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Axial Chirality and Supramolecular Interactions: The Case of $[(\kappa^2\text{-}P,P\text{-}\{PPh_2NMe\}_2CO)Cu^ICl]_2$

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The title compound $[(\kappa^2\text{-}P,P\text{-}\{PPh_2NMe\}_2CO)Cu^ICl]_2$ (**4**) is readily formed by the reaction between $(PPh_2NMe)_2CO$ and copper(I) chloride. Compound **4** forms a two-dimensional supramolecular network of Cu_2Cl_2-centered dimers that are linked by $\pi-\pi$ interaction between the phenyl substituents on phosphorus in the solid state. Because of the nature of these $\pi-\pi$ interactions, only one of the three possible enantiomers, the *meso* form, can be observed in the crystals.

Introduction

In the past few years, the chemistry of phosphinoureas has attracted renewed attention.[1] With the report of $PPh_2NMeC(O)NMeH$, the first monophosphinourea possessing an easy to activate functional group, a new field was opened up.[2] This led to the discovery of a facile route to unsymmetrically substituted bisphosphinoureas[3−5] and a novel chirality pattern for their complexes, both in the solid state and in solution. With the establishment of the chiral solid-state structure for $(R,S)_{A2'}$-$[Pd(\kappa^2\text{-}P,P\text{-}\{P(OC_6H_3Bu^t{}_2\text{-}2,4)_2N(Me)C(O)N(Me)PPh_2\}Cl_2]$ (**1**)[4] that prevails in solution and can also be observed for *cis*-$[Mo(CO)_4\{P(OC_6H_3Bu^t{}_2\text{-}2,4)_2N(Me)CON(Me)PPh_2\}_2]$ (**2**),[5] it became apparent that chirality is likely to be a general feature of all folded bisphosphinourea transition-metal complexes. The chirality is created by the fold vector.

However, all known phosphinourea chelate complexes involve metals with a square-planar[1] or octahedral[1,4−6] coordination sphere and thus a metal preferred bite angle of 90°. A notable exception is $[Ni\{\eta^2\text{-}(PPh_2NMe)_2CO\}\{\eta^1\text{-}(PPh_2NMe)_2CO\}]$ (**3**),[7] whose solid-state structure is unknown but, as a Ni^0 complex, should adopt either a tetrahedral or trigonal-planar structure. Because **3** is the only bisphosphino complex found to be dynamic in solution, it was interesting to investigate the dependence of the structural stability on the preferred bite angle of the metal.

From molecular modeling calculations[7] and the crystal structure of the monophosphinourea ligand $(PPh_2NMe)_2CO$,[2] it is known that phosphinoureas want to adopt a planar conformation with the phosphorus atoms coplanar with the planar NC(O)N unit of the urea core. However, the two electron lone pairs of the phosphorus atoms repel each other, resulting in one phosphorus atom moving above and the other one below the common plane. Upon coordination to a transition metal, both phosphorus atoms by necessity have to move back into the common plane in order to bond to the metal atom. This creates a considerable ring strain in this presumably planar system because now the differing bond lengths (ranging from about 136 to 240 pm) and unfavorable preferred bond angles (ranging from 90 to 120°) are no longer suited for a coplanar structure. As a consequence, the ring responds with folding along one of the two P−N vectors, creating a chiral compound (see Chart 1).

An obvious alternative to the tetrahedral d^{10} metal Ni^0 is the isoelectronic Cu^I cation. From Cu^I, only a small number of diphosphino complexes are structurally described in the

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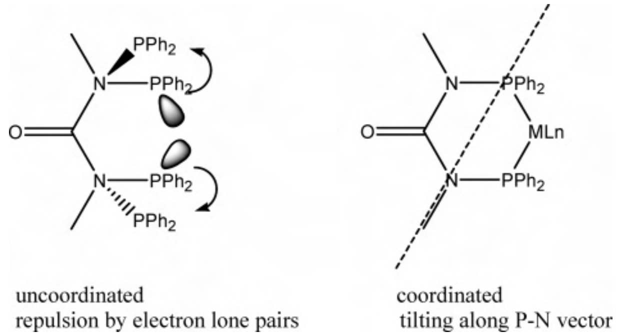
Chart 1. Structure of Bisphosphinoureas: Free and Coordinated



literature.[8,9] Most of these form dimers with a central and planar Cu_2Cl_2 ring. This feature introduces a second bisphosphinourea ligand and thus a second center of chirality into the molecule, making the number of stereoisomers equal to that in **2**.

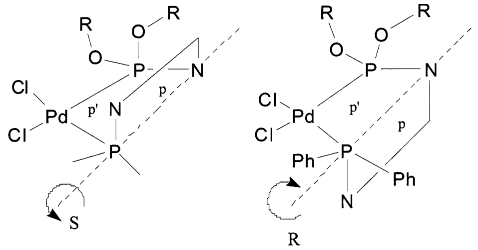
In the present paper, we report on the synthesis, crystal structure, and behavior in solution of ([κ^2-*P*,*P*-{PPh_2-NMe}$_2$CO)Cu^ICl]$_2$ (**4**) and shall discuss the stability of these chiral bisphosphinourea-derived metallacycles in solution.

Results and Discussion

The previously reported palladium complex **1**, easily accessible from the reaction between $P(OC_6H_3Bu^t{}_2\text{-}2,4)_2N$-(Me)C(O)N(Me)$PPh_2$ and [$PdCl_2$(cod)] (cod = 1,5-cyclooctadiene),[4] folds only along one of the two possible fold vectors. In this complex, the PPh_2 phosphorus atom is located on the fold vector, which is evidently the preferred position for the sterically less encumbered phosphorus group. This finding is corroborated by the related molybdenum complex *cis*-[$Mo(CO)_4P(OC_6H_3Bu^t{}_2\text{-}2,4)_2N$(Me)C(O)N(Me)-$PPh_2$], which realizes both diastereomers, 85% with the PPh_2 group and 15% with the phosphite unit on the fold vector.[5]

The P−N fold vector is an axial element of chirality and can be used to fully describe the chirality of the palladium complex (see Chart 2). Although there are two chiral axes (fold vectors) possible, denoted P1−N2 and P2−N1, respectively, the palladium complex utilizes only P1−N2, the axis with the lower priority P atom. It should thus be labeled A2 (A1 would be the axis P2−N1). If one now views the molecule along A2 from the near end (P1), the left-hand molecule in Chart 1 becomes *S* and the other *R*. *S* and *R* name the sense of direction along the shortest angle between the two planes going from the higher priority plane to the lower one. The racemate can be described as $(R/S)_{A2}$. For a description of the planar chiral elements, see ref 4.

Chart 2. Chirality of **1** As Described by the Axial Chiral Element A2 (Dotted Line)



The title compound **4** can be synthesized by mixing tetrahydrofuran (THF) solutions of the ligand and copper(I) chloride. Crystals were grown by concentrating the solution in vacuo and allowing the mother liquor to stand at room temperature for several days (Figure 1).

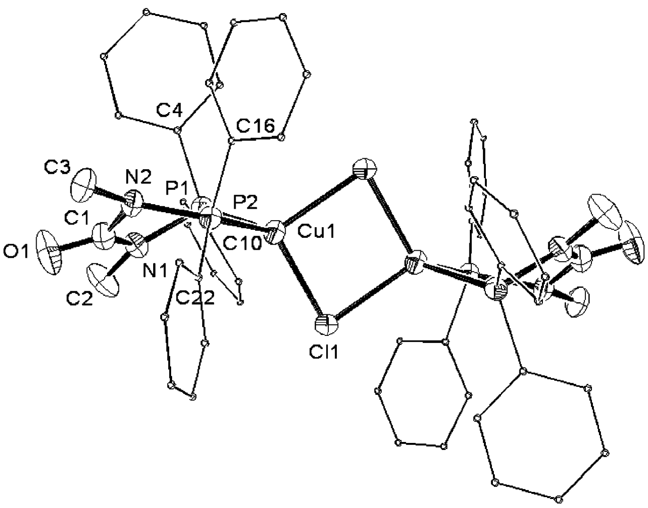


Figure 1. ORTEP drawing of **4** (*meso* form). Hydrogen atoms have been omitted and phenyl rings reduced in size for clarity.

It should be noted that utilizing the symmetric bisphosphinourea ligand $(PPh_2NMe)_2CO$ instead of the unsymmetric $P(OC_6H_3Bu^t{}_2\text{-}2,4)_2N$(Me)C(O)N(Me)$PPh_2$ simplifies the system significantly by eliminating half of the chiral elements. In the dimeric copper(I) complex, the number of possible enantiomers is reduced from 16 for the unsymmetric ligand to 4 for the symmetric one. The center of inversion in the middle of the Cu_2Cl_2 ring is responsible for a *meso* form that decreases the total number of stereoisomers further to 3.

Compound **4** crystallizes in the triclinic space group $P\bar{1}$ with $Z = 2$ and displays a dimeric structure with a planar Cu_2Cl_2 ring situated on a crystallographic center of inversion (Figure 2).[10−13] The two Cu−Cl bond lengths are 233.11(5) and 237.57(5) pm, indicating single and donor bonds, respectively. Both are significantly longer than the single

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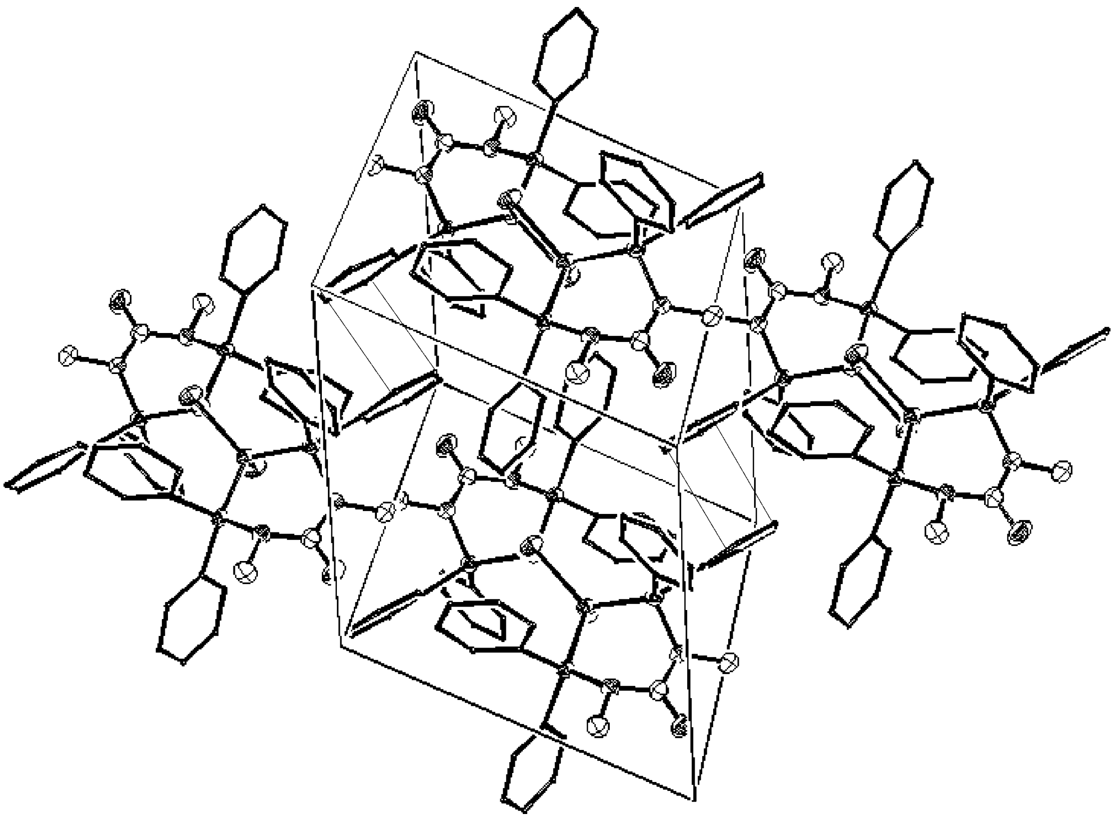

Figure 2. Unit cell of **4** (*meso* form) showing the $\pi-\pi$ stacking interaction between the C10−C16 rings (long bonds). The C23−C24 interaction is located in the center of the unit cell.

bond of 227 pm found in pure CuCl in the solid phase[14] or 217 pm of (CuCl)$_6$ in the gas phase[15] but within the range of Cu−Cl bonds of related structures, 232.0−242.2 pm.[8] The Cl1−Cu1−Cl1# angle of 95.896(17)° and the Cu1−Cl1−Cu1# angle of 84.104(17)° make this central ring almost square. The Cl−Cu−Cl angle is in the middle of its range (92.6−100.8°).[8] The two copper atoms are 315.3 pm apart and thus too far to consider a bonding interaction. The Cl−Cl distance at 349.5 pm is equally too long.[16,17] The copper atoms have the usual tetrahedral coordination, with the two phosphorus atoms of the ligand occupying the remaining two coordination sites. Thus, each ligand forms a six-membered ring with the respective copper atom. The two Cu−P bonds are very similar but not identical (Cu1−P1 222.80(6) pm and Cu1−P2 224.06(5) pm), lying very much at the low end of the range (221.9−229.5 pm),[8] and the P1−Cu1−P2 angle of 93.189(18)° is significantly smaller than tetrahedral. These metallacycles are folded along the P1−N2 vector, creating one axial and two planar elements of chirality.[4] The phosphorus atom on the fold vector (P1) forms the slightly shorter bond to copper. The chirality of each metallacycle is similar to that of a related palladium compound. Because the dimer displays two chiral rings that are crystallographically generated from each other by the center of inversion, compound **4** is seen to crystallize in the *meso* form.

The structure of the crystal comprises tapes of dimers that are held together by supramolecular $\pi-\pi$ stacking interactions between the C10−C15 phenyl rings of neighboring dimers in a slightly slipped fashion with a closest C−C distance of 351.9 pm, and the C23−C24 bonds of neighboring phenyl rings approach each other at 405.9−409.4 pm, which might be assignable to a $\pi-\pi$ interaction of a single double bond in the phenyl ring. No other carbon atoms approach each other closer than 510 pm. The ideal distance for phenyl−phenyl interaction in π stacking is about 370 pm.[18]

The $^{31}P\{^1H\}$ NMR spectrum of **4** displays two broad peaks at 98.6 and 58.3 ppm with equal intensity. The signal at 58.3 ppm is virtually unchanged from the spectrum of the free ligand,[7] and that at 98.6 ppm is in the expected range for coordination to copper. The observation is compatible with only one of the two phosphorus atoms of the ligand bonded to copper. It seems that one of the two phosphorus atoms dissociates from the copper center in solution even at room temperature. A similar situation was observed for the isoelectronic Ni^0 species **3**.[7] To investigate this behavior

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[13] Crystallographic study (220 K): $a = 1022.06(16)$ pm, $b = 1065.05(17)$ pm, $c = 1375.84(21)$ pm, $\alpha = 89.185(2)°$, $\beta = 74.812(2)°$, $\gamma = 62.911(2)°$ with $Z = 2$ in the triclinic space group $P\bar{1}$. R(int) = 0.0171, R1 = 0.0295, wR2 = 0.0739 for 6210 unique reflections. All hydrogen atoms were found and refined. Absorption correction was performed with *SADABS*.

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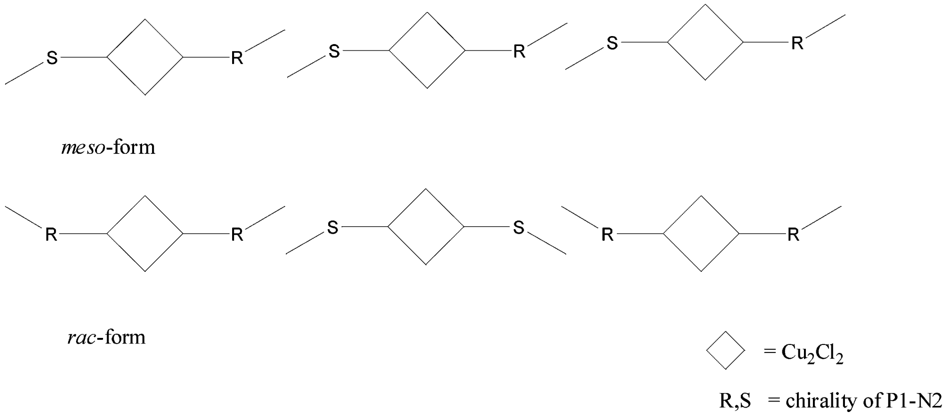
Chart 3. Schematic View of the Copper(I) Dimer Tapes



further, low-temperature NMR studies were carried out. No change in the $^{31}P\{^{1}H\}$ NMR spectrum could be detected even at 213 K. However, line broadening of the ^{31}P NMR signal in Cu−P complexes is expected because both NMR-active copper isomers (^{63}Cu and ^{65}Cu) have spin $^{3}/_{2}$ and thus possess a quadropolar moment. We conclude that in solution the CuP_2N_2C ring is dissociated and the closed-ring structure could not be frozen out even at low temperatures. By comparison with the isoelectronic Ni^0 complex **3** and the known lability of M−P donor bonds in solution, we assume dynamic behavior of complex **4** in solution, indicative of only one phosphorus atom of each bisphosphinourea ligand coordinated to copper.

In the IR spectrum, the ν_{CO} band of the ligand is observed at 1620 cm^{-1} and thus shifted to lower wavenumbers by about 28 cm^{-1} compared to the free ligand. Similar shifts could be observed for related palladium,[4] molybdenum,[1a,5] and nickel[7] complexes of bisphosphinoureas.

Dynamic behavior in solution of any bisphosphinourea complex has up to now only been reported once, for the tetrahedral d^{10} complex **3**.[7] The octahedral molybdenum and square-planar palladium and platinum representatives are structurally stable in solution. The main reason for these differences in stability seems to be the preferred coordination sphere of the central atom. In a recent study on **3**, one of us has investigated the natural bite angle of the ligand $(PPh_2NMe)_2CO$ with a view to explain the fluxional behavior of **3**. Using molecular mechanics calculations, a natural bite angle range of 95−104° for $(PPh_2NMe)_2CO$ was obtained. The observed P−Cu−P angle of 93.2° is very much on the lower end of this range and is similar to the bite angles observed in octahedral and square-planar complexes with a metal preferred bite angle of 90° instead of the tetrahedral angle of 109.5°. In octahedral complexes where the axial ligands on the central metal exert steric crowding on the aryl substituents on phosphorus, the ligand generally responds with a P−M−P contraction of around 10°.[1b,5]

The adaptability of the ligand finds its limits on the obtuse side of the spectrum. No P−M−P angles above 96° have been observed for bisphosphinourea metal complexes. It seems obvious that for tetrahedral (109.5°) and trigonal-planar (120°) complexes the central metal needs to adapt to the ligand rather than vice versa. As a consequence, there is an apparent bite angle “mismatch” situation, resulting in monodentate coordination and fluxional behavior of the ligand when the central atom fails to accommodate the ligand. In the case of **4**, this is precisely what occurs in solution, the ligand oscillates between η^1 and η^2 modes. The same is observed for the nickel complex. That means that a tetrahedral central atom can tolerate one “acute” bite angle in solution but not two. In the case of **4**, this “acute” angle seems to be Cl−Cu−Cl rather than P−Cu−P. The reason for this is not completely clear but is likely to be connected to the electronic differences between phosphorus and chlorine.[19,20]

However, why is it that **4** tolerates the bite angle “mismatch” in the solid state, and why is only one enantiomer (the *meso* form) observed in the solid state? One obvious answer to both these questions lies in the supramolecular $\pi-\pi$ stacking interaction observed in **4** but not observed in any related structure. The ideal $\pi-\pi$ stacking observed between the C10−C15 phenyl rings of different chiral metallacycles lowers the energy content of the dimer and thus serves to stabilize the strained four-coordinate copper atom. In order for the supramolecular interaction to be continuous and thus the dominant ordering force in the structure, the chirality on interacting metallacycles needs to be opposite, making it a “chiral handshake”. This can be achieved by both the *rac* and *meso* forms (see Chart 3). The additional C23−C24 interaction as well as the close approach of the stacked tapes is only achievable by the *meso* form. Thus, the *meso* form has a clear advantage over the *rac* form.

Because compound **4** racemizes in solution, only the thermodynamically more stable *meso* form crystallizes from the solution at the expense of the *rac* form.

In theory, interconversion in solution can occur by either of two mechanisms: ring inversion (see Scheme 1) or a dissociation−association mechanism (see Scheme 2). In ring inversion, the chemical shift value of the ^{31}P NMR spectrum experiences only a small change, resulting mainly in line broadening, and the ^{31}P NMR signal of the *rac* form should be almost identical with that of the *meso* form.

However, if the dissociation−association mechanism is operational, then the difference between coordinated and

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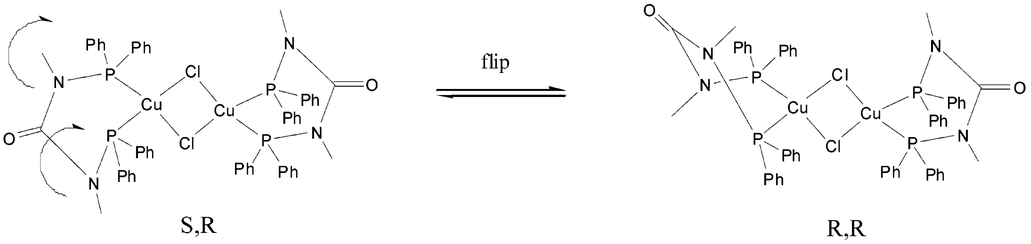
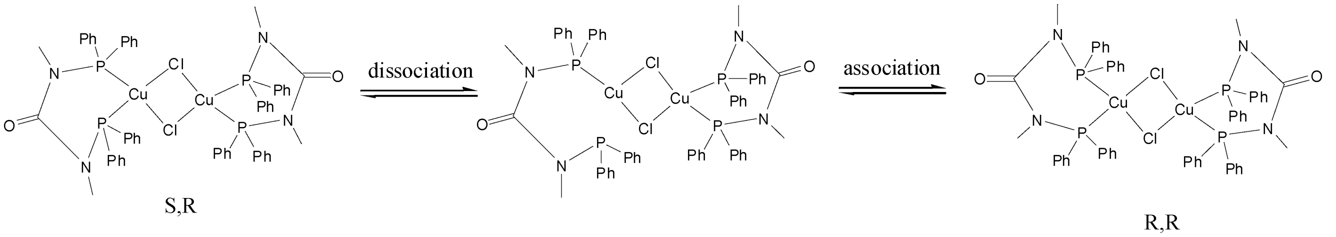
Scheme 1. Illustration of the Possible Ring Inversion Mechanism for Compound **4**



Scheme 2. Illustration of the Dissociation−Association Mechanism Operative in **4**



uncoordinated phosphorus will be observable in the ^{31}P NMR spectrum by a large chemical shift difference between the two signals. In the spectrum of **4**, two broad peaks separated by 40.3 ppm are observed at room temperature, indicative of a dissociation−association mechanism. Further evidence comes from a study on rhodium complexes performed by Suarez et al. Suarez et al. showed that a bisphosphino chelate complex is not subjected to ring inversion if it possesses four aryl rings arranged in the same manner as that in any of the chiral metallacycles of **4**.[21] Ring inversion for **4** would therefore be impossible by this argument.

The central Cu_2Cl_2ring displays another key feature vital to the stability of the solid-state structure; it aligns the two chelate ligands in a parallel fashion. The dimers are thus aligned to form a tape structure. In the related nickel complex **3** lacking the central four-membered ring, there is no parallel alignment of metallacycles. On the contrary, the metallacycles would be perpendicular to each other and thus would be prevented from forming a similar tape structure. In all other known structures, the coligands on the metal atoms prevent tape structures.

Conclusion

We have shown that the chirality displayed by the tilted metallacycles in transition-metal complexes of bisphosphinoureas is best described in terms of axial chirality. Whereas there is no evidence for dynamic behavior in complexes with metal preferred bite angles of 90°, tetrahedrally coordinated metal centers such as Ni^0 and Cu^I show rapid racemization via a dissociation−association mechanism. In the case of **4**, we could show that the two-dimensional supramolecular $\pi-\pi$ stacking interactions determine the diastereomer displayed in the solid-state structure. This is achieved by fractional crystallization of the preferred diastereomer in conjunction with a rapid equilibrium between the diastereomers in solution.

Experimental Section

All experiments were carried out under purified dry argon. Solvents were dried with sodium and freshly distilled under argon. The ligands $\{PPh_2N(Me)\}_2CO$ and $P(OC_6H_3Bu^t{}_2\text{-}2,4)_2N(Me)C(O)N(Me)PPh_2$ were prepared as described in refs 1b and 5, respectively. $[Pd\{\kappa^2\text{-}P,P\text{-}P(OC_6H_3Bu^t{}_2\text{-}2,4)_2N(Me)C(O)N(Me)PPh_2\}Cl_2]$ (**1**) was prepared as described in ref 4. NMR spectra were measured with ARX 300 (Bruker), standards: ^{1}H NMR (300.1 MHz), trace amounts of protonated solvent, $CDCl_3$; ^{13}C NMR (75.5 MHz), internal solvent; ^{31}P NMR (121.5 MHz), external standard 85% H_3PO_4. Elemental analyses were carried out with an elemental analyzer LECO model CHNS-932 with standard combustion conditions and handling of the samples in air. Melting points were determined in sealed capillaries under argon and are uncorrected.

$[(\kappa^2\text{-}P,P\text{-}\{PPh_2NMe\}_2CO)Cu^ICl]_2$ (4). Complex **4** was prepared by adding 198 mg (2 mmol) of CuCl to a solution of 908 mg (2 mmol) of $\{PPh_2N(Me)\}_2CO$ in 20 mL of THF. After stirring for 2 h, the solution was concentrated under reduced pressure and left standing at ambient temperature for several days. The colorless crystals were filtered off and dried in vacuo. Some suitable crystals were submitted for single-crystal X-ray diffractometry. Yield: 907 mg (82%). Mp: 167−70 °C (dec). ^{1}H NMR ($CDCl_3$, 213 and 300 K): δ 8.18−6.80 (m, br, 20H, Ph), 2.77 (s, br, 3H, Me), 2.42 (s, br, 3H, Me). $^{31}P\{^1H\}$ NMR ($CDCl_3$, 213 and 300 K): δ 98.6 (s, CuP), 58.3 (s, P). IR (KBr, cm^{-1}): 1620 (s, CO). Elem anal. Calcd for $C_{54}H_{52}Cl_2Cu_2N_4O_2P_4$ (1110.86): C, 58.39; H, 4.72; N, 5.07. Found: C, 58.14; H, 5.09; N, 4.86.

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Supporting Information Available: Crystallographic details given in a CIF file. This material is available free of charge via the Internet at http://pubs.acs.org.

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