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Dinuclear Allylpalladium Complexes of C_2-Symmetric Pyrazolate-Bridged Bis(oxazoline) Ligands (pyrbox's): Structures, Dynamic Behavior, and Application in Asymmetric Allylic Alkylation

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A series of new chiral binucleating pyrazolate-based N-donor ligands (**3a**−**d**) with oxazoline side arms (coined pyrbox's) have been synthesized. Bimetallic methallylpalladium complexes (**4a**−**d**) of these ligands were obtained, and the solid-state structures of complexes **4a**,**c** were characterized by X-ray diffraction. NMR spectroscopy revealed that in solution **4a**−**d** exist as three different isomers that differ in the orientation of the two methallyl ligands. Exchange between the isomers (i.e., allyl rotation) was observed in two-dimensional NOESY NMR experiments as syn/syn and anti/anti interconversion of the allylic hydrogen atoms; kinetic parameters for the fluxional behavior have been determined. The catalytic activity of the complexes was tested in palladium-catalyzed allylic alkylation of *rac*-(*E*)-1,3-diphenylallyl acetate. By comparison of the set of complexes **4a**−**d** that feature different ligand scaffolds, both steric and electronic factors were found to be important for enantiocontrol, and a model has been proposed for rationalizing the observed enantioselectivities.

Introduction

C_2-symmetric bis(oxazolines), usually called box's, were introduced as a new class of ligands for asymmetric catalysis in the early 1990s.[1] Since then, the list of applications of these ligands has rapidly grown, as has the number of differently substituted box derivatives.[2−4] Further developments in the field comprise, inter alia, the tris(oxazolines)[5,6] as well as box ligands with a range of bridges linking the chiral oxazoline rings, including bridges with additional donor atoms.[7] Prominent examples of the latter type are the so-called pybox ligands, which feature a central pyridine and provide a tridentate binding site.[8] Though oxazoline-based ligands have become very common, binucleating systems where a central bridging unit with appended oxazoline rings can host two metal centers have remained scarce so far. This is somewhat surprising, since recent chemical research has seen an increasing interest in two-center catalysis that offers the potential of cooperative effects of the proximate metal ions.[9−11] The principle is nothing new, as naturally occurring enzymes use this approach in various ways, and binucleating ligand design is indeed very popular in biomimetic and bioinspired coordination chemistry.[12,13] However, only a few reports have dealt with bimetallic C_2-symmetric complexes of the bis(oxazoline) type: Pfaltz and Fahrni developed a series of phenol-, 1,8-naphthyridine-, and pyridazine-bridged ligand scaffolds, each with oxazoline side arms,[14] and have studied some aspects of their coordination

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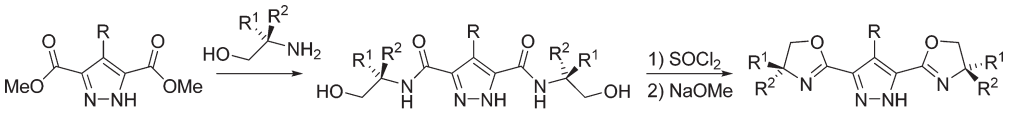
Scheme 1. Synthesis of Pyrazole-Bridged Ligands 3a−d



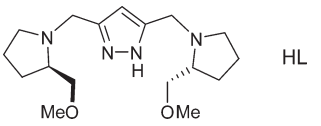
1a R = H
1b R = Ph

2a R = H, R^1 = H, R^2 = Ph
2b R = Ph, R^1 = H, R^2 = Ph
2c R = H, R^1 = *i*-Pr, R^2 = H
2d R = Ph, R^1 = *i*-Pr, R^2 = H

3a R = H, R^1 = H, R^2 = Ph
3b R = Ph, R^1 = H, R^2 = Ph
3c R = H, R^1 = *i*-Pr, R^2 = H
3d R = Ph, R^1 = *i*-Pr, R^2 = H

chemistry and their use in catalysis.[15] More recently, the structure of a binuclear η^3-allylpalladium complex of the pyridazine-centered pydbox ligand with appended oxazoline rings was also reported.[16]

Pyrazole, in its deprotonated form, is a well-known bridging unit that supports the formation of bimetallic complexes.[17] The generally adopted metal−metal separations are in the range of 3.4−4.5 Å and are thus suitable for exploiting cooperative reactivity toward substrate molecules. Further enhancement of preorganization of the two metal ions can be achieved by the attachment of chelating side arms to the 3,5-positions of the pyrazole heterocycle, and a variety of symmetrical and unsymmetrical 3,5-disubstituted ligands with mono-, bi-, and tridentate side arms have been developed over the past decade.[18] By varying the lengths of these side arms and the nature or the quantity of the donor atoms, a fine tuning of the metal−metal distance can be achieved.[19,20] Such highly preorganized pyrazolate-based bimetallic complexes have been successfully used in metallobiosite modeling,[21] and their favorable properties in two-center organometallic chemistry are increasingly recognized.[22−25] While a pyrazolate-bridged bimetallic array has inherent 2-fold symmetry, however, little is known as yet about C_2-symmetric systems with chiral chelate arms such as the ligand HL bearing two (*R*)-2-(methoxymethyl)pyrrolidine substituents at the central pyrazole core.[26]



In this work we report the synthesis of new chiral pyrazole-bridged ligands with oxazoline side arms (coined pyrbox's), as well as the synthesis and molecular structures of their binuclear allylpalladium complexes. Mutual interconversion of different isomers of the allylpalladium complexes in solution is studied in detail, using two-dimensional NMR techniques, and initial findings for the application of these C_2-symmetric binuclear pyrbox−palladium complexes in the asymmetric allylic alkylation of *rac*-(*E*)-1,3-diphenylallyl acetate are discussed in view of the fluxional behavior.

Results and Discussion

Synthesis of Ligands 3a−d. We prepared a set of four new ligands that differ in the C^4 substituent at the central pyrazole (H or Ph) and in the substituent of the outer oxazolines (Ph or ^{i}Pr), which allowed us to investigate the effect of steric and electronic modifications at both the bridging unit and the chelate arms. The synthesis was achieved in a straightforward approach (Scheme 1): in the first step, the pyrazole compounds **1a**[27] and **1b**[28] were reacted with an appropriate amino alcohol in the presence of a catalytic amount of acid. It was found beneficial to keep the amount of solvent very low, as dilution caused longer reaction times and favored the formation of the monosubstituted byproduct. Pyrazole compounds **2a−d** were obtained in moderate yields (55−73%) after recrystallization or chromatographic workup. Ring closure to form the oxazolines was then achieved by using thionyl chloride followed by the addition of sodium methoxide. The crude

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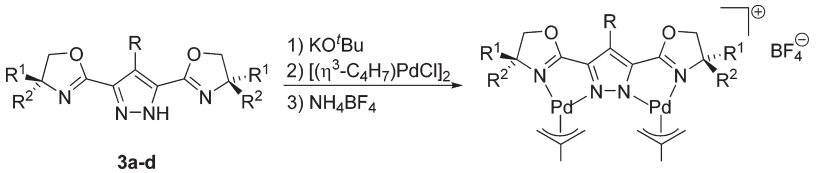
Scheme 2. Synthesis of Methallylpalladium Complexes 4a−d



3a-d

4a R = H, R^1 = H, R^2 = Ph
4b R = Ph, R^1 = H, R^2 = Ph
4c R = H, R^1 = *i*-Pr, R^2 = H
4d R = Ph, R^1 = *i*-Pr, R^2 = H

Table 1. C=N Stretching Vibrations for the Free Ligands (ν_L) and the Complexes (ν_C) Obtained from IR Spectroscopy

entry	ligand	ν_L(C=N), cm^{-1}	complex	ν_C(C=N), cm^{-1}	$\Delta\nu$, cm^{-1}
1	**3a**	1652	**4a**	1633	19
2	**3b**	1656	**4b**	1623	33
3	**3c**	1664	**4c**	1640	24
4	**3d**	1659	**4d**	1624	35

products were already quite pure and could be further purified by recrystallization or column chromatography, giving potential ligands **3a−d** in moderate to good yields (58−80%).

Synthesis and Characterization of Complexes 4a−d. The coordination properties of ligands **3a−d** were investigated in their monocationic bis(methallylpalladium) complexes. Deprotonation of the pyrazole with potassium *tert*-butoxide, addition of methallylpalladium chloride, and anion exchange with ammonium tetrafluoroborate afforded complexes **4a−d**, which were isolated as pale yellow solids after aqueous workup in good to excellent yields (80−98%; Scheme 2).

The products are soluble in polar solvents such as acetone, dichloromethane, and tetrahydrofuran but insoluble in hexane, pentane, or diethyl ether. Neat samples of the methallylpalladium complexes or solutions stored at −30 °C are stable in air for several weeks without any decomposition. However, at room temperature the compounds in solution gradually decompose within a few days, even when handled under inert conditions. All four complexes were fully characterized by IR, NMR, and mass spectrometry. As expected, the C=N stretching frequency is lower in the complexes **4a−d** compared to the corresponding free ligands **3a−d** due to coordination of the palladium (Table 1). This effect is somewhat more pronounced for **4b**,**d**, presumably because the phenyl substituent in the 4-position of the pyrazole weakens the electron donation of the pyrazole-N, which is balanced by a more pronounced binding of the oxazoline. However, ^{13}C NMR chemical shifts of the oxazoline C=N group are very similar in all cases (**4a**, 166.6 ppm; **4b**, 167.0 ppm; **4c**, 165.9 ppm; **4d**, 166.3 ppm) and only marginally larger for complexes bearing the backbone phenyl substituent (**4b**,**d**) compared to the respective complexes with a backbone H (**4a**,**c**).

Solid-State Structures of 4a,c. Crystals of **4a**,**c** were obtained by slow diffusion of diethyl ether into dichloromethane solutions of the complexes. Molecular structures are shown in Figures 1 and 2. One $[LPd_2\{(CH_2)_2CCH_3\}_2]^+$ cation per asymmetric unit is found in **4a**, while two different $[LPd_2\{(CH_2)_2CCH_3\}_2]^+$ cations with crystallographically imposed C_2 symmetry are present in **4c**. In one of the latter cases the (η^3-methallyl)Pd moieties are disordered about two

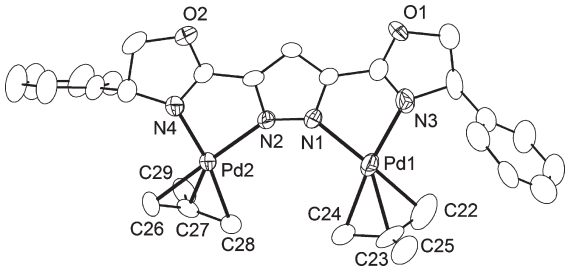


Figure 1. ORTEP plot (50% probability thermal ellipsoids) of the molecular structure of the cation of **4a**. Hydrogen atoms and the BF_4^- anion have been omitted for clarity. Selected bond distances (Å) and angles (deg): Pd(1)−N(1) = 2.133(7), Pd(1)−N(3) = 2.104(8), Pd(1)−C(22) = 2.127(12), Pd(1)−C(23) = 2.130(10), Pd(1)−C(24) = 2.131(11), C(22)−C(23) = 1.42(2), C(23)−C(24) = 1.380(15), Pd(2)−N(2) = 2.132(7), Pd(2)−N(4) = 2.100(7), Pd(2)−C(26) = 2.113(8), Pd(2)−C(27) = 2.128(9), Pd(2)−C(28) = 2.142(8), C(26)−C(27) = 1.412(13), C(27)−C(28) = 1.417(12), Pd(1)···Pd(2) = 4.6070(9); N(1)−Pd(1)−N(3) = 78.2(3), N(1)−Pd(1)−C(24) = 109.3(4), N(3)−Pd(1)−C(22) = 103.9(5), C(22)−Pd(1)−C(24) = 68.8(6), N(1)−Pd(1)−C(22) = 176.1(4), N(3)−Pd(1)−C(24) = 171.3(4), N(2)−Pd(2)−N(4) = 78.0(3), N(2)−Pd(2)−C(28) = 110.8(3), N(4)−Pd(2)−C(26) = 103.5(3), C(26)−Pd(2)−C(28) = 67.8(3), N(2)−Pd(2)−C(26) = 178.5(3), N(4)−Pd(2)−C(28) = 170.9(3).

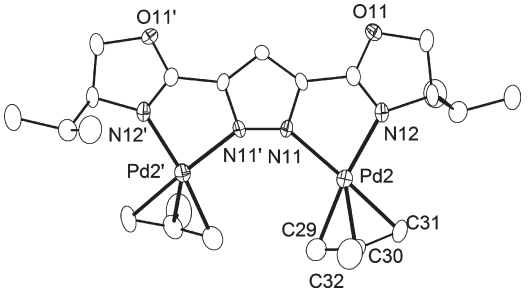


Figure 2. ORTEP plot (50% probability thermal ellipsoids) of the molecular structure of the cation of **4c**. Hydrogen atoms and the PF_6^- anion have been omitted for clarity. Only one of the two crystallographically independent molecules is shown. Selected bond distances (Å) and angles (deg): Pd(2)−N(11) = 2.098(9), Pd(2)−N(12) = 2.108(6), Pd(2)−C(29) = 2.098(9), Pd(2)−C(30) = 2.137(8), Pd(2)−C(31) = 2.117(8), C(29)−C(30) = 1.397(14), C(30)−C(31) = 1.428(12), Pd(2)···Pd(2′) = 4.6313(7); N(11)−Pd(2)−N(12) = 78.2(2), N(11)−Pd(2)−C(29) = 109.0(3), N(12)−Pd(2)−C(31) = 104.1(3), C(29)−Pd(2)−C(31) = 68.7(3), N(11)−Pd(2)−C(31) = 177.6(3), N(12)−Pd(2)−C(29) = 172.7(3). Symmetry transformation used to generate equivalent atoms: (′) 1 − *x*, *y*, −*z*.

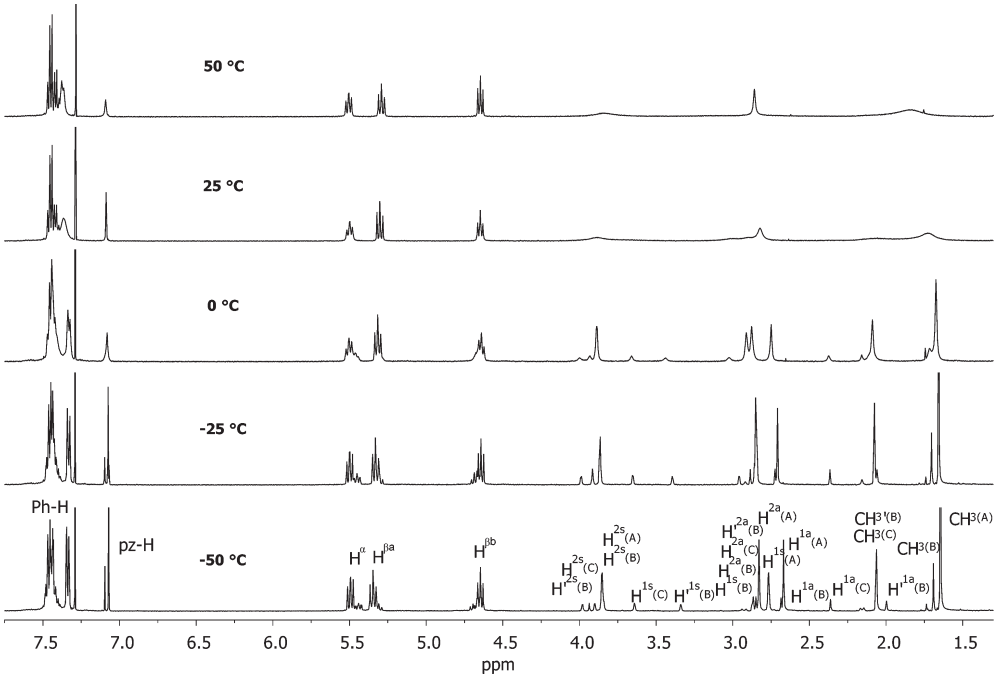


Figure 3. Variable-temperature ^{1}H NMR spectra ($CDCl_3$, 500 MHz) of complex **4a**.

positions (Figure S4 in the Supporting Information). Complexes **4a**,**c** both consist of a bimetallic monocation with two methallylpalladium moieties hosted in the two $\{N_2\}$ binding pockets of the ligand, as anticipated. The bite angle of the ligand is approximately 78° in both coordination sites, only for the disordered cation in **4c** it differs somewhat. The distance between the two palladium atoms (~4.6 Å) is relatively long for binuclear complexes of compartmental pyrazolate-based ligands,[18,24] which is probably due to (i) the short oxazoline chelate arms that pull the metal ions outward and (ii) steric crowding between the two methallyl groups in the bimetallic pocket that pushes the (η^3-methallyl)Pd moieties apart. Both methallyl CH_3 groups point in the same direction as the phenyl groups on the neighboring oxazoline rings in **4a** (exo/exo isomer); this is also the major isomer in solution (vide infra). Since the (η^3-methallyl)Pd moiety is disordered between exo and endo isomers and the cation is located on a 2-fold axis, all possible orientations of the η^3-bound methallyl group, giving a C_2-symmetric $[LPd_2\{(CH_2)_2CCH_3\}_2]^+$ cation, are present within the unit cell of **4c**. This finding suggests that fluxional behavior due to rotation of the methallyl groups might occur in solution, as is indeed observed.

Pd−C bond lengths in **4a**,**c** are found as expected for palladium(II) allyl compounds,[29,30] and Pd−N bond lengths are common for pyrazolate- and oxazoline-derived ligands. A closer inspection of atom distances reveals that all Pd−N bond lengths are found in a rather narrow range (2.133(7)−2.098(9) Å), as are the Pd−CH_2 bonds (2.142(8)−2.098(9) Å). This suggests similar trans influences of the pyrazolate-N and oxazoline-N atoms, in accordance with NMR data (vide infra). Interestingly, a subtle distinction is discernible when comparing **4a** and **4c** (although differences are barely significant at the 3σ level): in **4a** the Pd−N(pyrazolate) bonds are slightly longer than the Pd−N(oxazoline) bonds, and hence the Pd−CH_2 bonds trans to N(pyrazolate) are slightly shorter than the Pd−CH_2 bonds trans to N(oxazoline), while the situation is reversed in the case of **4c**. Indeed, this reversal is also reflected in the ^{13}C NMR spectra for the methallyl CH_2 groups (vide infra).

Dynamic Behavior of 4a−d in Solution. The behavior of complexes **4a−d** in solution was studied by one- and two-dimensional NMR experiments at variable temperatures. At room temperature, the spectrum of **4a** in chloroform-*d* shows very broad signals in the allylic region, which indicates that the methallyl groups are dynamic (Figure 3). Cooling to 0 °C results in single, albeit somewhat broad peaks, and at −50 °C the methallyl resonances are sufficiently resolved to allow assignment by two-dimensional NOESY experiments (Figure S1 in the Supporting Information).

Multiple NMR peaks are due to two possible orientations of each η^3-bound methallyl group, resulting in three distinct isomers (Scheme 3): two C_2-symmetric species (**A** and **C**) with antiparallel oriented allyl groups and a fully asymmetric species (**B**) with parallel oriented allyl groups that gives rise to twice the number of NMR resonances (denoted H and H′). A similar situation is encountered for the other complexes **4b−d** (not shown). From specific NOE correlations between the oxazoline phenyl protons and H^{1s}(**A**) and CH_3(**A**) we could assign the major isomer of complex **4a** to structure **A**, where the phenyl groups and the adjacent methallyl CH_3 group face the same direction. This isomer is also the one observed in the solid-state structure of **4a** (vide supra). In solution, isomers **A−C** are populated with a ratio of approximately 4:2:1 (Table S1 in the Supporting Information). Also, the phenyl groups induce substantial shielding of the "outer" protons H^{1s} and H^{1a} relative to the "inner" protons H^{2s} and H^{2a}.

At −25 °C, the NOESY spectra contain not only NOE correlations but also cross-peaks that arise from exchange

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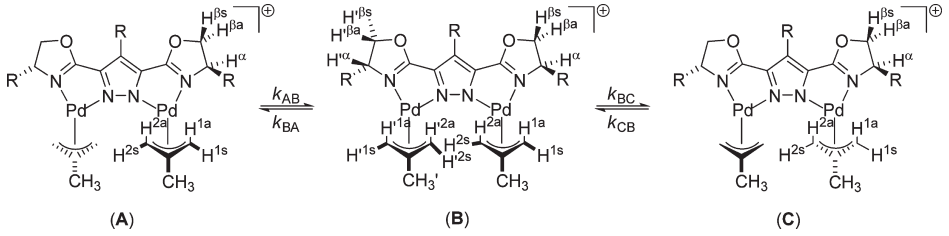
Scheme 3. Three Possible Isomers of the Allylpalladium Complexes 4a−d



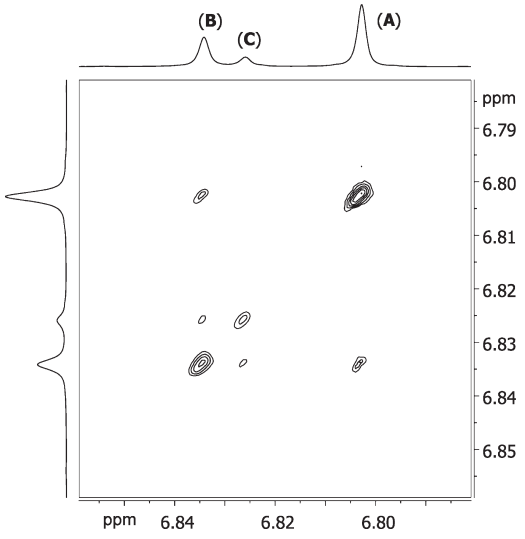
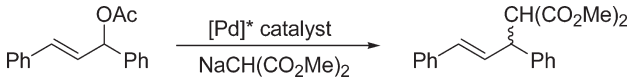


Figure 4. Part of the 2D NOESY spectrum of **4c** ($CDCl_3$, 500 MHz, −25 °C, mixing time 0.5 s) showing the pz H^4 region. The spectrum was acquired with 957 × 512 data points and a spectral width of 0.3 ppm.

between the isomers **A** and **B** and between **B** and **C** (Figure 4). For the allyl protons, exchange is strictly syn/syn and anti/anti (Figure S2 in the Supporting Information) and therefore indicates a rotation of the allyl plane, consistent with former reports about allylpalladium systems with other N-donor ligands.[29,31] A $\eta^3-\eta^1-\eta^3$ mechanism,[32] which has often been observed in the case of phosphorus or N-heterocyclic carbenes coordinated to Pd,[25c,33,34] requires syn/anti exchange of the transiently η^1-bound allyl CH_2 protons and can be ruled out here. Quantitative analysis of the peak integrals with a 3 × 3 exchange matrix approach yielded typical values of $k_{AB} \approx k_{BC} \approx 0.1\ s^{-1}$ and $k_{BA} \approx k_{CB} \approx 0.2\ s^{-1}$ for **4a**,**b**, while the rate constants in **4c** are somewhat larger, presumably due to a less pronounced steric interference with the peripheral isopropyl groups on the ligand. The values for k_{AC} and k_{CA} were always close to zero, indicating that no direct exchange occurs between **A** and **C** and that the two methallyl groups rotate sequentially, independent from each other.

Table 2. Allylic Alkylation of *rac*-(*E*)-1,3-Diphenylallyl Acetate with Dimethyl Malonate



entry	catalyst[a]	yield, %[b]	ee, %[c]
1	**4a**	40	68 (*R*)
2	**4b**	53	28 (*R*)
3	**4c**	67	44 (*S*)
4	**4d**	54	5 (*S*)
5	**3a**/[(methallyl)PdCl]$_2$[d]	69	58 (*R*)
6	**3a**/[(allyl)PdCl]$_2$[d]	72	56 (*R*)

[a] Reaction of the catalyst (2 mol %) with *rac*-(*E*)-1,3-diphenylallyl acetate (1.0 mmol), dimethyl malonate (3.0 mmol), and NaH (3.0 mmol); 48 h reaction time at 45 °C. [b] Isolated yields after workup. [c] Determined by ^{1}H NMR using Eu(hfc)$_3$ as chiral shift reagent; absolute configurations were determined by comparing the optical rotation values to literature data.[38a] [d] Catalyst was generated in situ from ligand (5 mol %) and [Pd] source (2 mol %).

Exchange rate constants in chloroform-*d* were determined at −25, −12.5, and 0 °C for complexes **4a**,**b** and at −25 °C for complex **4c** (the results are given in Table S2 in the Supporting Information) and converted into activation free energies $\Delta G^{\ddagger}$.[35] The $\Delta G^{\ddagger}$ value of the transition **B** → **C** is approximately 65 kJ/mol in complexes **4a**,**b** and about 3 kJ/mol lower in complex **4c** (Figure S3 in the Supporting Information), which is in agreement with values reported for similar allylic systems.[29,31] The temperature dependence obtained for **4a** indicates a negative activation entropy and thus a highly organized transition state as part of an associative mechanism.[33] This is further supported by the much lower activation free energy (56 kJ/mol) observed for complex **4c** in the coordinating solvent THF. In acetonitrile the rate constants could not be determined due to coalescence of peaks already at −25 °C, but we estimated them to be at least another 20 times higher (corresponding to another 6-7 kJ/mol less) than in THF. Since apparent allyl rotation is orbitally forbidden unless the coordination number is altered in the transition state, these findings suggest that the solvent serves as a fifth donor to initiate allyl rotation around the Pd−allyl bond via an associative process.[36]

Palladium-Catalyzed Asymmetric Allylic Alkylation. The catalytic activity of the bis(methallylpalladium) complexes was tested in the allylic alkylation of the model substrate *rac*-(*E*)-1,3-diphenylallyl acetate, using dimethyl malonate as a nucleophile under basic conditions. Palladium-catalyzed

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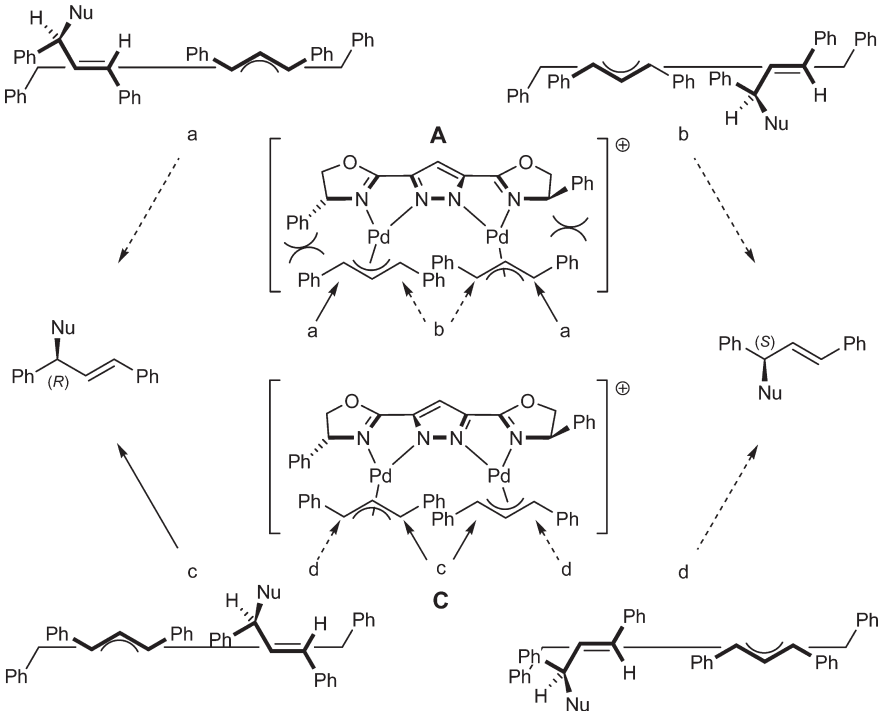
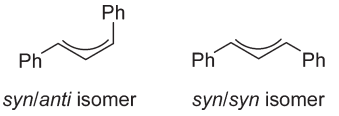
Scheme 4. Enantiocontrol Provided by Dinuclear Pyrazole-Bridged Pd Catalyst 4a



allylation of carbon nucleophiles is a versatile method for carbon−carbon bond formation in organic synthesis,[37] and it is a common benchmark reaction for probing new ligands in enantioselective catalytic reactions.[38] Whereas there are many reports on Pd-catalyzed allylic substitutions employing chiral phosphine derivatives, it should be noted that systems with purely N-donor ligands are comparatively few.[36,39] Complexes **4a**−**d** were either used directly or generated in situ from an allylpalladium precursor and the appropriate ligand. All palladium complexes showed activity in the alkylation reaction with isolated (nonoptimized) yields after 48 h of 40−72% (2 mol % catalyst; Table 2). The catalysts generated in situ seem to have slightly higher activities; possibly this effect arises from the presence of chloride rather than tetrafluoroborate as counteranion. The best enantioselectivity (68% ee) was achieved with **4a**, whereas **4d** gave only 5% ee. The (electron-withdrawing) phenyl group on the backside of the central pyrazole bridge (**4b**,**d**) apparently reduces the selectivity, as does replacement of the phenyl group on the oxazoline side arm by an isopropyl group (**4a**,**b** versus **4c**,**d**). Note that changes in the absolute configuration of the product are caused by different configurations of the stereocenters on the ligand (**4a**,**b** versus **4c**,**d**).

Dinuclear species similar to complexes **4a**−**d**, but with two 1,3-diphenylallyl ligands instead of methallyl ligands, could be identified by ESI mass spectrometry in the reaction mixtures. As an initial working model, the observed enantioselectivities may thus be rationalized by the scenario shown in Scheme 4. If one assumes that the syn/syn isomer of the 1,3-diphenylallyl moiety predominates,[40,41] due to steric repulsion of the bulky phenyl substituents within the bimetallic pocket the two 1,3-diphenylallyl groups in the intermediates can only adopt an antiparallel orientation, which corresponds to isomers **A** (exo/exo) and **C** (endo/endo) of complexes **4a**−**d** (Scheme 3). In the case of 1,3-diphenylallyl instead of methallyl, however, it is reasonable to suppose that isomer **A** is strongly disfavored because of interference with the oxazoline substituents.



Nucleophilic attack is generally expected to occur at the allyl C that is trans to the stronger trans-effect donor atom, which can usually be identified by the lower field ^{13}C NMR chemical shift of that allylic carbon atom.[41−43] In accordance with what has been concluded from the crystallographic data for **4a**,**c**, however, there seems to be no substantial difference in ground-state trans influence (and likely also in kinetic trans effect) between the pyrazolate and oxazoline donors of the pyrbox ligands. ^{13}C NMR resonances are detected in the very narrow range 58.2−59.4 ppm for the methallyl CH_2 trans to the pyrazolate N and 58.8−59.9 ppm for the methallyl CH_2 trans to the oxazoline N. The locus of nucleophilic attack is therefore not evident

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from the spectroscopic and structural data, and it is quite likely that the lack of electronic difference of the pyrazolate and oxazoline donors, which propagates itself in a lack of electronic differentiation of the allylic termini, is a reason for the only modest enantiomeric excess of the present systems.[41] On a more subtle level, it is interesting to note that the allylic carbon trans to the pyrazolate N resonates at slightly lower field than the carbon trans to the oxazoline N in the case of **4a**,**b** (^{13}C at 59.3/59.4 versus 58.8/58.8 ppm), while this order is reversed in **4c**,**d** (58.3/58.2 versus 59.6/59.9 ppm). One has to bear in mind, though, that various factors, including the shielding effect of the oxazoline phenyl substituents in **4a**,**b**, will contribute to these minor differences. According to ^{13}C NMR data, the presence or absence of a phenyl group at the pyrazolate C^4 has no obvious ground-state electronic effect on the allyl groups; thus, the significant effect of the backbone C^4 substituent on enantioselectivities remains unexplained at this stage.

Starting from the predominant isomer **C**, nucleophilic attack trans to the oxazoline N (pathway c in Scheme 4) would lead to the experimentally observed *R* enantiomer in the case of precatalyst **4a**. Given a late-transition-state model, the alternative pathway d might be disfavored because of repulsive steric interactions with the ligand substituents in the intermediate Pd(0)−olefin complex (Scheme 4). It has to be noted, though, that this picture represents just a preliminary working scheme, since it is well-known that species which are present in only low amounts may react much more quickly than the major rotational isomer and may carry most of the reaction flux.[40,44] In addition, it is quite conceivable that syn/syn−syn/anti isomerism of the bulky 1,3-diphenylallyl ligands[45] may play a role in the present bimetallic systems due to unfavorable steric interactions of the two proximate 1,3-diphenylallyl groups, even though fluxionality in the methallyl precatalyst complexes was found to proceed via apparent allyl rotation rather than syn/anti exchange.

Conclusions

New pyrazolate-bridged ligands **3a**−**d**, coined pyrbox's, have been successfully synthesized and characterized. A first glance at their coordination properties has been obtained from their methallylpalladium complexes **4a**−**d**. In the solid state, complex **4a** was found as a single isomer, while **4c** displays disorder in the coordinated methallyl fragment with all possible isomers present. In solution the complexes each exist as three isomers in a 4:2:1 ratio in chloroform. Fluxional behavior was observed and identified as an apparent allyl rotation process. Rate constants and activation free energies were determined from NOESY NMR experiments for selected cases and were found to be strongly solvent dependent, in accordance with an associative mechanism. Allyl rotation in systems with isopropyl substituents at the oxazolines is around 2 times faster than in systems with phenyl groups at the oxazolines, whereas the substituent on the pyrazole backbone of the ligand scaffold has only a minor effect.

The set of complexes **4a**−**d** was evaluated in palladium-catalyzed asymmetric allylic alkylation. While all complexes showed similar activities, drastic differences in enantiocontrol were observed. Enantioselectivities are much better for the systems with phenyl groups at the oxazolines (**4a**,**b**) compared to isopropyl substituents (**4c**,**d**) and much better for complexes bearing just a proton instead of an electron-withdrawing phenyl substituent at the central pyrazole bridge (**4a**,**c** versus **4b**,**d**). Hence, both steric and electronic factors play a key role in determining enantioselectivities, which offers a multitude of options for tuning and improving the new pyrbox ligand scaffolds. Recent reports on enantioselective allylic substitution using a binuclear allylpalladium complex with a single-stranded helicate structure showed that ee values crucially depend on many factors, such as the base and the solvent.[46] An ee of 68% in our nonoptimized preliminary experiments thus represents a promising starting point for further optimization. Studies of tris(oxazoline)-based and related catalysts for allylic substitution showed that complexes with the least internal degrees of freedom display the highest activity and stereoselectivity,[6] which may represent a guiding line for further elaboration of the present bimetallic systems.

Future work will also focus on the application of the pyrbox ligands in other enantioselective metal-mediated reactions and on the study of possible cooperative effects of the proximate metal ions. In the context of palladium-catalyzed allylic substitution reactions, these highly preorganized bimetallic systems offer interesting prospects in view of a recent report by the Pfaltz group, where the reversible formation of allyl-bridged binuclear Pd^I reservoir species has been observed under catalytic conditions.[47]

Experimental Section

General Procedures. All air- and/or water-sensitive reactions were performed under a nitrogen atmosphere in a glovebox or using standard Schlenk line techniques. Tetrahydrofuran and dichloromethane were dried over potassium and calcium hydride, respectively, and distilled prior to use. Dimethyl 1*H*-pyrazole-3,5-dicarboxylate hydrochloride (**1a**),[27] dimethyl 4-phenyl-1*H*-pyrazole-3,5-dicarboxylate (**1b**),[28] (*S*)-valinol,[48] and (*R*)-phenylglycinol[48] were prepared according to literature procedures. All other chemicals were used as purchased without further purification. Flash chromatography was performed on silica gel from Macherey-Nagel (Kieselgel 60 M, 0.04−0.063 mm, 230−400 mesh ASTM). Thin-layer chromatography was performed on Fluka aluminum-based plates with silica gel and fluorescent indicator 254 nm. For indication, UV light (λ 254 nm/366 nm), potassium permanganate solution (1.0 g of $KMnO_4$, 6.7 g of K_2CO_3, 0.1 g of NaOH, 100 mL of H_2O), or ninhydrin solution (1.0 g of ninhydrin, 0.2 mL of acetic acid, 100 mL of EtOH) was used. Melting points were determined in open glass capillary tubes on a Stanford Research Systems OptiMelt MPA 100 device; values are uncorrected. Optical rotation values were determined on a Perkin-Elmer 241 polarimeter device. Infrared spectra were recorded as KBr pellets on a Digilab Excalibur Series FTS 3000 spectrometer. Mass spectrometry was performed using an Applied Biosystems API 2000 (ESI) or a Bruker FTICR (HR-ESI) instrument.

X-ray Diffraction. The crystal data and details of the data collections for **4a**,**c** are given in Table 3. X-ray data were

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Table 3. Summary of X-ray Crystallographic Data for Complexes 4a,c

	4a	4c
empirical formula	$C_{29}H_{31}BF_4N_4O_2Pd_2$	$C_{26}H_{42.50}F_6N_4O_{2.75}PPd_2$
formula wt	767.19	812.91
cryst size, mm	0.50 × 0.23 × 0.22	0.22 × 0.17 × 0.07
cryst syst	hexagonal	monoclinic
space group	$P6_1$ (No. 169)	$C2$ (No. 5)
a, Å; α, deg	13.5487(4); 90	28.2448(10); 90
b, Å; β, deg	13.5487(4); 90	8.7037(4); 97.382(3)
c, Å; γ, deg	27.8944(10); 120	13.8195(5); 90
V, Å^3	4434.5(2)	3369.1(2)
ρ_{calcd}, g cm^{-3}	1.724	1.603
Z	6	4
$F(000)$	2292	1638
μ, mm^{-1}	1.276	1.179
T_{max}/T_{min}	0.5979/0.7586	0.9201/0.6937
hkl range	±16, ±16, −31 to +33	±34, ±10, ±16
θ range, deg	1.74−25.68	1.45−25.63
no. of measd rflns	38 453	13 640
no. of unique rflns (R_{int})	5482 (0.0416)	6334 (0.0541)
no. of obsd rflns, $I > 2\sigma(I)$	5283	5630
refined params/restraints	377/43	386/19
goodness of fit	1.065	1.029
Abs. structure param.	−0.03(5)	0.00(5)
R1/wR2 ($I > 2\sigma(I)$)	0.0547/0.1244	0.0533/0.1341
R1/wR2 (all data)	0.0566/0.1256	0.0611/0.1386
resid electron dens, e Å^{-3}	3.487/−2.309 (near Pd)	2.399/−1.037 (near Pd)

collected on a STOE IPDS II diffractometer (graphite -monochromated Mo Kα radiation, λ = 0.710 73 Å) by use of ω scans at −140 °C. The structures were solved by direct methods and refined on F^2 using all reflections with SHELX-97.[49] Most nonhydrogen atoms were refined anisotropically. Most hydrogen atoms were placed in calculated positions and assigned to an isotropic displacement parameter of 0.08 Å^2. The BF_4^- anion in **4a** was found to be disordered and was refined using SADI restraints (d_{B-F} and $d_{F\cdots F}$). One (η^3-methallyl)Pd moiety in **4c** was found to be disordered about two positions. The occupancies were set to 0.75 and 0.25. The main component also includes one diethyl ether solvent molecule with an occupancy of 0.75. Atoms of the disordered parts (except Pd) were refined isotropically. SAME and, for the diethyl ether molecule, DFIX restraints (d_{C-C} = 1.51 Å and d_{C-O} = 1.43 Å) were used to model the disorder. Allyl protons of the disordered methallyl moiety were first calculated and later refined at fixed positions. A DFIX restraint (d_{C-H} = 0.93 Å) was applied in the case of the nondisordered allyl protons. The absolute structure parameters were determined according to Flack[50] with SHELX-97. Face-indexed absorption corrections were performed numerically with the program X-RED.[51]

NMR Spectroscopy. ^{1}H NMR and ^{13}C NMR spectra were recorded on Bruker Avance 300 and 500 MHz spectrometers using the indicated solvent as internal reference. Full-range NOESY spectra were acquired with 512 × 1024 data points and a spectral width of 9.0 ppm; in particular cases the spectral width was reduced to increase the resolution. Mixing times were chosen between 50 and 500 ms, depending on the rate of the exchange. For the measurement of exchange rate constants in complexes **4a**,**c** the pz H^4 proton and in complexes **4a**,**b** alternatively the allyl H^{1S}/H$'^{1S}$ proton was used. Peak volumes were determined manually using MNova, and rate constants were calculated with an estimated error of 10% using EXSYCalc.[52]

Synthesis of N^3,N^5-Bis((*R*)-2-hydroxy-1-phenylethyl)-1*H*-pyrazole-3,5-dicarboxamide (2a). A solution of **1a** (1.93 g, 8.75 mmol), (*R*)-2-phenylglycinol (3.60 g, 26.2 mmol), and potassium cyanide (120 mg, 1.84 mmol) in methanol (30 mL) was heated to reflux for 4 days. The solvent was removed in vacuo, and the residue was washed thoroughly with dichloromethane. The crude product was recrystallized from methanol/diethyl ether to give the intended product as a white solid. Yield: 2.23 g (65%). R_f = 0.30 (silica gel, CH_2Cl_2/MeOH, 10:1). Mp: >250 °C. $[\alpha]_D^{20}$ = +39.1° (c = 2.3 mg/mL, MeOH). IR (KBr): ν 3406.9 (N−H), 3370.2, 3331.3, 3160.1, 2945.3, 2850.5, 2638.0, 1651.0 (C=O), 1619.4, 1527.5, 1447.4, 1384.5, 1277.1, 1262.1, 1192.0, 1068.1, 1042.8, 852.5, 773.5, 698.9, 570.7, 544.4, 445.6 cm^{-1}. ^{1}H NMR (MeOD, 300 MHz, 298 K): δ (ppm) 7.46−7.21 (m, 10H, Ph *H*), 7.15 (s, 1H, pz *H*4), 5.17 (t, $^3J_{HH}$ = 6.4 Hz, 2H, α-C*H*), 3.85 (d, $^3J_{HH}$ = 6.4 Hz, 4H, β-CH_2). ^{13}C NMR (MeOD, 75 MHz, 298 K): δ (ppm) 166.2 (*C*=O), 148.0 (pz *C*3, pz *C*5), 141.6 (Ph *C*1), 129.5 (Ph *C*3, Ph *C*5), 128.4 (Ph *C*2, Ph *C*6), 128.1 (Ph *C*4), 108.0 (pz *C*4), 66.6 (β-*C*H$_2$), 56.8 (α-*C*H). MS (m/z, ESI$^+$, MeOH): 417.1 (100) [M + Na]$^+$. HRMS (m/z, ESI$^-$, MeOH): found 393.1569, calcd for $C_{21}H_{21}N_4O_4^-$ 393.1568.

Synthesis of N^3,N^5-Bis((*R*)-2-hydroxy-1-phenylethyl)-4-phenyl-1*H*-pyrazole-3,5-dicarboxamide (2b). A solution of **1b** (4.40 g, 16.9 mmol), (*R*)-2-phenylglycinol (6.96 g, 50.7 mmol), and potassium cyanide (110 mg, 1.69 mmol) in methanol (13 mL) was heated to reflux for 4 days. The solvent was removed in vacuo, and the residue was cleaned by column chromatography (dichloromethane/methanol, 10:1) on silica media. For purification the crude product was washed thoroughly with dichloromethane to give the intended product as a white solid. Yield: 4.40 g (55%). R_f = 0.41 (silica gel, CH_2Cl_2/MeOH, 10:1). Mp: 113 °C. $[\alpha]_D^{20}$ = +27.3° (c = 2.2 mg/mL, MeOH). IR (KBr): ν 3392.6 (N−H), 2935.2, 1655.5 (C=O), 1535.7, 1454.6, 1293.6, 1240.4, 1189.0, 1071.9, 1030.8, 877.6, 760.9, 699.9 cm^{-1}. ^{1}H NMR (MeOD, 300 MHz, 298 K): δ (ppm) 7.43−7.13 (m, 16H, Ph *H*, pz *H*4), 4.99 (t, $^3J_{HH}$ = 5.9 Hz, 2H, α-C*H*), 3.69 (dd, $^3J_{HH}$ = 5.9 Hz, $^2J_{HH}$ = 11.0 Hz, 2H, β-C*H*^{a}H^b), 3.69 (dd, $^3J_{HH}$ = 5.9 Hz, $^2J_{HH}$ = 11.0 Hz, 2H, β-CH^a*H*^{b}). ^{13}C NMR (MeOD, 75 MHz, 298 K): δ (ppm) 162.2 (*C*=O), 140.7 (Ph *C*1), 132.4 (pz Ph *C*1), 131.5 (pz Ph *C*3, pz Ph *C*5), 130.0 (pz Ph *C*4), 129.6 (pz Ph *C*2, pz Ph *C*6), 129.5 (Ph *C*3, Ph *C*5), 128.5 (Ph *C*2, Ph *C*6), 127.9 (Ph *C*4), 123.2 (pz *C*4), 66.0 (β-*C*H$_2$), 56.7 (α-*C*H), pz *C*3 and pz *C*5 were not observed. MS (m/z, ESI$^+$, MeOH): 493.1 (100) [M + Na]$^+$. HRMS (m/z, ESI$^-$, MeOH): found 469.1879, calcd for $C_{27}H_{25}N_4O_4^-$ 469.1881.

Synthesis of N^3,N^5-Bis((*S*)-1-hydroxy-3-methylbutan-2-yl)-1*H*-pyrazole-3,5-dicarboxamide (2c). A solution of **1a** (2.00 g, 9.07 mmol) and (*S*)-valinol (2.81 g, 27.2 mmol) in methanol (15 mL) was heated to reflux for 3 days. The solvent was removed in vacuo, and the residue was cleaned by column chromatography (dichloromethane/methanol, 10:1) on silica media to give the product as a white solid. Yield: 1.62 g (55%). R_f = 0.67 (silica gel, CH_2Cl_2/MeOH, 5:1). Mp: 232 °C. $[\alpha]_D^{20}$ = −60.5° (c = 2.1 mg/mL, MeOH). IR (KBr): ν 3152.5, 2961.4, 1655.7 (C=O), 1617.1, 1560.4, 1535.1, 1450.6, 1318.8, 1294.7, 1260.7, 1187.1, 1147.6, 1067.8, 1021.6, 870.4, 819.7 cm^{-1}. ^{1}H NMR (MeOD, 300 MHz, 298 K): δ (ppm) 7.28 (s, 1H, pz *H*4), 3.87 (m, 2H, α-C*H*), 3.69 (m, 4H, β-CH_2), 1.97 (octet, $^3J_{HH}$ = 7.0 Hz, 2H, *i*Pr C*H*), 1.00 (d, $^3J_{HH}$ = 7.0 Hz, 6H, *i*Pr CH_3), 0.96 (d, $^3J_{HH}$ = 7.0 Hz, 6H, *i*Pr CH_3). ^{13}C NMR (MeOD, 75 MHz, 298 K): δ (ppm) 162.8 (*C*=O), 106.3 (pz *C*4), 63.1 (β-*C*H$_2$), 58.2 (α-*C*H), 30.3 (*i*Pr *C*H), 20.1 (*i*Pr *C*H$_3$), 19.2 (*i*Pr *C*H$_3$), pz *C*3 and pz *C*5 were not observed. MS (m/z, ESI$^+$, MeOH): 349.1 (100) [M + Na]$^+$. HRMS (m/z, ESI$^-$, MeOH): found 325.1877, calcd for $C_{15}H_{25}N_4O_4^-$ 325.1881.

Synthesis of N^3,N^5-Bis((*S*)-1-hydroxy-3-methylbutan-2-yl)-4-phenyl-1*H*-pyrazole-3,5-dicarboxamide (2d). A solution of **1b** (2.00 g, 7.68 mmol), (*S*)-valinol (2.38 g, 23.1 mmol), and

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(52) Cobas, J. C.; Martín-Pastor, M. *EXSYCalc 1.0*; Mestrelab Research, Escondido, CA, **2007**.

trifluoromethanesulfonic acid (133 mg, 0.77 mmol) in methanol (15 mL) was heated to reflux for 3 days. The solvent was removed in vacuo, and the residue was cleaned by column chromatography (dichloromethane/methanol, 10:1) on silica media to give the intended product as a white solid. Yield: 2.25 g (73%). R_f = 0.34 (silica gel, CH_2Cl_2/MeOH, 10:1). Mp: 85 °C. $[\alpha]_D^{20}$ = −51.9° (*c* = 2.1 mg/mL, MeOH). IR (KBr): *ν* 3398.2, 2961.5, 1651.4 (C=O), 1539.3, 1464.9, 1386.7, 1311.6, 1234.7, 1073.2, 1028.0, 871.8, 794.6, 764.7, 701.7 cm^{-1}. ^1H NMR (MeOD, 300 MHz, 298 K): *δ* (ppm) 7.51−7.39 (m, 5H, Ph *H*), 3.73 (q, $^3J_{HH}$ = 5.4 Hz, 2H, α-C*H*), 3.49 (m, 4H, *β*-CH_2), 1.77 (m, 2H, *i*Pr C*H*), 0.85 (d, $^3J_{HH}$ = 6.7 Hz, 6H, *i*Pr CH_3), 0.70 (br s, 6H, *i*Pr CH_3). ^{13}C NMR (MeOD, 75 MHz, 298 K): *δ* (ppm) 162.6 (*C*=O), 132.7 (pz Ph *C*1), 131.6 (pz Ph *C*3, pz Ph *C*5), 130.1 (pz Ph *C*2, pz Ph *C*6), 129.7 (pz Ph *C*4), 122.7 (pz *C*4), 62.8 (*β*-*C*H_2), 57.6 (α-*C*H), 29.9 (*i*Pr *C*H), 20.0 (*i*Pr *C*H_3), 18.4 (*i*Pr *C*H_3), pz *C*3 and pz *C*5 were not observed. MS (*m*/*z*, ESI^-, MeOH): 401.2 (100) $[M - H]^-$. HRMS (*m*/*z*, ESI^-, MeOH): found 401.2193, calcd for $C_{21}H_{29}N_4O_4^-$ 401.2194.

Synthesis of 3,5-Bis((*R*)-4-phenyl-4,5-dihydro-2-oxazolyl)-1*H*-pyrazole (3a). To a solution of **2a** (1.36 g, 3.45 mmol) in 1,2-dichloroethane (100 mL) was added thionyl chloride (5 mL). The mixture was heated to 40 °C for 2 h, followed by the removal of the solvent in vacuo. The resulting white solid was added to a solution of sodium methanolate (1.49 g, 27.6 mmol) in methanol (125 mL) and heated to reflux for an additional 5 h. The solvent was removed, and the resulting solid was dissolved in dichloromethane (50 mL). The organic phase was washed with water (3 × 30 mL) and dried over magnesium sulfate. The crude product was recrystallized from dichloromethane to give a white solid. Yield: 982 mg (79%). R_f = 0.50 (silica gel, EtOAc). Mp: 187 °C. $[\alpha]_D^{20}$ = +81.1° (*c* = 1.9 mg/mL, $CHCl_3$). IR (KBr): *ν* 3420.2, 3109.6, 2899.9, 1652.1 (C=N), 1557.6, 1491.0, 1449.1, 1394.5, 1348.4, 1269.2, 1200.4, 1142.2, 1068.6, 990.3, 943.2, 878.4, 754.2, 696.8, 542.0 cm^{-1}. ^1H NMR ($CDCl_3$, 500 MHz, 298 K): *δ* (ppm) 14.0 (br s, 1H, N*H*), 7.32−7.23 (m, 11H, Ph *H*, pz *H*), 5.47 (t, $^3J_{HH}$ = 8.6 Hz, 2H, α-C*H*), 4.80 (t, $^3J_{HH}$ = 8.6 Hz, 2H, *β*-CH^aH^b), 4.29 (t, $^3J_{HH}$ = 8.6 Hz, 2H, *β*-CH^aH^b). ^{13}C NMR ($CDCl_3$, 125 MHz, 298 K): *δ* (ppm) 158.6 (N=*C*−O), 141.6 (Ph *C*1), 128.8 (Ph *C*3, Ph *C*5), 127.8 (Ph *C*4), 126.6 (Ph *C*2, Ph *C*6), 109.2 (pz *C*4), 75.3 (*β*-*C*H_2), 69.5 (α-*C*H), pz *C*3 and pz *C*5 were not observed. MS (*m*/*z*, ESI^+, CH_2Cl_2): 359.3 (100) $[M + H]^+$. HRMS (*m*/*z*, ESI^-, MeOH): found 357.1356, calcd for $C_{21}H_{17}N_4O_2^-$ 357.1357.

Synthesis of 3,5-Bis((*R*)-4-phenyl-4,5-dihydro-2-oxazolyl)-1*H*-4-phenylpyrazole (3b). The same procedure was followed as for **3a**, except for purifying the crude product by column chromatography (dichloromethane/methanol, 25:1) on a silica media to give the intended product as a white solid. Yield: 3.04 g (80%). R_f = 0.23 (silica gel, CH_2Cl_2/MeOH, 25:1). Mp: 99 °C. $[\alpha]_D^{20}$ = +65.0° (*c* = 3.6 mg/mL, $CHCl_3$). IR (KBr): *ν* 3126.7, 3060.4, 3029.6, 2900.3, 1950.5, 1883.8, 1809.8, 1655.6 (C=N), 1606.7, 1494.0, 1477.4, 1450.5, 1344.9, 1288.4, 1259.5, 1184.3, 1128.2, 1076.5, 993.9, 943.2, 914.5, 895.1, 757.0, 698.1, 536.9 cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz, 298 K): *δ* (ppm) 13.9 (br s, 1H, N*H*), 7.45−7.15 (m, 15H, Ph *H*), 5.41 (dd, $^3J_{HH}$ = 8.2 Hz, $^3J_{HH}$ = 9.9 Hz, 2H, α-C*H*), 4.64 (t, $^3J_{HH}$ = 8.2 Hz, $^2J_{HH}$ = 9.9 Hz, 2H, *β*-CH^aH^b), 4.12 (t, $^3J_{HH}$ = 9.9 Hz, $^2J_{HH}$ = 9.9 Hz, 2H, *β*-CH^aH^b). ^{13}C NMR ($CDCl_3$, 75 MHz, 298 K): *δ* (ppm) 158.9 (N=*C*−O), 141.8 (Ph *C*1), 130.7, 128.6, 127.7, 127.5, 127.3, 126.5, 74.9 (*β*-*C*H_2), 69.0 (α-*C*H), pz *C*3 and pz *C*5 were not observed. MS (*m*/*z*, ESI^+, CH_2Cl_2): 435.1 (100) $[M + H]^+$. HRMS (*m*/*z*, ESI^-, MeOH): found 433.1677, calcd for $C_{27}H_{21}N_4O_2^-$ 433.1670.

Synthesis of 3,5-Bis((*S*)-4-isopropyl-4,5-dihydro-2-oxazolyl)-1*H*-pyrazole (3c). The same procedure was followed as for **3a**, except for purifying the crude product by column chromatography (dichloromethane/methanol, 10:1) on a silica media to give the intended product as a white solid. Yield: 136 mg (62%). R_f = 0.87 (silica gel, CH_2Cl_2/MeOH, 5:1). Mp: 74 °C. $[\alpha]_D^{20}$ = −94.3° (*c* = 2.1 mg/mL, $CHCl_3$). IR (KBr): *ν* 3425.6, 3139.5, 2962.1, 1664.1 (C=N), 1561.6, 1468.0, 1349.7, 1263.7, 1230.2, 1136.3, 1065.9, 988.8, 950.3, 891.1, 801.6, 730.5 cm^{-1}. ^1H NMR ($CDCl_3$, 500 MHz, 298 K): *δ* (ppm) 14.2 (br s, 1H, N*H*), 7.11 (s, 1H, pz *H*), 4.42 (m, 2H, α-C*H*), 4.17 (m, 4H, *β*-CH_2), 1.81 (m, 2H, *i*Pr C*H*), 0.96 (d, $^3J_{HH}$ = 6.9 Hz, 6H, *i*Pr CH_3), 0.88 (d, $^3J_{HH}$ = 6.9 Hz, 6H, *i*Pr CH_3). ^{13}C NMR ($CDCl_3$, 125 MHz, 298 K): *δ* (ppm) 157.6 (N=*C*−O), 108.6 (pz *C*4), 72.0 (*β*-*C*H_2), 70.7 (α-*C*H), 32.8 (*i*Pr *C*H), 18.7 (*i*Pr *C*H_3), 18.2 (*i*Pr *C*H_3), pz *C*3 and pz *C*5 were not observed. MS (*m*/*z*, ESI^+, CH_2Cl_2): 289.1 (100) $[M - H]^-$. HRMS (*m*/*z*, ESI^+, MeOH): found 313.1636, calcd for $C_{15}H_{22}N_4NaO_2^-$ 313.1635.

Synthesis of 3,5-Bis((*S*)-4-isopropyl-4,5-dihydro-2-oxazolyl)-1*H*-4-phenylpyrazole (3d). The same procedure was followed as for **3a**, except for purifying the crude product by column chromatography (dichloromethane/methanol, 10:1) on a silica media to give the intended product as a white solid. Yield: 1.16 g (58%). R_f = 0.62 (silica gel, CH_2Cl_2/MeOH, 10:1). Mp: 76 °C. $[\alpha]_D^{20}$ = −127.9° (*c* = 1.9 mg/mL, $CHCl_3$). IR (KBr): *ν* 2960.6, 1658.8 (C=N), 1607.1, 1556.3, 1514.1, 1475.5, 1425.6, 1341.2, 1266.9, 1122.6, 991.5, 950.7, 894.6, 759.2, 697.0 cm^{-1}. ^1H NMR ($CDCl_3$, 500 MHz, 298 K): *δ* (ppm) 14.1 (br s, 1H, N*H*), 7.37−7.30 (m, 5H, Ph *H*), 4.26 (t, $^3J_{HH}$ = 8.7 Hz, 2H, α-C*H*), 4.11−3.97 (m, 4H, *β*-CH_2), 1.72 (octet, $^3J_{HH}$ = 6.8 Hz, 2H, *i*Pr C*H*), 0.92 (d, $^3J_{HH}$ = 6.8 Hz, 6H, *i*Pr CH_3), 0.84 (d, $^3J_{HH}$ = 6.8 Hz, 6H, *i*Pr CH_3). ^{13}C NMR ($CDCl_3$, 125 MHz, 298 K): *δ* (ppm) 157.8 (N=*C*−O), 130.9, 130.7, 127.4, 127.2, 124.9, 71.9 (*β*-*C*H_2), 70.6 (α-*C*H), 33.0 (*i*Pr *C*H), 18.7 (*i*Pr *C*H_3), 18.4 (*i*Pr *C*H_3), pz *C*3 and pz *C*5 were not observed. MS (*m*/*z*, ESI^-, CH_2Cl_2): 365.2 (100) $[M + H]^+$. HRMS (*m*/*z*, ESI^+, MeOH): found 389.1946, calcd for $C_{21}H_{26}N_4NaO_2^-$ 389.1948.

Synthesis of Bis(*η*^{3}-methallyl)[3,5-bis((*R*)-4-phenyl-4,5-dihydro-2-oxazolyl)-pyrazolate-*N*,*N*′,*N*′]dipalladium(II) Tetrafluoroborate (4a). A mixture of **3a** (100 mg, 0.28 mmol) and potassium *tert*-butoxide (32 mg, 0.28 mmol) in dry dichloromethane (30 mL) was stirred for 15 min. (Methallyl)palladium chloride dimer (110 mg, 0.28 mmol) was then added. The reaction mixture was stirred at room temperature overnight. Ammonium tetrafluoroborate (176 mg, 1.68 mmol) was added, and the reaction mixture was stirred for an additional 5 h. The organic phase was washed with water (4 × 20 mL) and dried over magnesium sulfate. After removal of the solvent the intended product was obtained as a yellow solid. Yellow needles suitable for X-ray crystallographic analysis were obtained by slow diffusion of diethyl ether into a concentrated dichloromethane solution. Yield: 203 mg (95%). Mp: 204 °C. IR (KBr): *ν* 3434.1, 3127.0, 2971.2, 2909.7, 1633.0 (C=N), 1535.7, 1518.0, 1495.0, 1471.7, 1455.9, 1431.9, 1380.0, 1320.8, 1277.9, 1241.8, 1192.0, 1055.5, 927.8, 891.8, 837.2, 763.8, 699.4, 645.4, 543.9 cm^{-1}. ^1H NMR ($CDCl_3$, 500 MHz, 223 K): *δ* (ppm) isomer **A** (53%), 7.42−7.27 (m, 10H, Ar *H*), 7.01 (s, 1H, pz *H*), 5.44 (t, $^3J_{HH}$ = 9.3 Hz, $^3J_{HH}$ = 9.3 Hz, 2H, H^{α}), 5.29 (t, $^2J_{HH}$ = 9.3 Hz, $^3J_{HH}$ = 9.3 Hz, 2H, $H^{\beta a}$), 4.58 (t, $^2J_{HH}$ = 9.3 Hz, $^3J_{HH}$ = 9.3 Hz, 2H, $H^{\beta s}$), 3.80 (s, 2H, H^{2s}), 2.77 (s, 2H, H^{2a}), 2.73 (s, 2H, H^{1s}), 2.62 (s, 2H, H^{1a}), 1.59 (s, 6H, CH_3); isomer **B** (31%), 7.42−7.27 (m, 10H, Ar *H*), 7.03 (s, 1H, pz *H*), 5.44 (t, $^3J_{HH}$ = 9.3 Hz, $^3J_{HH}$ = 9.3 Hz, 1H, H^{α}), 5.39 (t, $^3J_{HH}$ = 9.3 Hz, $^3J_{HH}$ = 9.3 Hz, 1H, H'^{α}), 5.29 (t, $^2J_{HH}$ = 9.3 Hz, $^3J_{HH}$ = 9.3 Hz, 1H, $H^{\beta a}$), 5.26 (t, $^2J_{HH}$ = 9.3 Hz, $^3J_{HH}$ = 9.3 Hz, 1H, $H'^{\beta a}$), 4.62 (t, $^2J_{HH}$ = 9.3 Hz, $^3J_{HH}$ = 9.3 Hz, 1H, $H'^{\beta s}$), 4.58 (t, $^2J_{HH}$ = 9.3 Hz, $^3J_{HH}$ = 9.3 Hz, 1H, $H^{\beta s}$), 3.92 (s, 1H, H'^{2s}), 3.79 (s, 1H, H^{2s}), 3.30 (s, 1H, H'^{1s}), 2.85 (s, 1H, H^{1s}), 2.81 (s, 1H, H^{2a}), 2.77 (s, 1H, H'^{2a}), 2.64 (s, 1H, H^{1a}), 2.01 (s, 3H, CH_3'), 1.96 (s, 1H, H'^{1a}), 1.64 (s, 3H, CH_3); isomer **C** (16%), 7.42−7.27 (m, 10H, Ar *H*), 7.01 (s, 1H, pz *H*), 5.39 (t, $^3J_{HH}$ = 9.3 Hz, $^3J_{HH}$ = 9.3 Hz, 2H, H^{α}), 5.26 (t, $^2J_{HH}$ = 9.3 Hz, $^3J_{HH}$ = 9.3 Hz, 2H, $H^{\beta a}$), 4.62 (t, $^2J_{HH}$ = 9.3 Hz, $^3J_{HH}$ = 9.3 Hz, 2H, $H^{\beta s}$), 3.85 (s, 2H, H^{2s}), 3.59 (s, 2H, H^{1s}), 2.79 (s, 2H, H^{2a}), 2.31 (s, 2H, H^{1a}), 2.01 (s, 6H, CH_3). ^{13}C NMR ($CDCl_3$, 125 MHz, 223 K): *δ* (ppm) isomer **A**, 166.6 (N=*C*−O), 141.4 (Ph *C*1), 139.8 (methallyl *C*), 130.8 (Ph *C*3, Ph *C*5), 129.0 (Ph *C*4), 127.3 (Ph *C*2, Ph *C*6), 106.4 (pz *C*4), 78.9 (*β*-*C*H_2), 67.7 (α-*C*H),

59.3 (methallyl CH_2 *trans* to pyrazolate-N), 58.8 (methallyl CH_2), 23.1 (methallyl CH_3 *trans* to oxazoline N), pz *C*3 and pz *C*5 not observed. MS (*m*/*z*, ESI$^+$, CH_2Cl_2): 681.0 (100) $[M - BF_4]^+$. HRMS (*m*/*z*, ESI$^+$, MeOH): found 679.0511, calcd for $C_{29}H_{31}N_4O_2Pd_2^+$ 679.0511.

Synthesis of Bis(η^3-methallyl)[3,5-bis((*R*)-4-phenyl-4,5-dihydro-2-oxazolyl)-4-phenylpyrazolate-*N*,*N*,*N*′,*N*′]dipalladium(II) Tetrafluoroborate (4b). The same procedure was followed as for **4a**. The intended product was obtained as a yellow solid. Yield: 324 mg (80%). Mp: 166 °C. IR (KBr): ν 3424.5, 3059.0, 3030.0, 2962.1, 2917.4, 1964.4, 1887.1, 1823.6, 1680.0, 1622.8 (C=N), 1531.5, 1496.3, 1444.2, 1365.6, 1308.5, 1263.2, 1178.8, 1052.5, 933.5, 837.4, 761.3, 698.2, 574.5, 450.1 cm^{-1}. ^{1}H NMR ($CDCl_3$, 500 MHz, 223 K): δ (ppm) isomer **A** (62%), 7.50−7.24 (m, 15H, Ar *H*), 5.40 (t, $^3J_{HH}$ = 9.3 Hz, $^3J_{HH}$ = 9.3 Hz, 2H, H^{α}), 5.17 (t, $^2J_{HH}$ = 9.3 Hz, $^3J_{HH}$ = 9.3 Hz, 2H, $H^{\beta a}$), 4.43 (t, $^2J_{HH}$ = 9.3 Hz, $^3J_{HH}$ = 9.3 Hz, 2H, $H^{\beta s}$), 3.81 (s, 2H, H^{2s}), 2.79 (s, 2H, H^{2a}), 2.68 (s, 2H, H^{1s}), 2.64 (s, 2H, H^{1a}), 1.59 (s, 6H, CH_3); isomer **B** (23%), 7.50−7.24 (m, 15H, Ar *H*), 5.40 (t, $^3J_{HH}$ = 9.3 Hz, $^3J_{HH}$ = 9.3 Hz, 1H, H^{α}), 5.36 (t, $^3J_{HH}$ = 9.3 Hz, $^3J_{HH}$ = 9.3 Hz, 1H, H'^{α}), 5.17 (t, $^2J_{HH}$ = 9.3 Hz, $^3J_{HH}$ = 9.3 Hz, 1H, $H^{\beta a}$), 5.15 (t, $^2J_{HH}$ = 9.3 Hz, $^3J_{HH}$ = 9.3 Hz, 1H, $H'^{\beta a}$), 4.48 (t, $^2J_{HH}$ = 9.3 Hz, $^3J_{HH}$ = 9.3 Hz, 1H, $H'^{\beta s}$), 4.43 (t, $^2J_{HH}$ = 9.3 Hz, $^3J_{HH}$ = 9.3 Hz, 1H, $H'^{\beta s}$), 3.94 (s, 1H, H'^{2s}), 3.81 (s, 1H, H^{2s}), 3.29 (s, 1H, H'^{1s}), 2.87 (s, 1H, H^{1s}), 2.79 (s, 1H, H^{2a}), 2.79 (s, 1H, H'^{2a}), 2.64 (s, 1H, H^{1a}), 2.04 (s, 3H, CH_3′), 1.92 (s, 1H, H'^{1a}), 1.65 (s, 3H, CH_3); isomer **C** (15%), 7.50−7.24 (m, 15H, Ar *H*), 5.36 (t, $^3J_{HH}$ = 9.3 Hz, $^3J_{HH}$ = 9.3 Hz, 2H, H^{α}), 5.15 (t, $^2J_{HH}$ = 9.3 Hz, $^3J_{HH}$ = 9.3 Hz, 2H, $H^{\beta a}$), 4.48 (t, $^2J_{HH}$ = 9.3 Hz, $^3J_{HH}$ = 9.3 Hz, 2H, $H^{\beta s}$), 3.86 (s, 2H, H^{2s}), 3.61 (s, 2H, H^{1s}), 2.79 (s, 2H, H^{2a}), 2.27 (s, 2H, H^{1a}), 2.04 (s, 6H, CH_3). ^{13}C NMR ($CDCl_3$, 125 MHz, 223 K): δ (ppm) isomer **A**, 167.0 (N=*C*−O), 140.0 (methallyl C), 139.3 (Ph *C*1), 131.0 (Ph *C*3, Ph *C*5), 130.5, 129.0 (Ph *C*4), 128.7, 127.8, 127.5, 127.3 (Ph *C*2, Ph *C*6), 125.1 (pz *C*4), 79.2 (β-CH_2), 66.9 (α-*C*H), 59.4 (methallyl CH_2 *trans* to pyrazolate N), 58.8 (methallyl CH_2 *trans* to oxazoline N), 23.0 (methallyl CH_3), pz *C*3 and pz *C*5 not observed. MS (*m*/*z*, ESI$^+$, CH_2Cl_2): 757.0 (100) $[M - BF_4]^+$. HRMS (*m*/*z*, ESI$^+$, MeOH): found 755.0831, calcd for $C_{35}H_{35}N_4O_2Pd_2^+$ 755.0824.

Synthesis of Bis(η^3-methallyl)[3,5-bis((*S*)-4-isopropyl-4,5-dihydro-2-oxazolyl)-pyrazolate-*N*,*N*,*N*′,*N*′]dipalladium(II) Tetrafluoroborate (4c). The same procedure was followed as for **4a**. The intended product was obtained as a yellow solid. Yield: 940 mg (98%). Mp: 140 °C. IR (KBr): ν 3136.3, 3068.6, 2962.4, 2875.1, 1640.0 (C=N), 1518.9, 1466.8, 1381.0, 1329.0, 1283.5, 1242.2, 1192.0, 1054.2, 930.3, 837.1, 802.6, 761.8, 724.7 cm^{-1}. ^{1}H NMR ($CDCl_3$, 500 MHz, 223 K): δ (ppm) isomer **A** (64%), 6.80 (s, 1H, pz *H*), 4.70 (t, J_{HH} = 9.7 Hz, 2H, $H^{\beta a}$), 4.56 (dd, $^2J_{HH}$ = 9.7 Hz, $^3J_{HH}$ = 6.5 Hz, 2H, $H^{\beta s}$), 4.18 (m, 2H, H^{α}), 4.01 (s, 2H, H^{2s}), 3.99 (s, 2H, H^{1s}), 3.00 (s, 2H, H^{2a}), 2.97 (s, 2H, H^{1a}), 2.09 (s, 6H, CH_3), 2.03 (m, 2H, *i*Pr C*H*), 0.97 (d, $^3J_{HH}$ = 7.1 Hz, 6H, *i*Pr CH_3), 0.88 (d, $^3J_{HH}$ = 7.1 Hz, 6H, *i*Pr CH_3); isomer **B** (27%) 6.80 (s, 1H, pz *H*), 4.73 (m, 1H, $H'^{\beta a}$), 4.70 (t, J_{HH} = 9.7 Hz, 1H, $H^{\beta a}$), 4.56 (dd, $^2J_{HH}$ = 9.73 Hz, $^3J_{HH}$ = 6.5 Hz, 1H, $H^{\beta s}$), 4.54 (m, 1H, $H'^{\beta s}$), 4.23 (m, 1H, H'^{α}), 4.18 (m, 1H, H^{α}), 4.09 (s, 1H, H'^{2s}), 4.00 (s, 1H, H^{1s}), 3.97 (s, 1H, H^{2s}), 3.94 (s, 1H, H'^{1s}), 3.01 (s, 1H, H^{2a}), 3.00 (s, 1H, H'^{2a}), 2.95 (s, 1H, H^{1a}), 2.92 (s, 1H, H'^{1a}), 2.18 (s, 3H, CH_3′), 2.10 (s, 3H, CH_3), 2.03 (m, 1H, *i*Pr C*H*), 1.96 (m, 1H, *i*Pr C*H*′), 0.96 (d, $^3J_{HH}$ = 7.1 Hz, 3H, *i*Pr CH_3), 0.96 (d, $^3J_{HH}$ = 7.1 Hz, 3H, *i*Pr CH_3′), 0.88 (d, $^3J_{HH}$ = 7.1 Hz, 3H, *i*Pr CH_3), 0.83 (d, $^3J_{HH}$ = 7.1 Hz, 3H, *i*Pr CH_3′); isomer **C** (9%), 6.82 (s, 1H, pz *H*), 4.73 (m, 2H, $H^{\beta a}$), 4.54 (m, 2H, $H^{\beta s}$), 4.32 (m, 2H, H^{α}), 4.06 (s, 2H, H^{2s}), 4.01 (s, 2H, H^{1s}), 3.00 (s, 2H, H^{2a}), 2.99 (s, 2H, H^{1a}), 2.09 (s, 6H, CH_3), 1.96 (m, 2H, *i*Pr−C*H*′), 0.96 (d, $^3J_{HH}$ = 7.1 Hz, 6H, *i*Pr CH_3′), 0.75 (d, $^3J_{HH}$ = 7.1 Hz, 6H, *i*Pr CH_3′). ^{13}C NMR ($CDCl_3$, 125 MHz, 223 K): δ (ppm) isomer **A**, 165.9 (N=*C*−O), 141.4 (pz *C*3, pz *C*5), 131.7 (methallyl *C*), 105.6 (pz *C*4), 72.5 (β-CH_2), 68.8 (α-*C*H), 59.6 (methallyl CH_2 trans to oxazoline N), 58.3 (methallyl CH_2 trans to pyrazolate N), 31.0 (*i*Pr *C*H), 23.5 (methallyl CH_3), 18.3 (*i*Pr CH_3), 15.7 (*i*Pr CH_3). MS (*m*/*z*, ESI$^+$, CH_2Cl_2): 613.1 (100) $[M - BF_4]^+$. HRMS (*m*/*z*, ESI$^+$, MeOH): found 611.0861, calcd for $C_{23}H_{35}N_4O_2Pd_2^+$ 611.0824.

Synthesis of Bis(η^3-methallyl)[3,5-bis((*S*)-4-isopropyl-4,5-dihydro-2-oxazolyl)-4-phenylpyrazolate-*N*,*N*,*N*′,*N*′]dipalladium(II) Tetrafluoroborate (4d). The same procedure was followed as for **4a**. The intended product was obtained as a yellow solid. Yield: 199 mg (94%). Mp: 174 °C. IR (KBr): ν 3061.5, 2961.2, 1624.1 (C=N), 1537.3, 1506.4, 1445.0, 1367.5, 1321.2, 1260.4, 1180.4, 1057.0, 931.6, 838.8, 804.6, 700.8 cm^{-1}. ^{1}H NMR ($CDCl_3$, 500 MHz, 223 K): δ (ppm) isomer **A**, 7.43−7.33 (m, 5H, Ph *H*), 4.60 (t, J_{HH} = 9.4 Hz, 2H, $H^{\beta a}$), 4.41 (t, $^2J_{HH}$ = 9.7 Hz, $^3J_{HH}$ = 6.9 Hz, 2H, $H^{\beta s}$), 4.14 (m, 2H, H^{α}), 4.04 (s, 2H, H^{2s}), 3.99 (s, 2H, H^{1s}), 3.02 (s, 2H, H^{2a}), 2.99 (s, 2H, H^{1a}), 2.11 (s, 6H, CH_3), 2.03 (m, 2H, *i*Pr C*H*), 0.95 (d, $^3J_{HH}$ = 6.7 Hz, 6H, *i*Pr CH_3), 0.84 (d, $^3J_{HH}$ = 6.7 Hz, 6H, *i*Pr CH_3). ^{13}C NMR ($CDCl_3$, 125 MHz, 223 K): δ (ppm) isomer **A**, 166.3 (N=*C*−O), 138.9 (pz *C*3, pz *C*5), 131.9 (methallyl *C*), 130.4 (Ph *C*2, Ph *C*6), 128.4 (Ph *C*4), 127.8 (Ph *C*3, Ph *C*5), 127.5 (Ph *C*1), 124.1 (pz *C*4), 72.4 (β-CH_2), 68.2 (α-*C*H), 59.9 (methallyl CH_2 trans to oxazoline N), 58.2 (methallyl CH_2 trans to pyrazolate N), 30.9 (*i*Pr *C*H), 23.5 (methallyl CH_3), 18.4 (*i*Pr CH_3), 15.6 (*i*Pr CH_3). MS (*m*/*z*, ESI$^+$, CH_2Cl_2): 689.1 (100) $[M - BF_4]^+$. HRMS (*m*/*z*, ESI$^+$, MeOH): found 687.1160, calcd for $C_{29}H_{39}N_4O_2Pd_2^+$ 687.1137.

Allylic Alkylation of *rac*-(*E*)-1,3-Diphenylallyl Acetate. The catalyst (0.02 mmol) was dissolved in tetrahydrofuran (2 mL) and was treated with a solution of *rac*-(*E*)-1,3-diphenylallyl acetate (252 mg, 1.00 mmol) in tetrahydrofuran (1 mL). In a second flask dimethyl malonate (0.34 mL, 396 mg, 3.00 mmol) was dissolved in tetrahydrofuran (1 mL) and sodium hydride (72 mg, 3.00 mmol) was slowly added to give a white solid which was then added to the solution containing the catalyst. The reaction mixture was stirred at 45 °C, and the conversion was monitored by TLC analysis. After the appropriate reaction time the solution was diluted with diethyl ether (20 mL) and washed with saturated aqueous ammonium chloride (3 × 20 mL). The organic phase was dried over magnesium sulfate, and the conversion was determined by ^{1}H NMR spectroscopy. The product was purified by column chromatography (hexane/EtOAc, 4:1) on a silica media to give the final product as a colorless oil (in some cases the oil became a white solid after a few hours). The enantiomeric excess was determined by ^{1}H NMR spectroscopy (200 MHz, $CDCl_3$, 0.5 equiv of Eu(hfc)$_3$, for the CO_2CH_3 singlet at lower field a splitting was observed).

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Supporting Information Available: CIF files giving crystal data for **4a**,**4c**, figures giving ^{1}H and ^{13}C NMR spectra for compounds **2a**−**d**, **3a**−**d**, and **4a**−**d**, 2D NOESY spectra of **4a** at −50 and −25 °C, tables giving the ratio of the three different isomers of methallyl complexes **4a**−**c** in $CDCl_3$, rate constants and activation free energies of the methallyl rotation, and a figure giving a plot of the molecular structure of the cation of **4c**, emphasizing the disorder of the (η^3-methallyl)Pd moiety. This material is available free of charge via the Internet at http://pubs.acs.org.