionic acid methyl ester **22**: Daicel Chiralcel OD-H column, 254 nm, 20 °C, 0.5 mL min^{-1}, *n*-heptane–2-propanol, 99.5:0.5, retention times (in min) = 21.5 (*R*), 25.4 (*S*).[37] 2-Methylsuccinic acid dimethyl ester **23**: Daicel Chiralcel OD-H column, 215 nm, 20 °C, 0.5 mL min^{-1}, *n*-heptane–2-propanol, 96:4, retention times (in min) = 13.7 (*R*), 18.9 (starting material), 21.6 (*S*).[38] *N*-Acetyl phenylalanine methyl ester **25**: Daicel Chiralcel OD-H column, 254 nm, 20 °C, 0.6 mL min^{-1}, *n*-heptane–2-propanol, 90:10, retention times (min) = 17.1 (*R*), 23.8 (*S*).[38]

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