[Bis(oxazolinyl)pyrrole]palladium Complexes as Catalysts in Heck- and Suzuki-Type C−C Coupling Reactions

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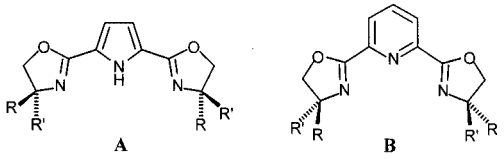
The two bis(oxazoline)pyrrole ligand precursors 2,5-bis(4,4′-dimethyl-4,5-dihydrooxazol-2-yl)pyrrole ("dmoxpH", **2**) and 2,5-bis(4,4′-dimethyl-4,5-dihydrooxazol-2-yl)-3,4-diethylpyrrole ("Et_2dmoxpH", **5**) have been synthesised and metallated by treatment with *n*-butyllithium at −78 °C in diethyl ether. Treatment of the lithium pyrrolide with 1.1 mol-equiv. of [$PdCl_2$(COD)] gave the corresponding helical dinuclear palladium complexes [Pd_2Cl_2(dmoxp)$_2$] (**6**) and [Pd_2Cl_2(Et_2dmoxp)$_2$] (**7**). In both complexes the tridentate bis(oxazolinyl)pyrrolide ligands bridge the two metal centres, with one of the oxazoline rings and the charged pyrrolide being coordinated to the one Pd centre while the second oxazoline ring is twisted relative to the pyrrolide unit and coordinates to the second palladium atom. Complexes **6** and **7** were found to be precursors for active catalysts for Heck coupling reactions of styrene and ethyl acrylate, with turnover numbers of over 9000 for the former, as well as for disubstituted alkenes such as methyl crotonate and methyl cinnamate. Complex **6** was found to be a very active catalyst for Suzuki coupling reactions of activated and deactivated bromoarenes.

Introduction

In recent years, nitrogen donor ligands have increasingly been employed as ancillary ligands in molecular catalysis.[1] This is due to the great variety of synthetic strategies available. Nitrogen-based catalysts may generate catalytically active complexes complementary to the known phosphane-based systems. Oxazolines and their derivatives have been intensely studied in a wide range of applications, particularly in asymmetric catalysis.[2,3]



A

B

We recently began to develop the coordination chemistry of a new class of potentially tridentate, monoanionic N-donor ligands based on the combination of two oxazoline rings and a central pyrrole unit (**A**).[4] This class of compounds may be viewed as precursors to monoanionic analogues of the well-established family of pybox ligands (**B**), which have found widespread application in asymmetric catalysis in recent years.[5] The monoanionic charge of the deprotonated molecule and the more open structure of this derivative of the five-membered pyrrole ring in comparison with the ligands containing a central pyridine unit would be expected to result in somewhat different complex structures in comparison to pybox complexes. In a preliminary study of their coordination chemistry we discovered that the arrangement of its three N-donor atoms does not permit meridional tris(coordination) to a single metal centre.[4] This gives rise to dinuclear complexes that dissociate in solution only at higher temperatures.[6]

In this paper we report the synthesis of two achiral type **A** bis(oxazolinyl)pyrroles, one of which is alkyl-substituted in the 3- and 4-positions of the pyrrole ring, and the synthesis of two helical dinuclear palladium complexes. The principle focus was to assess their suitability as precursors for efficient catalytic C−C coupling reactions. To this end, a series of Heck and Suzuki coupling reactions were carried out as benchmark reactions in order to test these novel molecular systems.

Results and Discussion

Synthesis of the Two Ligand Precursors 2,5-Bis[2-(4,4′-dimethyl-4,5-dihydrooxazolyl)]pyrrole ("dmoxpH", 2) and 2,5-Bis[2-(4,4′-dimethyl-4,5-dihydrooxazolyl)]-3,4-diethylpyrrole ("Et_2dmoxpH", 5)

As a starting material in the synthesis of 2,5-bis(4,4′-dimethyl-4,5-dihydrooxazol-2-yl)pyrrole ("dmoxpH", **2**) we chose pyrrole-2,5-dicarbonitrile (**1**), for which we had previously developed an efficient synthetic route.[6] Its cyclisation with two mol-equiv. of 2-amino-2-methyl-1-propanol was

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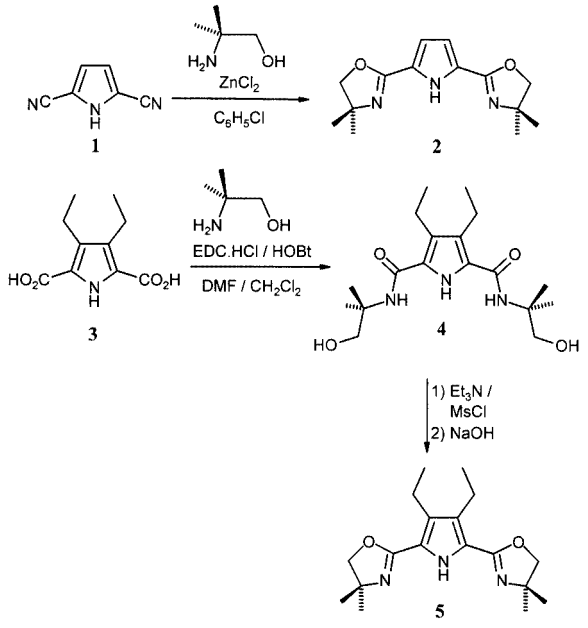
carried out by the method reported by Witte and Bolm.[7] Heating at reflux in chlorobenzene in the presence of 0.5 mol-equiv. of activated $ZnCl_2$ for 12 h gave crude **2**, which was purified by flash chromatography to give a cream-coloured solid. The formulation of compound **2** was confirmed by elemental analysis and mass spectrometry, while its ^1H, ^{13}C NMR and infrared spectra were consistent with the structure depicted in Scheme 1.

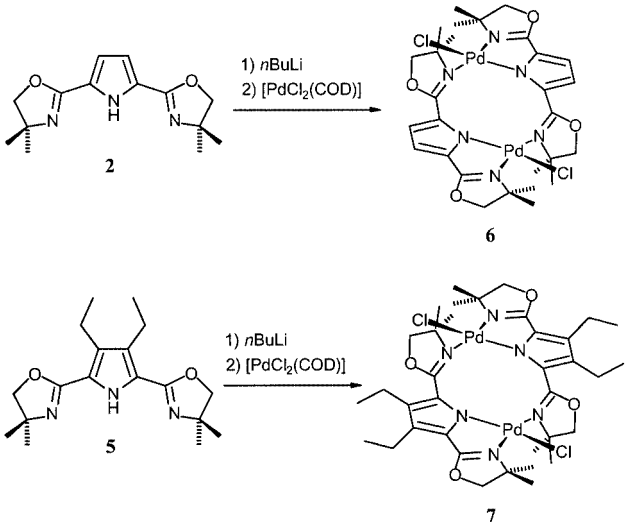


Scheme 1. Synthesis of the two bis(oxazolinyl)pyrroles **2** and **5**

The 3,4-diethylpyrrole analogue of **2**, 2,5-bis(4,4′-dimethyl-4,5-dihydrooxazol-2-yl)-3,4-diethylpyrrole ("Et_2dmoxpH", **5**) was synthesised in two steps, starting from the known 3,4-diethylpyrrole-2,5-dicarboxylic acid (**3**).[8] This has frequently been used as a starting material in porphyrin synthesis, and several efficient preparative procedures have been published in recent years.[9] The purpose behind the replacement of the central pyrrole ring by a diethylpyrrole unit was the variation of the donor capacity of the pyrrolide ligand, an approach previously pursued in oligopyrrole (notably porphyrin) chemistry.[9] In the first reaction step the dicarboxylic acid **3** was treated with 2.5 mol-equiv. of the amino alcohol in the presence of the well-established amide coupling reagent *N*′-[3-(dimethylamino)propyl]-*N*-ethylcarbodiimide (EDC·HCl) and 1-hydroxybenzotriazole (HOBt) (Scheme 1).[10] The diamide **4** was dimesylated and then cyclized in the presence of an excess of NaOH in methanol. After workup, the target compound **5** was obtained as a pale yellow oil, which was characterised by elemental analysis, mass spectrometry and infrared and ^1H and ^{13}C NMR spectroscopy.

Synthesis and Structural Characterisation of the Helical Dinuclear Palladium Complexes $[Pd_2Cl_2(dmoxp)_2]$ (6) and $[Pd_2Cl_2(Et_2dmoxp)_2]$ (7)

Deprotonation of the pyrrole rings in dmoxpH (**2**) and Et_2dmoxpH (**5**) with *n*-butyllithium at −78 °C in diethyl ether and subsequent stirring of the lithium pyrrolide with 1.1 mol-equiv. of $[PdCl_2(COD)]$ gave the corresponding palladium complexes $[Pd_2Cl_2(dmoxp)_2]$ (**6**) and $[Pd_2Cl_2(Et_2dmoxp)_2]$ (**7**) after chromatographic workup (Scheme 2).



Scheme 2. Synthesis of the helical dinuclear palladium complexes $[Pd_2Cl_2(dmoxp)_2]$ (**6**) and $[Pd_2Cl_2(Et_2dmoxp)_2]$ (**7**)

In order to establish their molecular structures, X-ray diffraction studies of both complexes **6** and **7** were carried out. Two views of their very similar molecular structures are depicted in Figures 1 and 2, together with the principal bond lengths and interbond angles.

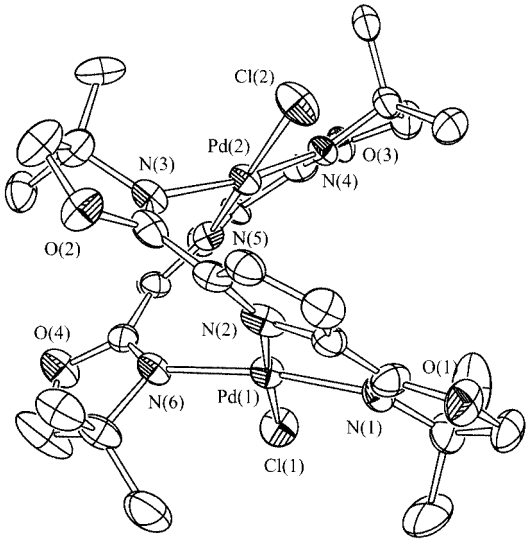


Figure 1. Molecular structure of the palladium complex $[Pd_2Cl_2(dmoxp)_2]$ (**6**); selected bond lengths [Å] and angles [°]: Pd(1)−N(1) 2.052(8), Pd(1)−N(2) 2.039(8), Pd(1)−N(6) 2.036(8), Pd(1)−Cl(1) 2.296(3), Pd(2)−Cl(2) 2.287(3), Pd(2)−N(3) 2.043(8), Pd(2)−N(4) 2.025(7), Pd(2)−N(5) 2.039(8); N(2)−Pd(1)−N(6) 97.7(3), N(1)−Pd(1)−N(2) 79.8(3), Cl(1)−Pd(1)−N(1) 96.5(2), N(3)−Pd(2)−N(5) 97.7(3), N(4)−Pd(2)−N(5) 79.9(3), N(2)−C(28)−C(8)−N(3) 29.3(5), N(5)−C(19)−C(22)−N(6) 26.4(5)

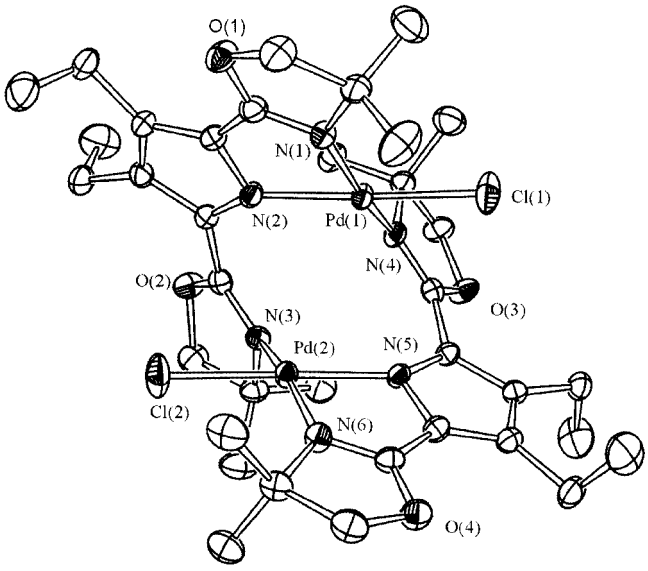


Figure 2. Molecular structure of the palladium complex $[Pd_2Cl_2(Et_2dmoxp)_2]$ (**7**); selected bond lengths [Å] and angles [°]: Pd(1)−N(1) 2.031(2), Pd(2)−N(3) 2.043(2), Pd(1)−Cl(1) 2.2922(7), Pd(1)−N(2) 2.036(2), Pd(2)−N(5) 2.031(2), Pd(2)−Cl(2) 2.0311(7), Pd(1)−N(4) 2.035(2), Pd(2)−N(6) 2.036(2); N(1)−Pd(1)−Cl(1) 94.94(6), N(6)−Pd(2)−Cl(2) 95.75(6), N(1)−Pd(1)−N(2) 80.01(8), N(3)−Pd(2)−N(5) 94.48(8), N(2)−Pd(1)−N(4) 96.80(8), N(5)−Pd(2)−N(6) 79.86(8), N(2)−C(7)−C(14)−N(3) 21.4(5), N(4)−C(21)−C(24)−N(5) 28.3(5)

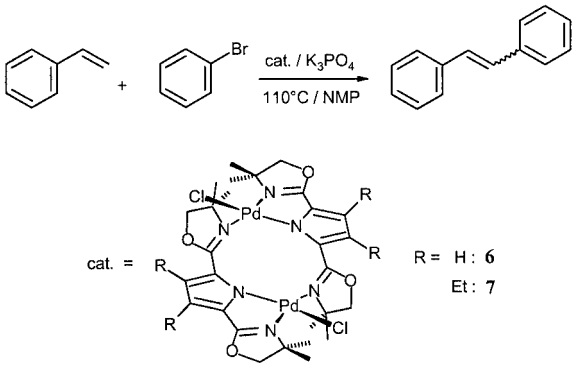
Both compounds **6** and **7** are dinuclear complexes in which the tridentate bis(oxazolinyl)pyrolide ligands bridge the two metal centres. Whereas one of the oxazoline rings and the charged pyrrolide are coordinated to the one Pd centre, adopting an almost coplanar arrangement, the second oxazoline ring is twisted relative to the pyrrolide unit [**6**: 26.4 and 29.3°; **7**: 21.4 and 28.3°] and coordinates to the second palladium atom. The coordination geometry at each metal centre is distorted square-planar, with the chloro ligand disposed *trans* to the pyrrolide. Although neither of the complexes **6** and **7** possesses exact crystallographic symmetry, both have an approximate twofold molecular symmetry axis relating the {Pd(ligand)Cl} fragments. Overall, the two bis(oxazolinyl)pyrrolide ligands are wrapped around the two metal centres to give helical arrangements,[11] with Pd−Pd distances of 3.389 and 3.426 Å for **6** and **7**, respectively. It is interesting to note that complex **6** crystallised in the polar space group *C*2 as a conglomerate of (*P*)- and (*M*)-helical enantiomers, although we were unable to separate them mechanically. For the solution of the crystal structure of **6** we selected by chance a crystal containing the (*M*) enantiomer, which is depicted in Figure 1.

The dimerisation of both **6** and **7** to give the helical dinuclear complexes implies the loss of all local symmetry elements at the metal centres. Only the two tridentate ligands as a whole are related by a twofold rotational axis. This loss in local symmetry is reflected in the signal patterns of the ^1H and ^{13}C NMR spectra of both compounds, in which all the ^1H and ^{13}C nuclei in the individual ligands are chemically inequivalent. Consistent with this reduced symmetry with respect to the ligand precursors **2** and **5** is the observation of two vibrational C=N bands for the two inequivalent oxazoline rings at 1632 and 1608 cm^{-1} for **6** and at 1622 and 1600 cm^{-1} for **7**.

Heck Coupling Reactions with Mono- and 1,2-Disubstituted Alkenes, Catalysed by $[Pd_2Cl_2(dmoxp)_2]$ (6) and $[Pd_2Cl_2(Et_2dmoxp)_2]$ (7)

Originally, Pd-catalysed Heck and Suzuki coupling reactions were based almost entirely on phosphane or phosphane-derived systems.[12] In recent years, however, a whole range of alternative ligand systems for this reaction has been successfully tested. These include *N*-heterocyclic carbenes,[13,14] N-, O- and S-containing palladacycles,[15,16] cyclometallated imines[17] and diazabutadienes[18] which act as mono- or polydentate ancillary ligands.

We tested the activities of compounds **6** and **7** in Heck coupling reactions. In an initial study, the reaction conditions (solvent, base, reaction temperature) were optimised for the reference reaction between bromobenzene and styrene, in the presence of 0.1 mol % of the catalyst precursor (Scheme 3). The best results were obtained at 110 °C in *N*-methylpyrrolidone with K_3PO_4 as a base, and these reaction conditions were chosen for all subsequent catalytic runs. It should be pointed out that the palladium catalysts were stable under these conditions throughout the conversions. Precipitation of "Pd-black", potentially due to the degradation of the molecular catalysts, was not observed in any case. The results of a comparative study with $[Pd_2Cl_2(dmoxp)_2]$ (**6**) and $[Pd_2Cl_2(Et_2dmoxp)_2]$ (**7**) are depicted in Table 1.



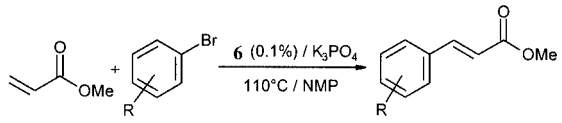
Scheme 3. Application of the palladium complexes $[Pd_2Cl_2(dmoxp)_2]$ (**6**) and $[Pd_2Cl_2(Et_2dmoxp)_2]$ (**7**) in the Heck reaction between bromobenzene and styrene

Table 1. Comparative study of the catalytic activities of catalysts **6** and **7** in the Heck reaction between bromobenzene and styrene

Entry	Catalyst	Cat./Sub.	Time	Conv. [(*Z*) + (*E*)]	T.O.N.
1	6	10^{-3}	3 d	97.1%	971
2	7	10^{-3}	3 d	96.6%	966
3	6	10^{-4}	3 d	87.3%	8730
4	7	10^{-4}	3 d	85.4%	8540
5	6	$5{\cdot}10^{-5}$	4 d	47.4%	9480
6	7	$5{\cdot}10^{-5}$	4 d	43.2%	8640

In general, there does not seem to be a significant difference in the catalytic performances of complexes **6** and **7**. A minimum catalyst/substrate ratio of $5 \cdot 10^{-5}$ was employed, and this, after 4 d reaction time at 110 °C, gave degrees of conversion to the product stilbene of 47 and 43%, respectively. The electronic effect expected from the introduction of the ethyl substituent on the pyrrolide ring[9] is not reflected in a modulation of the catalytic activity. It should be noted, though, that the turnover numbers of 9480 and 8640 place these catalysts among the most efficient systems containing exclusively nitrogen donor ligands.[19,20]

The results of the coupling of methyl acrylate with several substituted bromobenzene derivatives catalysed by compound **6** (Scheme 4) is shown in Table 2. The degree of conversion after a reaction time of 3 d was high and the stereoselectivity in favour of the (*E*) isomers essentially quantitative. In none of the cases did we observe traces of the geminally disubstituted coupling product.[21] No activity was observed for derivatives of chlorobenzene for the coupling either of styrene or of methyl acrylate.

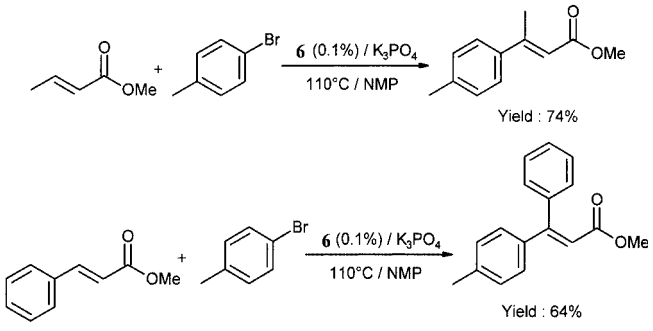


Scheme 4. Coupling of methyl acrylate with substituted bromobenzene derivatives

Table 2. Results of the Heck reactions between methyl methacrylate and substituted bromobenzene derivatives, catalysed by **6**

Entry	R	Time	Conversion	(*E*)/(*Z*)
1	2-Me	3 d	77%	100:0
2	4-Me	3 d	97%	100:0
3	4-OMe	3 d	85%	99:1

The use of the Heck coupling reaction for the synthesis of trisubstituted alkenes has received much less attention than the standard conversions affording disubstituted C=C double bonds.[20,22,23] We therefore carried out several tests to investigate the activity of **6** towards (*E*)-1,2-disubstituted alkenes. With a catalyst loading of 0.1 mol %, the reactions of methyl crotonate and methyl cinnamate with 4-bromotoluene gave the corresponding trisubstituted olefins after a reaction time of 7 d (Scheme 5).



Scheme 5. Heck reactions giving trisubstituted alkenes

The most remarkable aspect of these conversions is the complete stereoselectivity in the positioning of the entering aryl group in the reaction products. The configuration was established by NOESY experiments, NOEs between the α-olefin proton and the *ortho*-protons of the tolyl group providing the key assignment. It was not possible to detect any other stereoisomer even in trace quantities by GC, GCMS or by NMR spectroscopy. The exclusive formation of the (*E*) stereoisomers may be explained by the stereospecificity of the migratory insertion step resulting in the coupling of the olefin and the Pd-bonded aryl group and of the subsequent β-elimination step (Scheme 6).

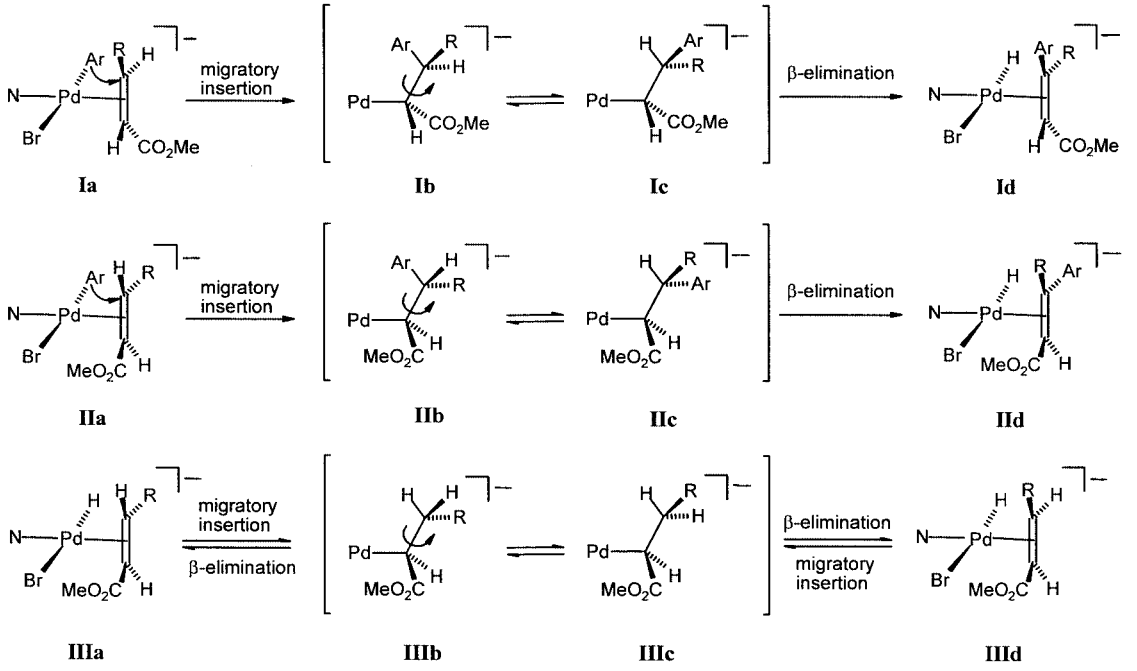
We have shown in a previous study that these dissociate in solution at temperatures above 70 °C,[6] and it is within this thermodynamic regime that their catalytic activities in Heck and Suzuki C−C coupling reactions have been observed. We therefore only consider monomeric species in the following mechanistic discussion. The *endo* approach of the aryl group in the intermediates **Ia** and **IIa** stereospecifically generates the alkyl complexes **Ib** and **IIb**, in which rotation around a C−C bond gives access to a conformation (**Ic** and **IIc**, respectively) in which the β-H is oriented towards the metal centre and from which β-elimination occurs. This gives the intermediates **Id** and **IId**, both of which liberate exclusively the (*E*) isomer.

Buchwald et al. have previously found a high degree of stereoselectivity in non-phosphane/palladium-catalysed Heck reactions of 1,2-substituted α,β-unsaturated carboxyl esters.[20] They also pointed out that the generally accepted mechanism of the catalytic Heck coupling implied a stereospecific reaction sequence as detailed above. The deviations from ideal stereoselection were interpreted as being due to an isomerisation of the configuration at the C=C double bond after the Heck coupling step. For the two cases described above we were unable to establish such an post-Heck equilibration, which may be due to the short lifetime of the hydridopalladium intermediate after decoordination of the product olefin. In fact, such a hydrido species may play a role either before or after the Heck reaction:

a) It may in principle coordinate the disubstituted alkene starting material (**IIIa** in Scheme 6), which is isomerised to the (*Z*)-1,2-disubstituted alkene in a sequence of migratory insertion and β-elimination (liberated from **IIId** in Scheme 6).

b) Alternatively, given a sufficient lifetime of the hydridopalladium complex, the reaction products liberated from **Id** and **IId** may recoordinate to the metal centre, and the migratory insertion into the Pd−H bond may then take place in part with a reversed regioselectivity (migration of the H atom to the C atom adjacent to the carboxyl function). A subsequent β-elimination from such an intermediate may indeed give the other isomer and, since all steps are reversible, the product distribution may be under thermodynamic control.

The fact that no isomerisation is observed in the case at hand even after the considerable reaction time of 7 d, necessary because of the low catalyst loadings of 0.1 mol %, indicates the short lifetime of the hydridopalladium species.

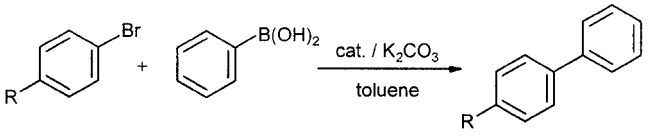


Scheme 6. Mechanistic scheme representing the stereospecific migratory insertion-β-elimination sequence in the Heck reaction involving 1,2-disubstituted alkenes

This may in part be due to the proximity of the relatively basic oxazoline functions attached to the pivotal pyrrolide ligand.

Suzuki Coupling Reactions Catalysed by $[Pd_2Cl_2(dmoxp)_2]$ (6)

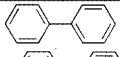
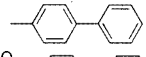
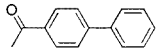
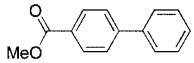
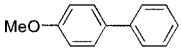
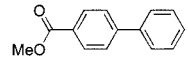
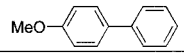
Compound **6** was found to be a highly active catalyst for the Suzuki-type coupling of phenylboronic acid with aryl bromides at relatively moderate temperatures (Table 3). In the general procedure a catalyst/substrate ratio of 10^{-4} was used and the aryl bromide and phenylboronic acid were stirred at 70 °C in toluene in the presence of K_2CO_3 as auxiliary base.



Scheme 7. Suzuki coupling between bromobenzene derivatives and phenylboronic acid

As observed for the Heck-type coupling reactions discussed above, catalyst **6** was found to be highly stable under Suzuki coupling conditions, and no palladium-black was formed during the reaction. The catalytic reaction was monitored by GC MS, and 100% conversion was obtained with both activated and deactivated bromides after 1−6 h. A decrease in the catalyst/substrate ratio to 10^{-5} still gave an 82% isolated yield of 4-bromoacetophenone and 54% of 4-methoxyacetophenone after 4 h, corresponding to turnover numbers of 82000 and 54000, respectively. In contrast to the reactivity towards aryl bromides, the catalyst proved to possess only very low activity towards the aryl chlorides, the reaction effectively stopping after a few cycles at 110 °C. As in the case of the Heck coupling reactions discussed in the previous section, the use of the diethyl-substituted derivative $[Pd_2Cl_2(Et_2dmoxp)_2]$ (**7**) gave essentially identical results in the catalytic conversions.

Table 3. Results of the Suzuki reactions between phenylboronic acid and substituted bromobenzene derivatives, catalysed by **6**

Entry	R	Product	Time	Cat./Sub.	Temp.	Yield	T.O.N.
1	H		2 h	10^{-4}	70 °C	97 %	9700
2	CH_3		2 h	10^{-4}	70 °C	89 %	8900
3	$C(O)CH_3$		1 h	10^{-4}	70 °C	92 %	9200
4	$C(O)OCH_3$		4 h	10^{-4}	70° C	95 %	9500
5	OCH_3		6 h	10^{-4}	70 °C	88 %	8800
6	$C(O)OCH_3$		4 h	10^{-5}	110 °C	82 %	**82000**
7	OCH_3		4 h	10^{-5}	110 °C	54 %	**54000**

Conclusions

Through the charging and deformation of the well-established pybox ligand **B** systems by replacement of the central pyridine unit by a formally charged pyrrolide ring, the more open "pyrrbox" ligands **A** have been obtained. The specific arrangement of the three nitrogen donor functions in these has given rise to helical dinuclear complexes if coordinated

to palladium(II). Whereas their activity is lower than those found for some Pd complexes bearing phosphane or N-heterocyclic arene ligands, they are nevertheless among the most active catalysts containing exclusively nitrogen-donor ligands. The observation of the high stereoselectivity in the Heck reactions with 1,2-disubstituted alkenes described in this work is remarkable and has initiated a more systematic investigation into this aspect, currently underway in our laboratory.

Experimental Section

General: Solvents were dried by standard procedures and saturated with nitrogen. Solids were separated from suspensions by centrifugation, thus avoiding filtration procedures, with a Hettich Rotina 48 centrifuge equipped with a specifically designed Schlenk tube rotor (Hettich Zentrifugen, Tuttlingen, Germany).[24] Optical rotations were recorded with a thermostated Perkin−Elmer Otopol III instrument in a 1.0-dm cell. The ^1H and ^{13}C NMR spectra were recorded with Bruker AC 300 (^1H 300 MHz; $^{13}C\{^1H\}$ 75 MHz), Bruker AM 400 (^1H 400 MHz; $^{13}C\{^1H\}$ 100 MHz), and Bruker ARX 500 (^1H 500 MHz; $^{13}C\{^1H\}$ 125 MHz) spectrometers. Infrared spectra were recorded with a Perkin−Elmer 1600 FT-IR spectrometer. EI mass spectra were recorded with a Shimadzu QP5050-GC/MS system. The elemental analyses were carried out by the Service Commun de Microanalyse de l'Université Louis Pasteur at Strasbourg. Pyrrole-2,5-dicarbonitrile,[6] 3,4-diethylpyrrole-2,5-dicarboxylic acid[8] and $[PdCl_2(1,5\text{-}COD)]$[25] were prepared by published procedures. All other chemicals used as starting materials were obtained commercially and used as received without further purification.

Preparation of 2,5-Bis(4,4′-dimethyl-4,5-dihydrooxazol-2-yl)pyrrole ("dmoxpH", 2): $ZnCl_2$ (1.164 g, 8.54 mmol, 0.5 equiv.) was melted under vacuum and then cooled under nitrogen for 15 min. A slurry of pyrrole-2,5-dicarbonitrile (2 g, 17.6 mmol) and 2-amino-2-methyl-1-propanol (4.263 g, 47.82 mmol, 2.8 equiv.) in chlorobenzene (25 mL) was added, and the mixture was heated at reflux for 24 h. The solvent was removed in vacuo and the orange-brown residue was chromatographed on silica gel (hexanes/EtOAc, 1:1); R_f = 0.43, yielding 4.263 g of an off-white solid (yield 72%). ^1H NMR (300 MHz. $CDCl_3$): δ = 11.40 (br. s, 1 H, NH_{pyrr}), 6.71 (s, 2 H, $H_{3/4,pyrr}$), 4.05 (s, 4 H, $CH_{2,oxa}$), 1.34 (s, 12 H, $CH_{3,oxa}$) ppm. $^{13}C\{^1H\}$ NMR (75 MHz. $CDCl_3$): δ = 155.6 ($C{=}N_{oxa}$), 123.0 (C-2/5$_{pyrr}$), 112.9 (C-3/4$_{pyrr}$), 79.0 ($CH_{2,oxa}$), 67.4 ($C_{quat,oxa}$), 28.2 ($CH_{3,oxa}$) ppm. IR (KBr): $\tilde{\nu}$ = 3436 (s), 2969 (m), 1660 (s), 1612 (m), 1499 (s), 1404 (m), 702 (m) cm^{-1}. MS (EI, 70 eV): *m*/*z* = 261 $[M]^+$, 246 $[M - CH_3]^+$, 174 $[M - CH_3 - (CH_3)_2CCH_2O]^+$. $C_{14}H_{19}N_3O_2$ (261.15): calcd. C 64.35, H 7.33, N 16.08; found C 63.89, H 7.25 N 15.99.

Preparation of Compound 4: A mixture of 3,4-diethylpyrrole-2,5-dicarboxylic acid (4.1 g, 19.4 mmol), amino alcohol (5.191 g, 58.2 mmol), EDC·HCl (11.164 g, 58.2 mmol), and HOBt (7.870 g, 58.2 mmol) in 75 mL of CH_2Cl_2 and 75 mL of DMF was stirred under nitrogen at room temperature for 48 h. The reaction mixture was poured into a saturated NH_4Cl/CH_2Cl_2 solution, and the aqueous layer was extracted with CH_2Cl_2. The combined organic layers were washed with 1 N HCl, water, saturated $NaHCO_3$ and brine, and then dried with anhydrous Na_2SO_4. After removal of the solvent, the product was isolated as a pale yellow oil (5.2 g, 14.7 mol, 77% yield). ^1H NMR (300 MHz, $CDCl_3$): δ = 10.4 (br. s, 1 H, NH_{pyrr}), 6.39 (s, 2 H, NH), 3.61 (s, 4 H, CH_2), 2.64 (q, 4 H, $CH_{2,pyrr}$), 1.38 (s, 12 H, CH_3), 1.20 (t, 6 H, $CH_{3,oxa}$) ppm. $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ = 162.1 (C-3/4$_{pyrr}$), 128.1 (C=O or C-2/5$_{pyrr}$), 123.9 (C-2/5$_{pyrr}$ or C=O), 69.9 (CH_2), 56.2 [*C*$(CH_3)_2$], 24.8 (CH_3), 17.9 ($CH_{2,pyrr}$), 15.8 ($CH_{3,pyrr}$) ppm. IR ($CHCl_3$): $\tilde{\nu}$ = 3423 (m), 2971 (s), 2253 (s), 1634 (s), 1516 (s), 1469 (s), 1301 (s), 1062 (m), 651 (s) cm^{-1}. $C_{18}H_{31}N_3O_4$ (353.23): calcd. C 61.17, H 8.84, N 11.89; found C 61.24, H 8.67 N 11.74.

Preparation of 2,5-Bis(4,4′-dimethyl-4,5-dihydrooxazol-2-yl)-3,4-diethylpyrrole ("Et$_2$dmoxpH", 5): MsCl (1.18 mL, 15.2 mmol) was slowly added to an ice-cold solution of **3** (2.440 g, 6.9 mmol) and Et_3N (3.30 mL, 30.4 mmol) in 20 mL of dichloromethane. The mixture was allowed to warm to room temperature and was then stirred for 1 h. After washing with water (5 mL), the organic phase was dried with Na_2SO_4, and the volatiles were removed in vacuo to give a yellow oil, which was used in the next step without purification. The bis(mesylated) compound was treated with KOH (0.4 g, 7.1 mmol) in 25 mL of an MeOH/H_2O mixture (5:1). The reaction mixture was stirred at room temperature for 3 d, then washed with water and dried with Na_2SO_4. The solvents were removed to give the ligand precursor as a pale yellow oil in 73% yield (1.6 g). ^1H NMR (300 MHz, $CDCl_3$): δ = 9.6 (br. s, 1 H, NH_{pyrr}), 4.24 (s, 4 H, $CH_{2,oxa}$), 2.70 (q, 4 H, $CH_{2,pyrr}$), 1.32 (s, 12 H, CH_3), 1.15 (t, 6 H, $CH_{3,oxa}$) ppm. $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ = 156.6 ($C{=}N_{oxa}$), 130.1 (C-2/5$_{pyrr}$), 118.6 (C-3/4$_{pyrr}$), 79.0 ($CH_{2,oxa}$), 66.9 [*C*$(CH_3)_2$], 28.2 (CH_3), 17.7 ($CH_{2,pyrr}$), 15.8 ($CH_{3,pyrr}$) ppm. IR ($CHCl_3$): $\tilde{\nu}$ = 3437 (m), 2969 (s), 1640 (s), 1461 (m), 1353 (m), 1305 (m), 1197 (m), 651 (s) cm^{-1}. MS (EI, 70 eV): *m*/*z* = 317 $[M]^+$, 302 $[M - CH_3]^+$, 160 $[M - 2\,CH_2CH_3]^+$. $C_{18}H_{27}N_3O_2$ (317.21): calcd. C 68.11, H 8.57, N 13.24; found C 68.02, H 8.52 N 13.15.

General Procedure for the Preparation of the Palladium Complexes [Pd$_2$Cl$_2$(dmoxp)$_2$] (6) and [Pd$_2$Cl$_2$(Et$_2$dmoxp)$_2$] (7): A solution of *n*BuLi (1.6 M) in hexanes (3.59 mL) was added to a diethyl ether (50 mL) solution of the bis(oxazolinyl)pyrrole (5.74 mmol), which was cooled to −78 °C. The reaction mixture was stirred for 15 min and then allowed to warm to room temperature. After an additional hour, a suspension of dichlorobis(1,5-cyclooctadiene)palladium (1.639 g; 5.74 mmol) in diethyl ether (20 mL) was added and the resulting mixture was stirred for 12 h at room temperature. The reaction mixture was then filtered and the resulting orange oil was purified by flash chromatography (silica gel, hexanes/EtOAc, 1:1) to give **6** (and **7**) as orange, air-stable solids.

[Pd$_2$Cl$_2$(dmoxp)$_2$] (6): Yield: 42%. R_f = 0.56. ^1H NMR (300 MHz, $CDCl_3$): δ = 6.64 (br. d, 2 H, 3/4-H_{pyrr}), 4.38 (d, 1 H, $CH_{2,oxa}$), 4.24 (t, 2 H, $CH_{2,oxa}$), 4.17 (d, 1 H, $CH_{2,oxa}$), 1.92 (s, 3 H, $CH_{3,oxa}$), 1.57 (s, 3 H, $CH_{3,oxa}$), 1.43 (s, 3 H, $CH_{3,oxa}$), 1.15 (s, 3 H, $CH_{3,oxa}$) ppm. $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ = 167.8 ($C{=}N_{oxa}$), 164.9 ($C{=}N_{oxa}$), 133.1 (C-2/5$_{pyrr}$), 131.9 (C-5/2$_{pyrr}$), 117.1 (C-3/4$_{pyrr}$), 112.2 (C-3/4$_{pyrr}$), 83.2 ($CH_{2,oxa}$), 80.0 ($CH_{2,oxa}$), 67.9 [*C*$(CH_3)_2$], 65.9 [*C*$(CH_3)_2$], 30.4 ($CH_{3,oxa}$), 27.8 ($CH_{3,oxa}$), 27.5 ($CH_{3,oxa}$), 26.7 ($CH_{3,oxa}$) ppm. IR (KBr): $\tilde{\nu}$ = 2964, 1632, 1608, 1521, 1376, 721, 362 cm^{-1}. $C_{28}H_{38}Cl_2N_6O_5Pd_2$ (822.36): calcd. C 41.81, H 4.51; found C 41.95, H 4.73.

[Pd$_2$Cl$_2$(Et$_2$dmoxp)$_2$] (7): Yield 30%. R_f = 0.47. ^1H NMR (500 MHz, C_6D_6): δ = 3.72 (m, 3 H, $CH_{2,oxa}$), 3.52 (d, $^3J_{H,H}$ = 8.3 Hz, 1 H, $CH_{2,oxa}$), 2.92 (m, 1 H, $CH_{2,pyrr}$), 2.79 (m, 2 H, $CH_{2,pyrr}$), 2.68 (m, 1 H, $CH_{2,pyrr}$), 1.77 (s, 3 H, $CH_{3,oxa}$), 1.53 (s, 3 H, $CH_{3,oxa}$), 1.41(m, 6 H, $CH_{3,oxa}$ and $CH_{3,pyrr}$), 1.32 (t, $^3J_{H,H}$ = 8 Hz, 3 H, $CH_{3,pyrr}$), 1.04 (s, 3 H, $CH_{3,oxa}$) ppm. $^{13}C\{^1H\}$ NMR (125 MHz, C_6D_6): δ = 168.3 ($C{=}N_{oxa}$), 165.5 ($C{=}N_{oxa}$), 133.0 (C-2/5$_{pyrr}$), 131.1 (C-3/4$_{pyrr}$), 130.0 (C-3/4$_{pyrr}$), 128.4 (C-3/4$_{pyrr}$), 83.2

($CH_{2,oxa}$), 80.0 ($CH_{2,oxa}$), 67.4 [$C(CH_3)_2$], 65.2 [$C(CH_3)_2$], 31.0 ($CH_{3,oxa}$), 27.6 ($CH_{3,oxa}$), 27.4 ($CH_{3,oxa}$), 26.6 ($CH_{3,oxa}$), 18.8 ($CH_{2,pyrr}$), 17.9 ($CH_{2,pyrr}$), 17.3 ($CH_{3,pyrr}$), 17.2 ($CH_{3,pyrr}$) ppm. IR (KBr): $\tilde{\nu}$ = 2965 (m), 1622 (s), 1600 (s), 1519 (m), 1406 (s), 1189 (s), 1151 (s), 965 (m), 742 (m), 349 (w) cm^{-1}. $C_{36}H_{52}Cl_2N_6O_5Pd_2$ (914.15): calcd. C 47.17, H 5.72; found C 47.21, H 5.56.

General Procedure for the Heck Coupling Reactions: The aryl bromide (1.1 mmol), the olefinic substrate (1.0 mmol, 6.0 mmol in the case of methyl acrylate) and K_3PO_4 (1.1 mmol) were dissolved in 3 mL of dry NMP. The catalyst (or a solution of the catalyst) was then added the reaction mixture was purged three times with nitrogen and heated to 110 °C. The reaction was monitored by GCMS analysis until the generation of the product olefin had ceased. The (*Z*)/(*E*) ratio and the degree of conversion were determined by GC analysis.

General Procedure for the Heck Coupling Reactions with 1,2-Disubstituted Alkenes: The aryl bromide (1.1 mmol), the olefin (1.0 mmol) and K_3PO_4 (1.1 mmol) were dissolved in 3 mL of dry NMP. The catalyst (0.1%) was then added and the reaction mixture was purged three times with nitrogen and heated to 110 °C. When the reaction was complete, as determined by GCMS analysis, the reaction mixture was allowed to cool to room temperature, diluted with diethyl ether and washed three times with water. The organic layer was dried with $MgSO_4$ and concentrated in vacuo to give the crude product. Purification by flash chromatography (hexane 100%, then hexanes/EtOAc, 1:1) afforded the analytically pure alkene product.

General Procedure for the Suzuki Cross-Coupling Reactions: The arylboronic acid and K_2CO_3 (2 equiv.) were placed in a Schlenk tube equipped with a stirring bar. Three nitrogen/vacuum cycles were performed before addition of dry toluene (5 mL), the aryl bromide (1.1 equiv.) and the palladium catalyst (or a solution of the palladium catalyst). The reaction was performed at the temperature indicated in Table 3. On completion of the reaction, the mixture was diluted with Et_2O, filtered through a pad of Celite, washed three times with water, concentrated and purified by column chromatography or recrystallisation. All the products were characterised by standard spectroscopic and analytical methods. Their spectroscopic data are in agreement with those found in the literature.[26]

X-ray Crystallographic Study of 6 and 7: Suitable crystals of the complexes **6** and **7** were obtained by layering concentrated solutions of the compounds in dichloromethane with *n*-hexane and allowing slow diffusion at room temperature. The crystal data were collected at −100 °C with a Nonius Kappa CCD diffractometer and transferred to a DEC Alpha workstation; for all subsequent calculations the Nonius OpenMoleN package was used.[27] The structures were solved by 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_{equiv}(C) Å^2] but not refined. Full least-squares refinements 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 ref.[28] Crystal data and experimental details for the crystals of compounds **6** and **7** are given in Table 4. CCDC-173019 (**6**) and -194957 (**7**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: (internat.) + 44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

Table 4. X-ray experimental data of compounds **6** and **7**

	6	**7**
Empirical formula	$C_{28}H_{36}Cl_2N_6O_4Pd_2{\cdot}H_2O$	$C_{36}H_{52}Cl_2N_6O_4Pd_2$
Formula mass	822.36	916.56
Crystal system	monoclinic	monoclinic
Space group	*C*2	$P2_1/c$
a [Å]	19.733(1)	11.4766(1)
b [Å]	9.9775(5)	18.3485(3)
c [Å]	16.8832(9)	19.8285(3)
β [°]	95.021(5)	103.820(5)
V [Å^3]	3311.3(3)	4054.58(9)
Z	4	4
$D_{calcd.}$ [g cm^{-3}]	1.65	1.50
F(000)	1656	1872
μ [mm^{-1}]	1.293	1.063
T [K]	173	173
λ [Å]	0.71073	0.71073
Radiation	Mo-K_α	Mo-K_α
θ limits [°]	2.5/27.09	2.5/30.03
Number of data measured	5478	20064
Number of data with $I > 3\sigma(I)$	4263	7971
Number of variables	387	451
R	0.048	0.029
Rw	0.066	0.036
GOF	1.179	1.159
Largest peak in final difference [e·Å^{-3}]	1.758	1.267

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