

four-line patterns with the signs ( $\pm$ ) due to the coupling between the active spins  $A_1$  and  $A_2$ , as indicated in Figure 1.<sup>14</sup> Each passive spin  $P$  splits the basic four-peak pattern into two identical patterns which are displaced by the coupling constants  $J_{PA_1}$  in the  $\omega_1$ - and  $J_{PA_2}$  in the  $\omega_2$ -dimension or vice versa. Even if one of these coupling constants, e.g.,  $J_{PA_2}$ , in the  $\omega_2$ -dimension, is smaller than the line width, it can still be determined by comparing two traces parallel to the  $\omega_2$ -axis cut through multiplet peaks separated from the rest of the multiplet by  $2\pi J_{PA_1}$  in the  $\omega_1$ -dimension (indicated by arrows in Figure 1). Examples are shown in Figure 2. The shift of the (identical) multiplets in the pair of traces indicates the desired passive coupling constant. The couplings  $^3J_{\alpha\beta_1}$  and  $^3J_{\alpha\beta_2}$  determined from Figure 2a,b are sufficiently resolved to be already visible in the 2D spectrum of Figure 1. However, the two couplings  $^4J_{\beta_1H_2}$  and  $^4J_{\beta_2H_2}$  do not lead to a resolved structure in the 2D spectrum.  $^4J_{\beta_2H_2}$ , for example, can be determined from the  $C_2H-C_\beta H_1$  cross-peak by the relative shift induced parallel to the  $\omega_1$ -axis of the traces obtained by integration over the multiplet patterns (marked by brackets) which are displaced in the  $\omega_2$ -dimension by the coupling  $2\pi^2 J_{\beta_1\beta_2}$  (Figure 2c). In the same manner,  $^4J_{\beta_1H_2}$  can be measured from the cross-peak  $C_2H-C_\beta H_2$  (Figure 2d).

The proposed E. COSY experiment appears powerful for the determination of magnitude and signs of coupling constants in complex spin systems. Furthermore, the E. COSY procedure favors the diagonal peaks (at  $\omega_1 = \omega_2$ ) in the diagonal multiplets (see Figure 1a). This allows the analysis of cross-peak multiplets even closer to the diagonal than for 2Q-filtered COSY spectra. Finally, the basic principle of E. COSY is not limited to the experiment discussed but can also be applied in connection with multiple quantum spectroscopy and for the simplification of cross-peak multiplets in NOESY spectra.

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(14) In some cases, passive couplings cause square patterns to partially overlap leading to rectangular patterns due to annihilation of peaks of opposite sign (see Figure 1b).

### Palladium-Promoted Diels-Alder Cycloadditions to 1-Phenyl-3,4-dimethylphosphole. Facile Synthesis of a New Class of Rigid Chiral Bidentate Phosphines: 5-Phosphino-7-phosphabicyclo[2.2.1]hept-2-enes

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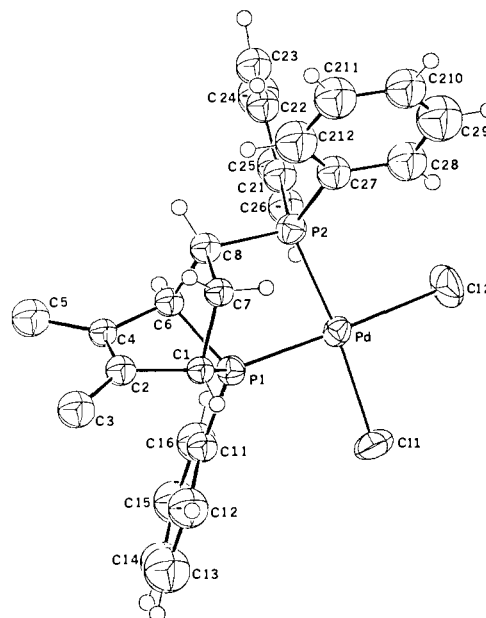
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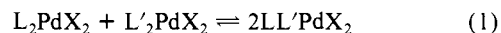
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We have previously investigated<sup>1</sup> the synthesis of mixed-ligand palladium complexes of the type  $LL'PdX_2$ , palladium complexes of phospholes,<sup>2</sup> and reviewed the coordination chemistry of phospholes.<sup>3</sup> From these previous studies we noted that (1) the

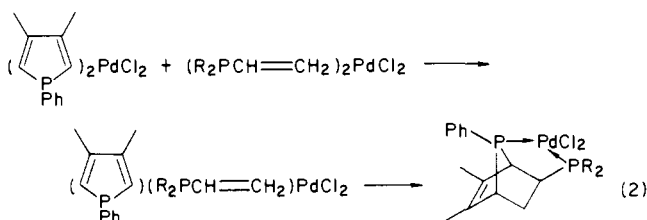


**Figure 1.** Structure of dichloro[5-(diphenylphosphino)-2,3-dimethyl-7-phenylphosphabicyclo[2.2.1]hept-2-ene]palladium(II) showing the 50% probability ellipsoids. Selected bond distances (Å): PdP<sub>1</sub>, 2.213 (4); PdP<sub>2</sub>, 2.251 (4); PdCl<sub>1</sub>, 2.344 (4); PdCl<sub>2</sub>, 2.351 (4); P<sub>2</sub>C<sub>8</sub>, 1.868 (13); P<sub>1</sub>C<sub>1</sub>, 1.818 (13); P<sub>1</sub>C<sub>6</sub>, 1.823 (14). Selected bond angles (deg): P<sub>1</sub>PdP<sub>2</sub>, 83.5 (1); Cl<sub>1</sub>PdCl<sub>2</sub>, 92.6 (2); Cl<sub>1</sub>PdP<sub>1</sub>, 89.2 (1); Cl<sub>2</sub>PdP<sub>1</sub>, 173.6 (1); Cl<sub>1</sub>PdP<sub>2</sub>, 171.4 (1); C<sub>1</sub>P<sub>1</sub>C<sub>6</sub>, 82.5 (6). The molecule of CH<sub>2</sub>Cl<sub>2</sub> was located and refined.

mixed-ligand complexes were rapidly formed in solution according to reaction 1, (2) the mixed-ligand complexes generally possessed



the *cis* geometry, (3) coordination of a phosphole polarizes its double bonds resulting in increased electron density at the  $\alpha$ -carbon centers, and (4) coordination of a phosphole increases its propensity to undergo [4 + 2]-Diels-Alder cycloadditions with dieneophiles. Thus, we reasoned that reaction of a palladium phosphole complex with a palladium vinylphosphine complex should likewise produce the *cis*-(phosphole)(vinylphosphine)palladium complex which might then undergo an internal Diels-Alder-[4 + 2] cycloaddition to yield a new class of chiral diphosphines, the 5-phosphino-7-phosphabicyclo[2.2.1]hept-2-enes according to reaction 2.



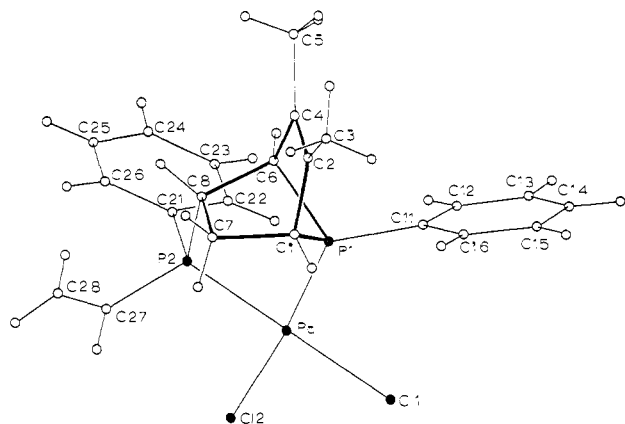
Accordingly, when a solution containing dichlorobis(1-phenyl-3,4-dimethylphosphole)palladium(II) ( $\delta^{31}P$  26.4) was added to a solution containing an equal molar amount of dichlorobis(diphenylvinylphosphine)palladium(II) ( $\delta^{31}P$  19.4, *cis* isomer; 11.2, *trans* isomer; 40:60, respectively) in CH<sub>2</sub>Cl<sub>2</sub> at ambient temperature an AX<sup>31</sup>P NMR spectrum ( $\delta^{31}P$  124.0, 34.5,  $J_{PP} = 5$  Hz) was immediately observed. The low-field resonance (124.0 ppm) is typical<sup>4</sup> of phosphorus contained in a 7-phosphabicyclo[2.2.1]hept-2-ene. This <sup>31</sup>P NMR spectrum suggested that reaction 2 proceeded to completion and that none

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**Figure 2.** Structure of dichloro[5-(phenylvinylphosphino)-2,3-dimethyl-7-phenylphosphabicyclo[2.2.1]hept-2-ene]palladium(II) in a skeletal view to show the norbornene unit clearly. Selected bond distances (Å): PdP<sub>1</sub>, 2.224 (2); PdP<sub>2</sub>, 2.236 (2); PdCl<sub>1</sub>, 2.356 (2); PdCl<sub>2</sub>, 2.366 (2); P<sub>1</sub>C<sub>1</sub>, 1.832 (8); P<sub>1</sub>C<sub>6</sub>, 1.843 (7); P<sub>2</sub>C<sub>8</sub>, 1.832 (8). Selected bond angles (deg): P<sub>1</sub>PdP<sub>2</sub>, 83.1 (1); P<sub>1</sub>PdCl<sub>1</sub>, 91.2 (1); P<sub>2</sub>PdCl<sub>1</sub>, 171.9 (1); P<sub>1</sub>PdCl<sub>2</sub>, 174.3 (1); P<sub>2</sub>PdCl<sub>2</sub>, 91.4 (1); Cl<sub>1</sub>PdCl<sub>2</sub>, 94.5 (1); C<sub>1</sub>P<sub>1</sub>C<sub>6</sub>, 82.3 (4).

of the intermediate mixed ligand complex was observed in solution. After addition of 95% ethanol and standing at room temperature for 2 days, colorless needles deposited from this solution in quantitative yield: mp 307 °C dec; IR  $\nu_{\text{PdCl}}$  291, 314  $\text{cm}^{-1}$ . Anal. Calcd for  $\text{C}_{26}\text{H}_{26}\text{Cl}_2\text{P}_2\text{Pd}\cdot\text{CH}_2\text{Cl}_2$ : C, 48.96; H, 4.23; Cl, 21.41. Found: C, 48.68; H, 4.47; Cl, 21.20. Since this compound is not very soluble and its  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra are very complicated, an X-ray crystal structure<sup>5</sup> (Figure 1) was obtained to confirm its structure. The crystal structure reveals that this reaction is highly stereoselective forming a racemic mixture of a single diastereomer.<sup>6</sup> The phosphorus donors have quite different donor abilities ( $\text{dPdP} = 2.213$  (4),  $2.251$  (4) Å), the CPC angle for the bridging phosphorus is small ( $82.5$  (6)°) and the PdCl ( $2.344$  (4),  $2.351$  (4) Å) distances are only slightly different.

A similar reaction proceeded quantitatively between equimolar quantities of dichlorobis(phenyldivinylphosphine)palladium(II) ( $\delta(^{31}\text{P})$  11.5, cis isomer; 4.1, trans isomer; 70:30, respectively) in  $\text{CH}_2\text{Cl}_2$  at ambient temperature to produce, after addition of 95% ethanol, colorless needles of dichloro[5-(phenylvinylphosphino)-2,3-dimethyl-7-phenylphosphabicyclo[2.2.1]hept-2-ene]palladium(II);  $\delta(^{31}\text{P})$  124.0, 35.3,  $J_{\text{PP}} = 5$  Hz; mp 286–290 °C dec; IR  $\nu_{\text{PdCl}}$  285, 310  $\text{cm}^{-1}$ . Anal. Calcd for  $\text{C}_{22}\text{H}_{24}\text{P}_2\text{Cl}_2\text{Pd}\cdot\text{H}_2\text{O}$ : C, 48.83; H, 4.76; Cl, 13.00. Found: C, 48.72; H, 5.09; Cl, 12.94. Likewise, this compound<sup>7</sup> (Figure 2) is a racemic mixture of a single diastereomer.<sup>6</sup> Here, the phosphorus donors have only slightly different donor abilities ( $\text{dPdP}$ ,  $2.224$  (2),  $2.236$  (2) Å), the CPC angle for the bridging phosphorus is small ( $82.3$  (4)°), and the PdCl ( $2.356$  (2),  $2.366$  (2) Å) distances are also slightly different.

(5) Crystal data: space group  $P2_1/c$ ,  $a = 11.184$  (4) Å,  $b = 10.972$  (5) Å,  $c = 23.351$  (8) Å,  $\beta = 103.17$  (3)°,  $\rho_{\text{calcd}} = 1.58$   $\text{g cm}^{-3}$ ,  $Z = 4$ , 1886 unique reflections with  $I > 3\sigma(I)$  were collected with a Syntex P<sub>21</sub> four-circle diffractometer with use of Mo K $\alpha$  (0.710 69 Å) radiation. The structure was solved by heavy atom methods (with anisotropic thermal parameters for all non-hydrogen atoms). Refinement converged to  $R(F) = \sum(|F_o| - |F_c|)/\sum|F_o| = 0.060$  and  $R_w(F) = [\sum w(|F_o| - |F_c|)^2/\sum wF_o^2]^{1/2} = 0.056$ , and  $w = 1/(\sigma^2(F) + gF^2)$  with  $g = 0.0006$ . Tables of positional and thermal parameters are available as supplementary material.

(6) Four diastereomers are possible in this case: syn-exo; syn-endo; anti-exo, anti-endo. If the exocyclic phosphorus bears two different substituents eight diastereomers become possible.

(7) Crystal data: space group  $Fdd2$ ,  $a = 28.737$  (5) Å,  $b = 32.979$  (8) Å,  $c = 10.253$  (2) Å,  $\rho_{\text{calcd}} = 1.44$   $\text{g cm}^{-3}$ ,  $Z = 16$ , 2011 unique reflections with  $I > 3\sigma(I)$  were collected with a Syntex P<sub>21</sub> four-circle diffractometer with use of Mo K $\alpha$  (0.710 69 Å) radiation. The structure was solved by heavy atom methods (with anisotropic thermal parameters for all non-hydrogen atoms). Refinement converged to  $R(F) = 0.036$  and  $R_w(F) = 0.040$ , and  $w = 1/(\sigma^2(F) + gF^2)$  with  $g = 0.002$ . Tables of positional and thermal parameters are available as supplementary material.

We then wondered whether these reactions would also occur with the platinum analogues.<sup>8</sup> In these cases, we hoped that since platinum complexes are substitutionally much more inert than palladium complexes, we might be able to detect the mixed-ligand complex intermediates by  $^{31}\text{P}$  NMR spectroscopy. However, only starting materials and final Diels–Alder-[4 + 2] cycloaddition products were observable by  $^{31}\text{P}$  NMR spectroscopy of the reaction solutions. Thus, the Diels–Alder cycloaddition ensues very rapidly following formation of the mixed-ligand complex<sup>9</sup> and in all four cases studied the reaction proceeds to completion.<sup>10</sup> These new ligand systems possess two properties which are highly desirable for asymmetric catalysis. They are rigid<sup>11</sup> bidentate ligands with different donor abilities<sup>12</sup> for the two donor atoms. Research is currently in progress to assess the catalytic potential of these new complexes.

An attempted extension of these reactions to other similar systems showed that reaction of dichlorobis(1-phenyl-3,4-dimethylphosphole)platinum(II) with dichlorobis(diallylphenylphosphine)platinum(II) did not produce the analogous [4 + 2]-Diels–Alder cycloadduct but rather stopped at the cis-mixed-ligand complex ( $\delta(^{31}\text{P})$  8.4 ( $^1J_{\text{PP}} = 3363$  Hz),  $-2.7$  ( $^1J_{\text{PP}} = 3584$ ),  $^2J_{\text{PP}} = 17$  (Hz)). This is probably the result of the much lower dieneophilicity of diallylphenylphosphine compared to the vinylphosphines and not the result of steric effects. Further work to delineate the scope and limitations of this new reaction is in progress.

The ligands have been liberated from their complexes by cyanide displacement<sup>13</sup> and converted to the respective sulfides<sup>14</sup> with retention of stereochemical configuration.

Thermal gravimetric analyses and differential scanning calorimetry demonstrate that both the complexes and the ligand sulfides polymerize upon melting, probably by extrusion of the phosphinidene moieties,<sup>15</sup> “PhP” and “PhP=S”.

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**Supplementary Material Available:** Listings of atomic positional parameters, thermal parameters, interatomic distances and angles, and observed and calculated structure factors (30 pages). Ordering information is given on any current masthead page.

(8) See, for the phosphole complexes: MacDougall, J. J.; Nelson, J. H.; Mathey, F. *Inorg. Chem.* **1982**, *21*, 2145. The vinyl phosphine complexes will be described in a future publication.

(9) 1-Phenyl-3,4-dimethylphosphole and phenyldivinylphosphine were reacted in refluxing chloroform for 1 week under nitrogen and only the two phosphorus ligands were observable by  $^{31}\text{P}\{^1\text{H}\}$  NMR spectroscopy. Thus, the Diels–Alder cycloaddition requires the formation of the mixed-ligand complex. Further, if the reaction proceeded in the absence of the metal, the syn-endo diastereomer would be expected, see: Santini, C. C.; Fischer, J.; Mathey, F.; Mitschler, A. *J. Am. Chem. Soc.* **1980**, *102*, 5809.

(10) Dichloro[5-(diphenylphosphino)-2,3-dimethyl-7-phenylphosphabicyclo[2.2.1]hept-2-ene]platinum(II), colorless microcrystals: mp 370 °C dec; IR  $\nu_{\text{PtCl}}$  285, 325  $\text{cm}^{-1}$ ;  $\delta(^{31}\text{P})$  107.9 ( $^1J_{\text{PP}} = 3258$  Hz), 38.6 ( $^1J_{\text{PP}} = 3184$  Hz,  $J_{\text{PP}} = 17$  Hz). Anal. Calcd for  $\text{C}_{26}\text{H}_{26}\text{Cl}_2\text{P}_2\text{Pt}$ : C, 46.86; H, 3.90; Cl, 10.64. Found: C, 47.12; H, 4.03; Cl, 10.58. Dichloro[5-(phenylvinylphosphino)-2,3-dimethyl-7-phenylphosphabicyclo[2.2.1]hept-2-ene]platinum(II), colorless microcrystals, mp 348 °C dec; IR  $\nu_{\text{PtCl}}$  286, 312  $\text{cm}^{-1}$ ;  $\delta(^{31}\text{P})$  96.3 ( $^1J_{\text{PP}} = 3235$  Hz), 20.3 ( $^1J_{\text{PP}} = 3474$ ,  $J_{\text{PP}} = 17$  Hz). Anal. Calcd for  $\text{C}_{22}\text{H}_{24}\text{Cl}_2\text{P}_2\text{Pt}$ : C, 42.88; H, 3.89; Cl, 11.51. Found: C, 43.04; H, 4.09; Cl, 11.34.

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(13) Mercier, F.; Mathey, F.; Fischer, J.; Nelson, J. H. *Inorg. Chem.*, in press.

(14) 5-(Diphenylphosphino)-2,3-dimethyl-7-phenylphosphabicyclo[2.2.1]hept-2-ene disulfide, colorless microcrystals, mp 199–200 °C;  $\delta(^{31}\text{P})$  89.4, 46.1 ( $J_{\text{PP}} = 0$ ). Anal. Calcd for  $\text{C}_{26}\text{H}_{26}\text{P}_2\text{S}_2$ : C, 67.25; H, 5.60. Found: C, 67.15; H, 5.49. 5-(Phenylvinylphosphino)-2,3-dimethyl-7-phenylphosphabicyclo[2.2.1]hept-2-ene disulfide, colorless microcrystals, mp 172–174 °C;  $\delta(^{31}\text{P})$  88.0, 42.0 ( $J_{\text{PP}} = 0$ ). Anal. Calcd for  $\text{C}_{22}\text{H}_{24}\text{P}_2\text{S}_2$ : C, 63.78; H, 5.79. Found: C, 63.84; H, 5.65. The value of the PP coupling constant (0) confirms the syn-exo stereochemistry; see: Quin, L. D.; Mesch, K. A. *Org. Magn. Reson.* **1979**, *12*, 442.

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