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Regioselective palladation of 2-oxazolinyl-[2.2]paracyclophanes. Synthesis of planar-chiral phosphines

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In memoriam Professor Dr. Othmar Stelzer

Abstract

Palladations of the diastereomeric 4-(4-*tert*-butyl-2-oxazolinyl)-[2.2]paracyclophanes (S,R_p)-**3** and (S,S_p)-**3** have been investigated. Exclusive *ortho*-palladation occurs, when (S,R_p)-**3** is treated with $Pd(OAc)_2$ in glacial acetic acid. In contrast, (S,S_p)-**3** affords products from either metallation in the *ortho* or the benzylic position of the [2.2]paracyclophane skeleton depending on the reaction conditions. Upon treatment of the resulting complexes with LiCl followed by addition of PPh_3 mononuclear chloro{4-(2-oxazolinyl)-[2.2]paracyclophane,5-*C*,3-*N*}(triphenylphosphine)palladium(II) complexes (S,S_p)-**7**, (S,R_p)-**7**, and (S,S_p)-**9** have been obtained. The solid state structures of (S,S_p)-**7** and (S,R_p)-**7** have been determined by X-ray diffraction analysis. Reaction of *ortho*-palladated complexes (S,S_p)-**7** and (S,R_p)-**7** with $KPPh_2$ gives the corresponding planar-chiral phosphines (S,S_p)-**11** and (S,R_p)-**11**, respectively. From benzyl substituted complex (S,S_p)-**9** bromo derivative (S,S_p)-**12** was obtained.

Keywords: Cyclopalladation; Paracyclophanes; Palladacycles; Planar chirality; Regioselective palladation

1. Introduction

Recently, chiral palladacycles with oxazolinyl substituents have attracted much attention, due to their potential application as catalysts in asymmetric synthesis [1]. Some of them reveal high catalytic activity, and through the asymmetric environment created by the oxazoline moiety appreciable enantioselectivities have been achieved in various reactions. Palladacycles have also been used as intermediates in substitution reactions [2,3], where they react with both nucleophiles or electrophiles. In the latter case, the reactivity of the palladium-containing intermediate is similar to the one of other organometallic reagents, such as organolithium reagents, and analogous functionalizations can be achieved. Particularly in transformations of substrates having competing metalation sites, the use of palladacycles is advantageous, since the regioselectivity of the palladation can be tuned by the reaction conditions. As a consequence, even those substrates can be modified in a highly selective manner [4].

Within our research program on the use of planar-chiral ligands in asymmetric catalysis [5], we now investigated selective functionalizations of [2.2]paracyclophanes [6–8]. Based on the excellent results achieved in the ferrocene chemistry [9,10], the oxazolinyl substituent derived from *tert*-leucinol was chosen as metalation directing group. Lithiations and palladations of the resulting oxazolinyl-[2.2]paracyclophane were investigated for their potential in a selective functionalization of the [2.2]paracyclophane skeleton.

2. Results and discussion

2.1. Synthesis and lithiation studies

Through a reaction sequence involving treatment of racemic 4-carboxy-[2.2]paracyclophane (*rac*-**1**) [11] with thionyl chloride followed by reaction of the resulting

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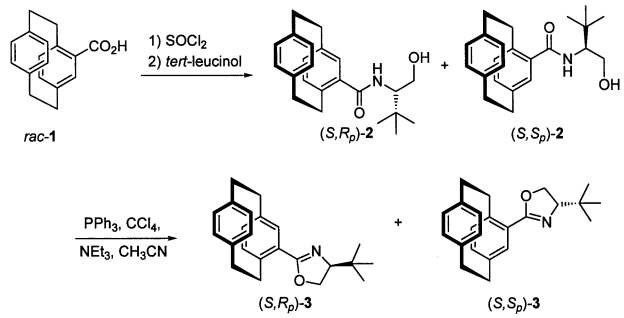
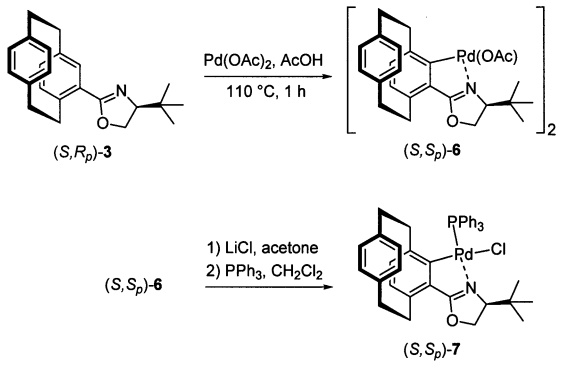


Scheme 1.

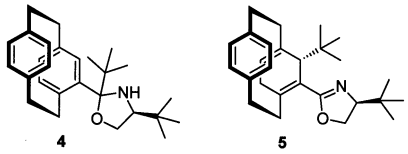


Scheme 2.

acid chloride with (*S*)-*tert*-leucinol, amides (S,R_p)-**2** and (S,S_p)-**2** were obtained as a mixture of diastereomers. Oxazoline formation by ring closure under *Appel* cyclization conditions [12] furnished diastereomeric 4-(4-*tert*-butyl-2-oxazolinyl)-[2.2]paracyclophanes (S,R_p)-**3** and (S,S_p)-**3** in 83% overall yield (Scheme 1).[1]

Column chromatography allowed to separate diastereomers (S,R_p)-**3** and (S,S_p)-**3**. For the unambiguous assignment of the relative stereochemistry, the reaction sequence shown in Scheme 1 was also performed using enantiopure (*S*)-**1** as starting material. Comparison of the spectral data revealed (S,R_p)-**3** to be the faster eluting stereoisomer (silica gel, pentane–ethyl acetate 19:1).

Unfortunately, all attempts to employ lithium bases such as *n*-BuLi, *sec*-BuLi and *tert*-BuLi for selective lithiations of (S,R_p)-**3** and (S,S_p)-**3** afforded complex product mixtures. Assuming that those products resulted from nucleophilic additions of the lithium reagents, the reaction of (S,R_p)-**3** with *tert*-BuLi at 0 °C in diethylether followed by quenching with water was studied in more detail. Besides remaining starting material, products **4** and **5** (ratio 2.4:2.8:1) stemming from 1.2- and 1.4-additions of the lithium reagents onto the oxazolinyl-[2.2]paracyclophane were identified. Reactions of such type are known and have previously been used by Meyers et al. in the synthesis of optically active naphthalene derivatives [13].



Attempted lithiation using lithium amides such as lithium diisopropylamide, lithium 2,2,6,6-tetramethylpiperidide and lithium bis(trimethylsilyl)amide (with or without TMEDA) led to no conversion of the starting material. Lithiation with *n*-BuLi, *sec*-BuLi, or *tert*-BuLi in the presence of TMEDA resulted in complex product mixtures after the addition of electrophiles (such as D_2O) to the lithiated intermediates. Similar observations were independently made by Hou et al., who used a diastereomeric mixture of lithiated 4-(4-isopropyl-2-oxazolinyl)-[2.2]paracyclophane for the synthesis of *S*,*N*- and *Se*,*N*-chelates [7]. There, treatment of the deprotonated species with PhSSPh or PhSeSePh also afforded product mixtures, revealing an unselective metalation at both the *ortho* and the benzylic position of the [2.2]paracyclophane skeleton.

2.2. Regioselective palladations

Since the use of lithium reagents proved unsatisfying, a potential functionalization of (S,R_p)-**3** and (S,S_p)-**3** via palladation was investigated next. Along these lines, a mixture of (S,R_p)-**3** and 1.1 equivalents of $Pd(OAc)_2$ was heated to 110 °C in glacial acetic acid for 1 h. After cooling of the reaction mixture to room temperature and removal of the solvent, palladacycle di-μ-acetatobis-{4-(2-oxazolinyl)-[2.2]paracyclophane,5-*C*,3-*N*}dipalladium(II) [(S,S_p)-**6**][2] was obtained. Without further purification (S,S_p)-**6** was dissolved in acetone and treated with LiCl followed by the addition of a solution of PPh_3 in dichloromethane. Upon addition of heptane to the concentrated reaction mixture, chloro{4-(2-oxazolinyl)-[2.2]paracyclophane,5-*C*,3-*N*}(triphenylphosphine)palladium(II) complex (S,S_p)-**7** was isolated in 90% yield (Scheme 2).

Crystals of (S,S_p)-**7** suitable for an X-ray diffraction analysis were obtained by recrystallization of the crude palladacycle from a mixture of heptane and chloroform. The precision of the structure of (S,S_p)-**5** is somewhat diminished by the presence of the slightly disordered $CHCl_3$ in the crystal lattice. The molecular structure of (S,S_p)-**7** is shown in Fig. 1.

[1] For reasons of clarity, the original numbering system of the oxazolinyl-[2.2]paracyclophane (**3**) was kept throughout the whole manuscript. Furthermore, only the absolute configuration of the stereogenic center at the oxazolinyl substituent steming from *tert*-leucine and that of the planar chirality is given, even when more elements of chirality are present in the molecule.

[2] Complexes (S,R_p)-**6**, (S,S_p)-**6**, and (S,S_p)-**8** were only identified by ^{1}H-NMR spectroscopy as crude products.

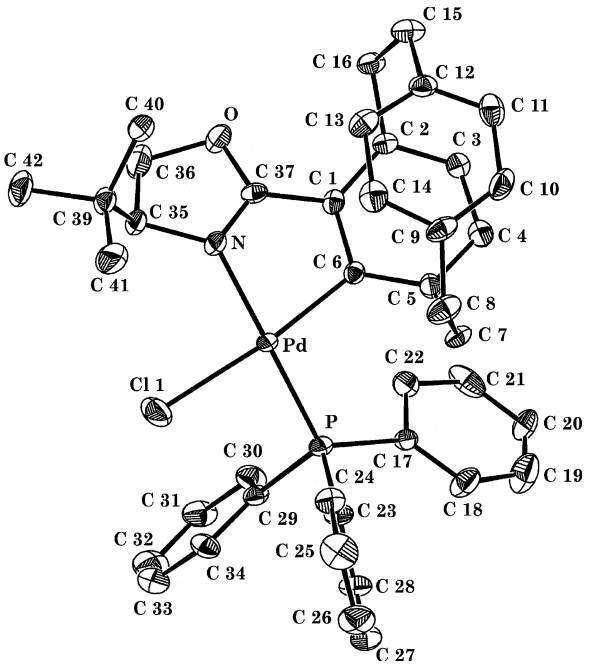


Fig. 1. The structure of palladacycle (S,S_p)-**7** in the solid state. The $CHCl_3$ molecule has been omitted for clarity. ORTEP plot (at the 30% probability level) [14].

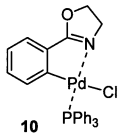
Diastereomer (S,S_p)-**3** reacted differently under the palladation conditions described above. In this case, the metal inserted preferentially into the C–H bond at the benzylic position of the [2.2]paracyclophane, and the *ortho*-palladated complex was only the minor product (ratio of benzylic vs. *ortho*-insertion ca. 4:1). Under high dilution conditions in refluxing acetic acid the regioselectivity was complete, and after treatment of an acetone solution of the initially formed palladium complex (S,S_p)-**8**[2] with LiCl followed by the addition of PPh_3 in dichloromethane, (S,S_p)-**9** was obtained in 82% yield (Scheme 3).

Knowing that the reaction medium could have a strong influence on the metalation path, we investigated the effect of the solvent on the palladium insertion. Gratifyingly, we found that by performing the metalation in toluene at 80 °C a complete regioselectivity change occurred. Thus under those conditions (S,S_p)-**3** gave exclusively *ortho*-palladated complex (S,R_p)-**6**. Treatment of an acetone solution of (S,R_p)-**6**[2] with LiCl followed by the addition of PPh_3 in dichloromethane afforded (S,R_p)-**7** in 94% yield (Scheme 4).

The molecular structure of (S,R_p)-**7** was also determined by X-ray diffraction analysis, and the result of this study is shown in Fig. 2.

2.3. X-ray crystallographic data

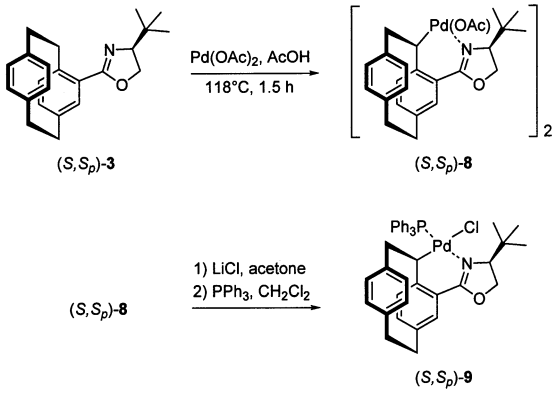
Recently, Smoliakova et al. reported on the synthesis and structure of the sterically unhindered chloro[(2-oxazolinyl)phenyl,2-*C*,3-*N*](triphenylphosphine)palladium(II) (**10**) [1j], where the immediate environment of the metal atom is quite similar to that in (S,S_p)-**7** and (S,R_p)-**7**.



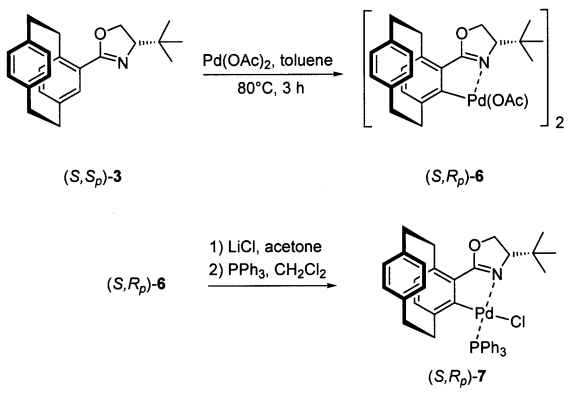
10

In Table 1 selected bond lengths and angles from (S,S_p)-**7**, (S,R_p)-**7**, and **10** are compared with unweighted average values for corresponding bonds given in the literature [15] and with some results of non-empirical quantum-chemical calculations.

While corresponding bond lengths in (S,S_p)-**7**, (S,R_p)-**7** and **10** are quite similar, marked differences occur as far as deviations of the environment of the Pd atom from planarity are concerned. At an interplanar angle of 4.3° between the (C,Pd,N) and the (P,Pd,Cl) planes coordination of the Pd atom is almost planar in **10**. However, corresponding angles of 16(2)° in (S,S_p)-**7** and even of 30.8(2)° in (S,R_p)-**7** indicate significant deviations from planarity especially for latter compound. Another measure of the degree of distortion are the average distances (Δ) of the coordinating C, P, N, and Cl atoms from their least-squares plane. The



Scheme 3.



Scheme 4.

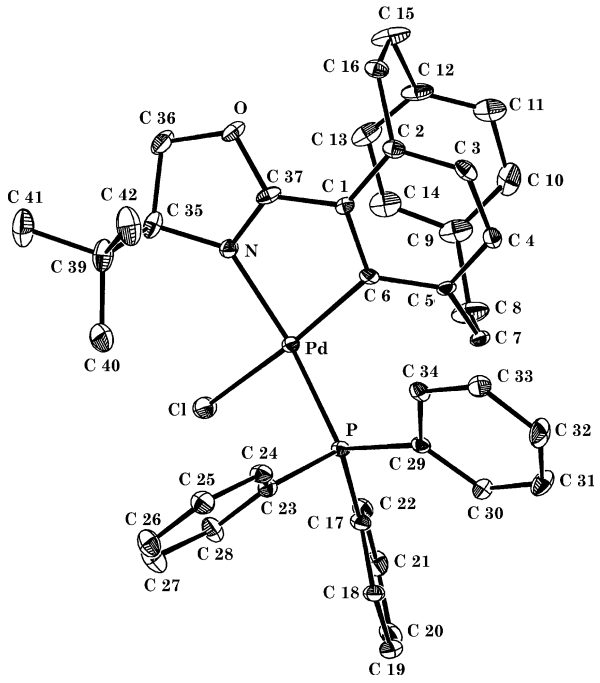


Fig. 2. The structure of palladacycle (S,R_p)-**7** in the solid state. ORTEP plot (at the 30% probability level) [14].

corresponding values are 0.15 Å in (S,S_p)-**7**, 0.34 Å in (S,R_p)-**7**, but only 0.06 Å in **10**. At $\Delta = 0.07$ Å in (S,S_p)-**7** and $\Delta = 0.09$ Å in (S,R_p)-**7**, the oxazoline rings in both compounds are close to planarity. The least-squares planes between the oxazoline systems and the directly bonded phenyl rings of the [2.2]paracyclophane substituents enclose angles of 15.5° in (S,S_p)-**7** and 13.3° in (S,R_p)-**7**, indicating a stronger torsion about the connecting C–C bonds in those compounds than in **10** where the corresponding angle is 6.2°. However, the expected differences in conjugative interaction between the five- and the six-membered ring in (S,S_p)-**7** and (S,R_p)-**7** on the one hand and in **10** on the other are not reflected by differences between the lengths of the connecting bonds (C1–C37 and the corresponding bond in **10**) which overlap within their single estimated standard deviations (Table 1). The [2.2]paracyclophane substituents in both complexes show the typical structural features. In both compounds, the atoms C1, C3, C4, C6 and C10, C11, C13, C14 define planes while C2, C5 and C9, C12 lie significantly below or above these planes. The average distances of these atoms from the planes are 0.17 Å in (S,R_p)-**7** and 0.18 Å in (S,S_p)-**7**. These values are close to the distance of 0.16 Å obtained from an ab initio calculation (for parent [2.2]paracyclophane (MP2/6-31+G*, total energy: −617.268156 Hartrees). In both complexes the strongest deviations from the planes occurs for C5 [(S,S_p)-**7**: 0.21, (S,R_p)-**7**: 0.22 Å] followed by C2 [(S,S_p)-**7**: 0.18 Å, (S,R_p)-**7**: 0.17 Å]. The average lengths of the C–C bonds in the CH_2CH_2 bridges connecting the six-membered rings of the [2.2]paracyclophane substituents is 1.58 Å and might be compared with the calculated value of 1.587 Å for parent [2.2]paracyclophane.

2.4. IR data

The coordination of the oxazoline nitrogen to palladium results in a significant shift of the strong C=N stretching vibration band to lower wave numbers. For the [2.2]paracyclophanyl palladacycles (S,S_p)-**7**, (S,R_p)-**7**, and (S,S_p)-**9** those shifts upon coordination were remarkably high. Whereas the bands of the uncomplexed compounds (S,R_p)-**3** and (S,S_p)-**3** occur at 1643

Table 1
Selected bond lengths (Å) and angles (°) in (S,S_p)-**7**, (S,R_p)-**7**, **10** and unweighted average values for corresponding bonds taken from Ref. [15]

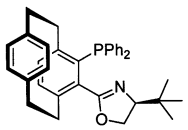
	(S,S_p)-**7**	(S,R_p)-**7**	**10**	Unweighted average values taken from Ref. [15] and calculated data
Bond lengths				
Pd–C	2.05(1)	2.016(6)	2.030(4)	1.981(32) (σ Pd–C_6R_5)
Pd–Cl	2.423(5)	2.403(2)	2.368(2)	2.331(67) (terminal Pd–Cl)
Pd–P	2.24(1)	2.261(2)	2.256(1)	2.308(38) (Pd–PPh_3)
Pd–N	2.06(3)	2.107(5)	2.062(3)	2.101 (Pd–N, in pyrazoles)
C1–C37	1.45(3)	1.443(9)	1.440(6)	
N–C37	1.31(3)	1.292(8)	1.266(6)	*1.310*
N–C35	1.50(3)	1.452(9)	1.471(6)	*1.474*
O–C36	1.50(3)	1.480(9)	1.457(4)	*1.483*
O–C37	1.31(3)	1.335(8)	1.335(5)	*1.308*
Bond angles				
C6–Pd–N	78.5(8)	79.8(2)	80.7(2)	
C6–Pd–P	98.9(5)	97.6(2)	94.8(1)	
N–Pd–P	164(2)	154.3(2)	174.1(1)	
N–Pd–Cl	94.6(8)	96.5(1)	88.6(1)	
P–Pd–Cl	88.2(3)	93.03(6)	96.07(4)	

Structural parameters in italics are from a MP2/6-31+G* geometry optimization of the oxazolium cation (proton at N). Bond lengths in Å, bond angles in °.

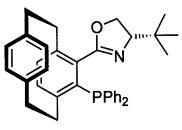
and 1641 cm^{-1}, respectively, those of the corresponding *ortho*-palladated [2.2]paracyclophanes occur at 1591 [$\Delta = -52$ cm^{-1}] for (S,S_p)-**7** and 1606 cm^{-1} [$\Delta = -35$ cm^{-1}] for (S,R_p)-**7**. In case of the benzylic complex (S,S_p)-**9** the C=N band was shifted from 1641 to 1618 cm^{-1} [$\Delta = -23$ cm^{-1}]. Compared to the respective shift upon formation of the sterically less encumbered palladacycle **10** (from 1649 to 1642 cm^{-1}; $\Delta = -7$ cm^{-1}) those large values for the [2.2]paracyclophane derivatives indicate the strong coordinative binding between the oxazoline nitrogen and palladium.

2.5. Substitution reactions of the palladacycles

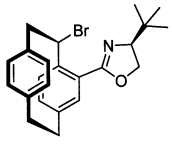
In order to demonstrate the capability of the palladacycles to undergo substitution reactions with nucleophiles, *ortho*-metalated (S,S_p)-**7** as well as its diastereomer (S,R_p)-**7** were reacted with potassium diphenylphosphide in toluene at room temperature. In both cases, the metal to phosphine exchange occurred smoothly affording phosphines (S,S_p)-**11** and (S,R_p)-**11**, respectively [16]. For the purification by column chromatography, the crude products was treated with an excess of boran dimethylsulfide complex, which led to the formation of the corresponding phosphine boran adducts. Their purification by column chromatography was followed by amine-mediated cleavage of the B–P bond to afford the unprotected phosphines (S,S_p)-**11** and (S,R_p)-**11** in 67 and 61% yield, respectively.



(S,S_p)-**11**



(S,R_p)-**11**



(S,S_p)-**12**

In preliminary studies the benzylic palladacycle (S,S_p)-**9** revealed a lower reactivity, and upon treatment with potassium diphenylphosphide at room temperature no palladium-to-phosphine substitution took place. However, at the same temperature (S,S_p)-**9** reacted with a mixture of bromine and sodium acetate to give bromide (S,S_p)-**12** in 72% yield after 1 h [17].

3. Summary and conclusions

Attempts to selectively lithiate oxazolinyl [2.2]paracyclophanes derived from *tert*-leucine remained unsuccessful, and after subsequent electrophilic trappings only complex product mixtures and addition products of the alkyllithium reagents were obtained. A palladium-based strategy offered an excellent alternative, and the selective palladation of oxazolinyl-[2.2]paracyclophanes **3** allowed the synthesis of new planar-chiral palladacycles. By appropriate adjustment of the reaction conditions, either the benzylic or the *ortho*-position of the [2.2]paracyclophane skeleton could be functionalized and bromo as well as phosphino substituents were selectively introduced into those positions. Thus, through the use of the palladacycles substituted [2.2]paracyclophanes were obtained regioselectively which previously remained inaccessible by the standard lithiation–bromination/phosphorylation protocol.

Our current efforts are firstly directed towards an expansion of the scope of the nucleophilic substitution reaction starting from palladacycles and, secondly, to an investigation of the applicability of the resulting planar-chiral [2.2]paracyclophanes as ligands in asymmetric catalysis. For example, preliminary experiments revealed a catalytic activity of palladacycle (S,S_p)-**9** and a ruthenium(II) complex of (S,S_p)-**11** in asymmetric hydroarylations of norbornene (in DMSO with phenyl iodide as aryl source) and transfer hydrogenations of acetophenone, respectively. The resulting products were obtained in good yields, alas as racemates or compounds with low enantiomeric excess. Further studies, which shall lead to a process optimization, are currently ongoing in our laboratories.

4. Experimental

4.1. General

^{1}H-, ^{13}C- and ^{31}P-NMR (400, 100 and 162 MHz, respectively), DEPT, COSY and HETCOR spectra were recorded in $CDCl_3$ using Me_4Si as an internal standard on an Inova 400 spectrometer (or a Gemini 300 for ^{13}C-NMR only). Chemical shifts are given in ppm and spin–spin coupling constants, J, are given in Hz. IR spectra were recorded on a Perkin–Elmer FTIR as KBr pellets. MS spectra were measured on a Varian MAT 212 and HRMS as well as SIMS-FAB spectra on a Finnigan MAT 95 mass spectrometer.

[2.2]Paracyclophane was purchased from Fluka, thionylchloride and $Pd(OAc)_2$ from Merck and potassium diphenylphosphide from Aldrich. 4-Carboxy-[2.2]paracyclophane [11] and (*S*)-*tert*-leucinol [18] were prepared according to literature protocols.

4.2. 4-(4-tert-Butyl-2-oxazolinyl)-[2.2]paracyclophanes [(S,R_p)-3 and (S,S_p)-3]

4-Carboxy-[2.2]paracyclophane (**1**) (3.02 g, 12 mmol) was refluxed in thionylchloride (30 ml) for 1 h. After removing the excess of thionylchloride under reduced pressure, the resulting acid chloride was dissolved in CH_2Cl_2 (20 ml) and added to a solution of (*S*)-*tert*-leucinol (1.55 g, 13.2 mmol) and Et_3N (1.84 ml, 13.2 mmol) in CH_2Cl_2 (20 ml). The resulting mixture was stirred at room temperature (r.t.) for 3 h and then

treated with water, and extracted with CH_2Cl_2. The combined organic phases were dried ($MgSO_4$), and the solvent was removed under reduced pressure. The resulting mixture of crude diastereomeric amides (S,R_p)-**2** and (S,S_p)-**2** was dissolved in MeCN (250 ml). After the addition of triphenylphosphine (5.5 g, 21 mmol), Et_3N (2.9 ml, 21 mmol) and tetrachloromethane (2.0 ml, 21 mmol), the mixture was stirred at r.t. overnight. Then, water was added and the mixture was extracted with CH_2Cl_2. The combined organic phases were dried ($MgSO_4$), and the solvents were removed under reduced pressure. Column chromatography (silica gel, C_5H_{12}–EtOAc 19:1) afforded the two diastereomers (S,R_p)-**3** ($R_f = 0.22$) as an oil and (S,S_p)-**3** ($R_f = 0.17$) as a colorless solid in an overall yield of 83%.

4.3. (*S,R_p*)-(4-tert-Butyl-2-oxazolinyl)-[2.2]paracyclophanes [(*S,R_p*)-**3**]

$[\alpha]_D^{20} = -128$ ($c = 1$, CH_2Cl_2); IR ($\tilde{\nu}$, cm^{-1}): 1643 (C=N); ^{1}H-NMR (δ, ppm): 7.17 (d, 1H, $J = 2.0$ Hz, H5), 6.64–6.34 (m, 6H, H_{Ar}), 4.33 (dd, 1H, $J = 9.4$, 7.7 Hz, CH_2O), 4.20–4.02 (m, 3H, CH_2O, CHN, CH_2), 3.22–2.96 (m, 6H, CH_2), 2.85 (ddd, 1H, $J = 7.4$, 9.3, 12.7 Hz, CH_2), 1.03 (s, 9H, C(CH_3)$_3$); ^{13}C{^{1}H}-NMR (δ, ppm): 163.6 (NCO), 141.0 (qC_{Ar}), 140.2 (qC_{Ar}), 139.7 (qC_{Ar}), 139.5 (qC_{Ar}), 135.9 (C_{Ar}), 134.9 (C_{Ar}), 134.5 (C_{Ar}), 133.1 (C_{Ar}), 133.0 (C_{Ar}), 132.6 (C_{Ar}), 131.4 (C_{Ar}), 128.6 (qC_{Ar}), 76.9 (CHN), 68.3 (CH$_2$O), 36.2 (CH$_2$), 35.7 (CH$_2$), 35.4 (CH$_2$), 35.2 (CH$_2$), 34.4 (C(CH$_3$)$_3$), 26.5 (C(CH$_3$)$_3$); *m/z* (%): 333.3 ([M$^+$], 59%), 229.2 ($C_{15}H_{19}NO$, 100); HRMS: Calc. for $C_{23}H_{27}NO$: 333.2093. Found: 333.2092.

4.4. (*S,S_p*)-4-(4-tert-Butyl-2-oxazolinyl)-[2.2]paracyclophanes [(*S,S_p*)-**3**]

M.p. 87 °C; $[\alpha]_D = +56.5$ ($c = 1$, CH_2Cl_2); IR ($\tilde{\nu}$, cm^{-1}): 1641 (C=N); ^{1}H-NMR (δ, ppm): 7.04 (d, 1H, $J = 1.9$ Hz, H5), 6.58–6.45 (m, 6H, H_{Ar}), 4.35 (ddd, 1H, $J = 3.3$, 9.0, 12.5 Hz, CH_2), 4.29 (dd, 1H, $J = 10.2$, 8.5 Hz, CH_2O), 4.21 (dd, 1H, $J = 8.5$, 8.0 Hz, CH_2O), 4.07 (dd, 1H, $J = 8.0$, 10.2 Hz, CHN), 3.20–3.07 (m, 4H, CH_2), 3.04–2.96 (m, 2H, CH_2), 2.89 (ddd, 1H, $J = 6.9$, 9.6, 12.7 Hz, CH_2), 1.07 (s, 9H, C(CH_3)$_3$); ^{13}C{^{1}H}-NMR (δ, ppm): 163.3 (NCO), 141.3 (qC_{Ar}), 140.2 (qC_{Ar}), 139.7 (qC_{Ar}), 139.6 (qC_{Ar}), 136.2 (C_{Ar}), 135.1 (C_{Ar}), 134.3 (C_{Ar}), 133.1 (C_{Ar}), 133.0 (C_{Ar}), 132.8 (C_{Ar}), 131.8 (C_{Ar}), 128.6 (qC_{Ar}), 77.1 (CHN), 67.9 (CH$_2$O), 35.9 (CH$_2$), 35.8 (CH$_2$), 35.5 (CH$_2$), 35.2 (CH$_2$), 34.7 (C(CH$_3$)$_3$), 27.7 (C(CH$_3$)$_3$); *m/z* (%): 333.3 ([M$^+$], 44%), 229.2 ($C_{15}H_{19}NO$, 100); HRMS: Calc. for $C_{23}H_{27}NO$: 333.2093. Found: 333.2098.

For characterization of the diastereomeric amides (S,R_p)-**2** and (S,S_p)-**2** an aliquot was taken from the reaction mixture, and the product was purified by column chromatography (silica gel; C_5H_{12}–EtOAc 1:1).

4.5. 4-(*S,R_p*/*S_p*)-N-2-(1-Hydroxy-3-dimethylbutyl)carboxyamide-[2.2]paracyclophane [(*S,R_p*/*S_p*)-**2**]

M.p. 159–162 °C; IR ($\tilde{\nu}$, cm^{-1}): 3449 (O–H), 3294 (O–H), 1638 (C=O), 1564 (N–H), 1545 (N–H); ^{1}H-NMR (δ, ppm): 6.81–6.36 (m, 14H, H_{Ar}), 5.85–5.81 (m, 2H, NH), 4.04–3.87 (m, 4H, CH_2O, CHN), 3.75–3.56 (m, 4H, CH_2O, CH_2), 3.30–2.82 (m, 14H, CH_2), 1.03 (s, 9H, C(CH_3)$_3$), 1.02 (s, 9H, C(CH_3)$_3$); ^{13}C{^{1}H}-NMR (δ, ppm): 170.7 (NCO), 170.5 (NCO), 140.5 (qC_{Ar}), 140.4 (qC_{Ar}), 140.0 (qC_{Ar}), 139.9 (qC_{Ar}), 139.6 (qC_{Ar}), 139.5 (qC_{Ar}), 139.4 (qC_{Ar}), 139.0 (qC_{Ar}), 136.3 (C_{Ar}), 136.2 (C_{Ar}), 135.7 (qC_{Ar}), 135.4 (C_{Ar}), 135.3 (C_{Ar}), 133.2 (qC_{Ar}), 132.9 (C_{Ar}), 132.9 (C_{Ar}), 132.8 (C_{Ar}), 132.7 (C_{Ar}), 132.7 (C_{Ar}), 132.6 (C_{Ar}), 132.1 (C_{Ar}), 132.0 (C_{Ar}), 132.0 (C_{Ar}), 131.8 (C_{Ar}), 63.6 (CH$_2$O), 63.4 (CH$_2$O), 60.1 (CHN), 59.9 (CHN), 36.0 (CH$_2$), 35.8 (CH$_2$), 35.7 (CH$_2$), 35.6 (CH$_2$), 35.6 (CH$_2$), 35.5 (CH$_2$), 35.3 (CH$_2$), 35.1 (CH$_2$), 34.4 (C(CH$_3$)$_3$), 34.3 (C(CH$_3$)$_3$), 27.6 (C(CH$_3$)$_3$), 27.5 (C(CH$_3$)$_3$); *m/z* (%): 351 ([M$^+$], 17%), 294 ([M$^+ - t$Bu], 79), 252 (PC–CONH$_2$, 100), 247 (C_8H_7*tert*-Leu, 74); HRMS: Calc. for $C_{23}H_{29}NO_2$: 351.2198. Found: 351.2194.

4.6. Reaction of (*S,R_p*)-(4-tert-butyl-2-oxazolinyl)-[2.2]paracyclophanes [(*S,R_p*)-**3**] with tert-butyllithium

To a solution of (S,R_p)-**3** (138 mg, 0.4 mmol) in Et_2O (5 ml) *tert*-butyllithium (0.36 ml of a 1.6 N solution, 0.53 mmol) at 0 °C was added. A spontaneous color change to violet occurred. The reaction was stopped after 45 min by the addition of a drop of water. After drying of the reaction mixture ($MgSO_4$) followed by evaporation of the solvent under reduced pressure, a product mixture was obtained. The crude ^{1}H-NMR spectrum showed three compounds in a ratio of 2.8:1:2.4. After column chromatography (silica gel, C_5H_{12}–EtOAc 29:1) the three fractions could be isolated: (S,R_p)-**4** (40%), (S,S_p)-**5** (13%), and remaining starting material (28%). Upon standing in solution (S,R_p)-**4** (40%) slowly decomposes by undergoing retro-Michael reaction.

4.7. (*S,R_p*)-4-(2,4-Di-tert-butyl-2-oxazolidinyl)-[2.2]paracyclophanes [(*S,R_p*)-**4**]

^{1}H-NMR (δ, ppm): 6.82 (br s, 1H, H5), 6.68 (m, 2H, H_{Ar}), 6.50 (d, 1H, $J = 8.2$ Hz, H8), 6.27 (m, 2H, H_{Ar}), 6.23 (dd, 1H, $J = 0.8$, 8.0 Hz, H7), 4.40 (ddd, 1H, $J =$ 2.4, 9.6, 12.6 Hz, CH_2), 4.02 (t (br), 1H, $J = 6.3$ Hz, CH_2O), 3.52 (s (br), 1H, CHN), 3.48 (dd, 1H, $J = 6.6$, 9.1 Hz, CH_2O), 3.22–3.11 (m, 3H, CH_2); 2.99–2.82 (m,

4H, CH_2), 2.20 (s (br), 1H, NH), 1.12 (s, 9H, NCOC(CH_3)$_3$), 0.64 (s, 3H, NCHC(CH_3)$_3$), 0.63 (s, 6H, NCHC(CH_3)$_3$); ^{13}C{^{1}H}-NMR (δ, ppm): 140.3 (qC_{Ar}), 139.7 (qC_{Ar}), 138.5 (qC_{Ar}), 137.1 (qC_{Ar}), 137.0 (qC_{Ar}), 136.1 (C_{Ar}), 132.8 (C_{Ar}), 132.4 (C_{Ar}), 132.2 (C_{Ar}), 132.1 (C8), 132.1 (C7), 131.1 (C5), 104.2 (NCO), 68.2 (CHN), 66.8 (CH$_2$O), 41.2 (C(CH$_3$)$_3$), 36.2 (CH$_2$), 35.8 (C(CH$_3$)$_3$), 35.7 (CH$_2$), 35.6 (CH$_2$), 35.5 (CH$_2$), 27.2 (C(CH$_3$)$_3$), 26.6 (CH$_3$), 26.2 (C(CH$_3$)$_2$); *m/z* (%): 391 ([M$^+$], 2%), 334 ([M$^+$ − *t*Bu], 100), 287 ([M$^+$ − C$_8$H$_8$], 6), 230 ([M$^+$ − C$_8$H$_8$ − *t*Bu], 40).

4.8. (*S*,*S*$_p$)-4-(4-tert-Butyl-2-oxazolinyl)-5-tert-butyl-5,8-dihydro-[2.2]paracyclophanes [(*S*,*S*$_p$)-**5**]

^{1}H-NMR (δ, ppm): 6.97 (dd, 1H, $J = 1.9$, 7.7 Hz, H_{Ar}), 6.89 (dd, 1H, $J = 1.9$, 8.0 Hz, H_{Ar}), 6.81 (dd, 1H, $J = 1.8$, 7.8 Hz, H_{Ar}), 6.71 (dd, 1H, $J = 1.8$, 7.7 Hz, H_{Ar}), 4.91 (d, 1H, $J = 6.9$ Hz, H7), 4.27 (dd, 1H, $J = 7.7$, 9.3 Hz, CH_2O), 3.98 (dd, 1H, $J = 9.3$, 11.0 Hz, CH_2O), 3.91 (dd, 1H, $J = 7.7$, 11.0 Hz, CHN), 3.62 (ddd, 1H, $J = 6.6$, 10.2, 13.2 Hz, CH_2), 3.00–2.90 (m, 3H, CH_2), 2.81 (ddd, 1H, $J = 6.6$, 9.4, 13.2 Hz, CH_2), 2.62 (dd, 1H, $J = 1.6$, 2.7 Hz, H5), 2.45–2.38 (m, 2H, CH_2), 2.30 (d (br), 1H, $J = 19.7$ Hz, H8), 2.17 (ddd, 1H, $J = 2.2$, 9.3, 12.1 Hz, CH_2), 1.98 (dd, 1H, $J = 6.6$, 19.7 Hz, H8), 0.98 (s, 9H, C(CH_3)$_3$), 0.72 (s, 9H, C(CH_3)$_3$); ^{13}C{^{1}H}-NMR (δ, ppm): 165.4 (NCO), 145.5 (C3), 139.2 (qC_{Ar}), 137.6 (qC_{Ar}), 137.1 (qC_{Ar}), 131.9 (C_{Ar}), 130.6 (C_{Ar}), 129.5 (C_{Ar}), 129.2 (C_{Ar}), 128.6 (C7), 76.5 (CHN), 66.8 (CH$_2$O), 53.9 (C5), 39.9 (C(CH$_3$)$_3$), 37.8 (CH$_2$), 34.9 (CH$_2$), 34.1 (CH$_2$), 33.5 (C(CH$_3$)$_3$), 33.0 (CH$_2$), 32.9 (CH$_2$), 28.1 (C(CH$_3$)$_3$), 26.5 (C(CH$_3$)$_3$); *m/z* (%): 391 ([M$^+$], 6%), 334 ([M$^+$ − *t*Bu], 72), 229 (C$_8$H$_8$–Oxa, 100), 104 (C$_8$H$_8$, 17).

4.9. (*S*,*S*$_p$)-Chloro{4-(4-tert-butyl-2-oxazolinyl)-[2.2]paracyclophane,5-*C*,3-*N*}(triphenylphosphine)palladium(II) [(*S*,*S*$_p$)-**7**]

A solution of (*S*,*R*$_p$)-**3** (1.08 g, 3.24 mmol) and palladium(II) acetate (0.8 g, 3.57 mmol) in glacial AcOH (15 ml) was heated to 110 °C for 1 h. After evaporation of the solvent under reduced pressure, the residue was dissolved in C$_3$H$_6$O (25 ml) and LiCl (275 mg, 6.48 mmol) was added. The mixture was stirred overnight and the excess of LiCl was extracted with water and CH$_2$Cl$_2$. The combined yellow organic layers were then dried (MgSO$_4$), the volume reduced to ca. 50 ml, the solution degassed, and triphenylphosphine (0.85 g, 3.24 mmol) was added. After stirring for 5 h at r.t. the solution was concentrated and addition of C$_7$H$_{16}$ afforded yellow crystals, which were isolated by filtration and dried in vacuo (2.14 g, 90%). M.p. 178–180 °C; $[\alpha]_D = +40.2$ ($c = 1$, CH$_2$Cl$_2$); IR ($\tilde{\nu}$, cm^{-1}): 1591; ^{1}H-NMR (δ, ppm): 7.65–7.58 (m, 6H, *ortho*-H of PPh$_3$), 7.36–7.31 (m, 3H, *para*-H of PPh$_3$), 7.27–7.22 (m, 6H, *meta*-H of PPh$_3$), 6.56–6.52 (m, 3H, H_{Ar}), 6.42 (dd, 1H, $J = 1.4$, 8.2 Hz, H_{Ar}), 5.92 (d, 1H, $J = 7.2$ Hz, H8), 5.54 (d (br), 1H, H7), 4.82 (ddd, 1H, $J = 1.0$, 3.6, 8.5 Hz, CH_2O), 4.63 (dd, 1H, $J = 8.5$, 9.8 Hz, CH_2O), 4.57 (dd, 1H, $J = 3.6$, 9.8 Hz, CHN), 3.65 (ddd, 1H, $J =$ 3.8, 10.1, 13.4 Hz, CH_2), 3.06–2.96 (m, 2H, CH_2), 2.90 (ddd, $J = 3.8$, 10.2, 14.3 Hz, CH_2), 2.81 (ddd, 1H, $J =$ 3.8, 10.2, 13.2 Hz, CH_2), 2.75–2.65 (m, 2H, CH_2), 1.80 (ddd, 1H, $J = 5.8$, 11.3, 14.9 Hz, CH_2), 1.22 (s, 9H, C(CH_3)$_3$); ^{13}C{^{1}H}-NMR (δ, ppm): 176.5 (d, $J_{PC} = 2.3$ Hz, NCO), 163.1 (d, $J_{PC} = 7.6$ Hz, qC_{Ar}), 146.7 (d, $J_{PC} = 6.1$ Hz, qC_{Ar}), 140.0 (qC_{Ar}), 139.2 (qC_{Ar}), 137.8 (qC_{Ar}), 135.6 (d, 6C, $J_{PC} = 10.3$ Hz, *ortho*-C of PPh$_3$), 135.2 (d, $J_{PC} = 2.3$ Hz, C7), 133.5 (qC_{Ar}), 132.8 (C_{Ar}), 132.6 (C_{Ar}), 132.5 (C_{Ar}), 132.3 (d, 3C, $J_{PC} = 29.6$ Hz, *ipso*-C of PPh$_3$), 131.5 (C_{Ar}), 131.4 (C_{Ar}), 130.3 (d, 3C, $J_{PC} = 2.3$ Hz, *para*-C of PPh$_3$), 127.8 (d, 6C, $J_{PC} = 10.7$ Hz, *meta*-C of PPh$_3$), 73.2 (CH$_2$O), 69.9 (d, $J_{PC} = 3.1$ Hz, CHN), 40.4 (d, $J_{PC} = 6.1$ Hz, CH$_2$), 36.2 (CH$_2$), 35.8 (CH$_2$), 35.6 (C(CH$_3$)$_3$), 32.6 (CH$_2$), 27.3 (C(CH$_3$)$_3$); ^{31}P{^{1}H}-NMR (δ, ppm): 33.49; Anal. Calc. for C$_{41}$H$_{41}$ClNOPPd·CH$_2$Cl$_2$: C, 61.40; H, 5.28; N, 1.70. Found: C, 61.30; H, 5.40; N, 1.64%; *m/z* (FAB, %): 735 ([M$^+$], 18%), 700 ([M$^+$ − Cl], 93), 438 ([M$^+$ − (PPh$_3$ + Cl)], 6), 332 (**3**-H, 9), 262 (PPh$_3$, 100).

4.10. Crystal structure analysis of (*S*,*S*$_p$)-**7**

Suitable crystals of (*S*,*S*$_p$)-**7** have been obtained from a mixture of C$_7$H$_{16}$ and CHCl$_3$ (ca. 2:1) at ca. 293 K. The compound crystallizes in monoclinic space group $P2_1(4)$ with one slightly disordered molecule of CHCl$_3$ in the asymmetric unit (C$_{41}$H$_{41}$ClNOPPd·CHCl$_3$). The cell parameters are $a = 11.531(5)$, $b = 13.9050(17)$, $c =$ 12.321(2) Å, and $\beta = 94.44(3)°$. At a cell volume of $V =$ 1969.6(9) Å^3, $Z = 2$, and $M_r = 856.01$, we obtain a calculated density of $\rho_{calc} = 1.443$. A total number of 6308 reflections ($0 \le h \le 16$, $0 \le k \le 19$, $-17 \le l \le 17$, $\Theta_{max} = 30.5°$) have been collected (ω–2Θ) at r.t. on an Enraf–Nonius CAD diffractometer employing graphite-monochromated Mo-K$_\alpha$ radiation ($\lambda = 0.71073$ Å). Data have been corrected for Lp but not for absorption effects ($\mu = 0.817$ mm^{-1}). The structure has been solved by direct methods as implemented in the Xtal3.7 set of crystallographic routines [19], employing GENSIN [20] for the generation of structure invariant relationships and GENTAN [21] for the general tangent phasing procedure. Four thousand two hundred and sixty-nine observed reflections ($I > 2\sigma(I)$) have been included in the final full-matrix least-squares refinement on F involving 451 parameters and converging at $r(r_w) =$ 0.069 (0.102, $w = \sigma^{-2}$) a residual electron density of −2.68/1.72 e Å^{-3}, and a goodness-of-fit of $S = 1.925$. Most hydrogen atoms could not be located in a difference Fourier map and have been calculated in

idealized positions. Their equivalent displacement parameters have been fixed at $1.5U$ of the relevant heavy atom. All hydrogen parameters have been kept constant in the refinement process.

4.11. (S,S_p)-Chloro{4-(4-tert-butyl-2-oxazolinyl)-[2.2]paracyclophane,2-C,3-N}(triphenylphosphine)palladium(II) [(S,S_p)-**9**]

A solution of (S,S_p)-**3** (0.8 g, 2.4 mmol) and palladium(II) acetate (0.59 g, 2.6 mmol) in glacial AcOH (120 ml) was heated to 118 °C for 1.5 h. After evaporation of the solvent under reduced pressure, the residue was dissolved in acetone (15 ml) and LiCl (0.3 g, 7.2 mmol) was added. The mixture was stirred overnight and the excess of LiCl was extracted with water and CH_2Cl_2. The combined yellow organic layers were dried ($MgSO_4$), the volume was reduced to ca. 40 ml, and the mixture was degassed. Then, triphenylphosphine (0.63 g, 2.4 mmol) was added, and the mixture was stirred for 5 h. The solvent was evaporated under reduced pressure, and the residue was purified by column chromatography (silica gel, EtOAc–DCM 1:1) to give 1.44 g (82%) of (S,S_p)-**9** as yellow solid, which was dried in vacuo (1.44 g, 82%). M.p. 151–155 °C; $[\alpha]_D = +667$ ($c = 1$, CH_2Cl_2); IR ($\bar{\nu}$, cm^{-1}): 1618; ^{1}H-NMR (δ, ppm): 7.87 (m, 6H, *ortho*-H of PPh_3), 7.50–7.40 (m, 9H, *para*–*meta*-H of PPh_3), 6.73 (d, 1H, $J = 1.6$ Hz, H5), 6.56 (dd, 1H, $J = 2.0$, 8.0 Hz, H_{Ar}), 6.43 (dd, 1H, $J = 1.9$, 8.0 Hz, H_{Ar}), 6.38 (dd, 1H, $J = 1.9$, 8.0 Hz, H_{Ar}), 6.27 (dd, 1H, $J = 1.9$, 8.0 Hz, H_{Ar}), 5.90 (d, 1H, $J = 8.0$ Hz, H8), 5.85 (dd, 1H, $J = 1.9$, 8.0 Hz, H_{Ar}), 5.29 (dd, 1H, $J =$ 4.1, 9.9 Hz, C*H*N), 4.60 (dd, 1H, $J = 4.1$, 9.1 Hz, CH_2O), 4.44 (dd, 1H, $J = 9.1$, 9.9 Hz, CH_2O), 3.42 (ddd, 1H, $J = 6.0$, 8.5, 13.8 Hz, CH_2), 3.20–3.04 (m, 2H, CH_2), 2.84–2.70 (m, 2H, CH_2), 2.66 (dd, 1H, $J = 8.8$, 13.2 Hz, CH_2), 2.40 (dt, 1H, $J = 8.8$, 13.2 Hz, C*H*), 1.42 (s, 9H, C(CH_3)$_3$); ^{13}C{^{1}H}-NMR (δ, ppm): 165.2 (d, $J_{PC} = 2.9$ Hz, N*C*O), 151.7 (d, $J_{PC} = 3.1$ Hz, qC_{Ar}), 140.7 (d, $J_{PC} = 2.3$ Hz, qC_{Ar}), 139.6 (qC_{Ar}), 139.0 (qC_{Ar}), 135.3 (C_{Ar}), 135.0 (d, 6C, $J_{PC} = 11.5$ Hz, *ortho*-C of PPh_3), 134.2 (C_{Ar}), 134.0 (C_{Ar}), 132.4 (d, $J_{PC} = 3.0$ Hz, C_{Ar}), 132.2 (C_{Ar}), 131.6 (d, 3C, $J_{PC} = 48.8$ Hz, *ipso*-C of PPh_3), 131.4 (C_{Ar}), 131.3 (C_{Ar}), 130.6 (d, 3C, $J_{PC} = 2.3$ Hz, *para*-C of PPh_3), 128.4 (d, 6C, $J_{PC} =$ 10.7 Hz, *meta*-C of PPh_3), 125.5 (qC_{Ar}), 71.6 (*C*H_2O), 71.2 (*C*HN), 48.0 (d, $J_{PC} = 2.3$ Hz, *C*H), 41.6 (*C*H_2), 35.9 (*C*(CH_3)$_3$), 35.7 (*C*H_2), 35.3 (*C*H_2), 27.6 (C(*C*H_3)$_3$); ^{31}P{^{1}H}NMR (δ, ppm): 38.04; *m/z* (FAB, %): 735 ([M^+], 12%), 700 ([$M^+ -$Cl], 100), 438 ([$M^+ -$(PPh$_3$+Cl)], 11), 332 (**3**-H, 17); Anal. Calc. for $C_{41}H_{41}ClNOPPd \cdot 0.5CH_2Cl_2$: C, 63.97; H, 1.80; N, 5.44. Found: C, 63.61; H, 1.71; N, 5.60%.

4.12. (S,R_p)-Chloro{4-(4-tert-butyl-2-oxazolinyl)-[2.2]paracyclophane,5-C,3-N}(triphenylphosphine)palladium(II) [(S,R_p)-**7**]

A solution of (S,S_p)-**3** (0.15 g, 0.45 mmol) and palladium(II) acetate (0.121 g, 0.54 mmol) in $C_6H_5CH_3$ (2 ml) was heated to 80 °C for 4 h. After evaporation of the solvent under reduced pressure, the residue was dissolved in acetone and LiCl (0.04 g, 0.9 mmol) was added. The mixture was stirred overnight and the excess of LiCl was extracted with water and CH_2Cl_2. The combined yellow organic layers were dried ($MgSO_4$), the volume was reduced to ca. 15 ml, and the solution was degassed. Then triphenylphosphine (0.12 g, 0.45 mmol) was added and the mixture stirred for 5 h. The solvent was evaporated under reduced pressure, and the residue was purified by column chromatography (silica gel, C_5H_{12}–EtOAc 2:1) to give 0.26 g (83% conversion, 94% yield based on recovered starting material) of (S,R_p)-**7**. M.p. 172–174 °C; $[\alpha]_D = +270$ ($c = 1$, CH_2Cl_2); IR ($\bar{\nu}$, cm^{-1}): 1606; ^{1}H-NMR (δ, ppm): 7.72 (m, 6H, *ortho*-H of PPh_3), 7.38 (m, 3H, *para*-H of PPh_3), 7.29 (m, 6H, *meta*-H of PPh_3), 6.98 (dd, 1H, $J =$ 1.9, 7.9 Hz, H_{Ar}), 6.48 (dd, 1H, $J = 1.9$, 7.9 Hz, H_{Ar}), 6.37–6.33 (m, 2H, H_{Ar}), 6.03 (d, 1H, $J = 7.7$ Hz, H8), 5.80 (dd, 1H, $J = 1.4$, 7.7 Hz, H7), 4.80 (dd, 1H, $J = 1.4$, 9.0 Hz, CH_2O), 4.66 (t, 1H, $J = 9.0$, 9.0 Hz, CH_2O), 4.43 (d (br), 1H, $J = 9.0$ Hz, C*H*N), 3.80 (ddd, 1H, $J = 1.6$, 10.6, 13.2 Hz, CH_2), 3.12–2.98 (m, 2H, CH_2), 2.91 (ddd, 1H, $J = 6.6$, 10.2, 13.6 Hz, CH_2), 2.80–2.54 (m, 3H, CH_2), 1.97 (ddd, 1H, $J = 4.1$, 10.2, 13.8 Hz, CH_2), 0.92 (s, 9H, C(CH_3)$_3$); ^{13}C{^{1}H}-NMR (δ, ppm): 175.8 (d, $J_{PC} = 3.4$ Hz, N*C*O), 159.2 (d, $J_{PC} = 6.8$ Hz, qC_{Ar}), 146.7 (d, $J_{PC} = 6.8$ Hz, qC_{Ar}), 140.0 (qC_{Ar}), 139.8 (qC_{Ar}), 139.2 (qC_{Ar}), 135.9 (d, $J_{PC} = 2.3$ Hz, C7), 135.4 (d, 6C, $J_{PC} = 10.7$ Hz, *ortho*-C of PPh_3), 132.9 (C8), 132.8 (C_{Ar}), 132.5 (C_{Ar}), 132.5 (qC_{Ar}), 132.2 (C_{Ar}), 131.5 (d, 3C, $J_{PC} = 46.6$ Hz, *ipso*-C of PPh_3), 130.5 (d, 3C, $J_{PC} = 2.3$ Hz, *para*-C of PPh_3), 129.9 (C_{Ar}), 128.0 (d, 6C, $J_{PC} = 10.7$ Hz, *meta*-C of PPh_3), 72.9 (d, $J_{PC} = 3.0$ Hz, *C*H_2O), 69.1 (d, $J_{PC} = 3.1$ Hz, *C*HN), 42.0 (d, $J_{PC} = 10.7$ Hz, *C*H_2), 36.0 (*C*H_2), 35.8 (*C*(CH_3)$_3$), 35.5 (*C*H_2), 34.0 (*C*H_2), 27.0 (C(*C*H_3)$_3$); ^{31}P{^{1}H}NMR (δ, ppm): 31.51; *m/z* (FAB, %): 735 ([M^+], 14%), 700 ([$M^+ -$Cl], 100), 438 ([$M^+ -$(PPh$_3$+Cl)], 5), 332 (**3**-H, 9); Anal. Calc. for $C_{41}H_{41}ClNOPPd \cdot CH_2Cl_2$: C, 61.40; H, 5.28; N, 1.70. Found: C, 61.04; H, 5.25; N, 1.59%.

4.13. Crystal structure analysis of (S,R_p)-7

Suitable crystals of (S,R_p)-**7** have been obtained from a mixture of C_5H_{12} and CH_2Cl_2 (1:1) at ca. 293 K. The compound ($C_{41}H_{41}ClNOPPd$) crystallizes in orthorhombic space group $P2_12_12_1$ (19) with the cell parameters $a = 12.0410(3)$, $b = 13.8171(3)$, $c = 24.4674(6)$ Å. At a cell volume of $V = 4070.68(17)$ Å^3, $Z = 4$, and

$M_r = 736.64$, we obtain a calculated density of $\rho_{calc} = 1.202$. A total number of 90 082 reflections ($-18 \le h \le 18$, $-21 \le k \le 21$, $-37 \le l \le 37$, $\Theta_{max} = 33.2°$) have been collected (ω scans) at r.t. on a Bruker SMART diffractometer employing graphite-monochromated Mo-K_α radiation ($\lambda = 0.71073$ Å). Data have been corrected for absorption effects ($\mu = 0.59$ mm^{-1}, $t_{min} = 0.8126$, $t_{max} = 0.8867$) employing a Gaussian correction followed by SADABS [22]. The structure has been solved by direct methods as implemented in the Xtal3.7 [19] set of crystallographic routines, employing GENSIN [20] for the generation of structure invariant relationships and GENTAN [20] for the general tangent phasing procedure. Eleven thousand one hundred and forty-one observed reflections ($I > 4\sigma(I)$) have been included in the final full-matrix least-squares refinement on F involving 415 parameters and converging at $r(r_w) = 0.071$ (0.095, $w = (\sigma^2(F) + 0.0004F^2))^{-1}$ a residual electron density of $-1.10/+2.96$ e Å^{-3}, and a goodness-of-fit of $S = 2.427$. The major part of the hydrogen atoms could not be located in a difference Fourier map and have been calculated in idealized positions. Their equivalent displacement parameters have been fixed at $1.5U$ of the relevant heavy atom, and all hydrogen parameters have been kept constant in the refinement process.

4.14. 4-(4-tert-Butyl-2-oxazolinyl)-5-diphenylphosphinyl-[2.2]-paracyclophane [(*S*,*S*$_p$)-**11** and (*S*,*R*$_p$)-**11**]

The palladacycle (*S*,*S*$_p$)-**7** [or (*S*,*R*$_p$)-**7**] was dissolved in dried $C_6H_5CH_3$ and three equivalents of potassium diphenylphosphide were added. The reaction mixture was stirred at r.t. for 2 h, and after cooling to 0 °C 12 equivalents of boran dimethylsulfide complex were added dropwise. The mixture was stirred overnight at r.t. and the resulting product was purified by column chromatography (silica gel, C_5H_{12}–EtOAc 24:1). After the addition of 10 equivalents of Et_2NH to the product the mixture was heated to 50 °C for 5 h. All volatiles were removed under reduced pressure, and another 10 equivalents of Et_2NH were added. The reaction mixture was heated to 40 °C overnight, and then all volatiles were removed. The residue was filtered through a pad of silica gel affording phosphines (*S*,*S*$_p$)-**11** and (*S*,*R*$_p$)-**11** in 67 and 61% yield, respectively.

4.15. (*S*,*S*$_p$)-4-(4-tert-Butyl-2-oxazolinyl)-5-diphenylphosphinyl-[2.2]paracyclophane [(*S*,*S*$_p$)-**11**]

From 200 mg of (*S*,*S*$_p$)-**7** (0.27 mmol) in 10 ml of $C_6H_5CH_3$; yield: 95 mg (67%); m.p. 121 °C (dec.); $[\alpha]_D = +158$ ($c = 1$, CH_2Cl_2); IR ($\tilde{\nu}$, cm^{-1}): 1655; ^{1}H-NMR (δ, ppm): 7.67–7.63 (m, 2H, *ortho*-H of PPh_2), 7.42–7.38 (m, 2H, *ortho*-H of PPh_2), 7.23–7.21 (m, 3H, *meta*–*para*-H of PPh_2), 7.17–7.15 (m, 3H, *meta*–*para*-H of PPh_2), 6.93 (dd, 1H, $J = 1.6$, 8.0 Hz, H_{Ar}), 6.75 (dd, 1H, $J = 1.4$, 8.0 Hz, H_{Ar}), 6.64–6.58 (m, 2H, H_{Ar}), 6.41 (dd, 1H, $J = 3.6$, 8.2 Hz, H7), 6.46 (d, 1H, $J = 7.8$ Hz, H8), 3.76–3.66 (m, 1H, CH_2O), 3.31–3.20 (m, 2H, CH_2O, C*H*N), 3.12–2.71 (m, 7H, CH_2), 2.51 (ddd, 1H, $J = 4.4$, 9.6, 13.7 Hz, CH_2), 0.97 (s, 9H, C(CH_3)$_3$); ^{13}C{^{1}H}-NMR (δ, ppm): 163.4 (N*C*O), 145.9 (d, $J_{PC} = 8.4$ Hz, qC_{Ar}), 142.1 (d, $J_{PC} = 13.0$ Hz, qC_{Ar}), 140.1 (d, $J_{PC} = 9.2$ Hz, qC_{Ar}), 139.8 (qC_{Ar}), 139.0 (qC_{Ar}), 138.9 (qC_{Ar}), 137.9 (d, $J_{PC} = 22.1$ Hz, qC_{Ar}), 135.9 (C_{Ar}), 134.9 (C_{Ar}), 133.7 (d, 2C, $J_{PC} = 22.1$ Hz, *ortho*-C of PPh_2), 133.1 (d, 2C, $J_{PC} = 22.1$ Hz, *ortho*-C of PPh_2), 132.1 (C_{Ar}), 131.8 (2C, C_{Ar}), 131.6 (d, $J_{PC} = 2.2$ Hz, C_{Ar}), 128.7 (d, $J_{PC} = 1.0$ Hz, *para*-C of PPh_2), 128.6 (d, 2C, $J_{PC} = 8.4$ Hz, *meta*-C of PPh_2), 128.2 (d, 2C, $J_{PC} = 8.4$ Hz, *meta*-C of PPh_2), 128.1 (d, $J_{PC} = 1.0$ Hz, *para*-C of PPh_2), 76.7 (*C*HN), 67.7 (*C*H$_2$O), 36.7 (d, $J_{PC} = 6.1$ Hz, *C*H$_2$), 35.2 (*C*H$_2$), 34.9 (*C*H$_2$), 33.7 (*C*H$_2$), 33.7 (*C*(CH$_3$)$_3$), 26.9 (C(*C*H$_3$)$_3$); ^{31}P{^{1}H}-NMR (δ, ppm): 1.87; *m*/*z* (%): 517 ([M$^+$]); HRMS: Calc. for $C_{31}H_{27}NOP$ ($C_{35}H_{36}NOP$–C_4H_9): 460.1830. Found: 460.1829.

4.16. (*S*,*R*$_p$)-4-(4-tert-Butyl-2-oxazolinyl)-5-diphenylphosphinyl[2.2]-paracyclophane [(*S*,*R*$_p$)-**11**]

From 264 mg (0.36 mmol) of (*S*,*R*$_p$)-**7** in 10 ml of $C_6H_5CH_3$; yield: 113 mg (61%); m.p. 212 °C (dec.); $[\alpha]_D = +84$ ($c = 0.1$, CH_2Cl_2); IR ($\tilde{\nu}$, cm^{-1}): 1649; ^{1}H-NMR (δ, ppm): 7.59–7.54 (m, 2H, *ortho*-H of PPh_2), 7.47–7.42 (m, 2H, *ortho*-H of PPh_2), 7.22–7.16 (m, 6H, *meta*–*para*-H of PPh_2), 6.82 (dd, 1H, $J = 1.6$, 8.0 Hz, H_{Ar}), 6.67–6.54 (m, 4H, H_{Ar}), 6.39 (dd, 1H, $J = 4.1$, 7.7 Hz, H7), 3.90 (dd, 1H, $J = 8.5$, 9.2 Hz, CH_2O), 3.73–3.67 (m, 1H, CH_2), 3.63 (dd, 1H, $J = 8.5$, 10.7 Hz, CH_2O), 3.12–2.71 (m, 7H, C*H*N, CH_2), 2.47 (ddd, 1H, $J = 4.1$, 9.7, 14.1 Hz, CH_2), 0.89 (s, 9H, C(CH_3)$_3$); ^{13}C{^{1}H}-NMR (δ, ppm): 163.0 (N*C*O), 145.2 (d, $J_{PC} = 9.9$ Hz, qC_{Ar}), 142.5 (d, $J_{PC} = 11.5$ Hz, qC_{Ar}), 139.7 (qC_{Ar}), 139.2 (qC_{Ar}), 138.2 (d, $J_{PC} = 9.1$ Hz, qC_{Ar}), 137.1 (d, $J_{PC} = 23.6$ Hz, qC_{Ar}), 135.6 (d, $J_{PC} = 6.1$ Hz, C_{Ar}), 135.6 (C_{Ar}), 133.5 (d, 2C, $J_{PC} = 22.1$ Hz, *ortho*-C of PPh_2), 133.2 (d, 2C, $J_{PC} = 22.9$ Hz, *ortho*-C of PPh_2), 132.6 (C_{Ar}), 132.4 (C_{Ar}), 131.7 (C_{Ar}), 131.2 (d, $J_{PC} = 2.2$ Hz, C_{Ar}), 128.7 (*para*-C of PPh_2), 128.6 (d, 2C, $J_{PC} = 8.4$ Hz, *meta*-C of PPh_2), 128.5 (*para*-C of PPh_2), 128.1 (d, 2C, $J_{PC} = 9.2$ Hz, *meta*-*C* of PPh_2), 76.4 (*C*HN), 67.6 (*C*H$_2$O), 36.8 (d, $J_{PC} = 9.1$ Hz, *C*H$_2$), 35.2 (*C*H$_2$), 35.1 (*C*(CH$_3$)$_3$), 34.5 (*C*H$_2$), 34.1 (*C*H$_2$), 26.8 (C(*C*H$_3$)$_3$); ^{31}P{^{1}H}-NMR (δ, ppm): 2.92; *m*/*z* (%): 517 ([M$^+$]); HRMS: Calc. for $C_{35}H_{36}NOP$: 517.2534. Found: 517.2534.

4.17. (S,S_p)-4-(4-tert-Butyl-2-oxazolinyl)-5-bromo-[2.2]paracyclophane [(S,S_p)-**12**]

To a solution of (S,S_p)-**9** (152 mg, 0.21 mmol) in CH_2Cl_2 (5 ml) a suspension of bromine (23 μl, 0.45 mmol) and AcONa (56 mg, 0.41 mmol) in tetrachloromethane was added dropwise over 1 h. After stirring of the resulting mixture for 1 h at r.t., the reaction was quenched with a saturated aq. solution of sodium hydrogensulfite. The mixture was extracted with water, and the combined organic layers were dried ($MgSO_4$). The solvent was evaporated under reduced pressure, and the residue was purified by column chromatography (silica gel, C_5H_{12}–EtOAc (9:1) to give 61 mg (72%) of (S,S_p)-**12**.

M.p. 127 °C; $[\alpha]_D = +307$ ($c = 1.0$; CH_2Cl_2); IR ($\tilde{\nu}$, cm^{-1}): 2956, 2915, 1657 cm^{-1}; ^{1}H-NMR (δ, ppm): 7.10 (dd, 1H, $J = 1.9$, 8.2 Hz, H_{Ar}), 6.73 (d, 1H, $J = 1.7$ Hz, H5), 6.62 (dd, 1H, $J = 1.7$, 8.0 Hz, H7), 6.57 (d, 1H, $J =$ 7.9 Hz, H8), 6.51–6.44 (m, 3H, H_{Ar}), 5.13 (t, 1H, $J = 9.1$ Hz, H2), 4.42 (dd, 1H, $J = 8.2$, 9.9 Hz, CH_2O), 4.24 (dd, 1H, $J = 8.5$, 9.6 Hz, CH_2O), 4.10 (t, 1H, $J = 9.9$ Hz, CHN), 3.84 (dd, 1H, $J = 9.3$, 13.2 Hz, H1), 3.70 (dd, 1H, $J = 8.5$, 13.2 Hz, H1), 3.25–3.17 (m, 2H, CH_2), 2.95–2.83 (m, 2H, CH_2), 1.04 (s, 9H, C$(CH_3)_3$); ^{13}C{^{1}H}-NMR (δ, ppm): 163.0 (NCO), 142.3 (qC_{Ar}), 139.9 (qC_{Ar}), 138.2 (qC_{Ar}), 137.0 (qC_{Ar}), 136.1 (C5), 134.6 (C8), 133.7 (C_{Ar}), 133.3 (C7), 132.7 (C_{Ar}), 132.4 (C_{Ar}), 131.6 (C_{Ar}), 129.0 (qC_{Ar}), 76.8 (CHN), 68.9 (CH$_2$O), 51.5 (C2), 46.5 (C1), 35.3 (CH$_2$), 35.3 (CH$_2$), 34.2 ($C(CH_3)_3$), 26.7 (C(CH_3)$_3$); *m/z* (%): 413/411 ([M^+], 10%), 332 ([$M^+ - Br$], 45), 331 ([$M^+ - HBr$]); HRMS: Calc. for $C_{23}H_{26}BrNO$: 411.1197. Found: 411.1197.

5. Supplementary material

The crystallographic data of structures (S,S_p)-**7** and (S,R_p)-**7** have been deposited with the Cambridge Crystallographic Data Centre, CCDC nos. 184930–184931 for compounds (S,S_p)-**7** and (S,R_p)-**7**. Copies of this data may be obtained free of charge on application to The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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References

[1] (a) M. Stark, C.J. Richards, Tetrahedron Lett. 38 (1997) 5881;
(b) S.E. Denmark, R.A. Stavernger, A.M. Faucher, J.P. Edwards, J. Org. Chem. 62 (1997) 3375;
(c) Y. Donde, L.E. Overman, J. Am. Chem. Soc. 121 (1999) 2933;
(d) T.K. Hollis, L.E. Overman, J. Organomet. Chem. 576 (1999) 290;
(e) A.M. Stevens, C.J. Richards, Organometallics 18 (1999) 1346;
(f) M.A. Stark, G. Jones, C.J. Richards, Organometallics 19 (2000) 1282;
(g) M. Ohff, A. Ohff, D. Milstein, Chem. Commun. (1999) 357;
(h) K. Kiewel, Y. Liu, D.E. Bergbreiter, G.A. Sulikowski, Tetrahedron Lett. 40 (1999) 8945;
(i) K. Hallman, C. Moberg, Adv. Synth. Catal. 343 (2001) 260;
(j) L.E. Overman, T.P. Remarchuk, J. Am. Chem. Soc. 124 (2002) 12;
(k) See also references in: I.P. Smoliakova, K.J. Keuseman, D.C. Haagenson, D.M. Wellmann, P.B. Colligan, N.A. Kataeva, A.V. Churakov, L.G. Kuz'mina, V.V. Dunina, J. Organomet. Chem. 603 (2000) 86.

[2] Selected reviews on palladacycles in synthesis or catalysis: (a) J. Dupont, M. Pfeffer, J. Spencer, Eur. J. Inorg. Chem. (2001) 1917;
(b) W.A. Herrmann, V.P.W. Böhm, C.-P. Reisinger, J. Organomet. Chem. 576 (1999) 23;
(c) A.D. Ryabov, Synthesis (1985) 233;
(d) G.R. Newkome, W.E. Puckett, V.R. Gupta, G.E. Kiefer, Chem. Rev. 86 (1986) 451.

[3] See, for examples of various substitution reactions: (a) H. Ossor, M. Pfeffer, J. Chem. Soc. Chem. Commun. (1985) 1540;
(b) R.C. Davis, TJ. Grinter, D. Leaver, R.M. O'Neil, G.A. Thomson, J. Chem. Soc. Perkin Trans. 1 (1990) 2881;
(c) T. Izumi, H. Watabe, A. Kasahara, Bull. Chem. Soc. Jpn. 54 (1981) 1711;
(d) J.C. Clinet, G. Balavoine, J. Organomet. Chem. 405 (1991) C29;
(e) G. Balavoine, J.C. Clinet, P. Zerbib, J. Organomet. Chem. 389 (1990) 259;
(f) J.-M. Valk, R. van Belzen, J. Boersma, A.L. Spek, G. van Koten, J. Chem. Soc. Dalton Trans. (1994) 2293;
(g) M. Benito, C. López, X. Morvan, X. Solans, M. Font-Bardia, J. Chem. Soc. Dalton Trans. (2000) 4470;
(h) K. Kamaraj, D. Bandyopadhyay, Organometallics 18 (1999) 438;
(i) P. Wadhwani, D. Bandyopadhyay, Organometallics 19 (2000) 4435;
(j) J. Vicente, J.-A. Abad, W. Förtsch, P.G. Jones, A.K. Fischer, Organometallics 20 (2001) 2704 and references therein.

[4] Examples: (a) A.D. Ryabov, V.A. Polyakov, I.K. Talwbarovskaya, V.A. Katkova, A.K. Yatsimirskii, I.V. Berezin, Izv. Akad. Nauk SSSR Ser. Khim. 1 (1988) 175, Int. Ed. Engl. 1 (1988) 162;
(b) V.V. Dunina, O.N. Grunova, E.B. Averina, Y.K. Grishin, L.G. Kuz'mina, J.A.K. Howard, J. Organomet. Chem. 603 (2000) 138 and references therein.

[5] (a) C. Bolm, K. Muñiz Fernandez, A. Seger, G. Raabe, Synlett (1997) 1051;
(b) C. Bolm, K. Muñiz-Fernandez, A. Seger, G. Raabe, K. Günther, J. Org. Chem. 63 (1998) 7860;
(c) C. Bolm, K. Muñiz, C. Ganter, New J. Chem. 22 (1998) 1371;
(d) C. Bolm, K. Muñiz, Chem. Soc. Rev. 28 (1999) 51;
(e) C. Bolm, K. Muñiz, N. Aguilar, M. Kesselgruber, G. Raabe, Synthesis (1999) 1251;

(f) C. Bolm, K. Muñiz, Chem. Commun. (1999) 1295;
(g) C. Bolm, K. Muñiz, J.P. Hildebrand, Org. Lett. 1 (1999) 491;
(h) K. Muñiz, C. Bolm, Chem. Eur. J. 6 (2000) 2309;
(i) C. Bolm, M. Kesselgruber, K. Muñiz, G. Raabe, Organometallics 19 (2000) 1648;
(j) C. Bolm, N. Hermanns, J.P. Hildebrand, K. Muñiz, Angew. Chem. 112 (2000) 3607; Angew. Chem. Int. Ed. Engl. 39 (2000) 3465;
(k) C. Bolm, M. Kesselgruber, A. Grenz, N. Hermanns, J.P. Hildebrand, New J. Chem. 25 (2001) 13;
(l) C. Bolm, N. Hermanns, M. Kesselgruber, J.P. Hildebrand, J. Organomet. Chem. 624 (2001) 157;
(m) C. Bolm, M. Kesselgruber, N. Hermanns, J.P. Hildebrand, G. Raabe, Angew. Chem. 113 (2001) 1536; Angew. Chem. Int. Ed. Engl. 40 (2001) 1488.

[6] Use of chiral [2.2]paracyclophanes as ligands in asymmetric catalysis: (a) C. Bolm, T. Kühn, Synlett 6 (2000) 899;
(b) Y. Belokon, M. Moscalenko, N. Ikonnikov, L. Yashkina, D. Antonov, E. Vorontsov, V. Rozenberg, Tetrahedron: Asymmetry 19 (1997) 3245;
(c) V.I. Rozenberg, D.Y. Antonov, R.O. Zhuravsky, E.V. Vorontsov, V.N. Khrustalev, N.S. Ikonnikov, Y.N. Belokon, Tetrahedron: Asymmetry 11 (2000) 2683;
(d) P.J. Pye, K. Rossen, R.A. Reamer, N.N. Tsou, R.P. Volante, P.J. Reider, J. Am. Chem. Soc. 119 (1997) 6207;
(e) K. Rossen, P.J. Pye, A. Maliakal, R.P. Volante, J. Org. Chem. 62 (1997) 6462;
(f) P.J. Pye, K. Rossen, R.A. Reamer, R.P. Volante, P.J. Reider, Tetrahedron Lett. 39 (1998) 4441;
(g) A.H. Vetter, A. Berkessel, Tetrahedron Lett. 39 (1998) 1741;
(h) U. Wörsdörfer, F. Vögtle, M. Nieger, M. Waletzke, S. Grimme, F. Glorius, A. Pfaltz, Synthesis (1999) 597;
(i) U. Wörsdörfer, F. Vögtle, F. Glorius, A. Pfaltz, J. Prakt. Chem. 341 (1999) 445;
(j) D.S. Masterson, D.T. Glatzhofer, J. Mol. Catal. A: Chem. 161 (2000) 65;
(k) D.S. Masterson, T.L. Hobbs, D.T. Glatzhofer, J. Mol. Catal. A: Chem. 145 (1999) 75;
(l) S. Banfi, A. Manfredi, F. Montannari, G. Pozzi, S. Quici, J. Mol. Catal. A 113 (1996) 77;
(m) M.J. Burk, W. Hems, D. Herzberg, C. Malan, A. Zanotti-Gerosa, Org. Lett. 2 (2000), 4173;
(n) S. Tanji, A. Ohno, I. Sato, K. Soai, Org. Lett. 3 (2001) 287;
(o) S. Dahmen, S. Bräse, Chem. Commun. (2002) 26;
(p) S. Dahmen, S. Bräse, Org. Lett. 3 (2001) 4119;
(q) R. Ruzziconi, O. Piermatti, G. Ricci, D. Vinci, Synlett (2002) 747.

[7] (a) X.-L. Hou, X.-W. Wu, L.-X. Dai, B.-X. Cao, J. Sun, Chem. Commun. (2000) 1195;
(b) See also: X.-W. Wu, X.-L. Hou, L.-X. Dai, J. Tao, B.-X. Cao, J. Sun, Tetrahedron: Asymmetry 12 (2001) 529.

[8] Recent examples on the functionalization of [2.2]paracyclophanes by directed metallation: (a) T. Focken, H. Hopf, V. Snieckus, I. Dix, P.G. Jones, Eur. J. Org. Chem. (2001) 2221;
(b) A. Pelter, B. Mootoo, A. Maxwell, A. Reid, Tetrahedron Lett. 42 (2001) 8391.

[9] Reviews: (a) T. Hayashi, A. Togni (Eds.), Ferrocenes, VCH, Weinheim, Germany, 1995;
(b) C.J. Richards, A.J. Locke, Tetrahedron: Asymmetry 9 (1998) 2377.

[10] For initial observations of *ortho*-directing effects in lithiations of oxazolinyl ferrocenes, see: (a) T. Sammakia, H.A. Latham, D.R. Schaad, J. Org. Chem. 60 (1995) 10;
(b) C.J. Richards, T. Damalidis, D.E. Hibbs, M.B. Hursthouse, Synlett (1995) 74;
(c) C.J. Richards, A.W. Mulvaney, Tetrahedron: Asymmetry 7 (1996) 1419;
(d) Y. Nishibayashi, S. Uemura, Synlett (1995) 79.

[11] V. Rozenberg, N. Dubrovina, E. Sergeeva, D. Antonov, Y. Belekon, Tetrahedron: Asymmetry 9 (1998) 653.

[12] R. Appel, Angew. Chem. 87 (1975) 863; R. Appel, Angew. Chem. Int. Ed. Engl. 14 (1975) 801.

[13] A.I. Meyers, K.A. Lutomski, D. Laucher, Tetrahedron 44 (1988) 3107.

[14] (a) C.K. Johnson, ORTEP: A Fortran Thermal-Ellipsoid Plot Program for Crystal Structure Illustrations, Report ORNL-3794, 1970;
(b) G. Davenport, S.R. Hall, W. Dreissig, in: S.R. Hall, D.J. du Boulay, R. Olthof-Hazekamp (Eds.), ORTEP. Xtal3.7 System, University of Western Australia, 2000.

[15] A.G. Orpen, L. Brammer, F.H. Allen, O. Kennard, D.G. Watson, R. Taylor, J. Chem. Soc. Dalton Trans. (1989) S1.

[16] For a related transformation, see: V.T. Sololov, L.L. Troitskaya, O.A. Reutov, J. Organomet. Chem. 202 (1980) C58.

[17] For a related transformation, see: Y. Zhao, M. Helliwell, J.A. Joule, Arkivoc 1 (2000) 352.

[18] M.J. McKennon, A.I. Meyers, K. Drauz, M. Schwarm, J. Org. Chem. 58 (1993) 3568.

[19] S.R. Hall, D.J. du Boulay, R. Olthof-Hazekamp (Eds.), Xtal3.7 System, University of Western Australia, 2000.

[20] V. Subramanian, S.R. Hall, in: S.R. Hall, D.J. du Boulay, R. Olthof-Hazekamp (Eds.), GENSIN. Xtal3.7 System, University of Western Australia, 2000.

[21] S.R. Hall, in: S.R. Hall, D.J. du Boulay, R. Olthof-Hazekamp (Eds.), GENTAN. Xtal3.7 System, University of Western Australia, 2000.

[22] G.M. Sheldrick, SADABS, University of Göttingen, 1996.