Charging and Deforming the Pybox Ligand: Enantiomerically Pure Double Helices and Their Interconversion

Clément Mazet and Lutz H. Gade*[a]

Abstract: Reaction of pyrrole-2,5-biscarbonitrile (**1**) with an excess of (*S*)- or (*R*)-valinol in boiling chlorobenzene selectively yielded the two enantiomeric bis(oxazolinyl)pyrroles (*S*,*S*)-bis[2-(4,4′-diisopropyl-4,5-dihydrooxazolyl)]pyrrole ("*S*,*S*-iproxpH", **2a**) and (*R*,*R*)-bis[2-(4,4′-diisopropyl-4,5-dihydrooxazolyl)]-pyrrole ("*R*,*R*-iproxpH", **2b**), respectively. Lithiation of **2a** and **2b** at $-78\,^{\circ}C$ and reaction with an equimolar amount of $[PdCl_2(cod)]$ (cod = 1,5-cyclooctadiene) gave the helical dinuclear palladium complexes (*M*)-[PdCl(*S*,*S*-iproxp)]$_2$ (**3a**) and (*P*)-[PdCl(*S*,*S*-iproxp)]$_2$ (**3b**) as well as (*P*)-[PdCl(*R*,*R*-iproxp)]$_2$ (**4a**) and (*M*)-[PdCl(*R*,*R*-iproxp)]$_2$ (**4b**). Reaction of a 1:1 mixture of lithiated **2a** and **2b** with an equimolar amount of $[PdCl_2(cod)]$ gave a mixture of the homochiral complexes **3a**,**b** and **4a**,**b** along with the racemic mixture of the heterochiral complex $[Pd_2Cl_2$(*S*,*S*-iproxp)(*R*,*R*-iproxp)] (**5**). The double helical structure as well as the absolute configuration of these neutral dinuclear palladium complexes was confirmed by X-ray diffraction studies of all five complexes. One of the oxazolyl units and the anionic pyrrolide occupy two coordination sites in an approximately square-planar ligand arrangement at the Pd centers whereas the second oxazolyl ring is twisted out of this plane and binds to the second metal center. The heterochiral complex **5** does not possess any element of molecular symmetry. The *P*-helical complexes **3b** and **4a** display a positive CD at 310 nm and a weaker negative CD at 350 nm, while the compounds possessing *M*-helicity have the corresponding mirror image CD spectra. Complexes **3a** and **4a** have an additional weak long wavelength CD feature between 380 and 420 nm which is absent in the spectra of **3b** and **4b**. Upon heating a solution of **3b**, interconversion to the diastereomer of opposite helicity **3a** sets in, for which a first-order rate law with respect to the concentration of the complex was established; activation parameters: $\Delta H^{\neq} = 68\ kJ\,mol^{-1}$, $\Delta S^{\neq} = -99\ J\,mol^{-1}\,K^{-1}$. A cross-over experiment monitored by ^1H NMR spectroscopy also gave the racemate of the mixed-ligand complex **5**: (*P*)-$[Pd_2Cl_2$(*S*,*S*-iproxp)(*R*,*R*-iproxp)] and (*M*)-$[Pd_2Cl_2$(*S*,*S*-iproxp)(*R*,*R*-iproxp)] indicating an intermolecular exchange involving mononuclear {PdCl(iproxp)} complex fragments.

Keywords: chiral ligands · helical structures · N ligands · palladium

Introduction

Helical chirality is ubiquitous in coordination chemistry and provided the basis for Alfred Werner's revolutionary studies at the beginning of the 20th century.[1] Elements of helicality, such as chiral axes and planes, originally formulated for mononuclear complexes, may provide the basic motif for the construction of polynuclear metal compounds.[2] Polydentate ligands then play the rôle of helical strands which assemble around two or more metal centers. First formulated in 1969 by Harris and McKenzie for a triply stranded dicopper helical complex,[3] a large number of helical structures have been characterized during the three decades which followed.[4, 5] An important development was the formulation of the general conceptual framework by Lehn and co-workers, who also introduced the term "helicate" for such structures.[6]

Generally, racemic mixtures of *P* (right handed) and *M* (left handed) helices are obtained when the starting ligands used are nonchiral. In recent years, the isolation of stereochemically pure transition-metal helical complexes has been the focus of much attention. However, there are still relatively few examples in the literature of enantiomerically or diastereomerically resolved helical structures to date.[7] The latter has been achieved inter alia by chromatography using a chiral stationary phase or selective crystallization. From a synthetic point of view, the most commonly applied strategy for achieving stereochemical uniformity is the introduction of chiral information into the ligand strand such that the $(S)_n$-*M* and $(S)_n$-*P* helicates are related as diastereomers instead of enantiomers.[8]

The conceptual background and the choice of the model system: We recently began to develop the coordination chemistry of a new class of potentially tridentate, mono-

[a] Prof. L. H. Gade, C. Mazet
Laboratoire de Chimie Organométallique et de Catalyse (UMR 7513)
Institut Le Bel, Université Louis Pasteur
4, rue Blaise Pascal, 67070 Strasbourg (France)
Fax: (+33) 390-241531
E-mail: gade@chimie.u-strasbg.fr

  0947-6539/02/0818-4308 $ 20.00+.50/0

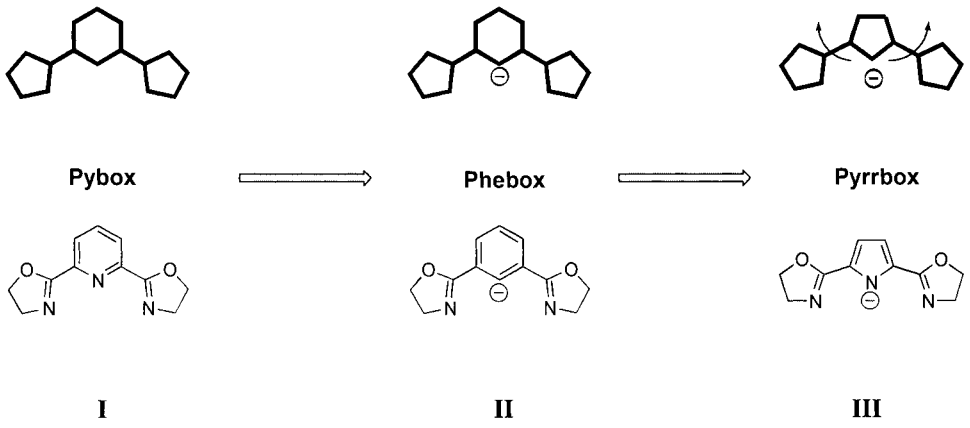
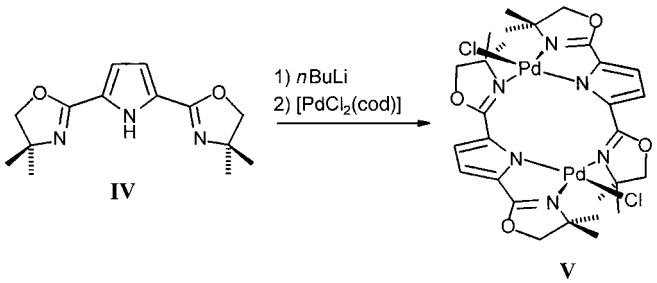


Figure 1. Charging and deforming the pybox ligand: the conceptual background and the choice of the model system.

anionic N-donor ligands based on the combination of two oxazoline rings and a central pyrrole unit.[9] This system may be viewed as being derived from the well established pyridine-bisoxazoline ("pybox") ligand (**I**) introduced to the field of asymmetric catalysis by Nishiyama and co-workers roughly a decade ago.[10, 11] Upon substitution of the pyridine ring by a phenyl unit, a formally anionic version of this system ("phebox", **II**) was obtained more recently by the same group.[12] Charging of the pybox system, while at the same time deforming the arrangement of the three donor atoms, was the intended result of introducing a central pyrrole ring in the tridentate ligand system **III** (Figure 1).

A preliminary study of the coordination chemistry of an achiral derivative of **III**, the bis[2-(4,4′-dimethyl-4,5-dihydrooxazolyl)]pyrrolide (dmoxp) (**IV**), revealed that the arrangement of its three N-donor atoms does not permit meridional tris-coordination to a single metal center.[9] For the square-planar palladium(II) complexes obtained with this ligand, the coordinatively unsaturated mononuclear species were stabilized instead by aggregation to form a racemic mixture of chiral helical dimers $[Pd_2(dmoxp)_2Cl_2]$ (**V**) (Scheme 1).

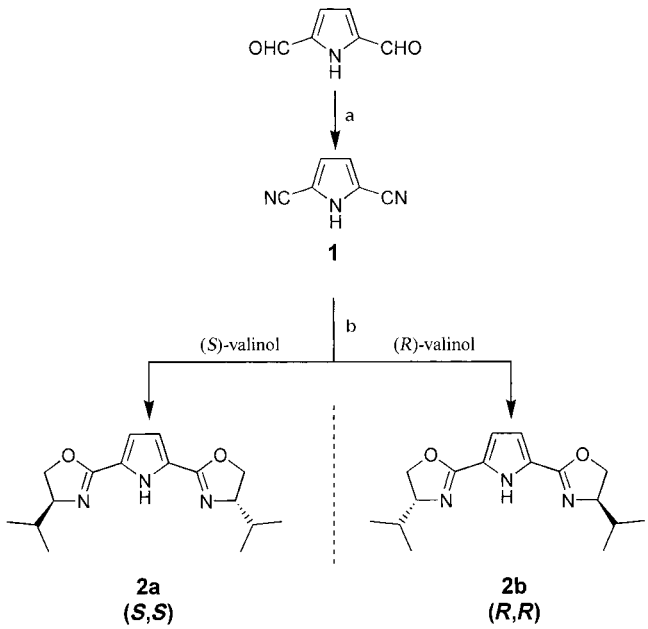


Scheme 1. Square-planar palladium(II) complexes obtained with the achiral bis[2-(4,4′-dimethyl-4,5-dihydrooxazolyl)]pyrrolide (dmoxp) ligand.

In view of the kinetic stability of the neutral dinuclear palladium complexes synthesized with the new ligand system,[13] this class of compounds appeared to be ideally suited for a detailed study of the structures of stereochemically well-defined helical complexes and the investigation of dynamic behavior of helix formation, dissociation and interconversion. Using chiral bis(oxazolinyl)pyrrole derivatives, it was thought that a diastereoselective access to such helical complexes might be feasible. Alternatively, the separation of mixtures of the kinetically stable diasteromeric helices could provide access to stereochemically uniform complexes. This paper is the first comprehensive report on the coordination chemistry of helical dipalladium complexes containing the new class of chiral bis(oxazolinyl)pyrrolide ligands, the dynamics of helix interconversion and the chiroptical properties of the complexes.

Results and Discussion

Synthesis of the ligands: Among the numerous established routes from amino alcohols to oxazolines,[14, 15] we focused on the one-step reaction using an amino alcohol/nitrile condensation to prepare the target molecules. An overview of the synthetic approach is given in Scheme 2. The key intermediate



Scheme 2. Synthesis of the chiral bis[2-(4,4′-isopropyl-4,5-dihydrooxazolyl)]pyrrole (iproxp) ligands **2a** and **2b**. a) $H_2NOH \cdot HCl$, Et_3N, CH_3CN, phthalic anhydride, 56%; b) $ZnCl_2$, (*R*)- or (*S*)-valinol, C_6H_5Cl, reflux, 70–72%.

  0947-6539/02/0818-4309 $ 20.00+.50/0

is the pyrrole-2,5-biscarbonitrile (**1**) which was reported previously by Barnett and co-workers.[16] These workers obtained compound **1** in very modest yield by reaction of chlorosulfonyl isocyanate with pyrrole. To prepare this important starting material for the ligand synthesis on a larger scale, the known pyrrole-2,5-biscarboxaldehyde was converted to its nitrile analogue by dehydration of its oxime derivative with phthalic anhydride using a one-pot protocol which has been recently described by Wang et al. for related transformations.[17]

Reaction of pyrrole-2,5-biscarbonitrile (**1**) with an excess of (*S*)- or (*R*)-valinol in boiling chlorobenzene in the presence of a catalytic amount of activated $ZnCl_2$ selectively yielded the two enantiomeric bis(oxazolinyl)pyrroles (*S*,*S*)-bis[2-(4,4′-diisopropyl-4,5-dihydrooxazolyl)]pyrrole ("*S*,*S*-iproxpH", **2a**) and (*R*,*R*)-bis[2-(4,4′-diisopropyl-4,5-dihydrooxazolyl)]pyrrole ("*R*,*R*-iproxpH", **2b**), respectively. Both compounds were readily purified by flash chromatography and isolated as air-stable off-white solids in 70–72% yield.

Synthesis and structural characterization of the helical palladium complexes containing the chiral bis(oxazolinyl)-pyrrole ligands: The bis(oxazolinyl)pyrrole *S*,*S*-iproxpH (**2a**) was lithiated at $-78\,^{\circ}C$ and the lithium pyrrolide then treated with a slight excess of $[PdCl_2(1,5\text{-cod})]$ at room temperature in dry diethyl ether to give a deep orange solution. After removal of the solvent and other volatile components, a ^1H NMR spectrum was recorded of the crude reaction mixture and indicated the presence of two novel compounds, the metalated derivatives of **2a**, in a ratio of 5:1 (along with a slight excess of palladium precursor). These air-stable reaction products were readily separated and purified by column chromatography on silica gel using CH_2Cl_2 as eluent. The first compound to be eluted, complex **3a**, ($R_f = 0.52$) was isolated in approximately 11% yield (based on **2a**), while the second orange band corresponded to the major species **3b** (48% yield; $R_f = 0.29$). These relative yields obtained after the workup are consistent with the ratio previously established by ^1H NMR integration for the crude product mixture.

The analytical data of both complexes were found to be identical and consistent with a formulation as $[PdCl(S,S\text{-iproxp})]_n$. The resonance patterns in the ^1H NMR spectra of **3a** and **3b** are very similar, however, the chemical shifts of the individual signals are different (Table 1). While the ^1H and ^{13}C NMR spectra of the free protonated ligand **2a** contain a half-set of signals due to its C_2 symmetry, the full signal set representing the chemical inequivalence of all proton environments is observed in the ^1H NMR spectra of **3a** and **3b**. This loss of the C_2 symmetry of the ligand upon complexation to palladium, which is also reflected in the doubling of the set of resonances in the ^{13}C NMR spectra of both compounds, was thought to be due to aggregation to form dimeric complexes or higher nuclearity oligomers. This interpretation was also confirmed by the splitting into two ν(C=N) vibrational IR bands of the two oxazolyl moieties, the position of which is consistent with their coordination to a metal center. These spectroscopic data, along with the observation of molecular ion peaks at m/z 861 ($[M+H]^+$) in their FAB mass spectra led us to propose that **3a** and **3b** were two isomeric helical dinuclear palladium complexes similar to the previously characterized complex dimer containing the achiral bis[2-(4,4′-dimethyl-4,5-dihydrooxazolyl)]pyrrolide (dmoxp) ligand. Given the chirality of the *S*,*S*-iproxp ligands, the presence of an additional element of chirality in a complex helix leads to the two diastereomers **3a** and **3b**.

Table 1. ^1H NMR spectroscopic data (500 MHz) of the ligands **2a** and **2b**, as well as the palladium complexes **3a**,**4a** and **3b**,**4b**, indicating the loss of the C_2 symmetry upon complexation. Whereas the protons in each ligand are thus inequivalent, the two tridentate ligands in the homochiral helicates are symmetry-equivalent. In contrast, the inequivalence of the two ligands in the helicate **5** is reflected in a further doubling of the signal sets.

	$H_{3/4}$	CH_{iPr}	$CH_{3\ iPr}$
2a,**2b**	6.73 s	1.81 sept	1.00 d 0.92 d
3a,**4a**	6.68 d 6.60 d	2.29 sept 2.20 sept	1.14 d 1.10 d 0.87 d 0.81 d
4a,**4b**	7.08 d 6.90 d	2.20 sept 1.52 sept	1.50 d 0.62 d 0.38 d 0.37 d
5	6.69 d 6.67 d	3.49 sept 2.81 sept	1.32 d 1.21 d 1.01 d
	6.63 d 6.61 d	2.53 sept 2.02 sept	0.86–0.77 m

Using the other ligand enantiomer, *R*,*R*-iproxp (**2b**), the corresponding enantiomeric pair of diastereomers, **4a** and **4b**, was obtained and isolated by a similar chromatographic work up. As expected, both complexes thus obtained possess identical spectroscopic and analytical data to those discussed above. Whereas the helical *homochiral* complex dimers **3a**,**b** and **4a**,**b** led to the expected set of pairs of *diastereomers*, it was reasoned that a *heterochiral* combination of the two ligands *S*,*S*-iproxp (**2a**) and *R*,*R*-iproxp (**2b**) in a dipalladium helix would lead to a single relative stereochemistry, that is a pair of *enantiomers* defined by the presence of the chiral molecular axis. Reaction of a 1:1 mixture of lithiated **2a** and **2b** with an equimolar amount of $[PdCl_2(cod)]$ gave a mixture of the homochiral complexes **3a**,**b** and **4a**,**b** along with an additional component which was separated from **3b** and **4b** by column chromatography on silica gel and, subsequently, from **3a** and **4a** by fractional crystallization. The analytical data along with the NMR spectra and the FAB mass spectrum established the identity of this new component as that of the desired *heterochiral* complex $[Pd_2Cl_2(S,S\text{-iproxp})(R,R\text{-iproxp})]$ (**5**). The resonance patterns in the ^1H and ^{13}C NMR spectra of **5** are similar to those of **3a** (**4a**) and **3b** (**4b**), albeit with double sets of signals and different chemical shifts, now indicating the inequivalence of all ^1H and ^{13}C nuclei in the complex. A splitting is also observed in the band pattern in the infrared spectrum of this complex.

The double-helical nature of these neutral dinuclear palladium complexes was confirmed by a series of X-ray diffraction studies of all five complexes. Suitable crystals were grown by layering dichloromethane solutions of the respective pure palladium complexes with hexane. The molecular structures of **4a**, **4b**, and **5** are depicted in Figure 2 along with the principal bond lengths and angles.

The molecular structures of complexes **4a** and **4b** represent the two diastereomeric forms of the dipalladium complexes containing a homochiral set of the *R*,*R*-iproxp ligand and are thus to be designated according to their helicity. This leads us to formulate complex **4a** as (*P*)-$[PdCl(R,R\text{-iproxp})]_2$ and complex **4b** as (*M*)-$[PdCl(R,R\text{-iproxp})]_2$. Accordingly, complexes **3a** and **3b**, containing the *S*,*S*-iproxp ligand, were

0947-6539/02/0818-4310 $ 20.00+.50/0 *Chem. Eur. J.* **2002**, *8*, No. 18

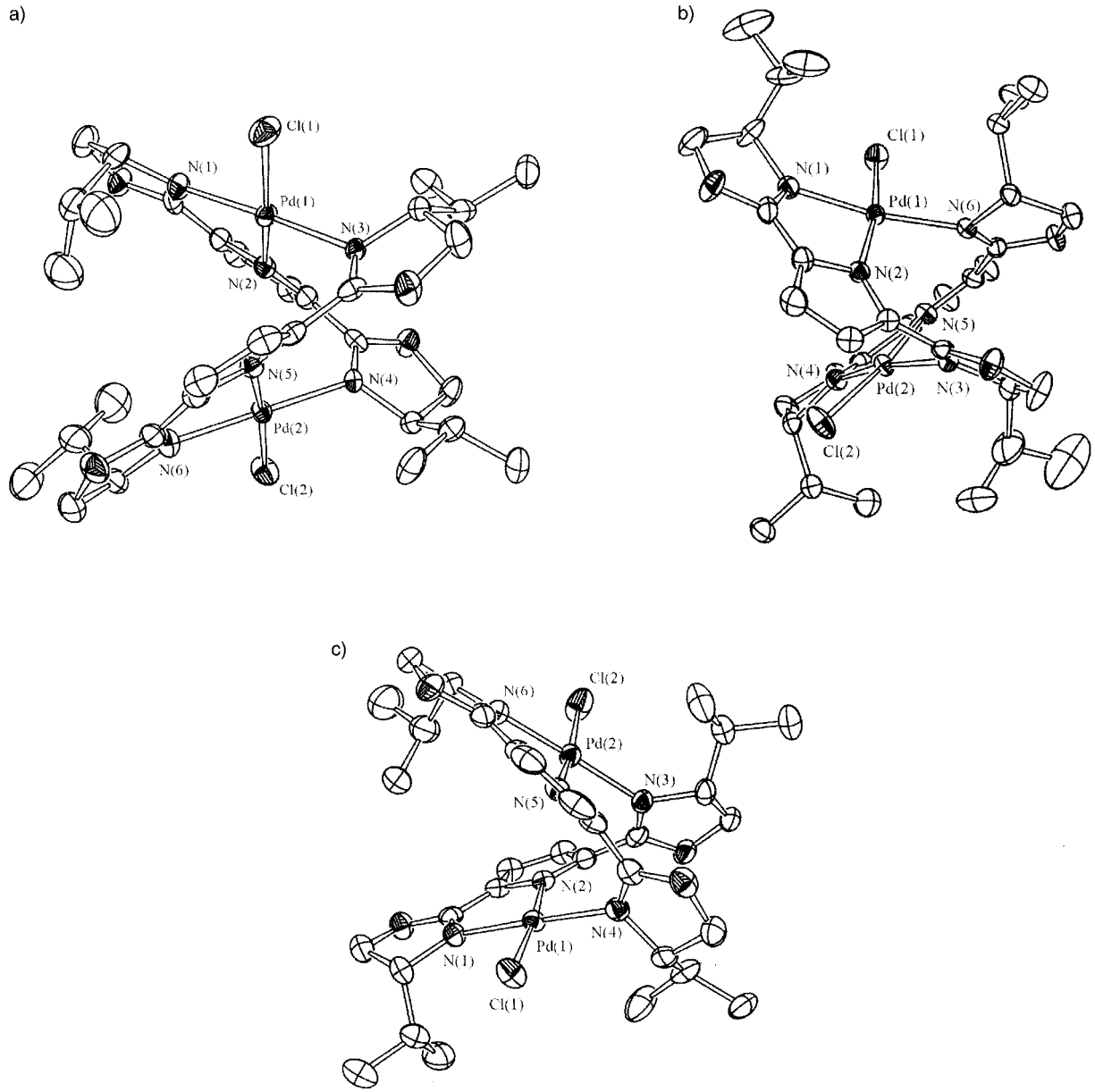


Figure 2. The molecular structures of **4a**, **4b**, and **5**. Principal bond lengths [Å] and angles [°]: **4a**: Pd(1)–Cl(1) 2.306(2), Pd(1)–N(1) 2.005(7), Pd(1)–N(2) 2.054(7), Pd(1)–N(3) 2.042(7), Pd(1)–Pd(2) 3.957; Cl(1)-Pd(1)-N(2) 167.1(2), N(1)-Pd(1)-N(2) 80.1(3), N(1)-Pd(1)-N(3) 176.7(3). **4b**: Pd(1)–Cl(1) 2.289(1), Pd(1)–N(1) 2.033(5), Pd(1)–N(2) 2.047(4), Pd(1)–N(6) 2.043(4), Pd(1)–Pd(2) 3.463; Cl(1)-Pd(1)-N(1) 92.9(1), N(1)-Pd(1)-N(6) 167.7(2), N(2)-Pd(1)-N(6) 99.0(2), N(5)-C(21)-C(24)-N(6) −31.4.

characterized as the corresponding enantiomers, (*M*)-[PdCl(*S*,*S*-iproxp)]$_2$ and (*P*)-[PdCl(*S*,*S*-iproxp)]$_2$, respectively. Whereas the enantiomers **3b** and **4b** crystallize in the same space group (*C*2), the single crystals of complexes **3a** and **4a** were crystallographically nonequivalent due to a different number of solvent molecules in the lattices. Compound **3a** crystallized in the hexagonal space group *R*32 with six molecules per unit cell and two molecules of dichloromethane in special positions. In contrast, the crystals of **4a** were orthorhombic ($P2_12_12_1$) with four molecules per unit cell and no solvent molecules included in the crystal lattice. Compound **5**, containing the heterochiral set of ligands, is characterized by the helical axis as the only effective element of chirality and crystallized as a racemate in the triclinic space group $P\bar{1}$. The unit cell is composed of the two enantiomers of **5**, (*P*)-[Pd$_2$Cl$_2$(*S*,*S*-iproxp)(*R*,*R*-iproxp)] and (*M*)-[Pd$_2$Cl$_2$(*S*,*S*-iproxp)(*R*,*R*-iproxp)], the latter of which is shown in Figure 2.

Using Piguet's classification of helicates,[5b] compounds **3a**,**b**, **4a**,**b** and **5** represent heterotopic double-stranded unsaturated helicates. In spite of the large number of helicates characterized to date there are only very few examples in the literature of either homo- or heterotopic multiply stranded unsaturated helicates.[18] We note that a previous example of a helical dinuclear palladium complex reported by Constable et al. does not fall into this category of double-stranded unsaturated helicates.[13]

Comparative discussion of the three structural types found for the chiral dipalladium helices: As stated in the introduction, the inability of the bisoxazolylpyrrolide ligands to act as

tridentate ligands for palladium(II) leads to the stabilization through the formation of the dinuclear complexes. In these dimers, one of the oxazolyl units and the anionic pyrrolide occupy two coordination sites in an approximately square planar ligand arrangement at the Pd centers and thus generate an essentially planar unit. The second oxazolyl ring, however, is twisted out of this plane and binds to the second metal center, and it is this twist in the two bridging ligands that is the key structural element in the helical overall arrangement of the compounds. Complexes **3a**,**b** and **4a**,**b** possess molecular twofold symmetry, the C_2 axis being orthogonal to the Pd···Pd vector which implies that the helical arrangement is associated with only one torsion angle between the pyrollide ring and the oxazolinyl unit bound to the second metal center. For the complexes **4a** and **4b** the twist angles are 37.1° and 31.4°, respectively. This decrease of the torsional angle upon going from **4a** to **4b** is matched by a decrease in the Pd–Pd distance from 3.975 to 3.463 Å. On the other hand, complex **5** does not possess any element of molecular symmetry resulting in two intraligand torsion angles. For the *M* enantiomer in the racemic crystal these were found to be 47.4° (*R*,*R*-iproxp) and 35.4° (*S*,*S*-iproxp), while the Pd–Pd distance was reduced to 3.208 Å.

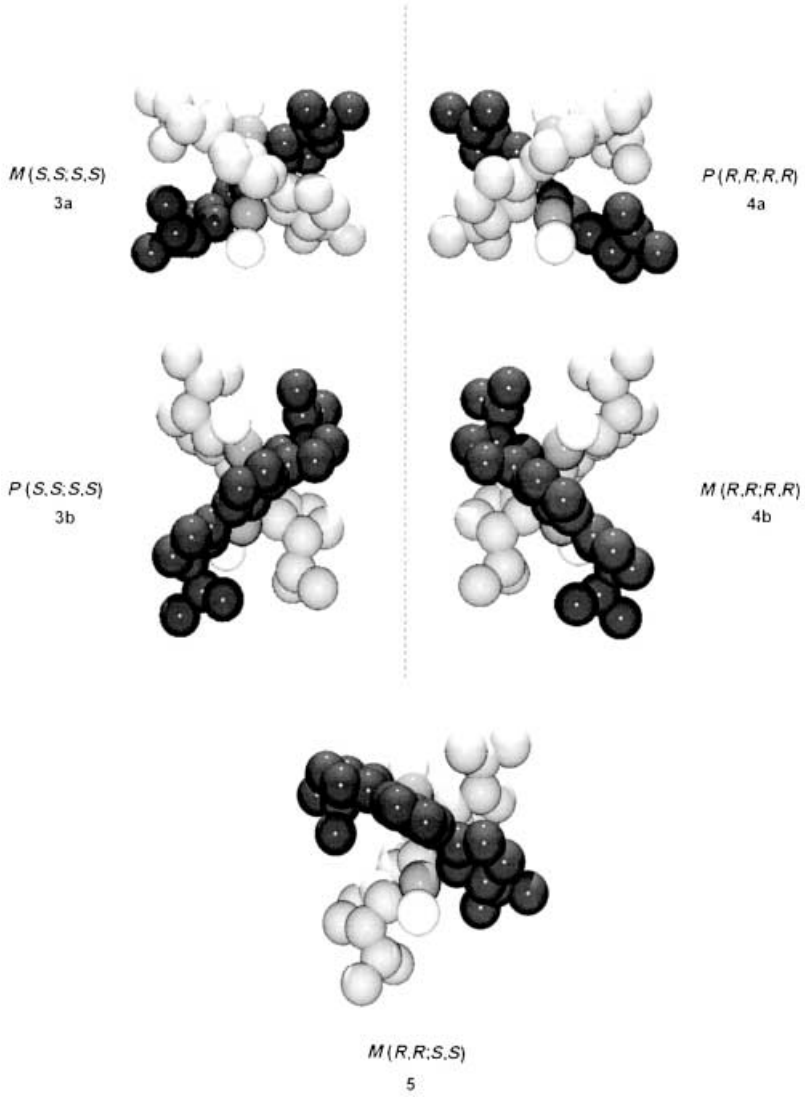


Figure 3. General overview of the isomers **3a** and **4a** (which are related to their respective enantiomers **3b** and **4b** by a virtual vertical mirror plane) as well as the heterochiral complex **5**.

The principal structural differences between molecular structures of complexes **3a**,**b**, **4a**,**b**, and **5** are most readily visualized by comparison of their molecular shapes represented by the space-filling models depicted in Figure 3. The most apparent consequence of the two different senses in which the *R*,*R*-iproxp ligands "wrap around" the two Pd centers in the helical isomers **4a** and **4b** is the orientation of the isopropyl substituents in the oxazoline rings vis-à-vis the groove of the helix. In the *P* isomer **4a** (*M* isomer **3a**) the isopropyl groups point inside the groove towards the other helical strand, whereas the *M* isomer **4b** (*P* isomer **3b**) displays the opposite orientation. In contrast, compound **5**, which contains a heterochiral set of ligands, and of which one of the two enantiomeric helical forms present in the racemic crystal is displayed in Figure 3, is distinguished by the combination of both types of isopropyl orientations: inside the groove for one of the two ligands and in the opposite direction for the other ligand enantiomer within the same helix. In all three types of molecular structures there is apparently no significant "interstrand" repulsion between the ligand peripheries (closest contact between the alkyl fragments >3.8 Å). There is thus no apparent energetic preference for a particular isomer based on factors related to steric repulsion. This may explain the statistical distribution of the isomers under the conditions of chemical equilibrium discussed below.

Absorption spectra and chiroptical properties of the chiral helical palladium complexes: The absorption spectra of the two diastereomeric complexes **3a** and **3b**, recorded in $CHCl_3$, are displayed in Figure 4. Whereas the absorption band of the free ligand **2a** is centered around 294 nm and corresponds to the $\pi^* \leftarrow \pi$ transition of the bisoxazolinylpyrrol chromophore, this absorption band is bathochromically shifted for the two helical complexes each possessing a broad band with a maximum intensity at 330 nm.

0947-6539/02/0818-4312 $ 20.00+.50/0 *Chem. Eur. J.* **2002**, *8*, No. 18

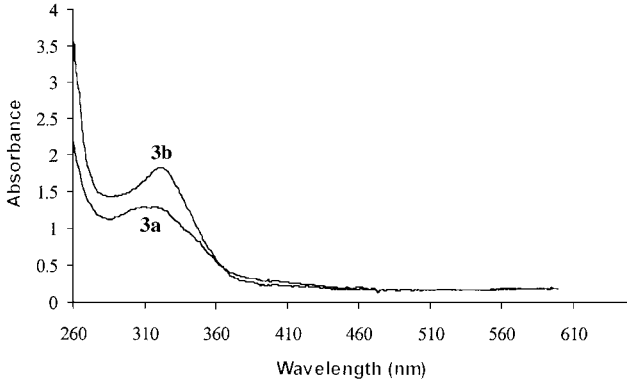


Figure 4. UV/Vis absorption spectra of the diastereomeric complexes **3a** and **3b**.

The optical rotations of the free pyrroles **2a**,**b** as well as the complexes **3a**,**b** and **4a**,**b** have been determined by polarimetry and are given in Table 2 in the form of their α_D and Φ_D (molar rotation) values. All compounds are spectroscopically transparent at 589 nm and therefore no anomalous optical rotatory dispersion needs to be considered. Since the chiral elements in the complexes appear to be sufficiently spacially disconnected to assume their additivity we may apply van't Hoff's empirical "Principle of Optical Superposition" to separate the components of the molar rotation due to the ligand on the one hand and originating from the complex helicality on the other.[19, 20] This has been taken into account calculating the values of the molar helical rotation $H_D = \Phi_D(\text{complex}) - 2\Phi_D(\text{ligand})$ listed in Table 1 which demonstrate a striking difference between the two diastereomers **3a**,**4a** and **3b**,**4b**.[21] The H_D values of the latter (+4904.0, −4876.9) are almost two orders of magnitude greater and inverse (**3a**,**4a**: −52.2, +73.3) which indicates a significantly higher degree of helicality for the diastereomer in which the isopropyl substituents point away from the helical groove.

Table 2. Polarimetric measurements (589-Na source) of the free ligands and the four diastereomers in $CHCl_3$ solutions ($c = 0.15\ g\,cm^{-3}$).

	$[\alpha]_D^{20}$ [$g^{-1}\,cm^{-3}\,dm^{-1}$]	$[\Phi]_D^{20}$ [$cm^3\,dm^{-1}\,mol^{-1}$]	$[H]_D^{20}$ [$cm^3\,dm^{-1}\,mol^{-1}$]
2a	−42.0	−121.4	–
2b	+44.6	+128.9	–
3a	−34.3	−295.0	−52.2
4a	+38.5	+331.1	+73.3
3b	+542.0	+4661.2	+4904.0
4b	−537.1	−4619.1	−4876.9

The difference between the two diastereomeric helices is also apparent in the CD spectra recorded of the four complexes which are shown in Figure 5. They all show a strong sinoidal CD in the region between 280 nm and 360 nm which we attribute to the intra ligand $\pi^* \leftarrow \pi$ as well as the MLCT transitions. The *P*-helical complexes **3b** and **4a** display a positive CD at 310 nm, as would be expected from exciton theory for coupled $\pi^* \leftarrow \pi$ transitions in a *P* helix, and a weaker negative CD at 350 nm (possibly due to a coupled MLCT excitation) while the compounds possessing *M*-helicity have the corresponding mirror image CD spectra. Interestingly, complexes **3a** and **4a** with the inward isopropyl orientation have an additional weak long wavelength CD feature between 380 and 420 nm (hidden in the long wavelength tail of the broad absorption band in the UV/Vis absorption spectrum discussed above) which is absent in the spectra of **3b** and **4b**. The deviation from the ideal sinoïdal

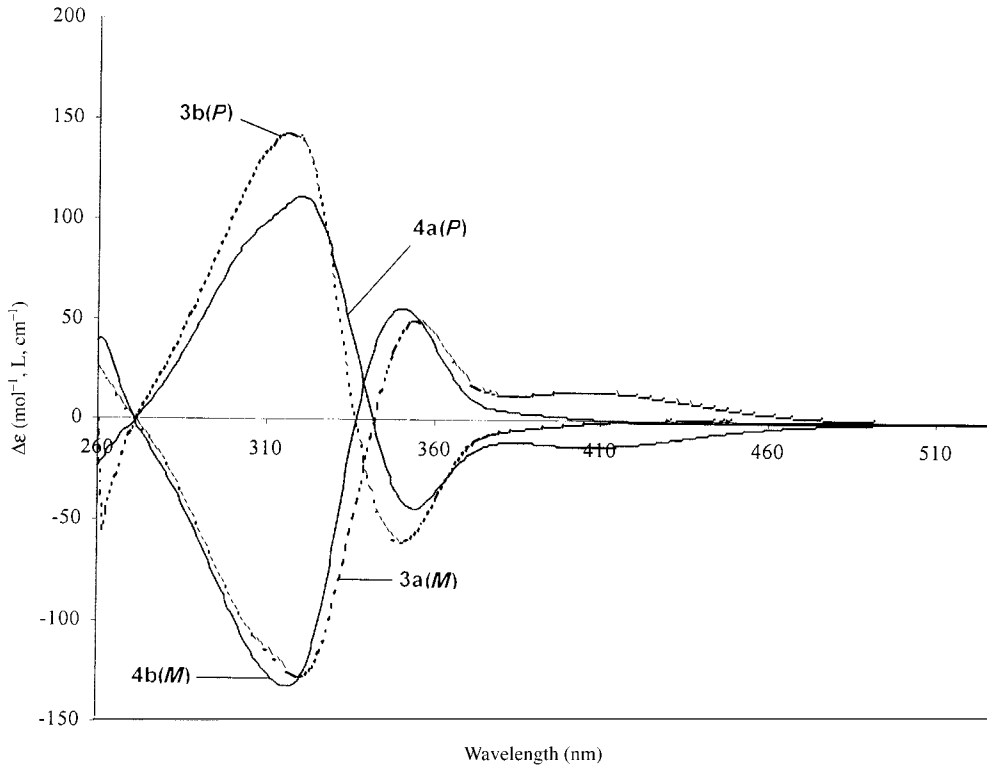


Figure 5. CD spectra of **3a(*M*)**, **3b(*P*)**, **4a(*P*)** and **4b(*M*)** (recorded in $CHCl_3$, concentrated $10^{-4}\ mol\,L^{-1}$.

  0947-6539/02/0818-4313 $ 20.00+.50/0

CD in **3a** and **4a** may be related to the reduced helicality of this diastereomeric form[22] as reflected in the results of the polarimetric study.

Dynamics of the interconversion of the diasteromeric palladium helices in solution: The helical dinuclear palladium complexes described in this paper are configurationally stable in solution at ambient temperature and no conversion to the other diastereomer was observed even after several weeks. However, upon heating a solution to above 70 °C, slow interconversion to the diastereomer of opposite helicity sets in. This conversion is decomposition free and may be conveniently monitored by ^{1}H NMR spectroscopy. A series of ^{1}H NMR spectra recorded in [D_8]toluene at 90 °C, representing the conversion of **3b** to **3a** is displayed in Figure 6 showing the AB spin system of the protons on the pyrrolide ring. The outer set of doublets ($\delta = 6.61$, 6.85 ppm) is assigned to the starting material **3b**, while the AB resonance system of **3a** slowly grows in ($\delta = 6.68$, 6.81 ppm). The corresponding conversion/time curve is displayed in Figure 6b.

Monitoring the conversion of **3b** to **3a** at variable concentration of the starting material established a first-order rate law with respect to the concentration of the complex (Figure 7) while the analysis of the initial reaction rates in the temperature range between 70 and 105 °C provided an estimate of the activation parameters: $\Delta H^{\neq} = 68\ \mathrm{kJ\,mol^{-1}}$, $\Delta S^{\neq} = -99\ \mathrm{J\,mol^{-1}\,K^{-1}}$. Prolonged heating at 90 °C led to the equilibrium distribution between **3a** and **3b** which was found to be 50.5:49.5, corresponding to the statistical 1:1 value. While there is a kinetic preference in the formation of **3b** over **3a** of about 80:20, as discussed in a previous section, neither of the two diastereomers appears to be thermodynamically favored. In other words, the orientation of the isopropyl groups in the two complexes does not have an enthalpic effect. This is consistent with the structural data obtained for the complexes which indicate that there is little inter-ligand repulsive interaction.

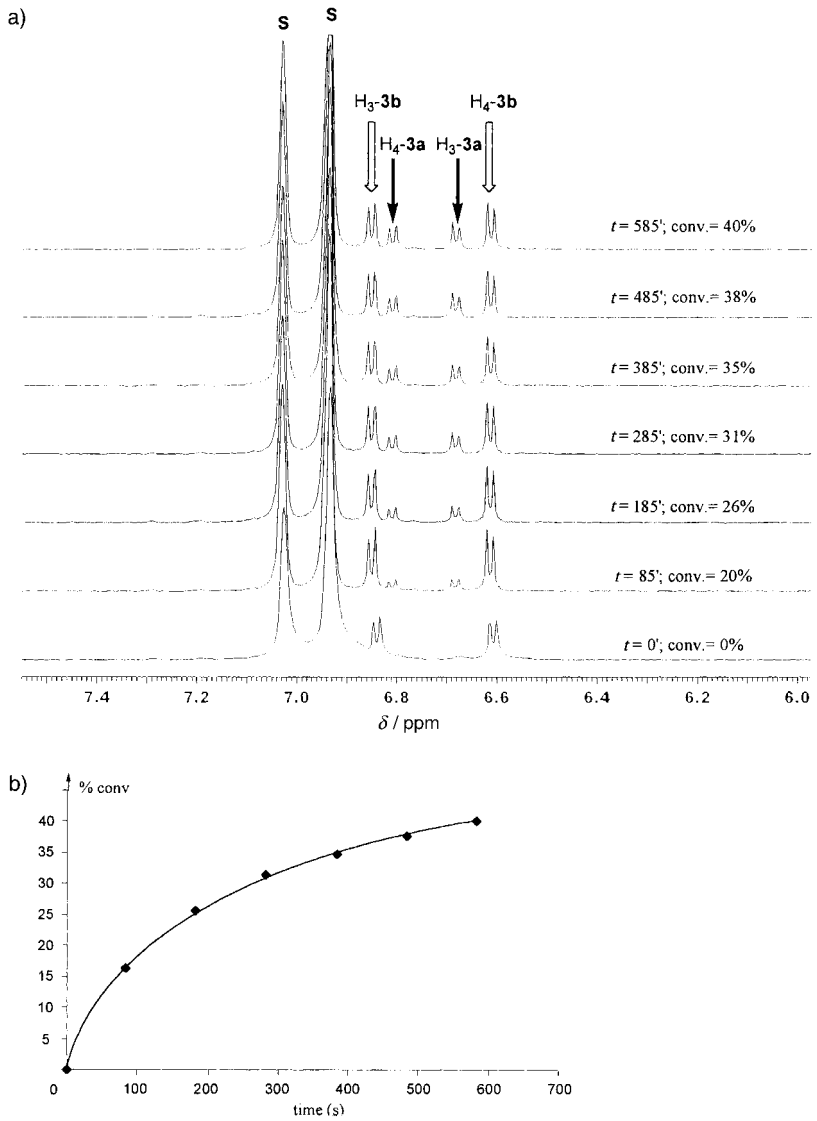


Figure 6. a) ^{1}H NMR spectra of the H_3 and H_4 aromatic protons of the pyrrole ring showing the progressive formation of **3a** when starting with pure **3b**. Experiment carried out at 363 K in C_7D_8 solution. b) The conversion/time curve for the conversion of **3b** to **3a**.

To establish whether the interconversion of the helices is an intramolecular process or occurs by means of a dissociative intermolecular pathway, a cross-over experiment was carried out. For this purpose a 1:1 mixture of the two enantiomers **3b** and **4b** was prepared and heated at 90 °C. If the rearrangement were intramolecular, the only reaction products to be observed are the diastereomers **3a** and **4a**, while an intermolecular exchange involving mononuclear {PdCl(iproxp)} complex fragments would also give the racemic mixture of the mixed-ligand complex **5**: (*P*)-[Pd_2Cl_2(*S*,*S*-iproxp)(*R*,*R*-iproxp)] and (*M*)-[Pd_2Cl_2(*S*,*S*-iproxp)(*R*,*R*-iproxp)] (Scheme 3). The latter was observed upon monitoring the cross-over experiment by ^{1}H NMR spectroscopy, which clearly indicated three sets of resonances attributable to the three stereoisomeric forms representing inequivalent relative configurations (Figure 8).

Due to the crowded nature of the spectra, a resolution of the different signal sets which was sufficient to study the kinetics of the formation of **5** was unfortunately not feasible. Qualitatively, the generation of **5** occurred more slowly than the helix interconversion **3b**,**4b** →

0947-6539/02/0818-4314 $ 20.00+.50/0 *Chem. Eur. J.* **2002**, *8*, No. 18

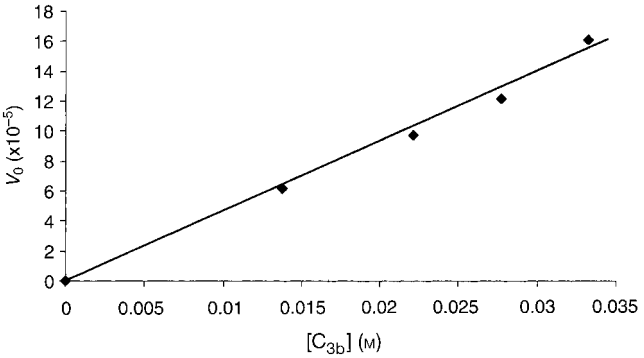


Figure 7. Determination of the kinetic reaction order of **3b** in the conversion to **3a**: Dependence of the initial reaction rate upon the initial concentration of **3b**.

3a,**4a** which may be due to a favored recombination of the two homochiral mononuclear fragments within the solvent cage.

Conclusion

The "distortion" of a tridentate ligand to the extent that planar tricoordination in d^8 palladium complexes is no longer feasible has led to the aggregation in the form of helical dimeric compounds. The use of chiral bis(oxazolinyl)pyrrolide ligands has enabled the separation and isolation of stereochemically uniform helices, representing the relatively rare case of heterotopic double-stranded unsaturated helicates in Piguet's system of classification. By using both enantiomers of the C_2-chiral ligands, the complete set of diastereomers and enantiomers was accessible and characterized by X-ray diffraction. We have also synthesized and isolated the helical dimer containing a heterochiral set of ligands which contains, as sole active element of chirality, the helical axis, and was thus isolated as the racemate of both enantiomeric forms.

All the helical complexes are configurationally stable in solution at ambient temperature, however, upon going to elevated temperatures their interconversion could be conveniently studied. These studies showed that while there is a strong kinetic preference for one of the diastereomeric helices, equilibration leads to 1:1 mixtures, indicating the absence of significant intramolecular repulsive forces favoring either of the two alternatives. A cross-over experiment using a racemate of two diastereomerically-uniform complexes revealed the formation of the heterochiral isomer apart from

$$[M(S,S;S,S)(\mathbf{3b}) + P(R,R;R,R)(\mathbf{4b})] \rightleftharpoons [P(S,S;S,S)(\mathbf{3a}) + M(R,R;R,R)(\mathbf{4a})] + [M(S,S;R,R) + P(S,S;R,R)(\mathbf{5})]$$

Scheme 3. Cross-over experiment for the thermal conversion of the Pd_2 helices with a 1:1 mixture of **3b** and **4b**.

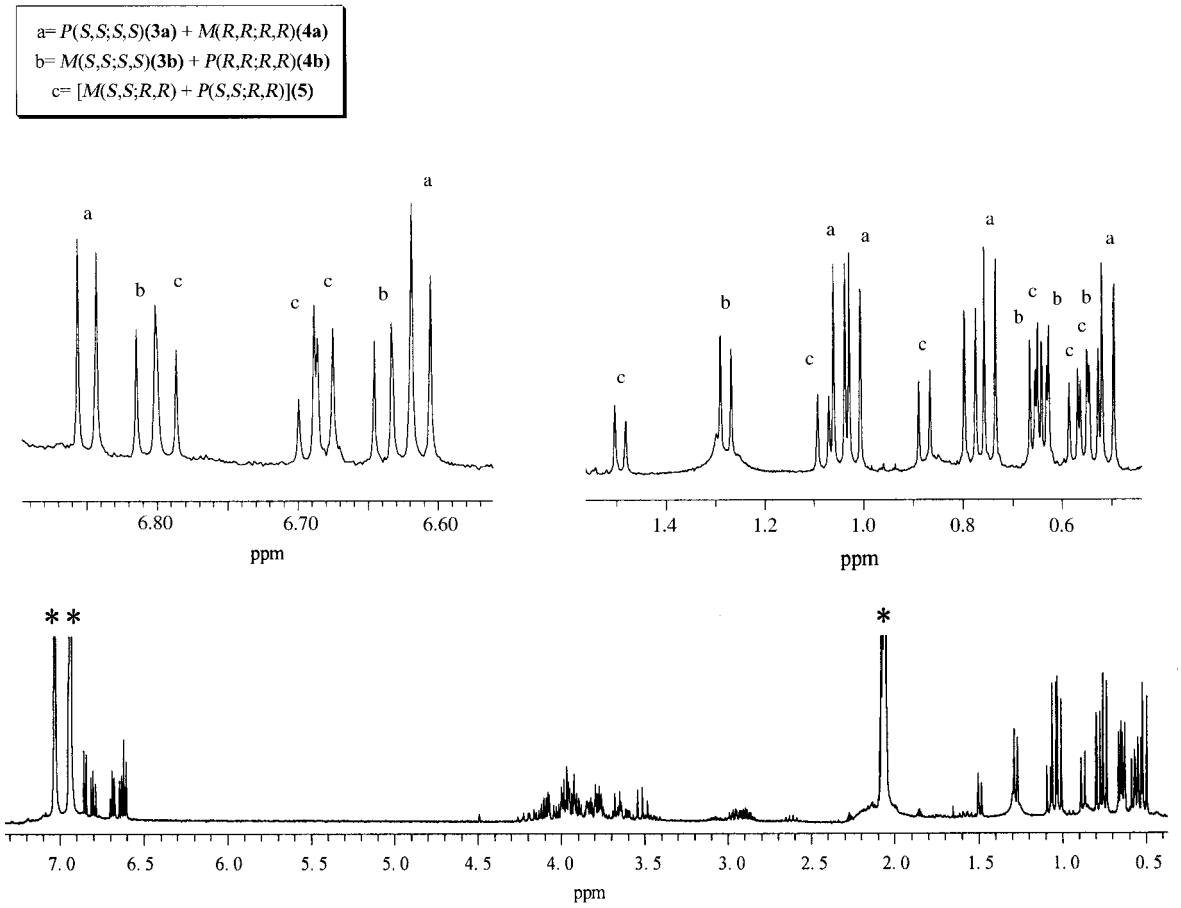


Figure 8. ^{1}H NMR spectrum recorded after the cross-over experiment performed with a 1:1 mixture of **3b** and **4b**.

  0947-6539/02/0818-4315 $ 20.00+.50/0

the helix interconversion of the homochiral species. This is consistent with the dissociation and subsequent re-aggregation of the dimeric complexes under the reaction conditions of the thermal rearrangement.

The aspect of configurational stability is an important issue in the application of these compounds in stereoselective catalytic transformations which are based on the activity displayed by the complexes containing the achiral bis(oxazolinyl)pyrrol ligand.[9] This is the focus of our current and future activities.

Experimental Section

Solvents were dried according to the standard procedures and saturated with nitrogen. Solids were separated from suspensions by centrifugation, thus avoiding filtration procedures, using a Hettich Rotina 48 centrifuge equipped with a specifically designed Schlenk tube rotor (Hettich Zentrifugen, Tuttlingen, Germany).[23] Optical rotations were recorded on a thermostated Perkin Elmer Otopol III using a 1.0 dm cell. The ^{1}H and ^{13}C NMR spectra were recorded on a Bruker AC 300 (^{1}H 300 MHz; ^{13}C{^{1}H} 75 MHz), a Bruker AM 400 (^{1}H 400 MHz; ^{13}C{^{1}H} 100 MHz), and a Bruker ARX 500 (^{1}H 500 MHz; ^{13}C{^{1}H} 125 MHz) spectrometers. Infrared spectra were recorded on a Perkin Elmer 1600 FTIR spectrometer. EI Mass spectra were recorded on a Shimadzu QP5050-GC/MS system. The elemental analyses were carried out by the Service Commun de Microanalyse de l'Université Louis Pasteur Strasbourg. The CD spectra were obtained using a Jobin-Yvon CD6 dichroism spectrometer equipped with a regulated base cell.

Pyrrole-2,5-biscarboxaldehyde[24] and [$PdCl_2$(1,5-cod)] were prepared according to the previously described procedures.[25] All other chemicals used as starting materials were obtained commercially and used as received without further purification.

Preparation of pyrrole-2,5-biscarbonitrile (1): To a solution of hydroxylamine hydrochloride (13.9 g , 0.2 mol) in dry acetonitrile (350 mL) were added successively freshly distilled triethylamine (24.3 mL, 0.2 mol) and pyrrole-2,5-biscarboxaldehyde (12.3 g, 0.1 mol) at 0 °C. After the mixture had been stirred for 30 min, phthalic anhydride (29.63 g, 0.2 mol) was added slowly over a period of 15 min. The mixture was then warmed to room temperature and refluxed overnight. The solvent was removed under reduced pressure, and the brown mixture added to cold dichloromethane and filtered. The filtrates were washed with an aqueous solution of ammonia (5 %), and the combined organic layers were then dried over $MgSO_4$. After removal of the solvent, the brownish residue was purified by flash chromatography using ethyl acetate as eluent, and the desired product was obtained as a yellow solid (7.03 g, 0.06 mol; 60 %). ^{1}H NMR ($CDCl_3$, 300 MHz): $\delta = 10.35$ (br s, 1H; NH_{pyrr}), 6.90 ppm (d, 2H; $H_{3/4pyrr}$); {^{1}H}^{13}C NMR ($CDCl_3$, 75 MHz): $\delta = 134.37$ ($C_{2/5pyrr}$), 123.61 (C≡N), 119.89 ppm ($C_{3/4pyrr}$); IR (KBr disk): $\tilde{\nu} = 2232$ (s), 1676 (m), 1514 (m), 1296 (s), 1195 (s), 814 (s), 632 (m), 495 (m) cm^{-1}; MS: m/z: 117 $[M]^+$, 91 $[M-CN]^+$, 65 $[M-2CN]^+$; elemental analysis calcd (%) for $C_6H_3N_3$ (117.11): C 61.54, H 2.58, N 35.88; found C 61.35, H, 2.77 N 35.67.

Preparation of (*S*,*S*)-bis[2-(4-diisopropyl-4,5-dihydrooxazolyl)]pyrrole ["(*S*,*S*-iproxpH)"] (2a) and (*R*,*R*)-bis[2-(4-diisopropyl-4,5-dihydrooxazolyl)]pyrrole ["(*R*,*R*-iproxpH)"] (2b): $ZnCl_2$ (582 mg, 8.54 mmol) was melted in vacuo and then cooled under an atmosphere of nitrogen. A slurry of pyrrole-2,5-biscarbonitrile (1.00 g, 8.54 mmol) and (*R*)- or (*S*)-valinol (2.465 g, 23.9 mmol) in chlorobenzene (25 mL) was added and the reaction mixture was subsequently stirred under reflux for 12 h. The solvent was removed in vacuo and the orange-brown residue chromatographed on silica gel using a 1:1 ethyl acetate/hexane mixture ($R_f = 0.35$) as eluent. The chiral ligand precursors (*S*,*S*)-bis[2-(4,4′-diisopropyl-4,5-dihydrooxazolyl)]pyrrole and (*R*,*R*)-bis[2-(4,4′-diisopropyl-4,5-dihydrooxazolyl)]pyrrole were isolated as off-white, microcrystalline solids in an average yield of 68 %. ^{1}H NMR (300 MHz, $CDCl_3$, 295 K): $\delta = 11.40$ (br s, 1H; NH_{pyrr}), 6.73 (s, 2H; $H_{3/4\,pyrr}$), 4.40 (m, 2H; CH_{2oxa}), 4.10 (m, 2H; CH_{2oxa} and CH_{oxa}), 1.81 (sept, 2H; CH_{iPr}), 1.00 (d, 6H; CH_{3iPr}), 0.92 ppm (d, 6H; CH_{3iPr}); {^{1}H}^{13}C NMR (75 MHz, $CDCl_3$, 295 K): $\delta = 156.15$ (C=N_{oxa}), 122.45 ($C_{2/5pyrr}$), 111.93 ($C_{3/4pyrr}$), 72.41 (CH_{oxa}), 70.36 (CH_{2oxa}), 33.02 (CH_{iPr}), 18.82 (CH_{3oxa}), 18.40 ppm (CH_{3oxa}); IR (KBr disk): $\tilde{\nu} = 2962$ (s), 1658 (s), 1500 (w), 1359 (m), 1264 (m), 981 (m) 908 (s), 734 (s) cm^{-1}; MS: m/z: 289 $[M]^+$, 246 $[M-i\mathrm{Pr}]^+$, 203 $[M-2i\mathrm{Pr}]^+$, 113 $[M-i\mathrm{Pr}-\mathrm{Oxa}]^+$; elemental analysis calcd (%) for $C_{16}H_{23}N_3O_2$ (289.37): C 66.41, H 8.01, N 14.52; found: C 65.62, H 8.27, N 14.58; $[\alpha]_D^{20}$ (**2a**) = −42.0; $[\alpha]_D^{20}$ (**2b**) = +44.6.

Preparation of [Pd_2{(*S*,*S*)-iproxp}Cl_2] (3a and 3b) and [Pd_2{(*R*,*R*)-iproxp}Cl_2] (4a and 4b): A solution of (*S*,*S*)-bis[2-(4,4′-diisopropyl-4,5-dihydrooxazolyl)]pyrrole (**2a**) (0.155 g, 0.54 mmol) in Et_2O (10 mL) was cooled under a nitrogen atmosphere to −78 °C. A 1.6 M solution of *n*BuLi in hexane (0.35 mL) was added and the mixture and stirred at this temperature for half an hour until a white suspension appeared. A suspension of [$PdCl_2$(1,5-cod)] (0.167 g, 0.58 mmol) in diethyl ether (15 mL) was then added with a cannula at −78 °C. After the addition was completed, the dry ice bath was immediately removed, the reaction mixture warmed to room temperature and then stirred overnight. The reaction mixture was then filtered and the solvent removed in vacuo. The orange residue was subjected to column chromatography (silica gel; CH_2Cl_2). Diastereomer **3a** appeared first ($R_f = 0.53$) and was isolated as an orange solid (53 mg; 11 % yield). The second orange band corresponded to diastereomer **3b** ($R_f = 0.29$) and was also isolated as an orange solid (231 mg; 48 % yield). The analogous procedure was employed in the synthesis of [Pd_2{(*R*,*R*)-iproxp}Cl_2] (**4a** and **4b**) using (*R*,*R*)-bis[2-(4,4′-diisopropyl-4,5-dihydrooxazolyl)]pyrrole (**2b**). Workup and the yield of the isolated complexes were the same.

3a,**4a**: ^{1}H NMR (500 MHz, C_6D_6; 295 K): $\delta = 6.68$ (d, 2H; $H_{3/4pyrr}$), 6.60 (d, 2H; $H_{3/4pyrr}$), 4.49 (m, 6H; CH_{2oxa}), 4.33 (m, 2H; CH_{2oxa}), 4.05 (m, 2H; CH_{2oxa}), 3.87 (m, 2H; CH_{2oxa}), 2.29 (sept, 2H; CH_{iPr}), 2.27 (sept, 2H; CH_{iPr}), 1.14 (d, 6H; CH_{3iPr}), 1.10 (2 d, 6H; CH_{3iPr}), 0.87 (d, 6H; CH_{3iPr}), 0.81 ppm (d, 6H; CH_{3iPr}); {^{1}H}^{13}C NMR (100 MHz, C_6D_6, 295 K): $\delta = 169.16$ ($C_{2/5pyrr}$), 166.98 ($C_{2/5pyrr}$), 131.65 (O−C=N_{oxa}), 130.89 (O−C=N_{oxa}), 117.31 ($C_{3/4pyrr}$), 113.00 ($C_{3/4pyrr}$), 72.13 (CH_{oxa}), 70.85 (CH_{2oxa}), 69.82 (CH_{2oxa}), 65.86 (CH_{oxa}), 30.72 (CH_{iPr}), 29.20 (CH_{iPr}), 20.35 (CH_{3iPr}), 18.37 (CH_{3iPr}), 16.71 (CH_{3iPr}), 14.03 ppm (CH_{3iPr}); IR (KBr disk): $\tilde{\nu} = 2961$ (m), 2959 (m), 1638 (s), 1636 (s), 1529 (s), 1526 (s), 1396 (vs), 1393 (vs), 717 (m), 715 (m) cm^{-1}; elemental analysis calcd (%) for $C_{32}H_{44}Cl_2N_6O_4Pd$ (860.48): C 44.67, H 5.15, N 9.77; found: C 44.33, H 5.02, N 9.84; MS (FAB): $[M+H]^+$ 861, $[M-Cl]^+$ 825, $[M-2Cl]^{2+}$ 394; $[\alpha]_D^{20}$ (**3a**) = −34.3; $[\alpha]_D^{20}$ (**3b**) = +542.0.

3b,**4b**: ^{1}H NMR (500 MHz, C_6D_6; 295 K): $\delta = 7.08$ (d, 2H; $H_{3/4pyrr}$), 6.90 (d, 2H; $H_{3/4pyrr}$), 4.27 (m, 2H; CH_{2oxa}), 4.00 (m, 2H; CH_{2oxa}), 3.80 (m, 4H; CH_{2oxa}), 3.51 (m, 4H; CH_{2oxa}), 2.20 (sept, 2H; CH_{iPr}), 1.52 (sept, 2H; CH_{iPr}), 1.50 (d, 6H; CH_{3iPr}), 0.62 (2 d, 12H; CH_{3iPr}), 0.38 ppm (d, 6H; CH_{3iPr}); {^{1}H}^{13}C NMR (100 MHz, C_6D_6; 295 K): $\delta = 169.12$ ($C_{2/5pyrr}$), 168.96 ($C_{2/5pyrr}$), 134.18 (O−C=N_{oxa}), 132.47 (O−C=N_{oxa}), 117.94($C_{3/4pyrr}$), 113.02 ($C_{3/4pyrr}$), 74.43 (CH_{oxa}), 72.46 (CH_{2oxa}), 72.09 (CH_{2oxa}), 65.43 (CH_{oxa}), 32.91 (CH_{iPr}), 30.69 (CH_{iPr}), 22.18 (CH_{3iPr}), 18.95 (CH_{3iPr}), 18.76 (CH_{3iPr}), 18.08 ppm (CH_{3iPr}); IR (KBr disk): $\tilde{\nu} = 2961$ (m), 2959 (m), 1634 (s), 1631 (s), 1531 (s), 1530 (s), 1400 (vs), 1395 (vs), 733 (m), 731 (m) cm^{-1}; MS (FAB): $[M+H]^+$ 861, $[M-Cl]^+$ 825, $[M-2Cl]^{2+}$ 394; $[\alpha]_D^{20}$ (**4a**) = +38.5; $[\alpha]_D^{20}$ (**4b**) = −537.1.

5: ^{1}H NMR (300 MHz, $CDCl_3$; 295 K): $\delta = 6.69$ (d, 1H; $H_{3/4\ pyrr}$), 6.67 (d, 1H; $H_{3/4pyrr}$), 6.63 (d, 1H; $H_{3/4pyrr}$), 6.61 (d, 1H; $H_{3/4pyrr}$), 4.66–4.30 (m, 8H; CH_{2oxa}), 4.09–3.83 (m, 4H; CH_{2oxa}), 3.49 (sept, 1H; CH_{iPr}), 2.81 (sept, 1H; CH_{iPr}), 2.53 (sept, 1H; CH_{iPr}), 2.02 (sept, 1H; CH_{iPr}), 1.32 (d, 3H; CH_{3iPr}), 1.21 (2 d, 3H; CH_{3iPr}), 1.01 (d, 3H; CH_{3iPr}) 0.86–0.77 ppm (m, 15H; CH_{3iPr}); {^{1}H}^{13}C NMR (75 MHz, $CDCl_3$, 295 K): $\delta = 168.40$ ($C_{2/5pyrr}$), 168.30 ($C_{2/5pyrr}$), 168.88 ($C_{2/5pyrr}$), 168.22 ($C_{2/5pyrr}$), 133.29 (O−C=N_{oxa}), 132.49 (O−C=N_{oxa}), 132.17 (O−C=N_{oxa}), 131.95 (O−C=N_{oxa}), 117.43 ($C_{3/4pyrr}$), 115.89 ($C_{3/4pyrr}$), 112.72 ($C_{3/4pyrr}$), 112.50 ($C_{3/4pyrr}$), 72.43 (CH_{2oxa}), 72.24 (CH_{2oxa}), 71.27 (CH_{2oxa}), 71.13 (CH_{2oxa}), 66.39 (CH_{oxa}), 65.16 (CH_{oxa}), 64.61 (CH_{oxa}), 64.58 (CH_{oxa}), 32.55 (CH_{iPr}), 32.19 (CH_{iPr}), 30.57 (CH_{iPr}), 30.46 (CH_{iPr}), 22.11 (CH_{3iPr}), 21.81 (CH_{3iPr}), 19.66 (CH_{3iPr}), 19.26 (CH_{3iPr}), 18.83 (CH_{3iPr}), 18.10 (CH_{3iPr}), 17.44 (CH_{3iPr}), 15.29 (CH_{3iPr}); MS (FAB): $[M+H]^+$ 861, $[M-Cl]^+$ 825, $[M-2Cl]^{2+}$ 394.

Kinetic study of the interconversion of 3a,4a and 3b,4b: A predetermined amount of complex **3b** was dissolved in [D_8]toluene (420 μL) and then transferred to an NMR tube. The kinetic experiments were performed on a Bruker AC 300 NMR spectrometer pre-heated to the desired temperature. The reaction order was determined by varying the complex concentrations between 1.38×10^{-2} mol L^{-1} and 3.87 mol L^{-1}, while the activation param-

  0947-6539/02/0818-4316 $ 20.00+.50/0 *Chem. Eur. J.* **2002**, *8*, No. 18

eters were derived from a series of experiment using 1.38×10^{-2} mol L^{-1} solutions of **3b**. For the latter, the reaction temperature was varied between 70 and 105 °C. The relative amount of the different diastereomers were determined by NMR integration with the pyrrole ring signals serving as a probe.[26]

X-ray crystallographic study of 3a, 3b, 4a, 4b and 5: Suitable crystals of the complexes **3a**, **3b**, **4a**, **4b** and **5** were obtained by layering concentrated solutions of the compounds in dichloromethane with hexane and allowing slow diffusion at room temperature. The crystal data were collected on a Nonius Kappa CCD diffractometer at −100 °C and transfered to a DEC Alpha workstation; for all subsequent calculations the Nonius OpenMoleN package was used.[27] The structures were solved using direct methods with absorption corrections being part of the scaling procedure of the data reductions. After refinement of the heavy atoms, difference Fourier maps revealed the maxima of residual electron density close to the positions expected for the hydrogen atoms; they were introduced as fixed contributors in the structure-factor calculations with fixed coordinates (C–H: 0.95 Å) and isotropic temperature factors ($B(H) = 1.3\,B_{eqv}(C)$ Å^2) but not refined. Full least-square refinements on F^2 were carried out. A final difference map revealed no significant maxima of electron density. The scattering-factor coefficients and the anomalous dispersion coefficients were take from reference [28]. Crystal data and experimental details for the crystals of **3a**, **3b**, **4a**, **4b** and **5** are given in Table 3.

CCDC-183845 – CCDC-183849 the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.can.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Center, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: (+44) 1223-336033; or deposit@ccdc.cam.ac.uk).

Acknowledgements

We thank the CNRS (France), the Institut Universitaire de France and the Ministère de l'Education Nationale, de la Recherche et de la Technologie (Ph. D. grant for C.M.) for funding. We are grateful to Dr. André De Cian and N. Gruber for X-ray diffraction studies and Dr. J.-A. Bousquet for help with the CD measurements.

[1] A. Werner, *Neuere Anschauungen auf dem Gebiete der Anorganischen Chemie*, 3rd ed., Vieweg, Braunschweig, **1913**.

[2] a) A. von Zelewsky, *Stereochemistry of Coordination Compounds*, Wiley, Chichester, **1996**; b) L. H. Gade, *Koordinationschemie*, Wiley-VCH, **1998**.

[3] C. M. Harris, E. D. McKenzie, *J. Chem. Soc. (A)* **1960**, 746.

[4] a) J. M. Lehn, A. Rigaut, J. Siegel, J. Harrowfield, B. Chevrier, D. Moras, *Proc. Natl. Acad. Sci. USA* **1987**, *84*, 2565; b) C. Piguet, G. Bernandinelli, A. F. Williams, *Inorg. Chem.* **1989**, *28*, 2920; c) E. C. Constable, S. M. Elder, J. Healy, M. D. Ward, D. A. Tocher, *J. Am; Chem. Soc.* **1990**, *112*, 4590; d) C. R. Woods, M. Benaglia, F. Cozzi, J. S. Siegel, *Angew. Chem.* **1996**, *108*, 1977; *Angew. Chem. Int. Ed. Engl.* **1996**, *35*, 1830; e) B. Hasenkopf, J. M. Lehn, *Helv. Chim. Acta* **1996**, *79*, 1643; g) J. W. Canary, C. S. Allen, J. M. Castagnetto, Y. Wang, *J. Am. Chem. Soc.* **1995**, *115*, 8484; h) A. Thompson, D. Dolphin, *J. Org. Chem.* **2000**, *65*, 7870; i) A. F. Williams, *Chem. Eur. J.* **1997**, *1*, 15.

[5] a) E. C. Constable, *Tetrahedron* **1992**, *48*, 10013; b) C. Piguet, G. Bernardinelli, G. Hopfgartner, *Chem. Rev.* **1997**, *97*, 2005; c) M. Albrecht, *Chem. Rev.* **2001**, *101*, 3457; d) U. Knof, A. von Zelewsky, *Angew. Chem.* **1999**, *111*, 312; *Angew. Chem. Int. Ed.* **1999**, *38*, 302.

[6] W. Zarges, J. Hall, J. M. Lehn, C. Bolm, *Helv. Chim. Acta* **1991**, *74*, 1843.

[7] a) F. R. Keene, *Coord. Chem. Rev.* **1997**, *166*, 121; b) R. Krämer, J. M. Lehn, A. De Cian, J. Fischer, *Angew. Chem.* **1993**, *105*, 764; *Angew. Chem. Int. Ed. Engl.* **1993**, *32*, 703; c) L. J. Charbonnière, G. Bernardinelli, C. Piguet, A. M. Sargesson, A. F. Williams, *Chem. Commun.* **1994**, 1419; d) G. Rapenne, B. T. Patterson, J. P. Sauvage, F. R. Keene, *Chem. Commun.* **1999**, 1853;

[8] a) H. Mürner, P. Besler, A. von Zelewsky, *J. Am. Chem. Soc.* **1996**, *118*, 7989; b) H. Mürner, A. von Zelewsky, H. Stoeckli-Evans, *Inorg. Chem.* **1996**, *35*, 3931; c) N. C. Fletcher, F. R. Keene, H. Viebrock, A. von Zelewsky, *Inorg. Chem.* **1997**, *36*, 1113; d) V. Amenola, L. Fabbrizzi, C. Mangano, P. Palavicini, E. Roboli, M. Zema, *Inorg. Chem.* **2000**, *39*, 5803; e) E. C. Constable, T. Kulke, M. Neuburger, M. Zehnder, *Chem. Commun.* **1997**, 489; f) G. Baum, E. C. Constable, D. Fenske, C. E. Housecroft, T. Kulke, *Chem. Commun.* **1999**, 195; g) C.

Table 3. Crystal data and structure refinement for compounds **3a**, **3b**, **4a**, **4b**, and **5**.

	3a	**3b**	**4a**	**4b**	**5**
formula	$C_{16}H_{22}ClN_3O_2Pd \cdot 0.33(CH_2Cl_2)$	$C_{32}H_{44}Cl_2N_6O_4Pd_2$	$C_{32}H_{44}Cl_2N_6O_4Pd_2$	$C_{32}H_{44}Cl_2N_6O_4Pd_2$	$C_{32}H_{44}Cl_2N_6O_4Pd_2$
M_r	860.45	860.45	860.45	860.45	860.45
crystal system	hexagonal	monoclinic	orthorhombic	monoclinic	triclinic
space group	$R3_2$	$C2$	$P2_12_12_1$	$C2$	$P\bar{1}$
a [Å]	19.0320(4)	25.320(1)	11.4445(2)	25.2181(7)	11.2314(2)
b [Å]	19.0320(4)	15.0837(3)	17.2729(3)	15.0284(4)	11.6406(3)
c [Å]	29.773(1)	10.2581(4)	17.6671(3)	10.2092(3)	14.1114(3)
α [°]	90	–	–	–	74.897(5)
β [°]	90	111.104(4)	–	111.055(2)	84.300(5)
γ [°]	120	–	–	–	82.776(5)
V [Å^3]	9339.4(4)	3655.0(2)	3492.4(1)	3610.8(2)	1762.79(7)
Z	6	4	4	4	2
ρ_{calcd} [g cm^{-3}]	1.47	1.56	1.64	1.58	1.62
radiation (λ [Å])	$Mo_{K\alpha}$ (0.71073)	$Mo_{K\alpha}$ (0.71073)	$Mo_{K\alpha}$ (0.71073)	$Mo_{K\alpha}$ (0.71073)	$Mo_{K\alpha}$ (0.71073)
μ [mm^{-1}]	1.121	1.173	1.228	1.187	1.216
F(000)	4176	1744	1744	1744	872
crystal size [mm]	$0.10 \times 0.10 \times 0.08$	$0.12 \times 0.10 \times 0.10$	$0.20 \times 0.10 \times 0.03$	$0.18 \times 0.14 \times 0.14$	$0.20 \times 0.20 \times 0.10$
θ range [°]	2.5 – 27.47	2.5 – 27.47	2.5 – 30.03	2 – 30.02	2.5 – 27.50
reflections collected	7827	7533	10051	9354	11012
independent reflections	2605	4226	5667	5465	4900
data/restraints/parameters	1943/8/199	3553/1/414	4039/0/415	4359/1/414	4900/0/415
S on F^2	1.617	1.009	1.247	1.043	1.028
final R indices[a] $[I > 3\sigma(I)]$					
R_1	0.055	0.026	0.030	0.031	0.039
wR_2	0.092	0.027	0.069	0.042	0.056
max/min $\Delta\rho$ [e Å^{-3}]	0.200/ – 0.178	0.228/ – 0.062	0.724/ – 0.235	0.784/ – 0.087	0.939/ – 0.304

[a] $S = [\Sigma w(F_o^2 - F_c^2)^2/(n-p)]^2$ where n = number of reflections and p = total number of parameters, $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$, $wR_2 = \Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]^2$, $w^{-1} = [R^2(F_o)^2 + (aP)^2 + bP]$, $P = [\max(F_o^2, 0) + 2(F_c^2)]/3$.

  0947-6539/02/0818-4317 $ 20.00+.50/0

Provent, S. Hewage, G. Brand, G. Bernardinelli, L. J. Charbonnière, A. F. Williams, *Angew. Chem.* **1997**, *109*, 1346; *Angew. Chem. Int. Ed.* **1997**, *36*, 1287; h) O. Mamula, A. von Zelewsky, G. Bernardinelli, *Angew. Chem.* **1998**, *110*, 301; *Angew. Chem. Int. Ed.* **1998**, *37*, 290; M. A. Masood, E. J. Enemark, T. D. P. Stack, *Angew. Chem.* **1998**, *110*, 973; *Angew. Chem. Int. Ed.* **1998**, *37*, 928; i) P. N. Baxter, J. M. Lehn, K. Rissanen, *Chem. Commun.* **1997**, 1323.

[9] C. Mazet, L. H. Gade, *Organometallics* **2001**, *20*, 4144.

[10] H. Nishiyama, H. Sakagushi, T. Nakamura, M. Horihata, M. Kondo, K. Itoh, *Organometallics* **1989**, *8*, 846.

[11] a) H. Nishiyama, M. Kondo, T. Nakamura, K. Itoh, *Organometallics* **1991**, *10*, 500; b) D. A. Evans, M. C. Kozlowski, J. A. Murry, C. S. Burgey, K. R. Campos, B. T. Connell, R. J. Staples, *J. Am. Chem. Soc.* **1999**, *121*, 669; c) D A. Evans, C. S. Burgey, M. C. Kozlowski, S. W. Tregay, *J. Am. Chem. Soc.* **1999**, *121*, 686; d) D. A. Evans, D. M. Barnes, J. S. Johnson, T. Lectka, P. von Matt, S. J. Miller, J. A. Murry, R. D. Norcross, E. A. Shaughnessy, K. R. Campos , *J. Am. Chem. Soc.* **1999**, *121*, 7582; e) D. A. Evans, Z. K. Sweeney, T. Rovis, J. S. Tedron, *J. Am. Chem. Soc.* **2001**, *123*, 12095; f) H. Nishiyama, Y. Itoh, H. Matsumoto, K. Itoh, *J. Am. Chem. Soc.* **1994**, *116*, 2223; g) H. Nishiyama, Y. Itoh, Y. Sugawara, H. Matsumoto, K. Aoti, K. Itoh, *Bull. Chem. Soc. Jpn.* **1995**, *68*, 1247; h) Y. Motoyama, K. Murata, O. Kurihara, T. Naitoh, K. Aoki, H. Nishiyama, *Organometallics* **1998**, *17*, 1251; i) H. Nishiyama, T. Naitoh, Y. Motoyama, K. Aoki, *Chem. Eur. J.* **1998**, *5*, 3509.

[12] a) Y. Motoyama, N. Makihara, Y. Mikami, K. Aoki, H. Nishiyama, *Chem. Lett.* **1997**, 951; b) Y. Motoyama, H. Narusawa, H. Nishiyama, *Chem. Commun.* **1999**, 131; c) Y. Motoyama, N. Makihara, Y. Mikami, K. Aoki, H. Nishiyama, *Organometallics* **1999**, *18*, 3584; d) Y. Motoyama, Y. Koga, H. Nishiyama, *Tetrahedron* **2001**, *53*, 853; e) Y. Motoyama, H. Okano, H. Narusawa, N. Makihara, K. Aoki, H. Nishiyama, *Organometallics* **2001**, *20*, 1580; f) S. E. Denmark, R. A. Stavenger, A. M. Faucher, J. P. Edwards, *J. Org. Chem.* **1997**, *62*, 3375; g) M. A. Stark, C. J. Richards, *Tetrahedron Lett.* **1997**, *38*, 5881; h) M. A. Stark, G. Jones, C. J. Richards, *Organometallics* **2000**, *19*, 1282.

[13] A helical dinuclear palladium complex was reported by: E. C. Constable, S. M. Elder, J. Healy, M. D. Ward, *J. Am. Chem. Soc.* **1990**, *112*, 4590.

[14] a) F. Fache, E. Schulz, L. Tommasino, M. Lemaire, *Chem. Rev.* **2000**, *100*, 2159; b) A. K. Ghosh, P. Mathivanan, J. Cappiello, *Tetrahedron Asymmetry* **1998**, *9*, 1; c) M. Gomez, G. Muller, M. Rocamora, *Coord. Chem. Rev.* **1999**, *193,* 769.

[15] a) C. Bolm, K. Weickhardt, M. Zehnder, D. Glasmacher, *Helv. Chim. Acta* **1991**, *74*, 717; b) C. Bolm, K. Weickhardt, M. Zehnder, T. Ranff, *Chem. Ber.* **1991**, *124*, 1173.

[16] G. H. Barnett, H. J. Anderson, C. E. Loader, *Can. J. Chem.* **1980**, *58*, 409.

[17] E. C. Whang, G. J. Lin, *Tetrahedron Lett.* **1998**, *39*, 4047.

[18] a) C. Piguet, G. Bernardinelli, B. Bocquet, A. Quattropani, A. F. Williams, *J. Am. Chem. Soc.* **1992**, *114*, 7440; b) E. C. Constable, *Prog. Inorg. Chem.* **1994**, *42*, 67; c) C. Piguet, G. Hopfgartner, A. F. Williams, J.-C. G. Bünzli, *J. Chem. Soc. Chem. Commun.* **1995**, 491; d) C. Piguet, C. Rivara-Minten, G. Hopfgartner, J.-C. G. Bünzli, *Helv. Chim. Acta* **1995**, *78*, 1541; e) D. M. L. Goodgame, S. P. W. Hill, D. J. Williams, *J. Chem. Soc. Chem. Commun.* **1993**, 1019; f) M. Barley, E. C. Constable, S. Corr, R. C. S. McQueen, J. C. Nutkins, M. D. Ward, *J. Chem. Soc. Dalton Trans.* **1988**, 2655.

[19] a) J. H. van't Hoff, *Die Lagerung der Atome im Raume*, Vieweg, Braunschweig, **1894**, p. 119; b) W. Kuhn in *Stereochemie* (Ed. K. Freudenberg), Franz Deuticke, Leipzig **1933**, pp. 394, 423.

[20] E. L. Eliel, S. H. Wilen, L. N. Mander, *Stereochemistry of Organic Compounds*, Wiley, New York, **1994**, p. 1080.

[21] G. Baum, E. C. Constable, D. Fenske, C. E. Housecroft, T. Kulke, *Chem. Eur. J.* **1999**, *5*, 1862.

[22] M. Ziegler, A. von Zelewsky, *Coord. Chem. Rev.* **1998**, *177*, 257.

[23] K. W. Hellmann, L. H. Gade, *Verfahrenstechnik (Berlin)* **1997**, *31*, 70.

[24] a) K. Olsson, P.-Å. Pernemalm, *Acta Chem. Scand. B* **1979**, *33*, 125; b) R. Miller, K. Olsson, *Acta Chem. Scand. B* **1981**, *35*, 303.

[25] D. Drew, J. R. Doyle, *Inorg. Synth.* **1972**, *13*, 47.

[26] R. G. Wilkins, *Kinetics and Mechanism of Reactions of Transition Metal Complexes*, VCH, Weinheim, **1991**.

[27] Nonius OpenMoleN, Interactive Structure Solution, Delft, **1997**.

[28] D. T. Cromer, J. T. Waber, *International Tables for X-ray Crystallography*, The Kynoch Press, Birmingham, **1974**.

Received: April 19, 2002 [F4029]

  0947-6539/02/0818-4318 $ 20.00+.50/0