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Synthesis of Axially Chiral 4,4′-Bipyridines and Their Remarkably Selective Self-Assembly into Chiral Metallo-Supramolecular Squares

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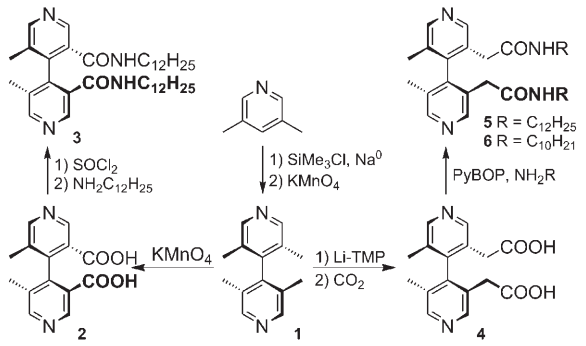
4,4′-Bipyridine is an extraordinarily versatile key intermediate: It is a precursor to the herbicide paraquat,[1] a useful building block in liquid crystals[2] as well as in supramolecular chemistry[3] and used in many other applications. In marked contrast to the large number of known atropisomeric biphenyls, surprisingly no axially chiral 4,4′-bipyridines are available in the literature except for a few biquinoline compounds,[4] although chirality plays a crucial role in these fields. Recently, we used racemic disubstituted dissymmetrical ligands[5] in the self-assembly of dendritic Stang-type[3d] metallo-supramolecular squares. Mass spectrometry[5,6] clearly ruled out the formation of assemblies other than squares, but the ^{1}H NMR spectra showed strong signal overlap from multiple slowly interconverting isomers formed in these dynamic combinatorial libraries.[7] Enantiopure axially chiral ligands decrease the number of possible isomers to only ten (see below), thus generating interesting chiral[8] assemblies,[9] while at the same time facilitating the analysis.

A convenient two-step synthesis for axially chiral 4,4′-bipyridines starts from commercial lutidine, which is converted on multi-gram scale into 3,3′,5,5′-tetramethyl-4,4′-bipyridine **1** (Scheme 1) by a procedure developed by Rebek et al.[10] Two routes to modify one methyl group at each pyridine ring yield axially chiral 4,4′-bipyridines: a) Oxidation of the methyl groups with potassium permanganate yields a mixture of the mono-, the achiral di-, the chiral di- (*rac*-**2**), the tri-, and the tetraacid. Due to mixture formation, the overall yield of *rac*-**2** is certainly not very satisfying. GCMS analysis of the corresponding esters revealed the chiral and achiral diesters to be formed in the statistical 2:1 ratio. The desired axially chiral bis-amide *rac*-**3** can be purified by column chromatography. b) More elegantly, selective deprotonation of two methyl groups with four equivalents of lithium tetramethylpiperidine[11] (Li-TMP) and quenching with gaseous carbon dioxide yields only the monoacid and the chiral diacid *rac*-**4**. Since deprotonation of one methyl group disfavors the deprotonation of the second methyl group at the same pyridine ring, neither the achiral diacid, nor the tri- and tetraacids are obtained by this procedure. The conversion into the desired axially chiral bis-amides *rac*-**5** and *rac*-**6** is achieved by standard amide coupling with PyBOP[12] and Hünig's base (Scheme 1).

Chromatography on a home-made immobilized Chiracel OD stationary phase[13] affords enantiomer separation of racemic **3**, **5**, and **6** with > 92 % *ee* (Supporting Information).



Scheme 1. Two routes to racemic, axially chiral 4,4′-bipyridines **3**, **5**, and **6** starting from 3,5-lutidine (only (*aS*)-enantiomers shown).

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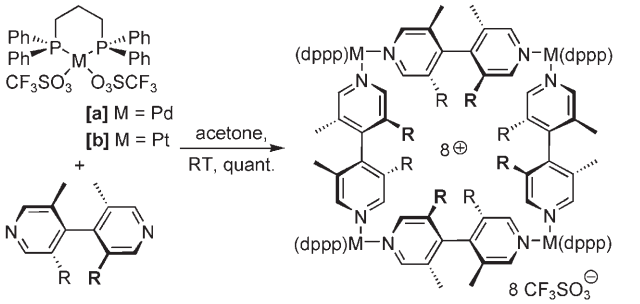
CD spectroscopy of the resulting pairs of enantiomers showed the appropriate mirror-inverted CD spectra. Tetrasubstituted bipyridyl compounds **3** and **5** are reasonably stable against racemization. After 70 h in methanol at 50 °C, only a minor decay of the CD signal of (*aR*)- or (*aS*)-**3** is observed. Bipyridine **5** racemizes somewhat more easily: After 26 h at 50 °C, racemization is observed in detectable amounts. We suggest the higher barrier for racemization of **3** to be caused by the flexibility-reducing conjugation of the amide carbonyl groups to the pyridyl rings.

Both types of ligands form chiral assemblies, when a pure enantiomer is mixed with equimolar amounts of [(dppp)Pd(OTf)$_2$] [**a**] and [(dppp)Pt(OTf)$_2$] [**b**] (Scheme 2).[3d] Not unexpectedly, the changes in the resulting CD spectra (Figure 1 and Supporting Information) and the differences between Pd (black lines) and Pt compounds (gray lines) are small, because the chiral information in the ligands' bipyridyl backbone is not changed much by the self-assembly process.



1 R = CH_3
3 R = CO-NH-$C_{12}H_{25}$
5 R = CH_2-CO-NH-$C_{12}H_{25}$

7a/b M = Pd/Pt, R = CH_3
8a/b M = Pd/Pt, R = CO-NH-$C_{12}H_{25}$
9a/b M = Pd/Pt, R = CH_2-CO-NH-$C_{12}H_{25}$

Scheme 2. Square formation through self-assembly of [(dppp)M(OTf)$_2$] (M = Pd [**a**] or Pt [**b**]) and **1** as well as axially chiral 4,4′-bipyridines **3**, **5**, and **6** (only one enantiomer shown).

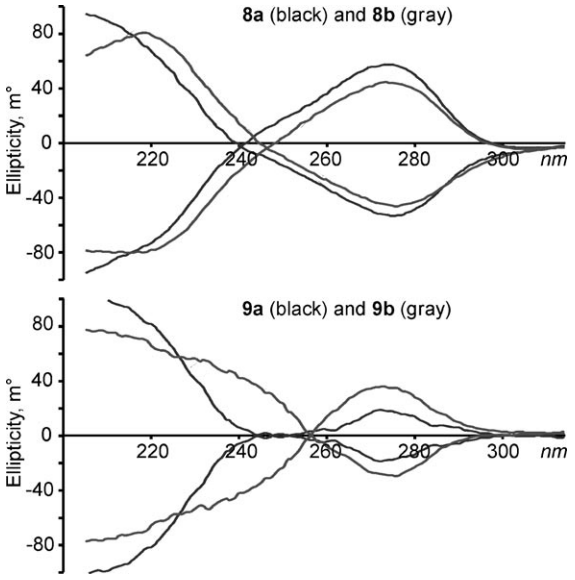


Figure 1. CD spectra of **8a**,**b** (top, 1 mm, methanol, $6\cdot10^{-5}$ M) and **9a**,**b** (bottom, 10 mm, methanol, $6\cdot10^{-5}$ M).

Electrospray mass spectrometry of **7a**,**b**–**9a**,**b** clearly rules out the formation of assemblies other than squares: Doubly (for **8a**,**b**) and triply (for **7a**,**b** and **9a**,**b**) positively charged complexes are formed by losses of triflate counterions (Figure 2). Elemental compositions of the resulting assemblies are confirmed by exact masses and high-resolution isotope patterns. For the Pd and Pt compounds, some typically observed[5,6] fragmentation occurs.

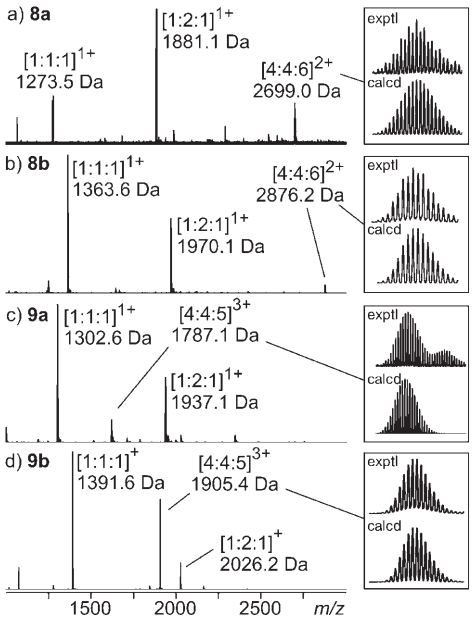


Figure 2. ESI-FTICR-MS spectra of **8a**,**b** and **9a**,**b** (all: acetone, $4\cdot10^{-4}$ M, labels represent the composition as [metal:ligand:OTf]$^{n+}$); insets: experimental and calculated isotope patterns. For **8a**,**b**, the [4:4:6]$^{2+}$ ion overlaps with fragment signals ([2:2:3]$^{+}$; < 10% intensity).

For an understanding of the NMR spectra of **7a**,**b**–**9a**,**b**, it is helpful to consider the following points: a) In contrast to 4,4′-bipyridine, its tetrasubstituted derivatives **1**–**6** have much larger torsional angles around the aryl–aryl bond. For example, this angle is −83° and 94° in two independent molecules in the unit cell of the solid-state structure of **1** (Figure 3, left).[14] b) Upon coordination to the metal corners, the pyridine rings usually[15] prefer an orientation perpendicular to the square's M-M-M-M plane and are stacked with neighboring dppp phenyl groups. This arrangement is not feasible here: If one pyridine were perpendicular, the other one would need to be coplanar with the square plane. Molecular modeling[16] suggests that the pyridines adopt a compromise in a tilted conformation with an angle of about 40–50° relative to the square plane (Figure 3, right). c) The bipyridines can thus adopt four different conformations by rotation around the metal–metal axis in about 90° steps. d) Based on earlier experiences with similar, racemic compounds,[5] the neighboring dppp phenyl groups make the ro-

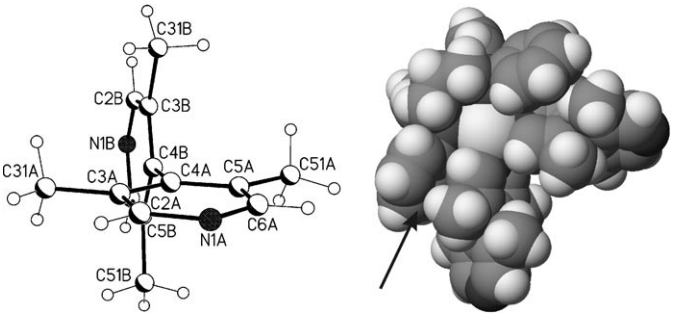
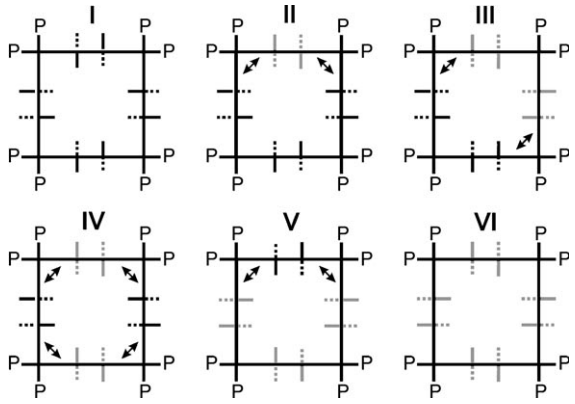


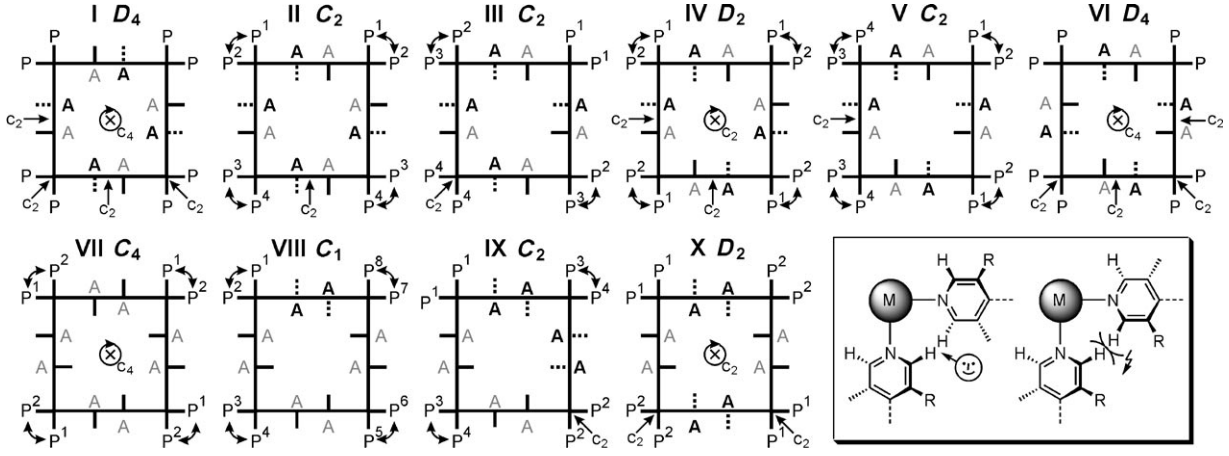
Figure 3. Left: X-ray single crystal structure of **1** (one of the two independent molecules).[14] The C3-C4-C4′-C3′ dihedral angle is −83.3(2)° and 93.8(2)°, respectively. Right: MM2 geometry-optimized structure of $[(dppp)Pd(\mathbf{1})_2]^{2+}$.[16] The coordinated pyridine rings adopt a tilted geometry. Arrow: The dppp phenyl ring hinders bipyridine rotation.



Scheme 3. Self-assembly of $[(dppp)M(OTf)_2]$ (M = Pd or Pt) and **1** can result in the formation of six conformers **I** to **VI**. The ligands' methyl groups are either above (thick) or below (dotted) the plane through the four metal atoms. Gray ligands are rotated by 90° around the M–M axis. Black arrows indicate steric repulsion between the *ortho*-hydrogen atoms of pyridine rings (also, see inset in Scheme 4).

tation of bipyridines around the M–M axis slow on the NMR time scale.

Taking these considerations into account, the self-assembly of **7a**,**b** can potentially give rise to six conformers **I**–**VI** (Scheme 3). The latter five conformations can be obtained from **I** by rotating one ligand (**II**, shown gray in Scheme 3), two adjacent ligands (**III**), two opposing ligands (**IV**), three (**V**), and all four ligands (**VI**) by 90° around the M–M axis. Two aspects should be noted: a) Rotation of one ligand around 180° yields the same conformer due to the ligand symmetry. b) Conformers **I** and **VI** as well as **II** and **V** are pairs of enantiomers. In conformers **II**–**V**, the pyridine rings marked with double arrows in Scheme 3 are tilted towards each other. This generates steric repulsion between two *ortho*-hydrogen atoms of adjacent pyridines (Scheme 4, inset right). In **I** and **VI**, no such repulsion occurs, because one of the two adjacent pyridines at each corner is tilted outwards, the second one inwards (Scheme 4, inset left). These two enantiomeric conformations should thus be energetically favored and are expected to be the major, if not exclusive, products of the self-assembly process. Indeed, exactly two signals for the *ortho*-hydrogen atoms and two signals for the methyl groups are observed in the ^{1}H NMR spectrum of **7a**,**b** in $[D_6]$acetone (Figure 4a). The *ortho*-hydrogens and methyl groups pointing towards the cavity feel the anisotropy of the second pyridine ring coordinated to the same corner. They are therefore shifted upfield with respect to those pointing away from the cavity ($\Delta\sigma = 0.4$ ppm for the *ortho*-H atoms and $\Delta\sigma = 0.3$ ppm for the CH_3 groups). All phosphorus nuclei are symmetry-equivalent and thus only one sharp signal is seen in the ^{31}P NMR spectrum. In $[D_7]$DMF, broadened signals are observed in the ^{1}H and ^{31}P NMR spectra at room temperature (Figure 4b). Below a coalescence temperature of 308 K at 500 MHz, the ligands' signals split into a pattern analogous to that observed in $[D_6]$acetone. This behavior is indicative of the inter-conversion of conformations **I** and **VI** which shows some solvent-



Scheme 4. Self-assembly of $[(dppp)M(OTf)_2]$ (M = Pd, Pt) and enantiomerically pure, axially chiral[4,4′]-bipyridines can result in the formation of ten conformers **I** to **X**. Ligand amides are either above (black **A**) or below (gray **A**) the square plane; methyl groups are indicated by solid (above) and dashed lines (below the plane). P atoms, which are chemically non-equivalent, are labeled with indices. Curved arrows indicate NMR coupling between non-equivalent P atoms. Inset: Steric repulsion between pyridine *otho*-hydrogen atoms (right) can be avoided (left).

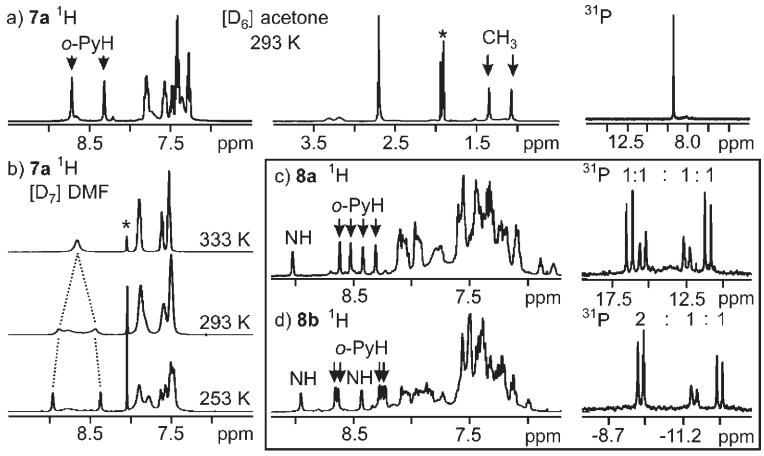


Figure 4. a) ^{1}H and ^{31}P NMR spectra of **7a** in [D$_6$]acetone at room temperature. b) Aromatic region of variable temperature ^{1}H NMR spectra of **7a** in [D$_7$]DMF. c) and d) Partial ^{1}H and ^{31}P NMR spectra of **8a** and **8b**, respectively in [D$_6$]acetone at room temperature. Asterisks indicate solvent peaks.

dependence and is faster in DMF than in acetone. In agreement with previous data,[5] these results confirm both the operation of slow exchange processes and the importance of avoiding the pyridine *ortho*-hydrogen repulsion.

Symmetry considerations for **8a**,**b** and **9a**,**b** are even more complex, but can be based on the same considerations (Scheme 4). Self-assembly of [(dppp)M(OTf)$_2$] with one pure enantiomer of **3** or **5** may result in the formation of up to ten conformers, *already excluding* those which suffer from steric repulsion between pyridine *ortho*-hydrogen atoms. In conformation **I**, all eight amide groups are pointing towards the cavity. Ligand rotations by 180° rather than 90° due to the lower ligand symmetry yields five additional conformers, **II**–**VI**, in analogy to those discussed for **7a**,**b** (Scheme 3). Conformer **VII** is obtained from **I** by rotation of *all* ligands by 90°. From **VII**, conformations **VIII**–**X** can again be generated by 180° rotations of the appropriate ligands. Any process, which involves a 90° ligand rotation of less than all four ligands would unavoidably lead to steric repulsion of pyridine *ortho*-H atoms. Based on the NMR results obtained for **7a**,**b**, they are expected not to be formed in the assembly process and thus are not listed here. The resulting symmetry elements for **I**–**X** are analyzed in Scheme 4. Table 1 provides the expected number of NMR signals and the expected ^{31}P NMR multiplicities.

Table 1. Symmetry considerations for conformers **I**–**X** and the resulting symmetry reductions in their ^{1}H and ^{31}P NMR spectra.

Conformer	Symmetry	Sets of signals (1H NMR)[a]	Signals (31P NMR)[b]
I	D_4	1	1 s
II	C_2	4	4 d
III	C_2	4	2 d & 1 s
IV	D_2	2	2 d
V	C_2	4	4 d
VI	D_4	1	1 s
VII	C_4	2	2 d
VIII	C_1	8	8 d
IX	C_2	4	2 d & 1 s
X	D_2	2	2 s

[a] Some of these signals may overlap. [b] s = singlet, d = doublet; coupling due to chemically nonequivalent ^{31}P atoms.

Mixtures of these ten, slowly interconverting conformations would certainly result in complex and hard-to-interpret NMR spectra. However, this is interestingly not the case. In the ^{31}P NMR spectrum of **8a** in [D$_6$]acetone, four doublets are observed in an exact 1:1:1:1 integration ratio, two sharp, two somewhat broadened (Figure 4c, right). From this result, we can draw three important conclusions: a) Exchange processes are still slow on the NMR time scale under the conditions applied here; otherwise, only one singlet would be observed. b) Only one conformer is formed exclusively.[17] Mixtures of conformers unlikely result in an exact 1:1:1:1 ratio of doublets. c) Only conformers **II** and **V** agree with the coupling pattern observed in the ^{31}P NMR spectrum. In the corresponding ^{1}H NMR spectrum, the reduction to a C_2 symmetry can be seen as well. Four signals are found for one of the two nonequivalent pyridine *ortho*-hydrogen atoms (arrows in Figure 4c). Similarly, four methyl signals are seen (not shown). The same situation is observed for the Pt analogue **8b**: The patterns are very similar and only differ from the NMR results obtained for **8a** in that minor peak shifts occur and two doublets coincide in the ^{31}P NMR spectrum (Figure 4d).[18]

It is impossible to safely deduce from the spectroscopic data alone, which of the two remaining conformers, that is **II** or **V**, is preferred. However, two structure-based arguments derived from simple molecular modeling calculations may be helpful for a tentative assignment: a) Stacking between each pyridine ring and one phenyl group from the dppp ligands is known to stabilize the squares.[15] The amide groups obstruct this favorable interaction more severely than the methyl groups. Consequently, we expect the amide groups to be energetically favored when pointing towards the square cavity. b) However, it is unlikely that the cavity of the square-type assembly can accommodate all amide groups. In order to relieve some of the strain, one ligand may turn outwards—thus optimizing the overall free energy of the assembly. Although somewhat speculative, the combination of these two arguments leads to the suggestion that conformer **II** is formed preferentially in the case of **8a**,**b**.

In conclusion, an effective two-step synthesis for axially chiral 4,4′-bipyridines was developed, which provides easy access to a long neglected class of chiral building blocks that are not only highly useful for supramolecular chemistry. As shown by a combination of CD spectroscopy and HPLC traces, a separation of the enantiomers is possible with the

appropriate chiral stationary phase. Two different classes of these bipyridines have been prepared: One offers rigidity due to carbonyl group conjugation with the pyridine π-system, the other is more flexible due to the CH_2 spacer between the carbonyl and the pyridine ring. The enantiomers obtained in more than 92% *ee* were quite stable in solution at room temperature and were successfully used in self-assembly reactions. Particularly remarkable is the strongly preferred formation of only one out of ten possible conformations, which can be deduced by a careful analysis of the ^{1}H and ^{31}P NMR spectra. Currently, we attempt to resolve the racemates of chiral diacids **2** and **4** by crystallization with chiral amines. When larger amounts of enantiopure diacids will become available, these chiral bipyridines will offer a versatile platform for further functionalization through ester or amide bond formation or the reduction of the acids to the corresponding aldehydes and alcohols.

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Keywords: bipyridines · chirality · metallo-supramolecular squares · N ligands · supramolecular chemistry

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[14] **1**: colorless crystals, $C_{14}H_{16}N_2$, $M_r = 212.29$, crystal size $0.25 \times 0.20 \times 0.10$ mm, monoclinic, space group *C*2/*c* (No.15): $a = 28.3010(5)$, $b = 11.4661(2)$, $c = 14.8096(3)$ Å, $\beta = 99.471(2)°$ $V = 4740.24(15)$ Å^3, $Z = 16$, $\rho(\text{calcd}) = 1.190\,\text{Mg m}^{-3}$, $F(000) = 1824$, $\mu = 0.071\,\text{mm}^{-1}$, 11 694 reflections ($2\theta_{max} = 50°$) measured on a Nonius Kappa-CCD diffractometer at 123(2) K using $Mo_{K\alpha}$ radiation ($\alpha = 0.71073$ Å), 4187 unique [$R_{int} = 0.0287$] used for structure solution (Direct Methods, SHELXS-97[19a]) and refinement (full-matrix least-squares on F^2, SHELXL-97[19b]) with 297 parameters, H-atoms with a riding model, $R1$ ($I > 2\sigma(I)$) = 0.0381, $wR2$ (all data) = 0.0984, largest diff. peak and hole 0.157 and $-0.185\,\text{e Å}^{-3}$. CCDC-664438 (**1**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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[18] P–Pt coupling constants are sensitive probes to confirm assembly formation: $^{1}J(^{195}Pt,P) = 3050$ Hz (**7b** and **8b**), $^{1}J(^{195}Pt,P) = 3600$ Hz (precursor [(dppp)Pt(OTf)$_2$]). Also, see, for example Ref. [3d, 5, 6].

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