# Double Bonds in Motion: Bis(oxazolinylmethyl)pyrroles and Their Metal-Induced Planarization to a New Class of Rigid Chiral $C_2$-symmetric Complexes

**Clément Mazet and Lutz H. Gade*[a]**

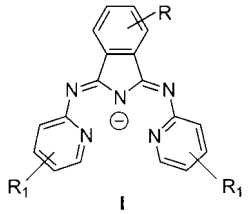
*In memory of Jacky Kress*

**Abstract:** The synthesis of a new class of chiral $C_2$-symmetric tridentate N-donor ligands, a series of 2,5-bis(2-oxazolinylmethyl)pyrroles, was achieved in four steps starting from the known 2,5-bis(trimethylammoniomethyl)pyrrole diiodide (**1**). Reaction of **1** with NaCN in dimethyl sulfoxide gave 2,5-bis(cyanomethyl)pyrrole (**2**) cleanly, which was then cyclized with amino alcohols to give the 2,5-bis(2-oxazolinylmethyl)pyrroles **3a–c** (**3a**: bis[2-(4,4′-dimethyl-5-hydrooxazolyl)methyl]pyrrole; **3b**: (*S*,*S*)-bis[2-(4-isopropyl-4,5-dihydrooxazolyl)methyl]pyrrole; **3c**: (*S*,*S*)-bis[2-(4-tertiobutyl-4,5-dihydrooxazolyl)methyl]-pyrrole). Metallation of **3a–c** with one molar equivalent of *t*BuLi and their subsequent reaction with a stoichiometric amount of $[PdCl_2(cod)]$ (cod = cyclooctadiene) gave the palladium(II) complexes **4a–c**. Whereas the arrangement of the N-donor atoms in the crystallographically characterized complex **4a** is almost ideally square planar, all three heterocycles in the ligand are twisted out of the coordination plane, leading to a chiral conformation of the complex. Attempts to freeze out these two conformers in solution at 200 K (NMR) failed, and this suggests that the activation barrier for conformational racemization is significantly below 10 kcal mol$^{-1}$. The palladium-induced shift of two double bonds as well as the porphyrinogen/porphyrin-type oxidation of the complexes **4a–c** led to the planarization of the 2,5-bis(oxazolinylmethyl)pyrrolide ligands in the palladium(II) complexes **5a–c, 6b**, and **6c**, and to the formation of rigid chiral $C_2$-symmetric systems as shown by X-ray diffraction studies. The formation of the conjugated system of double bonds in this transformation is accompanied by the emergence of an intra-ligand chromophore. This is evident in the absorption spectrum of **6c** which displays an intense band with a maximum at 485 nm attributable to an intra-ligand $\pi^* \leftarrow \pi$ transition and a characteristic vibrational progression of $\nu \approx 1350$ cm$^{-1}$. Complexes **4b** and **4c** were tested in the catalytic asymmetric Michael addition of ethyl 2-cyanopropionate to methyl vinylketone (catalyst loading: 1 mol%) and were found to give maximum *ee* values of 43% (**4b**) and 21% (**4c**) at low conversions.

**Keywords:** N ligands · NMR spectroscopy · palladium · porphyrinoids · X-ray diffraction

## Introduction

The pyrrole unit is the building block in porphyrin and porphyrin-related coordination chemistry.[1] The unique properties of oligopyrroles may not only explain their ubiquity in nature but have inspired the synthesis and investigation of a large variety of non-biotic artificial systems.[2, 3] Whereas the macrocyclic compounds may occupy centre stage, several classes of open-chain derivatives, as well as related ligands, have been studied in recent years.[4–7] Among these related systems, the bis(2-pyridylimino)isoindoles (**I**), first prepared in the 1950s,[8] are readily accessible monoanionic tridentate ligands that have found extensive application in oxidation catalysis.[9]



**I**

Meridionally coordinating chiral tridentate N-donor ligands have attracted much attention in asymmetric catalysis.[10, 11] The point of reference in this field is Nishiyama's chiral $C_2$-symmetric 2,6-bis(2-oxazolinyl)pyridine ('pybox') ligand **II**, which nowadays belongs to the basic 'tool kit' in stereoselective catalysis (Figure 1).[12, 13] Formally charging this ligand by exchanging the central pyridine ring for a

[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) 390-241-531
E-mail: gade@chimie.u-strasbg.fr

  0947-6539/03/0908-1759 $ 20.00+.50/0 

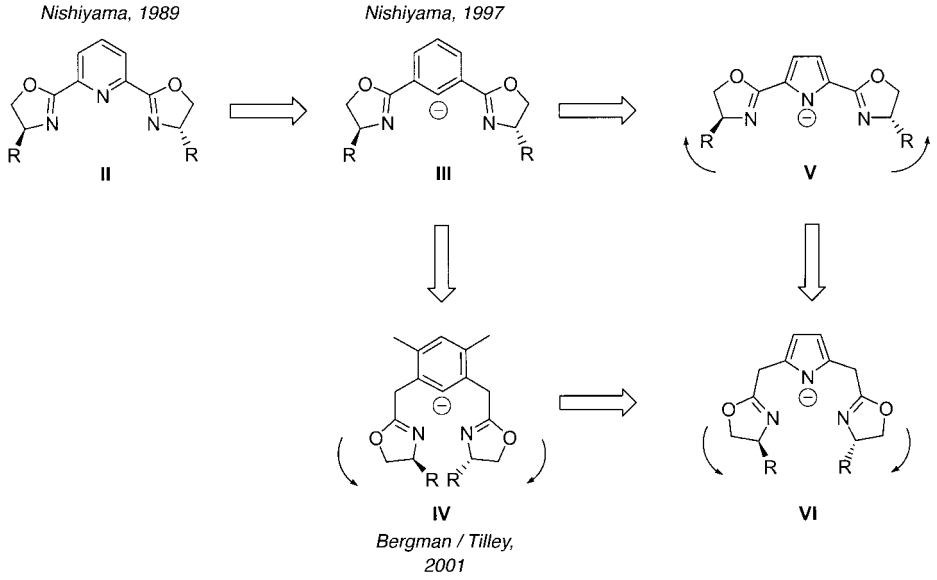



Figure 1. Charging and deforming the pybox ligand: the conceptual background and choice of the model system.

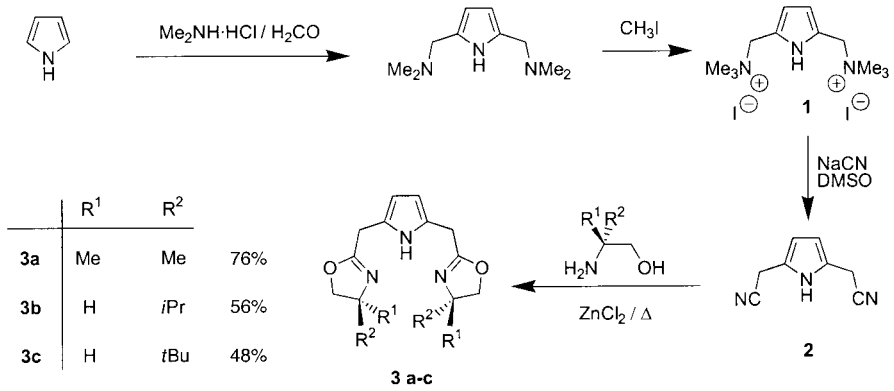
benzene ring, which is coordinated in its cyclometalated form, led to the analogous 'phebox' ligands **III** developed more recently by the same group.[14, 15] The same set of donor atoms, but in a different arrangement, is found in the 1,3-bis(2-oxazolinylmethyl)benzene derivatives **IV** that Bergman and Tilley reported very recently.[16] These are distorted analogues of 'phebox' ligand set and could lead to different coordination geometries.

We reported the synthesis of 2,5-bis(2-oxazolinyl)pyrrolides **V**, which are phebox analogues but which are distorted in the opposite sense, such that the outer N-donor functions are bent away from the charged central ligating unit (Figure 1).[17] This has led to preferential didentate coordination of this ligand or the formation of oligonuclear complexes. To regain mononuclear chiral $C_2$-symmetric complexes with a molecular geometry that is well adapted to their application in asymmetric catalytic conversions, we now report the synthesis and coordination chemistry of 2,5-bis(2-oxazolinylmethyl)pyrrolides **VI**. We will show that the presence of the 2,5-dimethylenepyrrole unit in these ligands leads to reactivity that is similar to that of open-chain oligopyrroles, of which these ligands are the chiral analogues.

## Results and Discussion

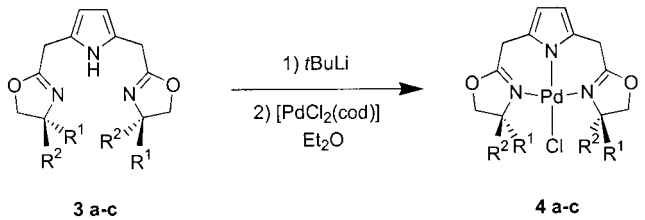
**Synthesis of 2,5-bis(2-oxazolinylmethyl)pyrroles and their coordination to palladium(II):** The 2,5-bis(2-oxazolinylmethyl)pyrroles were obtained in a four-step synthesis starting from the parent compound pyrrole (Scheme 1). The key intermediate was the 2,5-bis(trimethylammoniomethyl)pyrrole diiodide (**1**), which was obtained from the starting material by Mannich dimethylaminomethylation in the 2- and 5-positions and subsequent quaternization of the two dimethylamino groups with excess methyl iodide.[18] This strategy is based on work reported by Elsenbaumer et al. who demonstrated that the bis(trimethylammonium) derivative **1** is particularly suited to further functionalization in the $\alpha$-methylene positions by nucleophilic displacement of trimethylamine.[19] Reaction of compound **1** with NaCN in dimethyl sulfoxide gave 2,5-bis(cyanomethyl)pyrrole **2** cleanly, which was then cyclized with the appropriate amino alcohol to give the 2,5-bis(2-oxazolinylmethyl)pyrroles **3a–c**.[20]

Reaction of **3a–c** with one molar equivalent of *t*BuLi gave the corresponding lithium pyrrolides, which were then allowed to react in situ with a stoichiometric amount of $[PdCl_2(cod)]$ to give the palladium(II) complexes **4a–c** (Scheme 2). While the formulation of these complexes was confirmed by elemental analyses, the local $C_2$-symmetry of the ligands and their tridentate coordination was deduced from $^1$H NMR, $^{13}$C NMR, and IR spectroscopic data.




| | $R^1$ | $R^2$ | |
|---|---|---|---|
| **3a** | Me | Me | 76% |
| **3b** | H | *i*Pr | 56% |
| **3c** | H | *t*Bu | 48% |

Scheme 1. The four-step synthesis of the 2,5-bis(oxazolylmethyl)pyrrole ligand precursors.




| | $R^1$ | $R^2$ | |
|---|---|---|---|
| **4a** | Me | Me | 76% |
| **4b** | H | *i*Pr | 38% |
| **4c** | H | *t*Bu | 42% |

Scheme 2. Synthesis of the mononuclear palladium(II) complexes **4a–4c**.



0947-6539/03/0908-1760 $ 20.00+.50/0 *Chem. Eur. J.* **2003**, *9*, No. 8

A single-crystal X-ray analysis of compound **4a** was carried out to gain detailed insight into the molecular geometry and the way this novel ligand system binds to the metal center. Two views of its molecular structure are displayed in Figure 2, together with the principal bond lengths and interbond angles.

The coordination geometry in complex **4a** is almost square planar. The angles between mutally *trans*-disposed donor atoms are N(2)-Pd-Cl 179.74(7)° and N(1)-Pd-N(3) 172.6(1)°. This arrangement of the ligating atoms is associated with a characteristically twisted arrangement of the tridentate ligand system as a whole, as is apparent in the view along the Cl-Pd-N(2) axis which coincides with the virtual twofold molecular axis. All three heterocycles in the ligand are twisted out of the coordination plane; the dihedral angles are N(2)-C(10)-C(11)-C(12) 46.7°, C(10)-C(11)-C(12)-N(3) 53.2°, N(2)-C(7)-C(6)-C(3) 46.3, and C(7)-C(6)-C(3)-N(1) 53.9°. The planes spanned by the four donor atoms and the pyrrolide ring are inclined relative to each other by an angle of 29.7°. The overall arrangement of the tridentate ligand leads to a chiral conformation to the complex. Figure 2 displays the $\delta$ conformer of compound **4a**, in line with a generalized application of Bailar's designation of twisted chelates (Scheme 3).[21] There is a 1:1 distribution of both helically chiral conformers in the monoclinic crystal.

Attempts to freeze out these two conformers by low-temperature NMR spectroscopy were unsuccessful for all three complexes **4a–c** in solution. Even at 200 K, the spectrum of the achiral compound **4a** showed sharp singlet for the methylene proton resonance signal, not the AB system that is expected for frozen conformational chirality, which indicates an activation barrier for the conformational racemization below 10 kcal mol$^{-1}$. Similar observations were made for the chiral derivatives **4b** and **4c** at 200 K. Their $^1$H NMR spectra displayed the single AB system of the $CH_2$ protons that represents the high-temperature limit and did not coalesce or split to give the two multiplets of the frozen helical diastereomers. A potential preference of one conformer with respect to its helical diastereomer could therefore not be probed.

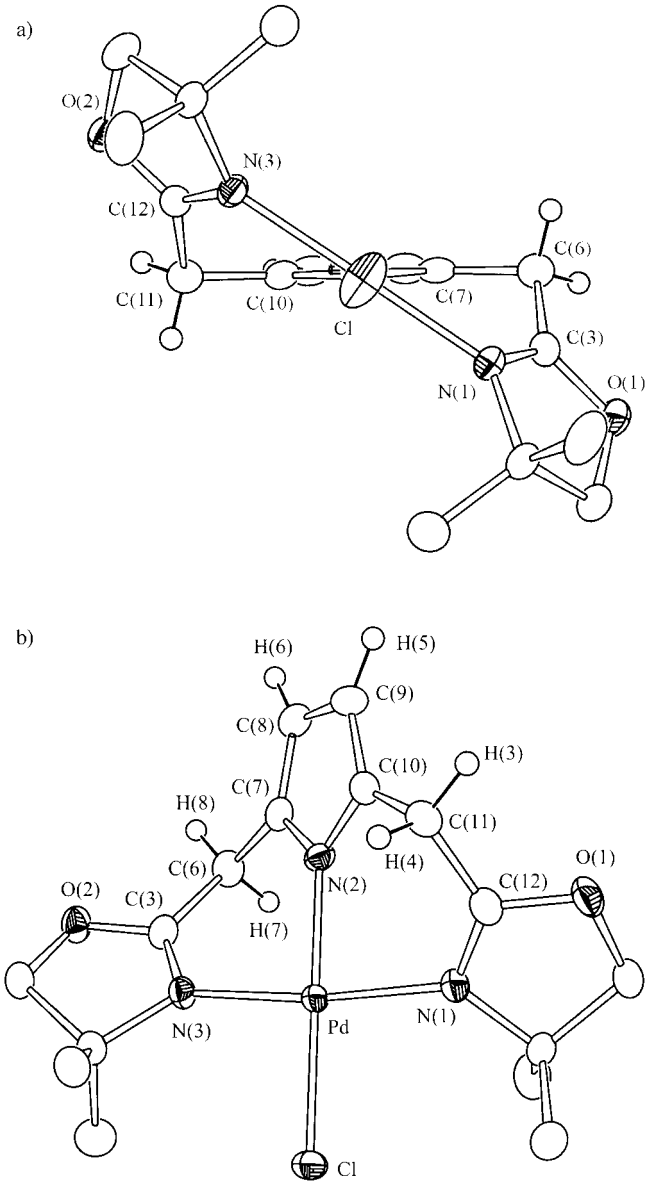
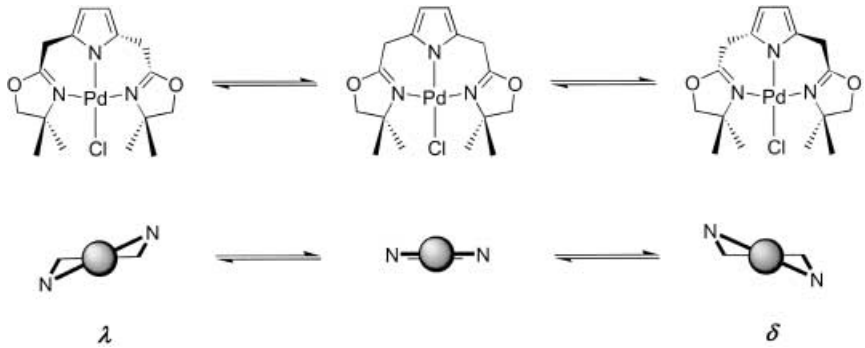


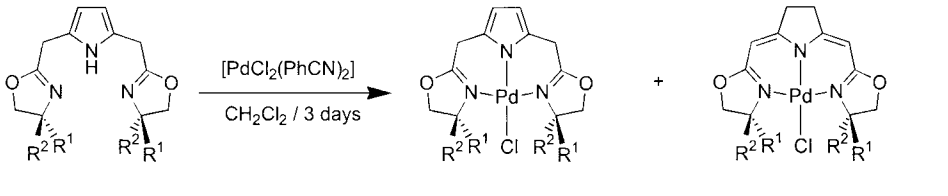

Figure 2. Two representations for the molecular structure of **4a**. Principal bond lengths [Å] and angles [°]: Pd–Cl 2.3176(9), Pd–N(1) 2.046(2), Pd–N(2) 1.995(3), Pd–N(3) 2.048(3), C(8)–C(9) 1.404(4), C(10)–C(11) 1.483(4), C(9)–C(10) 1.369(4), C(7)–C(8) 1.375(5), C(6)–C(7) 1.511(4), C(11)–C(12) 1.494(4), C(6)–C(3) 1.486(4); Cl-Pd-N(1) 94.07(7), Cl-Pd-N(2) 179.74(7), Cl-Pd-N(3) 93.33(7), N(1)-Pd-N(3) 172.6(1), C(10)-C(11)-C(3)-N(3) 53.2(5).

**The metal-induced shift of two double bonds: rearrangement and planarization of 2,5-bis(oxazolinylmethyl)pyrrolide ligands in the palladium(II) complexes**: The synthesis of the palladium(II) complexes **4a–c** described in the previous section was based on the initial lithiation of the pyrrole derivatives **3a–c** and the use of the lithium pyrrolides as ligand-transfer reagents. As an alternative route to Pd compounds without lithiation of the ligand precursor, we treated the protonated ligands **3a–c** directly with $[PdCl_2(NCPh)_2]$. This was a relatively slow reaction but complete metalation of the pyrroles was observed. However, in the conversions of **3a** and **3b**, a second reaction product was




Scheme 3. Schematic representation for the interconversion of two enantiomeric helical conformers (which is rapid on the NMR timescale).

  0947-6539/03/0908-1761 $ 20.00+.50/0 



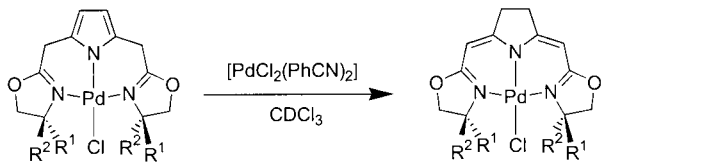

| | $R^1$ | $R^2$ | | | $R^1$ | $R^2$ | |
|---|---|---|---|---|---|---|---|
| **4a** | Me | Me | 17% | **5a** | Me | Me | 17% |
| **4b** | H | *i*Pr | 12% | **5b** | H | *i*Pr | 16% |
| **4c** | H | *t*Bu | 28% | **5b** | H | *t*Bu | 0% |

Scheme 4. Alternative synthesis of complexes **4a** and **4b** and their constitutional isomers **5a** and **5b**.

found apart from **4a** and **4b**, respectively, while the reaction of **3c** gave **4c** exclusively, albeit in moderate yield (Scheme 4).

After chromatographic workup, the two new complexes **5a** and **5b** were isolated from the product mixtures. While their $^1$H and $^{13}$C NMR spectroscopic patterns are similar to those of **4a** and **4b**, the chemical shifts of the individual signals differ markedly. Complexes **4a**–**c** display characteristic resonances for the 3- and 4-pyrrolide protons and $^{13}$C nuclei at $\delta = 5.85$–5.88 ppm and $\delta = 103.3$–104.6 ppm, respectively, as well as signals for the bridging $CH_2$ groups ($^1$H NMR: $\delta = 3.66$–3.76 ppm; $^{13}$C NMR: $\delta = 26.3$–29.1 ppm), whereas these are absent in the spectra of **5a** and **5b**. Instead, the resonances of an olefinic CH group (**5a**: $\delta = 4.94$ ppm; **5b**: $\delta = 4.99$ ppm) and a modified $CH_2$ unit (**5a**: $\delta = 2.79$ ppm; **5b**: $\delta = 2.85$ ppm) are observed. Based on these data, the structures of **5a** and **5b** were postulated (Scheme 3), which represent constitutional isomers of **4a** and **4b**. These isomeric forms are related by a formal 1,3-hydrogen shift which for **5a** and **5b** leads to a conjugated chromophore.

The relative amounts of **5a** and **5b** isolated from the reactions were found to be time-dependent (Scheme 4), and to become more abundant with time at the expense of **4a** and **4b**. To investigate whether the second isomer **5** was derived from **4** under the reaction conditions, a sample of **4a** was stirred in dichloromethane over a period of several days. Since no conversion was observed, a few milligrams of $[PdCl_2(NCPh)_2]$ were added, which induced the selective conversion of **4a** to **5a** (Scheme 5). This is not surprising since the $Pd^{II}$ reagent is only slowly consumed in the reaction with the nonmetalated bis(oxazolinylmethyl)pyrrole ligand and therefore acts as a catalyst for the conversion of **4a** to **5a** during the course of the reaction.




| | $R^1$ | $R^2$ | | | $R^1$ | $R^2$ | |
|---|---|---|---|---|---|---|---|
| **4a** | Me | Me | | **5a** | Me | Me | 100% / 11 days |
| **4c** | H | *t*Bu | | **5c** | H | *t*Bu | 100% / 7days |

Scheme 5. Pd-induced isomerization of **4a** and **4c** to **5a** and **5c**, respectively.

The isomerization was carried out at ambient temperature in an NMR tube and monitored by $^1$H NMR spectroscopy and was found to be complete after 11 days. At this stage, no trace of **4a** could be detected in the $^1$H NMR spectra above the noise level, which indicates that the ratio of **5a** to **4a** was greater than $10^3$. This amounts to a difference in free enthalpy between **5a** and **4a** of at least 4 kcal mol$^{-1}$. The thermodynamic driving force in this Pd-catalyzed conversion is clearly the generation of a planar delocalized π system in **5a**. An analogous experiment has established similar behavior in compound **5c**.

To establish the molecular structures of these isomers, an X-ray diffraction study of **5a** was carried out. Its molecular structure, along with the principal bond lengths, and interbond angles, is shown in Figure 3. A shift of the two double bonds from the pyrrole ring to the exocyclic C–C bond is evident from the elongation of the C(8)–C(9) bond (1.503(7) Å) and the contraction of the C(6)–C(7) (1.372(7) Å) and C10–C11 (1.341(8) Å) bonds relative to the analogous bond lengths in the structure of **4a** (Figure 2). The direct localization of the C-bonded hydrogen atoms in these positions confirmed the formulation of the structure.

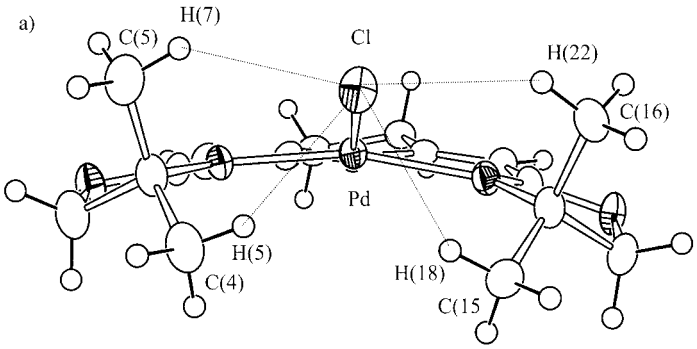
As a consequence of the rearrangement of the double bonds to the bridging methylene positions the ligand now possesses a conjugated π system and a planarized structure. This planarization induces a marked steric hindrance between the chloro ligand and the methyl substituents on the oxazoline ring. This repulsion leads to a distortion of the chloro ligand and the oxazoline ligands away from the idealized molecular plane and generates a coordination geometry which is reminiscent of the saddle-type conformation adopted by many porphyrin complexes.[1–3] The chloro ligand points out-of-plane (N(2)-Pd-Cl 160.0(2)°) and is almost equidistant with respect to the oxazoline methyl groups (Cl–C(5)/H(7) 3.362/2.607, Cl–C(16)/H(22) 3.355/2.597, Cl–C(4)/H(5) 3.286/2.502, Cl–C(15)/H(18) 3.351/2.590 Å). The strong interligand repulsion disfavors the conversion of **4a** to **5a** and thus the lower limit for the free reaction enthalpy discussed above must be interpreted with this constraint in mind. In other words, the net thermodynamic gain due to the planarization and generation of the conjugated π system is significantly greater.

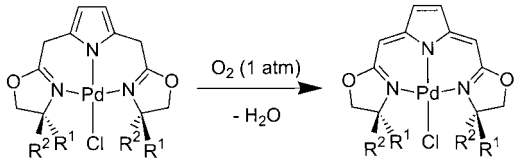
## The porphyrinogen–porphyrin analogy: oxidative planarization of the 2,5-bis(oxazolinylmethyl)pyrrolide–palladium complexes

The methylene-bridged tris-heterocyclic ligands **3a**–**3c** bear a certain resemblance to macrocyclic and open-chain oligopyrroles.[2–7] In the latter, in particular in their transition-metal complexes, there is a strong tendency to form planar ligands



0947-6539/03/0908-1762 $ 20.00+.50/0 *Chem. Eur. J.* **2003**, *9*, No. 8




| | $R^1$ | $R^2$ | |
|---|---|---|---|
| **6b** | H | *i*Pr | 100% / 14 h |
| **6c** | H | *t*Bu | 80% / 16 days |

Scheme 6. Oxidative planarization of complexes **4b** and **4c** to give the conjugated systems **6b** and **6c**, respectively.

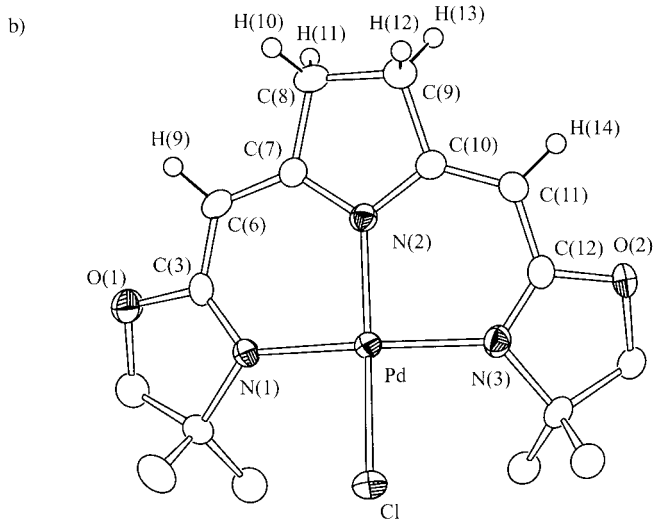



Figure 3. Two representations of the molecular structure of **5a**: a) View along the Pd–N(2) vector showing the repulsion between the chloro ligand and the methyl substituents on the oxazoline rings; b) view orthogonal to the idealized molecular plane. Principal bond lengths [Å] and angles [°]: Pd–N(1) 2.030(4), Pd–N(2) 2.022(4), Pd–N(3) 2.047(4), Pd–Cl 2.328(4), C(8)–C(9) 1.503(7), C(6)–C(7) 1.372(7), C(10)–C(11) 1.341(8); N(1)-Pd-N(3) 165.3(1), N(1)-Pd-N(2) 91.0(2), N(2)-Pd-N(3) 90.4(2), N(2)-Pd-Cl 160.0(2), C(10)-C(11)-C(12)-N(3) 13.6(4).

that are characterized by conjugated π systems which are generally formed by oxidation of the $CH_2$ bridges between the rings. This is the principle of the porphyrinogen–porphyrin conversion, a key step, which is generally induced by atmospheric oxygen, in the synthesis of porphyrins.[1] In view of this well established pattern of reactivity it was of interest to us to investigate the oxidation of the complexes **4a**–**4c** in air.

Whereas complex **4a** was unreactive towards oxidation with $O_2$, the chiral complexes **4b** and **4c** were cleanly converted to their planarized oxidation products **6b** and **6c**, respectively (Scheme 6). This transformation was accompanied by a change of color from yellow to orange-red which was monitored by UV/Vis spectroscopy. Monitoring the reaction by $^1$H NMR spectroscopy established the concomitant formation of $H_2O$ as the second reaction product. A series of absorption spectra recorded during the reaction of a solution of **4b** under an atmosphere of $O_2$ (1 bar) is shown in Figure 4.

The starting material **4b** displays a relatively featureless absorption spectrum in the visible region, with the long wavelength tailing of the metal–ligand charge transfer (MLCT) absorption band at 375 nm ($\lg(\varepsilon) = 2.60$) being responsible for the yellow color. This MLCT absorption band experiences a significant increase in intensity (hyperchromic effect: $\lg(\varepsilon) = 3.06$ with a maximum at 368 nm) upon conversion to the oxidized complex **6b**, and an intense band, which is assigned to an intraligand $\pi^* \leftarrow \pi$ transition in the conjugated planarized ligand, increases in intensity at 485 nm. This $\pi^* \leftarrow \pi$ band displays a characteristic vibrational progression of $\nu \approx 1350\ cm^{-1}$.

The details of the molecular structure of complex **6b** were established by an X-ray diffraction study. Two representations of the molecule are depicted in Figure 5 along with the principal bond lengths and interbond angles. The view along the Cl-Pd-N(2) vector in Figure 5a shows the almost ideal planarity of the ring system, the two isopropyl groups pointing in opposite directions, the methyl groups of which are oriented away from the bulky chloro ligand. In contrast to the structure of **5a**, the planarization of **6b** leads to a virtually

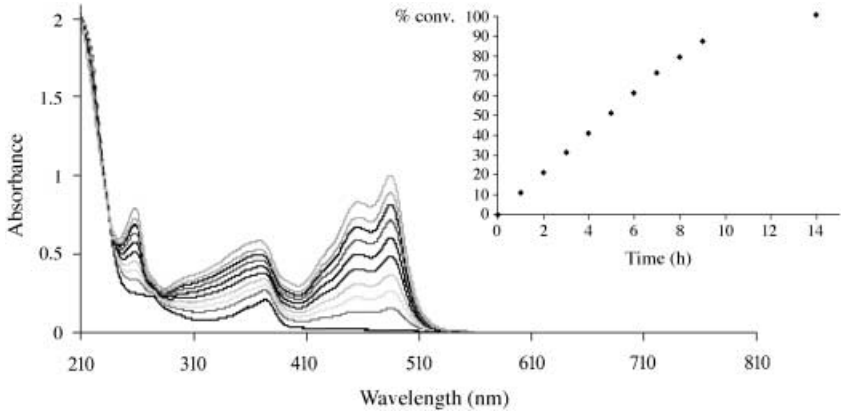



Figure 4. UV/Vis absorption spectra showing the progressive conversion of **4b** into **6b** (recorded in $CH_3CN$, concentration $5 \times 10^{-4}\ mol\,L^{-1}$).

  0947-6539/03/0908-1763 $ 20.00+.50/0 

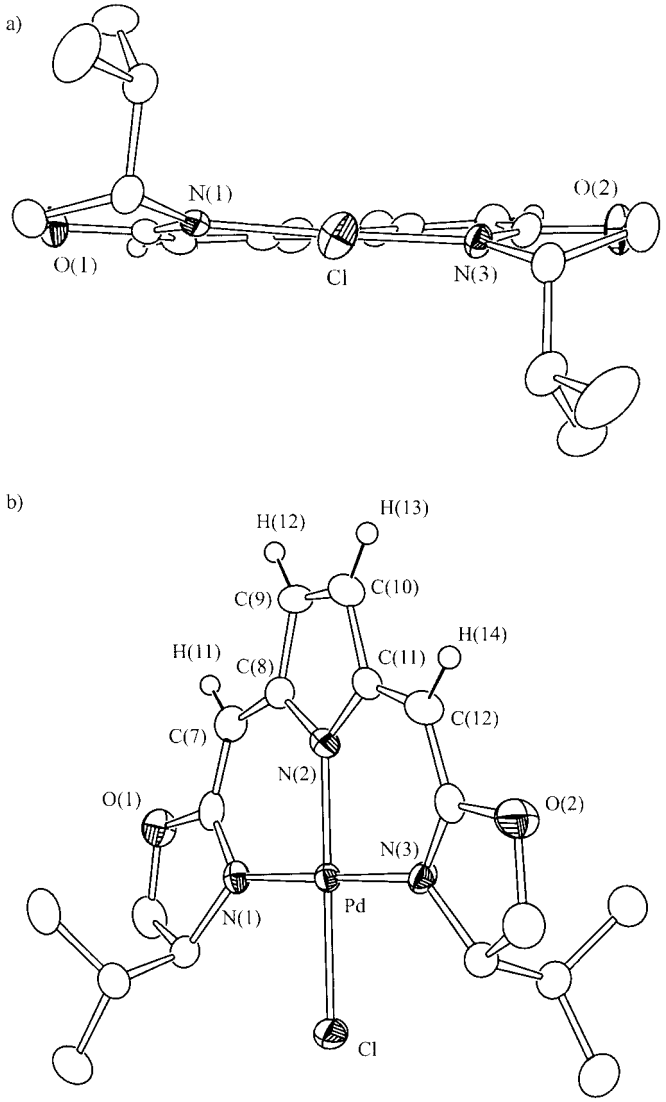


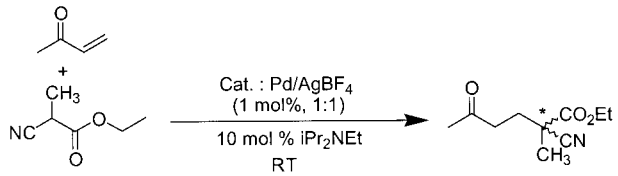

Figure 5. Two representations of the molecular structure of **6b**. a) View along the Cl-Pd-N(2) axis showing the almost ideal planarity of the ligand chromophore; b) view onto the coordination plane. Principal bond lengths [Å] and angles [°]: Pd–Cl 2.3211(9), Pd–N(1) 2.012(3), Pd–N(2) 2.003(3), Pd–N(3) 2.015(3), C(7)–C(8) 1.349(5), C(9)–C(10) 1.328(6), C(11)–C(12) 1.361(5); Cl-Pd-N(2) 179.82(7), N(1)-Pd-N(3) 177.8(1), C(8)-C(7)-C(3)-N(1) 2.3(2).

ideal square-planar arrangement of the four ligating atoms around the central atom (Cl-Pd-N(2) 179.82(7), N(1)-Pd-N(3) 177.8(1)°). While the C–C bond lengths of the exocyclic double bonds of the pyrrole ring are essentially identical to those found in complex **5a** (av 1.355 Å), the C(9)–C(10) bond length of 1.328(6) Å confirms the presence of an additional double bond in the converted pyrrole ring.

## Conclusion

In this work we have established a new class of chiral $C_2$-symmetric meridionally coordinating N-donor ligands which are ideally adapted to triscoordination in square-planar transition-metal complexes. These are interrelated by oligopyrrole-type planarization reactions of the $CH_2$/CH bridges that link the three heterocycles and constitute an alternative set of ancillary ligands to the well-established pybox/phebox systems.

All three types of $C_2$-symmetric palladium complexes may act as catalysts in Lewis acid catalyzed transformations. In a first step towards the application of these systems and in order to relate them to the known {(phebox)Pd}$^+$ catalysts, we have tested **4b** and **4c** in the catalytic asymmetric Michael addition of ethyl-2-cyanopropionate to methyl vinylketone (Scheme 7).[22, 23]




Scheme 7. Asymmetric Michael addition of ethyl-2-cyanopropionate to methyl vinyl ketone as catalyzed by **4b** and **4c**.

This reaction, for which Richards et al. found an enantioselectivity (*ee*) of 35% using [(phebox)Pd(OH$_2$)](SbF$_6$), was found to be catalyzed by both **4b** and **4c** (catalyst loading: 1 mol%) and gave rise to maximum *ee* values of 43% (**4b**) and 21% (**4c**) at low conversions (14% and 29%, respectively).[24] The limiting factor appears to be the relatively low activity of both complexes, accordingly significant competition from the noncatalyzed (non-stereoselective) reaction occurs, which reduces the overall enantioselectivity in this conversion. This is evident from the systematic decrease in stereoselectivity with longer reaction times.

Nishiyama and co-workers have very recently reported significantly superior results for this reaction (*ee* > 80%, 2 mol% cat.) with an in-situ generated phebox–rhodium complex [(phebox)Rh(SnMe$_3$)Cl] as catalyst.[25] The current activities in our group are aimed towards the extension of the coordination chemistry of these novel ligand systems and the exploration of the catalytic activity of their complexes with other transition metals in a variety of transformations

## Experimental Section

Solvents were dried according to the standard procedures and saturated with nitrogen. Solids were separated from suspensions by centrifugation to avoid filtration procedures with a Hettich–Rotina 48 centrifuge equipped with a specifically designed Schlenck tube rotor (Hettich Zentrifugen, Tuttlingen, Germany).[26] 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) spectrometer. Infrared spectra were recorded on a Perkin Elmer 1600 FT-IR spectrometer and UV spectra on a Varian Cary 05 E UV-VIS NIC spectrometer. EI mass spectra were recorded on a Shimadzu QP 5050-GC/MS system. The elemental analysis were carried out by the Service Commun de Microanalyse de l'Université Louis Pasteur of Strasbourg. 2,5-Bis[(trimethylammonio)methyl]pyrrole diiodide,[18, 19] 3,4-diethylpyrrole-2,5-dicarboxylic acid,[27] [Pd(PhCN)$_2$Cl$_2$],[28] and [PdCl$_2$(1,5-cod)] (cod = cyclooctadiene)[29] were prepared according to the previously described procedures. All other chemicals employed as starting materials were obtained commercially and used as received without further purification.

**Preparation of 2,5-biscyanomethylpyrrole (2)**: In a 1 L round bottom flask equipped with a gas trap, sodium cyanide (11.275 g, 0.23 mol) was dried



0947-6539/03/0908-1764 $ 20.00+.50/0 *Chem. Eur. J.* **2003**, *9*, No. 8

under vacuum at 110 °C for 1 h. The flask was then cooled to 0–10 °C and dimethyl sulfoxide (250 mL) was carefully added, followed by the dropwise addition of a slurry of 2,5-bis[(trimethylammonio)methyl]pyrrole diiodide (46.5 g, 0.1 mol) in dimethyl sulfoxide (350 mL). The mixture was heated and stirred at 40 °C for 1 h until the evolution of gas ceased. After cooling to room temperature, the suspension was poured onto 1 L of water and extracted with ethyl acetate. The combined organic phases were dried over sodium sulfate and solvents were removed by rotary evaporation to give a brown residue that was purified either by chromatography ($SiO_2$, EtOAc, $R_f = 0.70$) or recrystallization from dichloromethane (yield = 62 %).

$^1$H NMR ([D$_6$]DMSO; 300 MHz): $\delta = 11.16$ (broad s, 1H; pyrrole NH), 5.91 (d, $^4J = 3$ Hz, 2H; pyrrole H-3, H-4), 3.90 ppm (s, 4H; $CH_2$); $^{13}$C{$^1$H} NMR ([D$_6$]DMSO; 75 MHz): $\delta = 120.5$ (pyrrole C(2,5)), 118.1 (pyrrole C-3, C-4)), 107.1 (C=N), 15.6 ($CH_2$); IR (KBr disk): $\tilde{\nu} = 3444$ (m), 2251 (s), 1628 (w), 1592 (s), 1416 (s), 1328 (s), 1175 (s), 754 (s), 602 (m), 378 cm$^{-1}$ (m); MS: *m*/*z*: 145 $[M]^+$, 119 $[M - CN]^+$, 105 $[M - CH_2CN]^+$, 65 $[M - 2\,CH_2CN]^+$; elemental analysis (%) for $C_6H_3N_3$ (145.16): calcd: C 66.19, H 4.86, N 28.95; found: C 66.02, H 4.73, N 29.08.

**General procedure for the preparation of the 2,5-bis{(oxazolyl)methyl}-pyrroles 3a–3c**: $ZnCl_2$ (582 mg, 8.54 mmol) was melted in vacuo and then cooled under an atmosphere of nitrogen. 2,5-Biscyanomethylpyrrole (1.00 g, 8.54 mmol), chlorobenzene (20 mL), and the appropriate amino alcohol (23.9 mmol, 3.75 equiv) were added successively and the reaction mixture was subsequently stirred at 115 °C for 4–5 days in a closed system. The solvent was removed under vacuum and the dark brown residue was purified by chromatography on silica gel and eluted with a ethyl acetate–triethylamine mixture (95:5 % v/v) to afford the desired product as brown to light brown solids or oils.

**Bis{2-(4,4′-dimethyl-5-hydrooxazolyl)methyl}pyrrole (3a)**: Isolated as a pale brown solid after four days; yield: 76 %; $R_f = 0.42$; $^1$H NMR (300 MHz, $CDCl_3$, 295 K): $\delta = 9.33$ (br. s, 1H; pyrrole NH), 5.90 (d, $^4J =$ 2.6 Hz, 2H; pyrrole H-3, H-4), 3.93 (s, 4H; oxazolyl $CH_2$), 3.59 (s, 4H; $CH_2$), 1.28 ppm (s, 12H; $CH_3$); $^{13}$C{$^1$H} NMR (75 MHz, $CDCl_3$, 295 K): $\delta =$ 163.3 (oxazolyl C=N), 124.0 (pyrrole C-2, C-5), 106.9 (pyrrole C-3, C-4), 79.2 (oxazolyl $CH_2$), 67.2 (oxazolyl $C_{quat.}$), 28.4 ($CH_3$), 27.2 ppm ($CH_2$); IR (KBr disk): $\tilde{\nu} = 2967$ (s), 1663 (s), 1584 (w), 1362 (w), 1270 (m), 1143 (m) 981 cm$^{-1}$ (m); MS: *m*/*z*: 289 $[M]^+$, 246 $[M - i\mathrm{Pr}]^+$, 217 $[M - C(CH_3)_2CH_2O]^+$, 145 $[M - 2\,C(CH_3)_2CH_2O]^+$; elemental analysis (%) for $C_{16}H_{23}N_3O_2$ (289.37): calcd: C 66.41, H 8.01, N 14.52; found: C 65.62, H 8.27, N 14.58.

**(*S*,*S*)-Bis{2-(4-isopropyl-4,5-dihydrooxazolyl)methyl}pyrrole (3b)**: Isolated as a brown oil after four days; yield: 56 %; $R_f = 0.47$; $^1$H NMR (300 MHz, $CDCl_3$, 295 K): $\delta = 9.45$ (br. s, 1H; pyrrole NH); 5.90 (d, $^4J = 2.6$ Hz, 2H; pyrrole H-3, H-4), 4.24 (m, 2H; oxazolyl $CH_2$), 3.93 (m, 4H; oxazolyl $CH_2$, CH), 3.61 (s, 4H; $CH_2$), 1.72 (sept, 2H; *i*Pr CH), 0.97 (d, $^3J = 6.7$ Hz, 6H; *i*Pr $CH_3$), 0.87 ppm (d, $^3J = 6.7$ Hz, 6H; *i*Pr $CH_3$); $^{13}$C{$^1$H} NMR (75 MHz, $CDCl_3$, 295 K): $\delta = 164.8$ (oxazolyl C=N), 124.0 (pyrrole C-2, C-5), 106.9 (pyrrole C-3, C-4), 72.3 (oxazolyl CH), 70.4 (oxazolyl $CH_2$), 32.7 (*i*Pr CH), 26.9 ($CH_2$), 18.9 (*i*Pr $CH_3$), 18.3 ppm (*i*Pr $CH_3$); IR (KBr disk): $\tilde{\nu} = 2963$ (s), 1662 (s), 1517 (w), 1422 (m), 1369 (m), 1265 (s), 895 cm$^{-1}$ (m); MS: *m*/*z*: 317 $[M]^+$, 205 $[M - \mathrm{oxa}]^+$, 93 $[M - 2\,\mathrm{oxa}]^+$; elemental analysis (%) for $C_{18}H_{27}N_3O_2$ (317.43): calcd: C 68.11, H 8.57, N 13.24; found: C 67.73, H 8.66, N 12.97.

**(*S*,*S*)-Bis{2-(4-tertiobutyl-4,5-dihydrooxazolyl)methyl}pyrrole (3c)**: Isolated as a brown oil after five days; yield: 48 %; $R_f = 0.52$; $^1$H NMR (300 MHz, $CDCl_3$, 295 K): $\delta = 9.51$ (br. s, 1H; pyrrole NH), 5.90 (d, $^4J = 2.6$ Hz, 2H; pyrrole H-3, H-4), 4.15 (m, 4H; oxazolyl $CH_2$ and CH), 3.87 (m, 2H; oxazolyl $CH_2$), 3.62 (s, 4H; $CH_2$), 0.89 ppm (s, 18H; $CH_3$ *t*Bu); $^{13}$C{$^1$H} NMR (75 MHz, $CDCl_3$, 295 K): $\delta = 164.7$ (oxazolyl C=N), 124.0 (pyrrole C-2, C-5), 106.9 (pyrrole C-3, C-4), 75.8 (oxazolyl CH), 68.7 (oxazolyl $CH_2$), 33.6 (*t*Bu C), 26.9 ($CH_2$), 25.8 ppm (*t*Bu $CH_3$); IR (KBr disk): $\tilde{\nu} = 2958$ (s), 1665 (s), 1523 (w), 1414 (w), 1354 (m), 1265 (s), 744 cm$^{-1}$ (m); MS: *m*/*z*: 345 $[M]^+$, 288 $[M - C(CH_3)_3]^+$, 219 $[M - \mathrm{oxa}]^+$, 93 $[M - 2\ \mathrm{oxa}]^+$; elemental analysis (%) for $C_{20}H_{31}N_3O_2$ (345.48): calcd: C 69.53, H 9.04, N 12.16; found: C 69.17, H 9.11, N 12.05.

**Typical procedure for the preparation of the bis{2-(4,5-dihydrooxazolyl)-methyl}pyrrole(chloro)palladium complexes 4a–4c**: A solution of 2,5-bis[{(oxazolinyl)methyl}pyrrole] (0.100 g, 0.35 mmol) in diethyl ether (10 mL) was cooled under a nitrogen atmosphere to −78 °C. A solution of *t*BuLi (1.7 M) in hexane (0.20 mL) was added and the mixture stirred at this temperature for 30 min. A suspension of $[PdCl_2(1,5\text{-cod})]$ (0.108 g, 0.38 mmol) in $Et_2O$ (15 mL) was then added through a cannula at −78 °C. After the addition was completed, the dry ice bath was removed after one hour, the reaction mixture was allowed to warm to room temperature and then stirred overnight. The reaction mixture was filtered, the solvent removed under vacuum, and the orange or red residue was subjected to column chromatography (silica gel; $CH_2Cl_2$).

**[{Bis[2-(4,4′-dimethyl-5-hydrooxazolyl)methyl]pyrrole}PdCl] (4a)**: Isolated as a red solid; yield: 0.113 g, 76 %; $R_f = 0.45$; $^1$H NMR (300 MHz, $CDCl_3$, 295 K): $\delta = 5.85$ (s, 2H; pyrrole H-3, H-4), 4.08 (s, 4H; oxazolyl $CH_2$), 3.76 (s, 4H; $CH_2$), 1.66 ppm (s, 12H; $CH_3$); $^{13}$C{$^1$H} NMR (75 MHz, $CDCl_3$, 295 K): $\delta = 170.1$ (oxazolyl C=N), 124.9 (pyrrole C-2, C-5), 103.3 (pyrrole C-3, C-4), 81.9 (oxazolyl $CH_2$), 68.6 (oxazolyl $C_{quat.}$), 29.0 ($CH_3$), 26.3 ppm ($CH_2$); IR (KBr disk): $\tilde{\nu} = 2962$ (s), 1628 (s), 1466 (m), 1398 (m), 1261 (s), 1162 (m), 799 (s), 348 cm$^{-1}$ (w); elemental analysis (%) for $C_{16}H_{22}ClN_3O_2Pd$ (430.24): calcd: C 44.67, H 5.15, N 9.77; found: C 44.56, H 4.95, N 9.29.

**[{(*S*,*S*)-bis[2-(4-isopropyl-4,5-dihydrooxazolyl)methyl]pyrrole}PdCl] (4b)**: Isolated as a yellow solid; yield: 0.060 g, 38 %; $R_f = 0.37$; $^1$H NMR (300 MHz, $CDCl_3$, 295 K): $\delta = 5.87$ (s, 2H; pyrrole H-3, H-4), 4.65 (m, 2H; oxazolyl $CH_2$), 4.38 (m, 4H; oxazolyl $CH_2$ and CH), 3.90 (d, $J$(H,H) = 18.8 Hz, 2H; $CH_2$), 3.66 (d, $J$(H,H) = 18.8 Hz, 2H; $CH_2$), 2.55 (sept, 2H; *i*Pr CH), 0.93 (d, $^3J = 7.1$ Hz, 6H; *i*Pr $CH_3$), 0.71 ppm (d, $^3J = 7.1$ Hz, 6H; *i*Pr $CH_3$); $^{13}$C{$^1$H} NMR (75 MHz, $CDCl_3$, 295 K): $\delta = 169.4$ (oxazolyl C=N), 124.4 (pyrrole C-2, C-5), 104.6 (pyrrole C-3, C-4), 70.1 (oxazolyl CH), 67.7 (oxazolyl $CH_2$), 29.9 (*i*Pr CH), 29.1 ($CH_2$), 18.1 (*i*Pr $CH_3$), 14.2 ppm (*i*Pr $CH_3$); IR (KBr disk): $\delta = 2955$ (m), 1648 (s), 1539 (s), 1389 (m), 1262 (m), 1226 (s), 10023 (m), 730 (m), 348 cm$^{-1}$ (w); elemental analysis (%) for $C_{18}H_{26}ClN_3O_2Pd$ (458.29): calcd: C 47.17, H 5.72, N 9.17; found: C 46.97, H 5.33, N 9.37.

**[{(*S*,*S*)-bis[2-(4-tertiobutyl-4,5-dihydrooxazolyl)methyl]pyrrole}PdCl] (4c)**: Isolated as a pink solid; yield: 0.071 g, 42 %; $R_f = 0.32$; $^1$H NMR (300 MHz, $CDCl_3$, 295 K): $\delta = 5.88$ (s, 2H; pyrrole H-3, H-4), 4.52 (m, 4H; oxazolyl $CH_2$ and CH), 4.43 (m, 2H; oxazolyl $CH_2$), 3.95 (d, $J$(H,H) = 18.8 Hz, 2H; $CH_2$), 3.67 (d, $J$(H,H) = 18.8 Hz 2H; $CH_2$), 1.03 ppm (s, 18H; *t*Bu $CH_3$); $^{13}$C {$^1$H} NMR (75 MHz, $CDCl_3$, 295 K): $\delta = 169.5$ (oxazolyl C=N), 123.2 (pyrrole C2/5), 103.4 (pyrrole C-3, C-4), 70.1 (oxazolyl $CH_2$), 69.6 (oxazolyl CH), 33.3 (*t*Bu C), 28.5 ($CH_2$), 25.0 ppm (*t*Bu $CH_3$); IR (KBr disk): $\tilde{\nu} = 2965$ (s), 1632 (s), 1406 (m), 1414 (w), 1230 (s), 1070 (m), 996 (m), 743 (m), 313 cm$^{-1}$ (w); elemental analysis (%) for $C_{20}H_{30}ClN_3O_2Pd$ (486.34): calcd: C 49.39, H 6.22, N 8.64; found: C 49.67, H 6.05, N 8.87.

**General procedures for the preparation of 5a–c**

1) **Synthesis from 3a–b**: $[Pd(PhCN)_2Cl_2]$ (1.5 equiv) was added to the ligand (**3a–b**, 0.475 mmol) in dichloromethane (25 mL). The reaction mixture was stirred at room temperature for two days. The solvent was removed and the brown residue purified by column chromatography ($SiO_2$, $CH_2Cl_2$).

2) **Isomerization from 4a or 4c:** Compound **4a** (or **4c**) (10 mg) and one molar equivalent of $[Pd(PhCN)_2Cl_2]$ were dissolved in $CDCl_3$ (0.42 mL). The reaction was monitored by $^1$H NMR spectrocopy until completion.

**5a**: Isolated as a red solid; yield: 76 %; $R_f = 0.75$; $^1$H NMR (300 MHz, $CDCl_3$, 295 K): $\delta = 4.94$ (s, 2H; CH), 3.94 (s, 4H; oxazolyl $CH_2$), 2.79 (s, 4H; pyrrole $CH_2$), 1.77 ppm (s, 12H; $CH_3$); $^{13}$C{$^1$H} NMR (75 MHz, $CDCl_3$, 295 K): $\delta = 167.8$ (oxazolyl C=N), 161.2 (pyrrole C-2, C-5), 82.0 (CH), 81.7 (oxazolyl $CH_2$), 30.5 (pyrrole C-3, C-4), 28.2 ppm ($CH_3$); IR (KBr disk): $\tilde{\nu} = 2943$ (s), 1610 (s), 1539 (s), 1430 (m), 1262 (m), 1004 (m), 949 (m), 357 cm$^{-1}$ (w); elemental analysis (%) for $C_{16}H_{22}ClN_3O_2Pd$ (430.24): calcd: C 44.67, H 5.15, N 9.77; found: C 44.49, H 5.02, N 9.87.

**5b**: Isolated as an orange solid; $R_f = 0.75$; $^1$H NMR (300 MHz, $CDCl_3$, 295 K): $\delta = 4.99$ (s, 2H; CH), 4.34–4.20 (m, 6H; oxazolyl $CH_2$ and CH), 2.85 (s, 4H; pyrrole H-3, H-4), 2.52 (sept, 2H; *i*Pr CH), 0.86 (d, $^3J = 7.0$ Hz, 6H; *i*Pr $CH_3$), 0.59 ppm (d, $^3J = 7.0$ Hz, 6H; *i*Pr $CH_3$); $^{13}$C{$^1$H} NMR (75 MHz, $CDCl_3$, 295 K): $\delta = 169.2$ (oxazolyl C=N), 162.3 (pyrrole C-2, C-5), 81.1 (CH), 68.4 (oxazolyl CH), 67.4 (oxazolyl $CH_2$), 31.4 (*i*Pr CH), 30.6 (pyrrole C-3, C-4), 18.7 (*i*Pr $CH_3$), 13.9 ppm (*i*Pr $CH_3$); IR (KBr disk); 2954 (s), 1616 (s), 1539 (s), 1430 (m), 1262 (m), 1225 (s), 1024 (m), 956 (m), 735 (w), 357 cm$^{-1}$ (w); elemental analysis (%) for $C_{18}H_{26}ClN_3O_2Pd$ (4358.29): calcd: C 47.17, H 5.72, N 9.17; found: C 46.99, H 5.55, N 9.23.

**5c**: Isolated as a red-orange solid; $R_f = 0.70$; $^1$H NMR (300 MHz, $CDCl_3$, 295 K): $\delta = 4.91$ (s, 2H; CH), 4.75 (m, 2H; oxazolyl CH), 4.30 (m, 4H;

oxazolyl $CH_2$), 2.79 (m, 4H; pyrrole $CH_2$), 0.97 ppm (s, 18H; *t*Bu $CH_3$); $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$, 295 K): $\delta = 167.3$ (oxazolyl C=N), 162.5 (pyrrole C-2, C-5), 81.9 (oxazolyl CH), 69.6 (CH), 69.5 (oxazolyl $CH_2$), 35.4 (*t*Bu C), 30.4 (pyrrole C-3, C-4), 26.1 ppm (*t*Bu $CH_3$); IR (KBr disk): $\tilde{\nu} =$ 2944 (s), 1610 (s), 1551 (s), 1245 (s), 956 (m), 735 (w), 357 $cm^{-1}$ (w); elemental analysis (%) for $C_{20}H_{30}ClN_3O_2Pd$ (486.34): calcd: C 49.39, H 6.22, N 8.64; found: C 49.49, H 6.13, N 8.84.

**General procedure for the conversion of 4b – c to 6b – c:** Complex **4b** or **4c** (25 mg) was dissolved in $CH_2Cl_2$ (or $CH_3Cl_3$ or $CH_3CN$) and exposed to an oxygen atmosphere (1 bar). After the conversion was complete, $Na_2SO_4$ was added, the mixture was filtered and the solvent removed to give the product.

**Complex 6b:** Isolated as an orange solid; yield: 24 mg, 100%; $R_f = 0.82$; $^1H$ NMR (300 MHz, $CDCl_3$, 295 K): $\delta = 6.95$ (s, 2H; pyrrole H-3, H-4), 5.56 (s, 2H; CH), 5.07 (m, 2H; oxazolyl $CH_2$), 4.33 (m, 4H; oxazolyl $CH_2$ and CH), 2.61 (sept, 2H; *i*Pr CH), 0.91 (d, $^3J = 6.9$ Hz, 6H; *i*Pr $CH_3$), 0.59 ppm (d, $^3J = 6.9$ Hz, 6H; *i*Pr $CH_3$); $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$, 295 K): $\delta =$ 166.9 (oxazolyl C=N), 133.6 (pyrrole C-3, C-4), 131.0 (pyrrole C-2, C-5), 86.5 (CH), 69.6 (oxazolyl CH), 67.8 (oxazolyl $CH_2$), 31.4 (*i*Pr CH), 18.7 (*i*Pr $CH_3$), 13.9 ppm (*i*Pr $CH_3$); IR (KBr disk): $\tilde{\nu} = 2923$ (s), 1616 (s), 1539 (s), 1261 (m), 1226 (s), 1023 (m), 799 (w), 352 $cm^{-1}$ (w); elemental analysis (%) for $C_{18}H_{26}ClN_3O_2Pd$ (456.27): calcd: C 47.38, H 5.30, N 9.21; found: C 47.23, H 5.19, N 8.84.

**Complex 6c:** Isolated as a red solid; yield: 24 mg, 80%; $R_f = 0.73$; $^1H$ NMR (300 MHz, $CDCl_3$, 295 K): $\delta = 6.88$ (s, 2H; pyrrole H-3, H-4), 5.45 (s, 2H; CH), 5.00 (m, 2H; oxazolyl $CH_2$), 4.41 – 4.29 (m, 4H; oxazolyl $CH_2$ and CH), 0.95 ppm (s, 18H; *t*Bu $CH_3$); $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$, 295 K): $\delta = 167.3$ (oxazolyl C=N), 133.1 (pyrrole C-3, C-4), 130.9 (pyrrole C-2, C-5), 87.2 (CH), 69.9 (oxazolyl CH), 68.2 (oxazolyl $CH_2$), 36.4 (*t*Bu C), 26.3 ppm (*t*Bu $CH_3$); IR (KBr disk): $\tilde{\nu} = 2964$ (s), 1600 (s), 1521 (m), 1420 (m), 1327 (w), 1267 (s), 1225 (s), 1210 (s), 1042 (m), 999 (m), 818 (m), 759 (w), 348 $cm^{-1}$ (w); elemental analysis (%) for $C_{20}H_{30}ClN_3O_2Pd$ (484.33): calcd: C 49.60, H 5.83, N 8.68; found: C 49.72, H 5.91, N 8.53.

**General procedure for the asymmetric palladium-catalyzed Michael reaction:** In a glove box, the complex (0.01 mmol) and $CH_2Cl_2$ (2 mL) was added to $AgBF_4$ (0.01 mmol). After 45 min, the mixture was filtered under nitrogen through a pad of Celite directly into a test tube and the solvent was removed in vacuo. The solid was then redissolved in dry toluene (3 mL). Ethyl-2-cyanopropionate (1.0 mmol) and methyl vinyl ketone (1.0 mmol) were added to the solution at 25 °C. *N*-Ethyldiisopropylamine (0.1 mmol) was subsequently slowly added with a syringe. The reaction mixture was stirred at this temperature and followed by GC and GCMS analysis. The mixture was diluted with $CH_2Cl_2$ and washed with HCl (1 M) and water. The organic layers were combined, dried over $MgSO_4$. After removal of the volatile solvents, the product, ethyl-2-cyano-2-methyl-5-oxohexanoate, was purified by silica gel chromatography (2:1 v/v hexane/diethyl ether) to afford a pale yellow oil. $^1H$ NMR (300 MHz, $CDCl_3$, 295 K): $\delta = 4.25$ (q, 2H; $OCH_2CH_3$), 2.70 – 2.54 (m, 4H; (C*)$CH_2$), 2.20 – 1.94 (m, 2H; $CH_2$), 2.12 (s, 3H; C(O)$CH_3$), 1.56 (s, 3H; C(CN)$CH_3$), 1.30 ppm (s, 3H; $CH_2CH_3$); MS: *m*/*z* 197 $[M]^+$, 182, 169, 155, 124, 108, 96, 82, 68, 58, 43; GC analysis: Chiraldex G-TA, column temperature 125 °C; detection: $t_r = 20.1$ min (minor enantiomer), $t_r = 23.7$ min (major enantiomer).

**X-ray crystallographic study of 4a, 5a, and 6b:** Suitable crystals of the complexes **4a, 5a**, and **6b** 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 transferred to a DEC Alpha workstation; for all subsequent calculations the Nonius OpenMoleN package was used.[30] The structures were solved by using direct methods with absorption corrections as 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-matrix least-square refinements were made on $F^2$. A final difference map revealed no significant maxima of electron density. The scattering factor coefficients and the anomalous dispersion coefficients were taken from reference [31]. Crystal data and experimental details for the crystals of **4a**, **5a**, and **6b** are given in Table 1.

Table 1. Crystal data and structure refinement for compounds **4a**, **5a**, and **6b**.

| | **4a** | **5a** | **6b** |
|---|---|---|---|
| formula | $C_{16}H_{22}ClN_3O_2Pd$ | $C_{16}H_{22}ClN_3O_2Pd$ | $C_{18}H_{24}ClN_3O_2Pd$ |
| $M_r$ | 430.23 | 430.23 | 456.26 |
| crystal system | monoclinic | monoclinic | orthorhombic |
| space group | $P2_1/c$ | $Cc$ | $P2_12_12_1$ |
| $a$ [Å] | 11.6838(2) | 10.4133(5) | 8.0937(2) |
| $b$ [Å] | 10.2010(2) | 24.320(2) | 12.9910(3) |
| $c$ [Å] | 14.5161(3) | 7.1009(4) | 17.9425(4) |
| $\alpha$ [°] | 90 | 90 | 90 |
| $\beta$ [°] | 100.80(5) | 107.456(5) | 90 |
| $\gamma$ [°] | 90 | 90 | 90 |
| $V$ [Å$^3$] | 1697.24(6) | 1715.5(2) | 1886.57(8) |
| **Z** | 4 | 4 | 4 |
| $\rho_{calcd}$ [g cm$^{-3}$] | 1.68 | 1.67 | 1.61 |
| radiation ($\lambda$ [Å]) | $Mo_{K\alpha}$ (0.71073) | $Mo_{K\alpha}$ (0.71073) | $Mo_{K\alpha}$ (0.71073) |
| $\mu$ [mm$^{-1}$] | 1.263 | 1.250 | 1.141 |
| $F(000)$ | 872 | 872 | 928 |
| crystal size [mm] | 0.20 × 0.18 × 0.12 | 0.14 × 0.10 × 0.06 | 0.20 × 0.20 × 0.16 |
| $\theta$ range [°] | 2.5 – 30.00 | 2.5 – 30.06 | 2.5 – 30.03 |
| reflections collected | 8200 | 3989 | 5316 |
| independent reflect. | 4143 | 2063 | 2452 |
| data/restraints/param. | 4143/0/208 | 2063/2/206 | 2452/0/226 |
| $S$ on $F^2$ | 1.236 | 1.017 | 1.051 |
| final $R$ indices[a] $[I > 3\sigma(I)]$ | | | |
| $R_1$ | 0.029 | 0.025 | 0.026 |
| $wR_2$ | 0.063 | 0.033 | 0.026 |
| max/min $\Delta\rho$ [e Å$^{-3}$] | 0.828/ − 0.306 | 0.438/ − 0.105 | 0.501/ − 0.196 |

[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, $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$, $wR_2 = \Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]^2$, $w^{-1} = [R^2(F_o)^2 + (aP)^2 + bP]$, $P = [\max(F_o^2,0) + 2(F_c^2)]/3$.

CCDC-195952 (**4a**), CCDC-195953 (**5a**), and CCDC-195954 (**6b**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK (fax: + (44) 1223-336-033; or deposit@ccdc.cam.ac.uk)).

## Acknowledgement

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 and BASF (Ludwigshafen) as well as Degussa (Hanau) for gifts of valuable starting materials. We are grateful to Dr. André De Cian and N. Gruber for X-ray diffraction studies.

[1] K. M. Kadish, K. M. Smith, R. Guilard, *The Porphyrin Handbook*, Academic Press, San Diego, CA, **2000**.

[2] a) A. Jasat, D. Dolphin, *Chem. Rev.* **1997**, *97*, 2267—2340; b) L. R. Milgrom, *The Colours of Life, (An Introduction To The Chemistry of Porphyrins and Related Compounds)*, Oxford University Press, **1997**; c) R. Grigg in *The Porphyrins*, *Vol. 2*, (Ed.: D. Dolphin), Academic Press, New York, **1978**, Chapter 10; d) A. W. Johnson in *Porphyrins and Metalloporphyrins* (Ed.: K. M. Smith), Elsevier, Amsterdam, **1976**, p. 750.

[3] Some examples of porphyrins in various applications: photodynamic therapy: a) S. B. Brown, T. G. Truscott, *Chem. Ber.* **1993**, *29*, 955; b) H. van den Bergh, *Chem. Ber.* **1986**, *22*, 430; c) C. J. Gomer, *Photchem. Photobiol.* **1987**, *46*, 561; d) *Photodynamic Therapy: Basic Principles and Clinical Applications* (Eds.: B. Henderson, T. J. Dougherty), M. Dekker, New York, **1992**; e) R. Bonnett, *Chem. Soc. Rev.* **1995**, *24*, 19; f) D. Dolphin, *Can. J. Chem.* **1994**, *72*, 1005; pyrrolic photosensitizers:

g) E. Sternberg, D. Dolphin, *Curr. Med. Chem.* **1996**, *3*, 293; h) D. A. Bellnier, Y.-K. Ho, R. K. Pandey, J. R. Missent, T. J. Dougherty, *Photochem. Photobiol.* **1989**, *50*, 221; i) *Infrared Absorbing Dyes*, M. Matsuoka Ed., Plenum, New York, **1990**; for reviews on magnetic resonance imaging, see: j) R. B. Lauffer, *Chem. Rev.* **1987**, *87*, 901; k) R. Edelman, S. N. Warach, *Engl. J. Med.* **1993**, *328*, 708; k) S. W. Young, *Magnetic Resonance Imaging: Basic Principles*, Raven, New York, **1988**, 1–282.

[4] H. Falk, *The Chemistry of Linear Oligopyrroles and Bile Pigments*, Springer, Vienna, **1989**.

[5] For some examples of polypyrrole macrocycles, see for instance: a) *The Porphyrins Vols. 1–8* (Ed.: D. Dolphin), Academic Press, New York, **1978–1979**.; b) *Porphyrins and Metalloporphyrins*, (Ed.: K. M. Smith), Elsevier, Amsterdam, **1976**.

[6] a) M. Bröring, C. D. Brand, *Chem. Commun.* **2001**, 499; b) M. Bröring, C. D. Brand, *J. Chem. Soc. Dalton Trans.* **2002**, 1391.

[7] Selected publications on open-chain oligopyrrole chemistry: a) J. L. Sessler, A. Gebauer, V. Král and V. Lynch, *Inorg. Chem.* **1996**, *35*, 6636; b) F.-P. Montforts, *Angew. Chem.* **1981**, *93*, 795; *Angew. Chem. Int. Ed. Engl.* **1981**, *20*, 778; c) F.-P. Montforts, U. M. Schwartz, *Liebigs Ann. Chem.* **1985**, 1228; d) D. Eichinger, H. Falk, Monatsh. Chem. **1987**, *118*, 261; e) R. G. Khoury, M. O. Senge, J. E. Colchester, K. M. Smith, *J. Chem. Soc. Dalton Trans.* **1996**, 3937; A. Jaumà, J.-A. Farrera, J. M. Ribó, *Monatsh. Chem.* **1996**, *127*, 936.

[8] a) J. A. Elvidge, R. P. Linsted, *J. Chem. Soc.* **1952**, 5000; b) J. A. Elvidge, R. P. Linsted, *J. Chem. Soc.* **1952**, 5008.

[9] Selected publications: a) W. O. Siegl, *J. Org. Chem.* **1977**, *42*, 1872; b) W. O. Siegl, *Inorg. Nucl.Chem. Lett.* **1974**, *10*, 825; c) R. R. Gagné, W. A. Marritt, D. N. Marks, W. O. Siegl, *Inorg. Chem.* **1981**, *20*, 3260; d) L. Saussine, E. Brazi, A. Robine, H. Mimoun, J. Fischer, R. Weiss, *J. Am. Chem. Soc.* **1985**, *107*, 3534; e) E. T. Farinas, C. V. Nguyen, P. K. Mascharak, *Inorg. Chim. Acta* **1997**, *263*, 17; f) F. A. Chavez, P. K. Mascharak, *Acc. Chem. Res.* **2000**, *33*, 539; g) W. O. Siegl, *J. Heterocyclic Chem.* **1981**, *18*, 1613; h) C. A. Tolman, J. D. Druliner, P. J. Krusic, M. J. Nappa, W. C. Seidel, I. D. Williams, S. D. Ittel, *J. Mol. Catal.* **1988**, *48*, 129; i) M. A. Robinson, S. I. Trotz, T. J. Hurley, *Inorg. Chem.* **1967**, *6*, 392; j) D. N. Marks, W. O. Siegl, R. R. Gagné, *Inorg. Chem.* **1982**, *21*, 3140.

[10] A. Togni, L. M. Venanzi, *Angew. Chem.* **1994**, *106*, 517–546; *Angew. Chem. Int. Ed. Engl.* **1994**, *33*, 497

[11] a) F. Fache, E. Schulz, M. Lorraine Tommasino, M. Lemaire, *Chem. Rev.* **2000**, *100*, 2159; b) M. Gomez, G. Muller, M. Rocamora, *Coord. Chem. Rev.* **1999**, *193*, 769; c) A. K. Ghosh, P. Mathivanan, J. Cappiello, *Tetrahedron: Asymmetry* **1998**, *9*, 1–45.

[12] a) H. Nishiyama, H. Sakaguchi, T. Nakamura, M. Horihata, M. Kondo, K. Itoh, Organometallics, **1989**, *8*, 846; b) H. Nishiyama, *Advances in Catalytic Processes*, *Vol. 2*, JAI, **1997**, p. 153.

[13] 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, Br. T. Connell, R. J. Staples, *J. Am. Chem. Soc.* **1999**, *121*, 669; c) David 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.* **1999**, *5*, 3509.

[14] 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, Y. Mikami, H. Kawakami, 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.

[15] a) S. E. Denmark, R. A. Stavenger, A.-M. Faucher, J. P. Edwards, *J. Org. Chem.* **1997**, *62*, 3375; b) M. A. Stark, C. J. Richards, *Tetrahedron Lett.* **1997**, *38*, 5881; c) M. A. Stark, G. Jones, C. J. Richards, *Organometallics* **2000**, *19*, 1282.

[16] M. Gerisch, J. R. Krumper, R. G. Bergman, T. D. Tilley, *J. Am. Chem. Soc.* **2001**, *123*, 5818.

[17] a) C. Mazet, L. H. Gade, *Organometallics* **2001**, *20*, 4144; b) C. Mazet, L. H. Gade, *Chem. Eur. J.* **2002**, *8*, 4308.

[18] I. T. Kim, R. L. Elsenbaumer, *Tetrahedron Lett.* **1998**, *39*, 1087.

[19] I. T. Kim, R. L. Elsenbaumer, *Chem. Commun.* **1998**, 327.

[20] 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.

[21] E. J. Corey, J. C. Bailar, *J. Am. Chem. Soc.* **1959**, *81*, 2620.

[22] a) H.-G. Schmalz, *Comprehensive Organic Synthesis*, Pergamon, Oxford (Eds.: B. M. Trost, I. Flemming), **1991**; b) B. E. Rossiter, N. M. Swingle, *Chem. Rev.* **1992**, *92*, 771.

[23] Selected publications: a) T. Naota, H. Ta-ki, M. Masahiko, S.-I Murahashi, *J. Am. Chem. Soc.* **1989**, *111*, 5954; b) M. Sawamura, H. Hamashima, Y. Ito, *J. Am. Chem. Soc.* **1992**, *114*, 8295; c) M. Sawamura, H. Hamashima, H. Shinoto, Y. Ito, *Tetrahedron Lett.* **1995**, *36*, 6479; d) M. Sawamura, M. Sudoh, Y. Ito, *J. Am. Chem. Soc.* **1996**, *118*, 3309; e) R. Kuwano, H. Miazaky, Y. Ito, *Chem. Commun.* **1998**, 71; f) A. J. Blacker, M. L. Clarke, M. S. Loft, M. F. Mahon, J. M. J. Williams, *Organometallics* **1999**, *18*, 2867.

[24] M. A. Stark, G. Jones, C. J. Richards, *Organometallics* **2000**, *19*, 1282.

[25] Y. Motoyama, Y. Koga, K. Kobayashi, K. Aoki, H. Nishiyama, *Chem. Eur. J.* **2002**, *8*, 2968.

[26] K. W. Hellmann, L. H. Gade, *Verfahrenstechnik (Berlin)* **1997**, *31(5)*, 70.

[27] a) L. Knorr, *Ber.* **1884**, *17*, 1635; b) L. Knorr, *Annalen*, **1886**, *236*, 290; c) U. Eisner, A Lichtarowicz, R. P. Linstead, *J. Chem. Soc.* **1957**, 733; d) J. B. Paine III, R. B. Woodward, D. Dolphin, *J. Org. Chem.* **1976**, *41*, 2826; e) H. W. Whitelock, R. Hanauer, *J. Org. Chem.* **1968**, *33*, 2169–2171.

[28] G. K. Anderson, M. Lin, *Inorg. Synth.* **1990**, *28*, 61.

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

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

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

Received: October 23, 2002 [F4523]