

# Chiral Phosphine–Phosponium Ylide Rhodium Complexes

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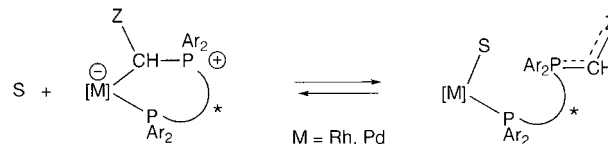
**Summary:** The phosphonium methylide of (*R*)-BINAP acts as a novel chiral dissymmetric chelating ligand in the stable  $[\text{Rh}(\text{cod})(\text{BINAPCH}_2)]^+$  complex. A rationale for the conformation of the eight-membered metallacycle derived from chiral phosphine–phosponium ylide ligands is proposed on the basis of DFT calculations on a model complex.

Whereas the coordination chemistry of chiral diphosphines with group 9 and group 10 metals has been widely studied, owing to their role in asymmetric catalysis,<sup>1</sup> complexes of chiral diylides have received little specific attention. Related to them, however, are chiral iminophosphoranes, which can be regarded as aza–phosphonium ylide ligands and which were shown to give efficient asymmetric catalysts for copper-mediated cyclopropanation<sup>2a,b</sup> and palladium-mediated allylic alkylation.<sup>2c</sup> A palladium iminophosphorane–phosphine complex derived from an achiral diphosphine has also been reported.<sup>3a</sup> A natural prolongation is the study of hybrid ligands containing both a  $\eta^1$ -phosphine terminus and a  $\eta^1$ -C nonstabilized phosphonium ylide terminus.<sup>3b,4</sup>

A phosphine–phosphonium precursor derived from the chiral skeleton BINAP<sup>5</sup> is considered. Indeed, this ligand lends itself to monoquaternization by methyl iodide to give a chiral phosphonio–phosphine termed as “methylbinapium” **2**.<sup>7</sup>

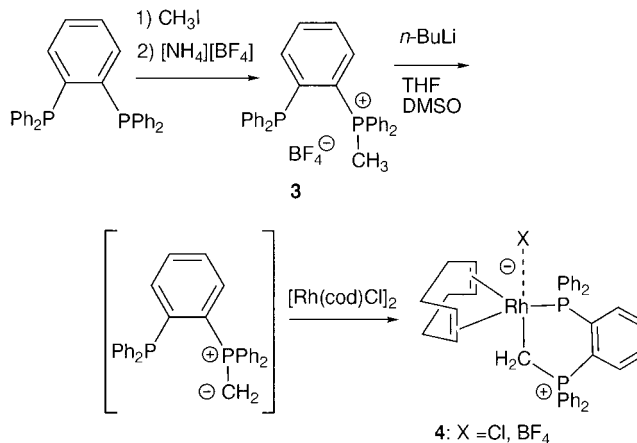
To the best of our knowledge, no chiral version of this hybrid type of ligand was reported until recently, when stabilized monophosphonium ylides of BINAP were shown to act as chelating ligands in Rh(I) and Pd(II) complexes.<sup>8a</sup> However, the stabilized nature of the free

**Scheme 1.** Decoordination of Stabilized Ylides of BINAP for  $\text{Z} = \text{CO}_2\text{R}^a$



<sup>a</sup> S denotes a solvent molecule. **1a** is the chelate form and **1b** the open form.

**Scheme 2.** Preparation of Rhodium Phosphine–Phosphonium Methylide Complex **4**



4: X = Cl, BF<sub>4</sub>

ylides gave rise to an equilibrium between a chelate form (**1a**) and an open form (**1b**) of the complex (Scheme 1). This is reminiscent of the hemilabile character of the BINAP monoxide ligand.<sup>8b</sup>

The design of a nonstabilized free ylide is anticipated to shift the equilibrium to the chelate form (**1a**). The ylide of methylbinapium **2** has thus been considered. As a model, the methylphosphonium tetrafluoroborate salt **3** was first prepared from 1,2-bis(diphenylphosphino)benzene.<sup>9</sup> Addition of 10% of DMSO was required to dissolve **3** in a THF/DMSO mixture, and deprotonation by *n*-BuLi afforded the non-salt-free ylide, which was then reacted in situ with  $[\text{Rh}(\text{cod})\text{Cl}]_2$ . <sup>1</sup>H and <sup>31</sup>P NMR analysis indicates that formation of complex **4** is quantitative.<sup>10</sup> In contrast to the reaction of stabilized ylides and diylides with  $\text{Pd}(\text{cod})\text{Cl}_2$ , the cyclooctadiene ligand is neither attacked<sup>11a</sup> nor displaced.<sup>11b</sup> Nevertheless, due to the presence of DMSO, chloride anions are present in the medium and the structure of **4** could be assigned to either an ionic or a zwitterionic form (Scheme 2).

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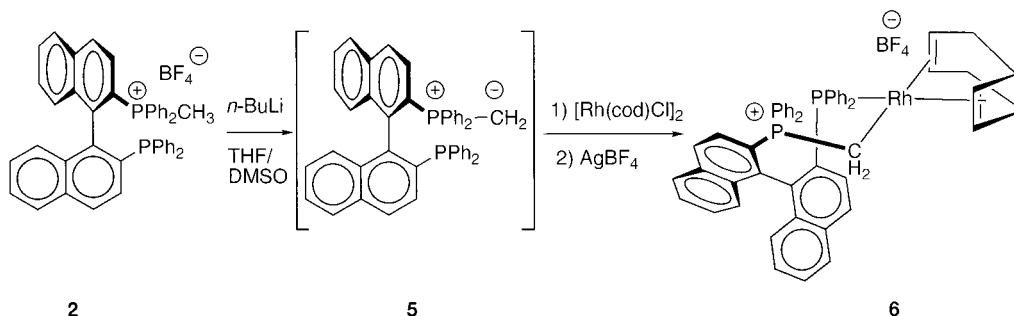
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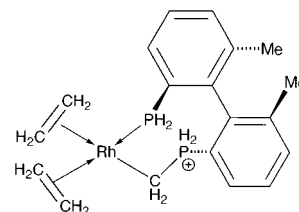
## Scheme 3. Synthesis of the Methylbinaprium Ylide Rhodium Complex 6



The tetrafluoroborate salt of methylbinaprium **2** was then reacted with a base (*n*-BuLi or LDA) in a 9/1 THF/DMSO mixture at 0 °C.<sup>12</sup> Ylide **5** was converted in situ to the non-salt-free oily complex **6** by reaction with [Rh(cod)Cl]<sub>2</sub> (Scheme 3). DMSO and inorganic salts could be extracted in water. Indeed, complex **6** is stable at 20–25 °C in CDCl<sub>3</sub>, in methanol and in CH<sub>2</sub>Cl<sub>2</sub>/water mixtures. Chloride ions could be removed by addition of AgBF<sub>4</sub> to a CH<sub>2</sub>Cl<sub>2</sub> solution of the crude product. The NMR data, however, remained the same, suggesting that the noncoordinating nature of the chloride counteranions was preexisting in a nonzwitterionic 16-electron Rh(I) structure.

Structure **6** is supported by a clean +ESMS three-peak fragmentation at *m/z* 847.2, which fits the calculated isotopic pattern for the [(BINAPCH<sub>2</sub>)Rh(cod)]<sup>+</sup> fragment. <sup>31</sup>P NMR data indicate a η<sup>1</sup> coordination of the ylide CH<sub>2</sub> group: δ 25.65 (dd, <sup>1</sup>J<sub>PRh</sub> = 155 Hz, <sup>3</sup>J<sub>PP+</sub> = 5.3 Hz, PRh) and 34.18 (dd, <sup>2</sup>J<sub>PRh</sub> = <sup>3</sup>J<sub>PP+</sub> = 5.2 Hz, P<sup>+</sup>CH<sub>2</sub>Rh). These chemical shifts and the coupling constant values are consistent with literature data for phosphorus atoms in similar environments.<sup>8a</sup> The ylidic CH<sub>2</sub> group is also characterized by shielded <sup>1</sup>H and <sup>13</sup>C NMR signals: in contrast with the reported difficulty in observing analogous signals in other Rh(I) ylide complexes,<sup>13</sup> the diastereotopic protons occur as resolved multiplets, at δ 0.58 and 1.22. The coupling constants were assigned by selective <sup>31</sup>P decoupling experiments (<sup>2</sup>J<sub>HH</sub> = 1.6 Hz, <sup>2</sup>J<sub>HRh</sub> ≈ 11.4 Hz, <sup>2</sup>J<sub>HP+</sub> ≈ 11 Hz, <sup>3</sup>J<sub>HP</sub> ≈ 5.5 Hz). All of the protons of the binaphthylene and the cyclooctadiene moieties were accurately assigned by <sup>1</sup>H, <sup>31</sup>P, <sup>13</sup>C, COSY <sup>1</sup>H–<sup>1</sup>H, and COSY <sup>1</sup>H–<sup>13</sup>C NMR analysis.<sup>14</sup> No evidence of a decoordination of the methylide terminus (Scheme 1 for Z = H) was observed from the <sup>31</sup>P NMR spectrum of **6**. A fast exchange on the NMR time scale between the resonances of open and chelate forms of the complex can indeed be ruled out: the <sup>3</sup>J<sub>PP+</sub>

Chart 1. Model 7 of Complex 6 Used for DFT Modeling



and <sup>2</sup>J<sub>PRh</sub> coupling constants would vanish in the open form, while the observed multiplet signals are sharp and consistent with a well-defined P–Rh–CH<sub>2</sub>–P<sup>+</sup> environment.<sup>8a,13b</sup>

Since no crystal structure could be obtained, structural information was extracted from geometry optimization of the model complex **7** at the B3PW91/6-31G\*/LANL2DZ(Rh) level. In **7**, the BINAP skeleton of **6** was simplified by exchanging PPh<sub>2</sub> for PH<sub>2</sub>, the binaphthyl for a bis(*o*-tolyl), and the cod ligand for two ethylene ligands (Chart 1).

The atropoisomeric chirality is thus retained in order to estimate the diastereoisomeric control of the *R/S* chirality element of the ligand on the conformation of the eight-membered metallacycle. The latter is regarded as resulting from the insertion of an ylide CH<sub>2</sub> unit into a seven-membered metallacycle: the structure is therefore discussed by reference to the λ,δ nomenclature coined for the seven-membered C<sub>2</sub>-symmetric metallacycles (Chart 2).<sup>15</sup> With an *R* ligand configuration, geometry optimization led to the λ-type conformation **7a** of the seven-membered cyclic sequence of atoms in the metallacycle, from which the ylide CH<sub>2</sub> group has

(10) NMR data for spectroscopically pure complex **4** are as follows. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 200 MHz): δ 1.30–1.40 (m, 1 H, PCH<sub>2</sub>); 1.41–1.50 (m, 1 H, PCH<sub>2</sub>); 1.70–2.20 (m, 8 H, CH<sub>2</sub>(cod)); 3.43–3.53 (m, 2 H, CH(cod)); 4.73–4.83 (m, 2 H, =CH(cod)); 7.24–7.72 (m, 24 H, aromatic CH). <sup>31</sup>P{<sup>1</sup>H} NMR (CDCl<sub>3</sub>, 81 MHz): δ 28.75 (dd, <sup>2</sup>J<sub>PRh</sub> = 5 Hz, <sup>3</sup>J<sub>P+P</sub> = 26 Hz, P<sup>+</sup>Ph<sub>2</sub>CH<sub>2</sub>Rh); 33.96 (dd, <sup>1</sup>J<sub>PRh</sub> = 163 Hz, <sup>3</sup>J<sub>PP+</sub> = 26 Hz, PPh<sub>2</sub>Rh). For an analogous phosphino–iminophosphorane rhodium complex displaying similar NMR characteristics, see: Reed, R. W.; Santarsiero, B.; Cavell, R. G. *Inorg. Chem.* **1996**, *35*, 4292.

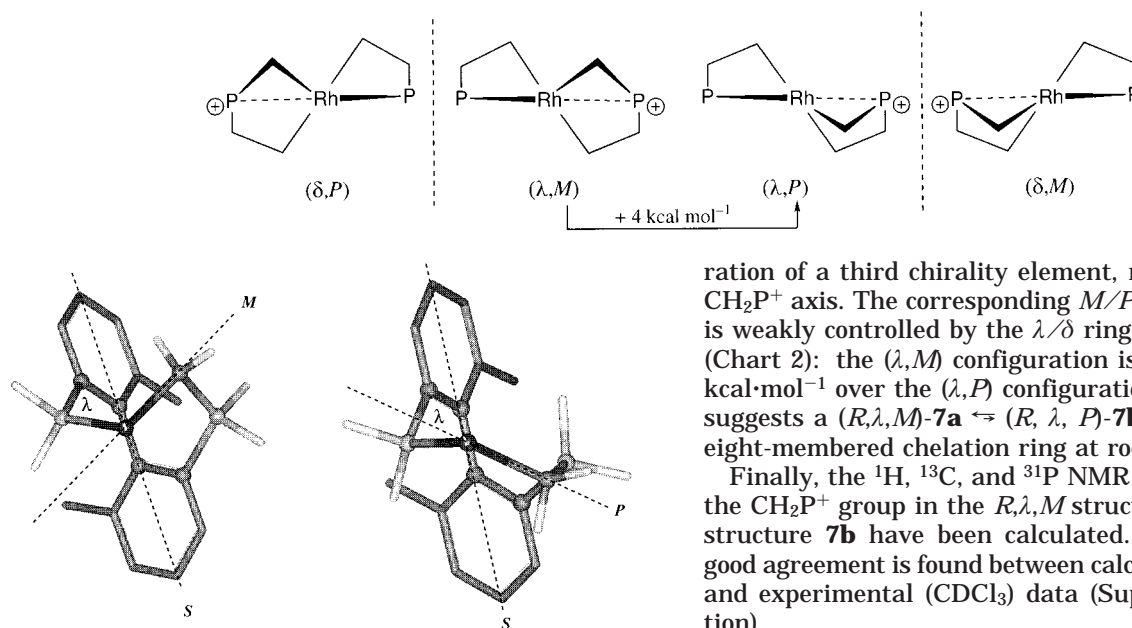
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(12) <sup>31</sup>P NMR data for **5** (81 MHz, THF/DMSO, external lock on C<sub>6</sub>D<sub>6</sub>): δ 26.55 (broad dd; <sup>2</sup>J<sub>PH</sub> = 10 and 13 Hz; (Np)Ph<sub>2</sub>PCH<sub>2</sub>); –14.03 (m; P(Np)Ph<sub>2</sub>). Np = naphthylene substituent.

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(14) Other NMR data for **6** are as follows (see atom numbering in the Supporting Information). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz): δ 0.58 (dddd; <sup>1</sup>J<sub>HH</sub> = 1.6 Hz, <sup>2</sup>J<sub>HRh</sub> = 11.4 Hz, <sup>2</sup>J<sub>HP+</sub> = 11 Hz, <sup>3</sup>J<sub>HP</sub> = 5.5 Hz, 1 H, P<sup>+</sup>CH<sub>2</sub>Rh); 1.11–1.18 (m, 1 H, H<sub>f</sub>); 1.18–1.25 (m, 1 H, P<sup>+</sup>CH<sub>2</sub>Rh); 1.34–1.37 (m, 1 H, H<sub>f</sub>); 1.50–1.60 (m, 1 H, H<sub>g</sub>); 1.60–1.75 (m, 2 H, H<sub>h</sub>, H<sub>h</sub>); 1.75–1.90 (m, 1 H, H<sub>g</sub>); 2.37–2.50 (m, 1 H, H<sub>e</sub>); 2.75–2.82 (m, 1 H, H<sub>d</sub>); 2.82–2.89 (m, 1 H, H<sub>e</sub>); 3.25–3.37 (m, 1 H, H<sub>e</sub>); 4.96–5.04 (m, 2 H, H<sub>a</sub>, H<sub>b</sub>); 5.60 (d, 1 H, <sup>3</sup>J<sub>HH</sub> = 8.5 Hz, H<sub>f</sub>); 5.90 (d, 1 H, <sup>3</sup>J<sub>HH</sub> = 8.5 Hz, H<sub>f</sub>); 6.42 (dd, <sup>3</sup>J<sub>HH</sub> = 8.2 Hz, <sup>3</sup>J<sub>HH</sub> = 7.2 Hz, 1 H, H<sub>f</sub>); 6.66 (dd, <sup>3</sup>J<sub>HH</sub> = 8.2 Hz, <sup>3</sup>J<sub>HH</sub> = 7.2 Hz, H<sub>f</sub>); 6.74–6.82 (m, 1 H, H<sub>n</sub>); 6.89–6.92 (m, 1 H, H<sub>m</sub>); 7.16 (dd, <sup>3</sup>J<sub>HH</sub> = 7.9 Hz, <sup>3</sup>J<sub>HH</sub> = 7.2 Hz, 1 H, H<sub>d</sub>); 7.30 (dd, <sup>3</sup>J<sub>HH</sub> = 7.9 Hz, <sup>3</sup>J<sub>HH</sub> = 7.2 Hz, 1 H, H<sub>e</sub>); 7.60–7.68 (m, 2 H, H<sub>f</sub>, H<sub>f</sub>); 7.79–7.84 (m, 1 H, H<sub>m</sub>); 8.06–8.12 (m, 1 H, H<sub>n</sub>); 6.9–8.1 (m, 20 H, C<sub>6</sub>H<sub>5</sub>P, C<sub>6</sub>H<sub>5</sub>P<sup>+</sup>). <sup>13</sup>C{<sup>1</sup>H, <sup>31</sup>P} NMR (CDCl<sub>3</sub>, 100 MHz): δ 8.29 (dd, <sup>1</sup>J<sub>CRh</sub> = 27.3 Hz, <sup>2</sup>J<sub>CP</sub> = 26.9 Hz, CH<sub>2</sub>Rh); 27.36 (s, C<sub>f</sub>); 31.21 (s, C<sub>g</sub>); 34.00 (s, C<sub>h</sub>); 35.37 (s, C<sub>e</sub>); 86.17 (dd, <sup>1</sup>J<sub>CRh</sub> = 7.0 Hz, <sup>2</sup>J<sub>CP</sub> = 18.5 Hz, C<sub>d</sub>); 89.05 (d, <sup>1</sup>J<sub>CRh</sub> = 8.0 Hz, C<sub>i</sub>); 92.12 (d, <sup>1</sup>J<sub>CRh</sub> = 8.0 Hz, C<sub>b</sub>); 96.73 (dd, <sup>1</sup>J<sub>CRh</sub> = 11.0 Hz, <sup>2</sup>J<sub>CP</sub> = 18.5 Hz, C<sub>a</sub>); 120.05–143.00 (m, aromatic C). <sup>13</sup>C{<sup>1</sup>H, <sup>31</sup>P} NMR (CDCl<sub>3</sub>, 100 MHz): δ 8.29 (d, <sup>1</sup>J<sub>CRh</sub> = 27.3 Hz, CH<sub>2</sub>Rh); 27.36 (s, C<sub>f</sub>); 31.21 (s, C<sub>g</sub>); 34.00 (s, C<sub>h</sub>); 35.37 (s, C<sub>e</sub>); 86.17 (d, <sup>1</sup>J<sub>CRh</sub> = 7 Hz, C<sub>d</sub>); 89.05 (d, <sup>1</sup>J<sub>CRh</sub> = 8 Hz, C<sub>i</sub>); 92.12 (d, <sup>1</sup>J<sub>CRh</sub> = 8 Hz, C<sub>b</sub>); 96.73 (d, <sup>1</sup>J<sub>CRh</sub> = 11 Hz, C<sub>a</sub>); 120–143 (m, aromatic C).

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**Chart 2. Rationale for the Conformational Analysis of Eight-Membered Phosphine–Phosphonium Methylene Metallacycles****Figure 1.** Two optimized  $R,\lambda$  type geometries of the model complex **7** at the B3PW91/6-31G\*/LANL2DZ level.  $sp^2$  CH and ethylene ligands have been omitted for clarity. The centroids X and Y of the ethylene ligands are almost in the  $\angle P-Rh-CH_2$  plane, which lies  $9.5^\circ$  off the  $\angle X\cdots Rh\cdots Y$  plane.

been excluded (Figure 1). In this configuration, denoted as  $R,\lambda$ , the ylide  $CH_2$  group is slightly tilted out of the  $P-Rh\cdots P^+$  plane, anti to the  $CH_2CH_2P^+$  ethylene sequence. This corresponds to an  $M$  configuration of the  $P-Rh-CH_2-P^+$  helicoidal axis.<sup>16</sup> A second  $R,\lambda$ -type conformation, **7b**, is found  $3.7\text{ kcal mol}^{-1}$  above the former, where the ylide  $CH_2$  group is switched syn to the  $CH_2CH_2P^+$  ethylene sequence and corresponds to a  $P$  configuration of the  $P-Rh-CH_2-P^+$  helicoidal axis (Figure 1).<sup>17</sup>

No  $R,\delta$ -type conformation could be obtained as a minimum. Therefore, the  $R/S$  configuration of the atropisomeric axis completely controls the  $\lambda/\delta$  configuration of the fictitious seven-membered metallacycle. The conformation of a real eight-membered metallacycle is characterized by another feature: the  $M/P$  configu-

ration of a third chirality element, namely the  $PRh-CH_2P^+$  axis. The corresponding  $M/P$  chirality element is weakly controlled by the  $\lambda/\delta$  ring chirality element (Chart 2): the  $(\lambda,M)$  configuration is favored by *c.a.*  $4\text{ kcal mol}^{-1}$  over the  $(\lambda,P)$  configuration (Chart 2). This suggests a  $(R,\lambda,M)\text{-7a} \rightleftharpoons (R,\lambda,P)\text{-7b}$  flexibility of the eight-membered chelation ring at room temperature.

Finally, the  $^1H$ ,  $^{13}C$ , and  $^{31}P$  NMR chemical shifts of the  $CH_2P^+$  group in the  $R,\lambda,M$  structure **7a** and  $R,\lambda,P$  structure **7b** have been calculated.<sup>18</sup> A qualitatively good agreement is found between calculated (gas phase) and experimental ( $CDCl_3$ ) data (Supporting Information).

In conclusion, methylbinapium methylene leads to a stable eight-membered chelated rhodium(I) complex with a novel type eight-membered metallacycle. In the presence of more or less coordinating anions, the metal would lie in the peculiar dissymmetric chiral electrostatic environment of formally  $\beta$ -zwitterionic organometalate complexes.<sup>19</sup> This feature should provide specific effects on the catalytic properties of such complexes, which are currently under investigation.<sup>20</sup>

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**Supporting Information Available:** Text giving experimental procedures and comprehensive NMR characteristics for compounds **3**, **4**, and **6** and detailed computational results. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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(16) See for example: Dodziuk, H.; Mirowicz, M. *Tetrahedron: Asymmetry* **1990**, *1*, 171.

(17) Other geometrical parameters of the two minima are similar. In particular, the  $H_2C-Rh-PH_2$  bite angles, *ca.*  $88$  and  $95^\circ$ , indicate an approximate square-planar crystal field around the rhodium atom in both the conformers.

(18) The NMR spectra were calculated at the B3PW91/6-31G\*/LANL2DZ(Rh) level within the framework of the GIAO formalism implemented in Gaussian98 (Wolinski, K.; Hinton, J. F.; Pulay, P. *J. Am. Chem. Soc.* **1990**, *112*, 8251. Cheeseman, J. R.; Trucks, G. W.; Keith, T. A.; Frisch, M. J. *J. Chem. Phys.* **1996**, *104*, 5497).

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