

**(6,6'-Dimethoxybiphenyl-2,2'-diyl)bis(diphenylphosphine)  
(MeO-BIPHEP) as a Six-Electron Donor in  
[Ru( $\eta^5$ -C<sub>8</sub>H<sub>11</sub>)(MeO-BIPHEP)]<sup>+</sup> Cations. Coordination of  
a Biaryl Double Bond, As Shown by <sup>13</sup>C NMR and X-ray  
Crystallography**

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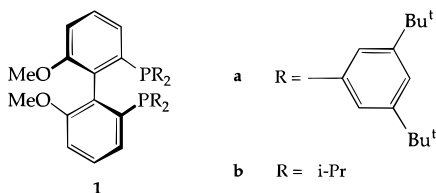
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The reaction of the MeO-BIPHEP complex Ru(OAc)<sub>2</sub>(**1a**) (**1a** = (6,6'-dimethoxybiphenyl-2,2'-diyl)bis(bis(3,5-di-*tert*-butylphenyl)phosphine), with HBF<sub>4</sub> and 1,5-COD affords [Ru( $\eta^5$ -C<sub>8</sub>H<sub>11</sub>)(**1a**)]BF<sub>4</sub> (**4**), in which **1a** functions as a 6e donor to Ru(II) via an unexpected coordination of one of the biaryl double bonds. The isopropyl analog [Ru( $\eta^5$ -C<sub>8</sub>H<sub>11</sub>)(**1b**)]CF<sub>3</sub>CO<sub>2</sub> (**6**; **1b** = (6,6'-dimethoxybiphenyl-2,2'-diyl)bis(diisopropylphosphine)) was prepared by starting from [Ru(CF<sub>3</sub>CO<sub>2</sub>)<sub>2</sub>(1,5-COD)]<sub>2</sub> and reveals the same  $\eta^4$ -bonding mode. Both complexes were characterized by detailed multidimensional NMR studies, and the X-ray structure for **6** is reported. Although the <sup>31</sup>P chemical shifts for this new  $\eta^4$ -bonding mode are informative, the <sup>13</sup>C resonance positions for the coordinated biaryl carbons are a more reliable criterion for recognizing this type of interaction. These chemical shift data are difficult to obtain using routine <sup>13</sup>C measurements, and a long-range <sup>13</sup>C,<sup>1</sup>H-correlation is recommended as the method of choice. Complex **4** exhibits dynamic behavior in solution, as shown by 2-D NOESY. This exchange process can be rationalized by assuming that the double bond dissociates; however, complex **6** does not show an analogous exchange process at ambient temperature.

### Introduction

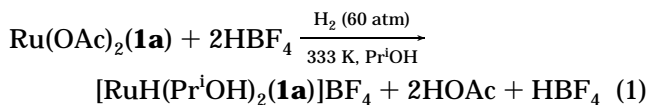
Homogeneous catalysts based on ruthenium complexes are now widely employed in enantioselective hydrogenation chemistry.<sup>1</sup> Within this context, the bidentate phosphine ligands MeO-BIPHEP (**1**), are now



recognized to be useful chiral auxiliaries for the enantioselective homogeneous hydrogenation of olefins.<sup>2,3</sup> The observed chemical and optical yields are often excellent, with enantiomeric excesses (ee's) frequently >95%. Thus, these MeO-BIPHEP auxiliaries represent

a useful complement to the well-known<sup>4</sup> BINAP class, where, for hydrogenation chemistry, there have been detailed mechanistic studies.<sup>5</sup> The preparative chemistry for **1** is sufficiently flexible such that the methoxy group can be replaced by a methyl substituent. Moreover, a variety of R groups can be introduced.<sup>2</sup> The precursor most often used in the catalytic work is of the form Ru(OAc)<sub>2</sub>(**1**) (**2**) or a related trifluoroacetate complex.

We have recently reported<sup>6</sup> that Ru(OAc)<sub>2</sub>(**1a**) (**2a**) under hydrogenation conditions, i.e., excess HBF<sub>4</sub>, a molecular hydrogen atmosphere, and 2-propanol as solvent, affords the novel five-coordinate bis(solvento) hydrido complex [RuH(2-propanol)<sub>2</sub>(**1a**)]BF<sub>4</sub> (**3**).



The structure for **3** was determined by X-ray diffraction methods<sup>6</sup> and is best described as a distorted square

<sup>®</sup> Abstract published in *Advance ACS Abstracts*, January 15, 1997.

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(5) (a) Ashby, M. T.; Khan, M. A.; Halpern, J. *Organometallics* **1991**, *10*, 2011. (b) Ashby, M. T.; Halpern, J. *J. Am. Chem. Soc.* **1991**, *113*, 589.

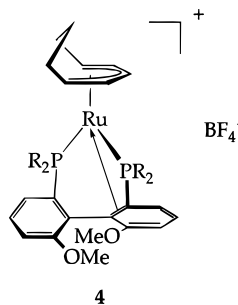
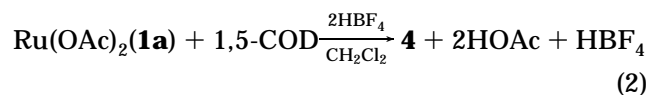
(6) Currao, A.; Feiken, N.; Macchioni, A.; Nesper, R.; Pregosin, P. S.; Trabesinger, G. *Helv. Chim. Acta* **1996**, *79*, 1587.

pyramid. This is a rare example of a chiral hydrido bis-(solvento) complex.

As **1a** stabilizes the five-coordinate coordinatively unsaturated complex **3**, and since there is little known on Ru(II)–organometallic chemistry with MeO-BIPHEP ligands, we attempted to prepare complexes of **1** containing 1,5-COD. We report here NMR and X-ray studies for two ruthenium complexes of **1** in which an unusual MeO-BIPHEP coordination mode is observed.

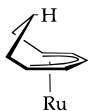
## Results and Discussion

**NMR Studies on [Ru( $\eta^5$ -C<sub>8</sub>H<sub>11</sub>)(**1a**)]BF<sub>4</sub>.** In methylene chloride, Ru(OAc)<sub>2</sub>(**1a**) reacts with 1,5-COD and HBF<sub>4</sub> to afford **4** in good yield.



Complex **4** affords satisfactory microanalytical and mass spectral data, with the molecular ion found at *m/e* 1239.7. The <sup>31</sup>P NMR spectrum (see Figure 1), shows a routine AX spin system; however, the phosphorus chemical shifts, at 69.6 ppm and –11.2 ppm (!) are unexpected, with the latter coming in a region often associated with uncoordinated phosphine. The BF<sub>4</sub><sup>–</sup> anion was also confirmed via its <sup>19</sup>F NMR spectrum. Initially, we considered an acetate complex; however, it was clear from infrared and <sup>13</sup>C measurements that this anion was not present.

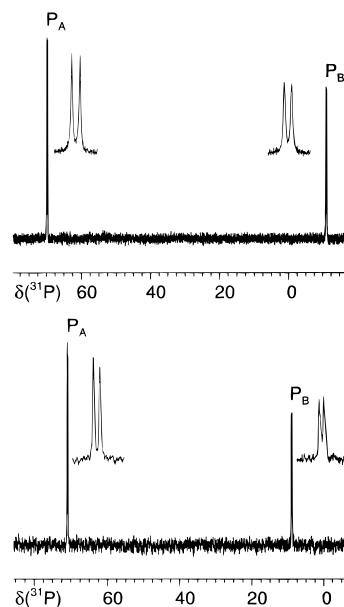
The nature of the organometallic ligand in **4** was not immediately obvious; however, a routine 2-D <sup>13</sup>C,<sup>1</sup>H correlation showed only three aliphatic CH<sub>2</sub> type signals, a clear indication that the 1,5-COD ligand had been transformed. There are *five* CH-absorptions in the region 57–114 ppm, and these <sup>13</sup>C chemical shift data are strongly suggestive of the ruthenium-cyclooctadienyl fragment Ru( $\eta^5$ -C<sub>8</sub>H<sub>11</sub>);<sup>7</sup> the following diagram shows one of the shielded protons of this fragment at –0.42 ppm:



The <sup>1</sup>H spectrum, assigned via NOESY (and ROESY, as the molecule is moderately large and moves slowly<sup>8,9</sup> at 193 K) plus the usual forms of proton correlation spectroscopy, confirms the presence of this  $\eta^5$  six-electron donor in that one of the two observed low-frequency

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(b) Macura, S.; Ernst, R. R. *Mol. Phys.* **1980**, *41*, 95.



**Figure 1.** <sup>31</sup>P NMR spectra for **4** (upper trace) and **6** (lower trace). Note the relatively large differences between the two <sup>31</sup>P chemical shifts. The <sup>2</sup>J(P,P) values are 47 and 40 Hz for **4** and **6**, respectively (500 MHz, CD<sub>2</sub>Cl<sub>2</sub>; **4** at 193 K, **6** at room temperature).

**Table 1.** <sup>1</sup>H and <sup>13</sup>C NMR Data for the  $\eta^5$ -C<sub>8</sub>H<sub>11</sub> Ligands in **4** and **6**<sup>a</sup>

position	<b>4</b>		<b>6</b>	
	<sup>1</sup> H	<sup>13</sup> C	<sup>1</sup> H	<sup>13</sup> C
9	4.14	57.8	4.16	49.6
10	5.08	89.8	4.92	85.4
11	5.37	114.7	5.27	114.3
12	0.95	97.7	0.85	99.2
13	2.32	69.5	2.84	62.3
14				
exo	0.79	ca. 21	1.87	
endo	–0.83		1.54	
15				
exo	0.48	ca. 18	1.09	19.4
endo	–0.42		0.02	
16				
exo		ca. 25	1.94	29.5
endo			1.60	

<sup>a</sup> Chemical shifts in ppm, relative to TMS.

absorptions, at –0.42 ppm, as an apparent quartet, is typical<sup>10–12</sup> for the  $\eta^5$ -C<sub>8</sub>H<sub>11</sub><sup>–</sup> ligand coordinated to ruthenium. This represents yet another example of the anisotropic effect of a  $\pi$ -system on aliphatic protons.<sup>13</sup> Interestingly, there is a second proton at even lower frequency, –0.83 ppm, stemming from one of the CH<sub>2</sub> groups. Further, one of the  $\eta^5$ -CH resonances appears at very low frequency at 0.95 ppm. The NMR characteristics for this  $\eta^5$ -C<sub>8</sub>H<sub>11</sub><sup>–</sup> ligand are given in Table 1.

At this point, we considered a possible five-coordinate structure, e.g., [Ru( $\eta^5$ -C<sub>8</sub>H<sub>11</sub>)(**1a**)]BF<sub>4</sub>, since **1a** can stabilize five-coordination; however, we noted two *non-*

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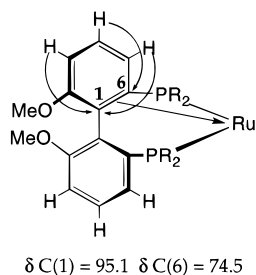
(13) Pretsch, E.; Seibl, J.; Simon, W. *Strukturaufklärung organischer Verbindungen*; Springer-Verlag: Berlin, 1986.

**Table 2.**  $^1\text{H}$  and  $^{13}\text{C}$  NMR Data for the MeO-BIPHEP Ligands in **4** and **6**<sup>a</sup>

<b>4</b>			<b>6</b>		
position	$^1\text{H}$	$^{13}\text{C}$	position	$^1\text{H}$	$^{13}\text{C}$
1		95.1	1		95.9
2		157.6	2		166.9
3	6.47	102.3	3	6.25	100.8
4	7.68	133.7	4	7.57	132.8
5	7.35	120.6	5	6.80	119.3
6		74.5	6		76.4
7	3.34	56.9	7	3.58	55.6
1'		139.7	1'		134.4
2'		168.3	2'		158.4
3'	6.19	112.7	3'	6.76	113.6
4'	6.93	131.4	4'	7.43	131.1
5'	7.09	122.5	5'	7.07	121.6
6'		135.4	6'		132.7
7'	3.69	58.0	7'	3.43	55.4
<i>ortho</i> - $\alpha$	7.18		$\alpha$ -CH	2.69	
<i>para</i> - $\alpha$	7.62		$\alpha$ -CH <sub>3</sub>	1.54	
<i>ortho</i> - $\beta$	6.53		$\alpha$ -CH <sub>3</sub> '	1.68	
<i>para</i> - $\beta$	7.06		$\beta$ -CH	-0.25	
<i>ortho</i> - $\gamma$	7.51		$\beta$ -CH <sub>3</sub>	0.67	
<i>ortho</i> - $\gamma'$	7.30		$\beta$ -CH <sub>3</sub> '	0.93	
<i>para</i> - $\gamma$	7.52		$\gamma$ -CH	3.16	
<i>ortho</i> - $\delta$	8.39		$\gamma$ -CH <sub>3</sub>	1.18	
<i>ortho</i> - $\delta'$	8.08		$\gamma$ -CH <sub>3</sub> '	1.59	
<i>para</i> - $\delta$	7.83		$\delta$ -CH	3.13	
			$\delta$ -CH <sub>3</sub>	0.99	
			$\delta$ -CH <sub>3</sub> '	0.93	

<sup>a</sup> Chemical shifts in ppm, relative to TMS. 7 = MeO.

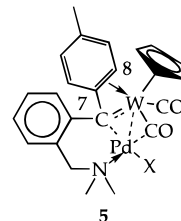
protonated  $^{13}\text{C}$  resonances at 74.5 ppm, as a strong doublet, and 95.1 ppm, as a very weak triplet, for which we had, as yet, no satisfactory explanation. A long-range  $^{13}\text{C}$ ,  $^1\text{H}$  correlation revealed connectivity between both of these nonprotonated carbons and the proton *ortho* to the P atom.



Further, the biphenyl proton *ortho* to the methoxy group correlated with the weak triplet signal at 95.1 ppm, and we show these connectivities in the fragment above. The  $^{13}\text{C}$  signals for C(1') (139.7 ppm) and C(6') (135.4 ppm) are at higher frequency. Given these assignments (see Table 2 for details), we conclude that the C(1)–C(6) biaryl double bond is coordinated to the metal, thereby affording an 18e coordinatively saturated complex and thus making the ligand **1a** a six-electron donor to the metal. Consistent with this bonding mode we note that the signals for the carbons *ortho* to the methoxy groups, at 102.3 and 112.7 ppm, are relatively far apart, suggestive of two different types of biaryl rings. The low-frequency  $^{31}\text{P}$  signal at  $-11.2$  ppm is associated with the unexpected coordination mode.

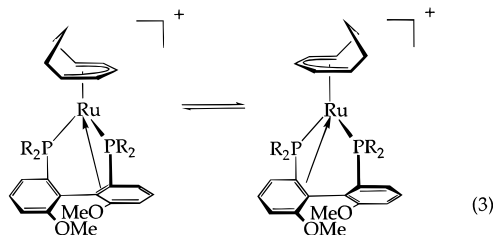
By coincidence, we recently<sup>14</sup> recorded the  $^{13}\text{C}$  NMR spectrum for the dinuclear tungsten–palladium complex **5** (X = Cl, and related derivatives). The observed

(14) Macchioni, A.; Pregosin, P. S.; Engel, P. F.; Mecking, S.; Pfeffer, M.; Daran, J.; Vaissermann, J. *Organometallics* **1995**, *14*, 1637.



$^{13}\text{C}$  resonances for the coordinated double bond, C(7)–C(8), are found at 101.8 and 76.5 ppm for C(7) and C(8), respectively, i.e., close to those values mentioned above, suggesting that our  $^{13}\text{C}$  values for **4** are reasonable for this type of bonding. Although the observed bonding is unprecedented for BIPHEP ligands, we note that Pathak et al.<sup>15</sup> have recently reported the solid-state structure for [Ru(Cp)(BINAP)]CF<sub>3</sub>SO<sub>3</sub>, in which they find the same type of six-electron donation from the BINAP ligand. They also note widely dispersed  $^{31}\text{P}$  chemical shifts (74.0 and 14.1 ppm) but did not consider the  $^{13}\text{C}$  approach to the solution structure proof. In retrospect, the  $^{31}\text{P}$  data are a useful indication (but not proof) of the unusual coordination mode.

The  $^1\text{H}$  phase-sensitive NOESY<sup>16</sup> for **4** at ambient temperature reveals a slow exchange process in which the halves of the MeO-BIPHEP ligand are exchanged (see Figure 2). Since the isomerization product has exactly the same structure, one observes only one set of resonances. Interestingly, there is *no exchange involving any of the  $\eta^5$ -C<sub>8</sub>H<sub>11</sub><sup>-</sup> protons*, i.e., the allyl protons do not exchange among themselves and the CH<sub>2</sub> protons do not exchange with the allyl protons, so that we can exclude a process involving sequential migration of H<sup>+</sup> (or H<sup>-</sup>) during the isomerization. Presumably, the biaryl double bond dissociates, thus making room for its counterpart in the second biaryl ring; however, this, by itself, does not rationalize our observations. A mechanism which contains both an  $\eta^5$ -C<sub>8</sub>H<sub>11</sub> "rotation"<sup>17</sup> by 180° plus a switch in biaryl olefin donation satisfies our observations, e.g. eq 3. The

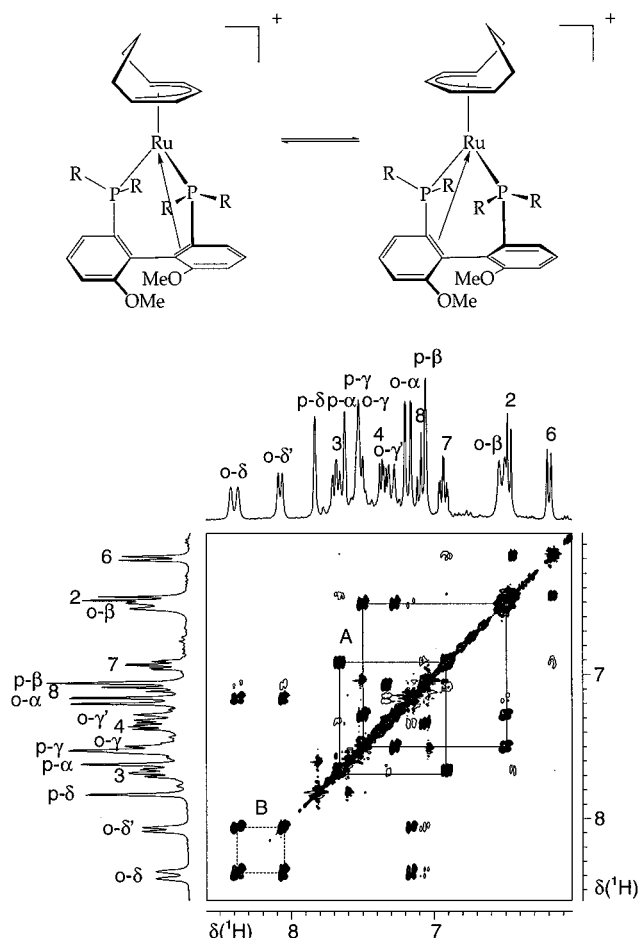


flexibility of coordinated **1a** is noteworthy in that its

(15) Pathak, D. D.; Adams, H.; Bailey, N. A.; King, P. J.; White, C. *J. Organomet. Chem.* **1994**, *479*, 237.

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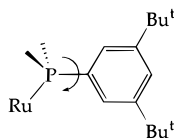
(17) "Rotation" is used to convey an image; there may be an  $\eta^3$ - $\pi$ -allyl intermediate. Moreover, one could also imagine that the BIPHEP, species **1a** dissociates the double bond and a phosphorus donor to afford a 14-electron complex which affects the necessary transformation without any  $\eta^5$ -C<sub>8</sub>H<sub>11</sub> isomerization (we thank Prof. A. Togni for calling our attention to this possibility); however, this is, to our knowledge, unprecedented, whereas there are examples of  $\eta^5$ -C<sub>8</sub>H<sub>11</sub> to  $\eta^3$ -C<sub>8</sub>H<sub>11</sub> transformation.<sup>10,18,19</sup>



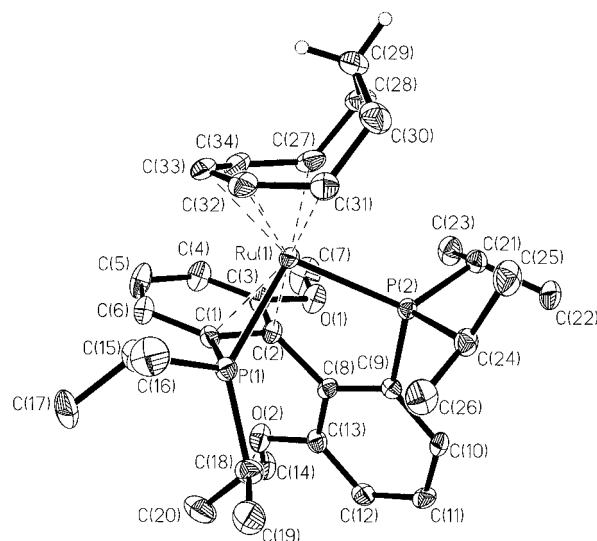
**Figure 2.** Aromatic section of the 2-D NOESY for **4** showing the exchange cross-peaks. The “open” cross-peaks arise from NOE and the filled-in cross-peaks from exchange. There are two exchange processes. The halves of the ligand **1a** are in equilibrium; i.e., cross-peak A indicates the exchange between 3 and 7, plus exchange of the nonequivalent *ortho* protons of the di-*tert*-butylphenyl rings, as shown by cross-peak B (300 MHz, CD<sub>2</sub>Cl<sub>2</sub>; room temperature, mixing time 0.6 s).

ability to act as a 6e donor might well help it stabilize reactive intermediates. Equally important, in this connection, is the relative ease with which **1a** can resume its “normal” bis(phosphine) coordination mode via double-bond dissociation.

We observe a second type of relatively slow dynamic process occurring simultaneously at room temperature. This involves restricted rotation around the P–C(ipsos) bonds for two of the four 3,5-disubstituted *tert*-butylphenyl rings:



These four nonequivalent *ortho* protons are, naturally, also involved in the exchange mentioned above, in that we observe cross-peaks linking these spins to the two sets of equivalent *ortho* protons. All eight *ortho* protons are nonequivalent at 193 K, the temperature for which the assignments are reported. Although this type of restricted rotation is rare, we have noted it previously in the complex [RuH(*p*-cymene)(**1a**)]BF<sub>4</sub>.<sup>6</sup>

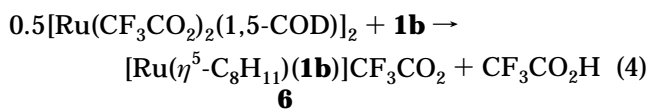


**Figure 3.** ORTEP plot for the cation of **6**. Note that the *exo* proton of the central CH<sub>2</sub> group is situated over the η<sup>5</sup>-C<sub>8</sub>H<sub>11</sub> π-system.

**Table 3.** Selected Bond Lengths (Å) and Bond Angles (deg) for **6**

Ru–P(1)	2.368(2)	Ru–P(2)	2.339(1)
Ru–C(1)	2.299(5)	Ru–C(2)	2.366(5)
Ru–C(27)	2.235(6)	Ru–C(31)	2.200(6)
Ru–C(32)	2.173(5)	Ru–C(33)	2.244(6)
Ru–C(34)	2.174(6)	C(27)–C(34)	1.416(9)
C(31)–C(32)	1.401(9)	C(32)–C(33)	1.425(10)
C(33)–C(34)	1.417(9)	C(27)–C(28)	1.504(9)
C(28)–C(29)	1.504(10)	C(29)–C(30)	1.486(10)
C(30)–C(31)	1.479(9)	O(1)–C(3)	1.359(6)
C(1)–C(2)	1.453(7)	O(2)–C(13)	1.354(6)
P(1)–Ru–P(2)	96.9(1)	P(1)–Ru–C(1)	45.2(1)
P(1)–Ru–C(2)	71.0(1)	P(2)–Ru–C(1)	107.8(1)
P(2)–Ru–C(2)	80.7(1)		
Ru–P(1)–C(1)	65.4(2)	Ru–P(2)–C(9)	104.4(2)
Ru–P(1)–C(15)	114.8(2)	Ru–P(1)–C(18)	135.4(2)

**X-ray Structure of 6.** The isopropyl analog [Ru(η<sup>5</sup>-C<sub>8</sub>H<sub>11</sub>)(**1b**)]CF<sub>3</sub>CO<sub>2</sub> (**6**) could be prepared by starting from [Ru(CF<sub>3</sub>CO<sub>2</sub>)<sub>2</sub>(1,5-COD)]<sub>2</sub>:



Suitable crystals could be obtained from CHCl<sub>3</sub>/EtOH/pentane solution, and the solid-state structure was determined by X-ray diffraction methods. An ORTEP plot for the cation is shown in Figure 3. Table 3 contains a list of selected bond lengths and bond angles, whereas Table 4 shows experimental parameters for the structure determination. A molecule of CF<sub>3</sub>CO<sub>2</sub>H cocrystallizes with the complex.

The immediate coordination sphere consists of the two P atoms, the biaryl double bond, C(1)–C(2), and the η<sup>5</sup>-pentadienyl moiety of the C<sub>8</sub>H<sub>11</sub><sup>−</sup> ligand. Of the two Ru–P separations, Ru–P(1) = 2.368(2) Å and Ru–P(2) = 2.339(1) Å, the Ru–P(1) adjacent to the coordinated double bond is (a) longer than Ru–P(2) and (b) significantly longer than that found by Pathak et al. (2.332(3) Å) in [Ru(Cp)(BINAP)]CF<sub>3</sub>SO<sub>3</sub>.<sup>15</sup> The two biaryl Ru–C distances, Ru–C(1) = 2.299(5) Å and Ru–C(2) = 2.366(5) Å, are also relatively long when compared to both (a) conventional Ru–C bond lengths in

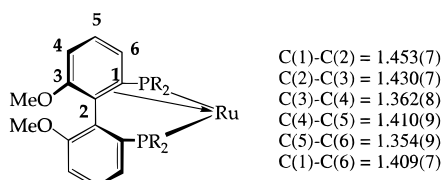
**Table 4. Crystal Data for Compound 6**

formula	C <sub>38</sub> H <sub>52</sub> F <sub>6</sub> O <sub>6</sub> P <sub>2</sub> Ru
fw	881.83
cryst syst	orthorhombic
space group	P2 <sub>1</sub> 2 <sub>1</sub> 2 <sub>1</sub> (No. 19)
a, Å	11.771(4)
b, Å	16.221(5)
c, Å	20.783(5)
V, Å <sup>3</sup>	3968(2)
Z	4
ρ <sub>calcd</sub> , g cm <sup>-3</sup>	1.476
F(000)	1824
residual R, R <sub>w</sub> <sup>a</sup>	0.0417, 0.0566

$$^a R = \sum (|F_o| - |F_c|) / \sum |F_o|; R_w = \sum (w^{1/2} (|F_o| - |F_c|)) / w^{1/2} (|F_o|).$$

Ru–arene,<sup>18–20</sup> Ru–olefin,<sup>21</sup> or Ru–butadienyl<sup>22</sup> compounds (ca. 2.10–2.30 Å) and (b) the analogous binaphthyl carbons in [Ru(Cp)(BINAP)]CF<sub>3</sub>SO<sub>3</sub> (2.258(7) and 2.281(9) Å). These long Ru–C(1) and Ru–C(2) bond lengths are consistent with a weak interaction.

The C–C separations (Å) within the coordinated biaryl ring suggest localized double bonds:



The corresponding values for the second biaryl ring involving carbons C(8)–C(13) are all much closer in value and lie in the range ca. 1.38(1)–1.41(1) Å. Both biaryl rings are perfectly flat.

The angle between the planes of the two biaryl rings is 104.6°. This angle is understandable in that the ring with the coordinated double bond is rotated toward the ruthenium, so as to facilitate complexation. There is an unexpected distortion in that the angle between the lines formed by C(2)–C(5) and C(8)–C(11) might be expected to be ca. 0°. In **6**, this angle is 32° and presumably arises due to the strained complexation mode of this BIPHEP ligand.

The coordinated η<sup>5</sup>-C<sub>8</sub>H<sub>11</sub><sup>-</sup> ligand has Ru–C separations in the range 2.173(5)–2.244(6) Å and C–C distances within the η<sup>5</sup> moiety of 1.401(9)–1.425(10) Å, in keeping with literature expectations.<sup>10,12,18</sup> One of the CH<sub>2</sub> protons lies above the π-system of the coordinated hydrocarbon. We note that the linkages from the methoxy oxygen atoms to the ring carbons, O(1)–C(3) = 1.359(6) Å and O(2)–C(13) = 1.354(6) Å, are essentially identical.

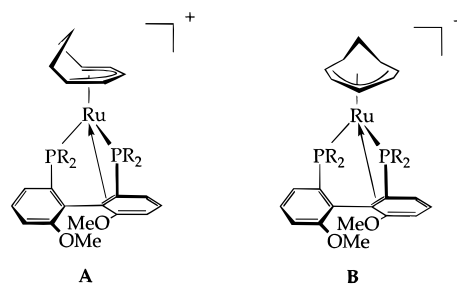
**NMR Studies on [Ru(η<sup>5</sup>-C<sub>8</sub>H<sub>11</sub>)(1b)]CF<sub>3</sub>CO<sub>2</sub> (**6**).** In many ways the NMR characteristics for **6** are similar to those for **4**. The two <sup>31</sup>P resonances are widely dispersed, 70.9 and 8.9 ppm (although less so than for **4**), and the five <sup>13</sup>CH absorptions from the η<sup>5</sup>-C<sub>8</sub>H<sub>11</sub><sup>-</sup> ligand fall in the range 49.6–114.3 ppm.

The long-range <sup>13</sup>C,<sup>1</sup>H correlation (see Figure 4), again reveals connectivity between the two nonprotonated coordinated carbons at 76.4 and 95.9 ppm and

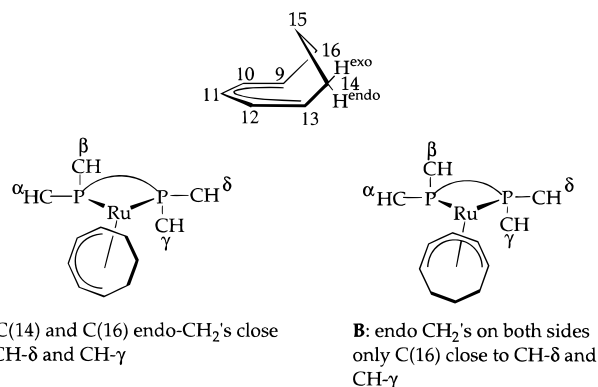
the biphenyl proton *ortho* to the P atom. The figure also reveals that the proton *ortho* to the methoxy group (sharp doublet at ca. 6.25 ppm) correlates with the coordinated biaryl carbon at 95.9 ppm. Figure 4 represents a rare example of the use of a 2-D long-range <sup>13</sup>C,<sup>1</sup>H correlation to find an extremely weak <sup>13</sup>C resonance. The conventional <sup>13</sup>C spectrum for **6** does not provide convincing evidence for the existence of a signal at 95.9 ppm.<sup>23</sup> Given all of these NMR data, we conclude that coordinated **1b** is also a six-electron donor in solution for **6**.

Surprisingly, **6** also shows two low-frequency protons. One of these arises from the cyclooctadienyl exo-CH positioned over the η<sup>5</sup> moiety, as mentioned above. The second stems from one of the four Pr<sup>i</sup> methine resonances.

The positioning of the η<sup>5</sup>-C<sub>8</sub>H<sub>11</sub><sup>-</sup> group relative to the P–Ru–P plane (**A** vs **B**) represents a subtle structural problem. The X-ray results clearly show that **A** is



correct in the solid state. In solution, one should observe NOE's from the isopropyl methine protons (shown as CH in the fragments below) to the endo C(14) and C(16) CH<sub>2</sub> protons of the η<sup>5</sup>-C<sub>8</sub>H<sub>11</sub><sup>-</sup> ligand:



If the **A** structure is correct, there will be NOE's from endo-14 (and endo-16) to the δ and γ CH's. If **B** is correct, then there will be NOE's from endo-14 to α and β and from endo-16 to δ and γ. Unfortunately, the endo protons are poorly resolved and resonate close to some of the CH methines, so that the "normal" NOESY was ambiguous. However, a ROESY measurement, combined with Hartmann–Hahn transfer<sup>24–26</sup> of the NOE

(23) It is not surprising that the coordinated biphenyl carbon C(1) observed at ca. 95 ppm is very weak in intensity. It has no close-by proton to facilitate relaxation, and it will be split by both <sup>31</sup>P spins. The analogous C(6) <sup>13</sup>C signal for [Ru(Cp)(BINAP)]CF<sub>3</sub>SO<sub>3</sub> was not observed (personal communication from C. White). The <sup>13</sup>C spin directly attached to phosphorus, ca. 75 ppm, has a proton neighbor. We have observed the expected doublet for C(6) in both **4** and **6**.

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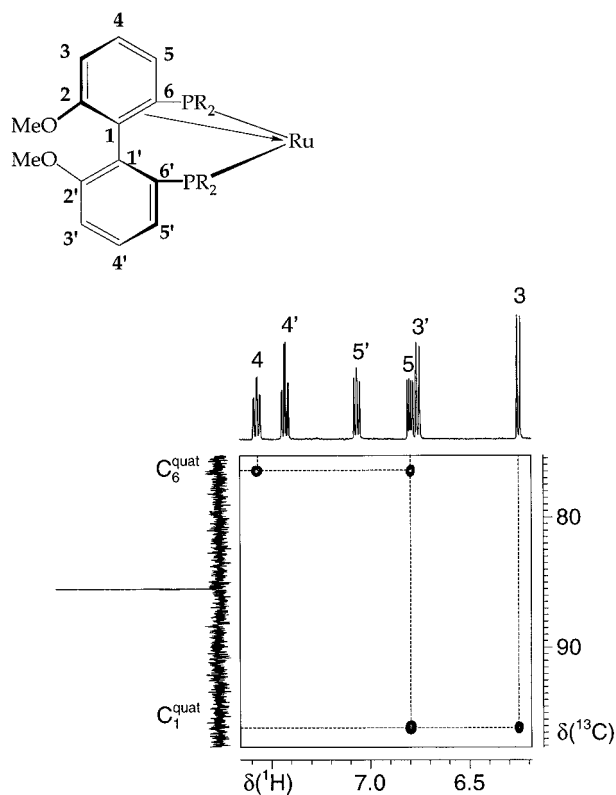
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**Figure 4.** Section of the long-range  $^{13}\text{C}, ^1\text{H}$  correlation (500 MHz,  $\text{CD}_2\text{Cl}_2$ , room temperature, optimized for  $J = 8.3$  Hz, magnitude spectrum) for **6** showing the key cross-peaks which link the resonances for the coordinated biaryl carbon to several of the biaryl proton resonances, via  $^2J(^{13}\text{C}, ^1\text{H})$  and, more importantly,  $^3J(^{13}\text{C}, ^1\text{H})$ . The intense signal in the  $^{13}\text{C}$  direction stems from one of the five  $\eta^5\text{-C}_8\text{H}_{11}$  pentadienyl carbons.

from the endo protons to their corresponding exo protons (which are well-resolved), clarified the question and revealed **A** to be correct (see Figure 5). The NOE spectrum is shown in the top trace and the ROESY/Hartmann–Hahn spectrum in the lower trace. The magnetization is transferred selectively from the  $\delta$ - and  $\gamma$ -CH's to the endo resonances (not seen) and then again, via Hartmann–Hahn, to the exo-14 and exo-16 spins, as shown.

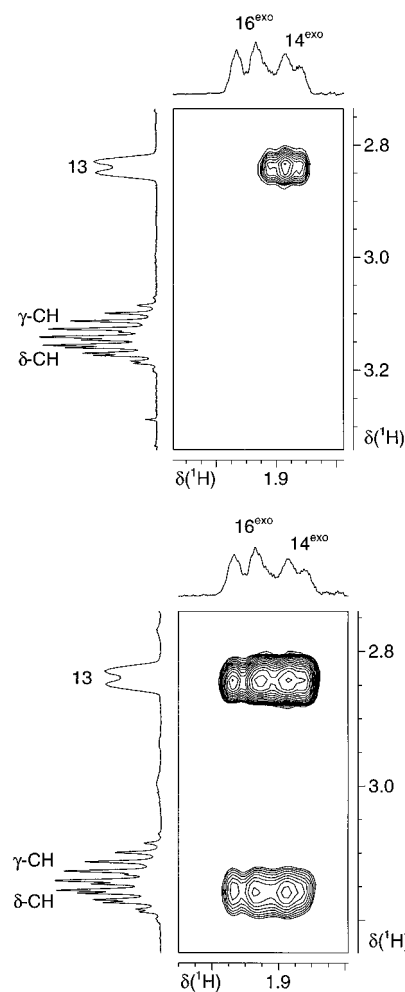
In contrast to the case for **4** the 2-D NOESY for **6** shows no exchange at ambient temperature.

## Conclusions

We have shown that the ligands **1** can function as  $\sigma$  donors to Ru(II) via an unexpected coordination of one of the biaryl double bonds. This mode of bonding might contribute to the capability of BIPHEP and BINAP type ligands to stabilize otherwise reactive species. Although the  $^{31}\text{P}$  NMR characteristics for this new  $\eta^4$ -bonding mode have empirical value, the  $^{13}\text{C}$  chemical shifts for the two biaryl carbons in question are a more reliable criterion.

## Experimental Section

**General Considerations.** All reactions were performed under an atmosphere of Ar using standard Schlenk techniques. Dry and oxygen-free solvents were used.  $\text{Ru}(\text{OAc})_2$  (**1a**), **2** was provided by F. Hoffman La Roche, Basel, Switzerland. Routine  $^1\text{H}$  (300.13 MHz) and  $^{31}\text{P}$  (121.5 MHz) NMR spectra were



**Figure 5.** (a, top) Section of the NOESY spectrum of **6** (300 MHz,  $\text{CD}_2\text{Cl}_2$ , room temperature, mixing time 0.8 s) showing no cross-peaks from the  $\text{Pr}^1$  methines to the two exo protons. This is as expected. (b, bottom) ROESY/Hartmann–Hahn spectrum of **6** (500 MHz,  $\text{CD}_2\text{Cl}_2$ , room temperature, spinlock 0.4 s, carrier frequency at 1.75 ppm), in which the magnetization is transferred selectively from the  $\delta$ - and  $\gamma$ -CH's to the endo resonances (not seen) and then again to the exo spins, as shown (see text).

recorded with a Bruker DPX-300 spectrometer.  $^{19}\text{F}$  (188.3 MHz) NMR spectra were recorded with a Bruker AC200 spectrometer. The two-dimensional studies were carried out at 500 MHz for  $^1\text{H}$ . Chemical shifts are given in ppm, and coupling constants ( $J$ ) are given in Hz. The ROESY/Hartmann–Hahn spectrum (500 MHz,  $\text{CD}_2\text{Cl}_2$ ) was measured at room temperature, with a 0.4 s spinlock and the carrier frequency set at 1.75 ppm. IR spectra were recorded with a Perkin-Elmer 882 infrared spectrophotometer. Elemental analyses and mass spectroscopic studies were performed both at ETHZ and by the Analytical Research Services at Hoffmann-La Roche.

**X-ray Structure Analysis of  $[\text{Ru}(\eta^5\text{-C}_8\text{H}_{11})\{(\text{R})\text{-1b}\}]\text{-CF}_3\text{COO}\cdot\text{CF}_3\text{COOH}$ , **6**.** Crystallographic data are collected in Table 4. Orange-brown crystals ( $0.25 \times 0.4 \times 0.8$  mm) suitable for X-ray determination were grown by slow diffusion of pentane into a  $\text{CHCl}_3/\text{EtOH}$  solution of **6**. Geometry and intensity data were collected at 233 K on a Siemens R3m/V diffractometer equipped with a graphite monochromator using  $\text{Mo K}\alpha$  (0.710 73 Å) radiation. Unit cell parameters were determined from the least-squares refinement of a set of 20 centered reflections. Two standard reflections were monitored periodically; they showed no change during data collection. Data were collected using the  $\omega$ -scan mode with a  $\omega$ -scan width of  $0.50^\circ$  and  $\omega$ -scan speed of  $1.50\text{--}19.53^\circ \text{min}^{-1}$ ; 5362 reflec-

tions were measured (index ranges  $0 \leq h \leq 15$ ,  $0 \leq k \leq 21$ ,  $0 \leq l \leq 27$ ), 4716 of which were unique with  $F > 5.0\sigma(F)$ . The selected crystal had the linear absorption coefficient  $\mu(\text{Mo K}\alpha) = 0.55 \text{ mm}^{-1}$ . The structure was determined by direct methods and subsequent Fourier maps. Full-matrix least-squares refinement was employed with all non-hydrogen atoms anisotropic and hydrogens in calculated positions. The weighting scheme  $w = 1/\sigma^2(F_o) + 0.001|F_o|^2$  gave satisfactory agreement analyses. Final  $R$  and  $R_w$  values are 0.0417 and 0.0566, respectively: goodness of fit 1.41, maximum  $\Delta/\sigma$  0.14, largest difference peak  $0.90 \text{ e } \text{\AA}^{-3}$ , largest difference hole  $-0.46 \text{ e } \text{\AA}^{-3}$ , data-to-parameter ratio 9.8:1. Data collection, cell refinement, data reduction, structure solution, structure refinement, molecular graphics and preparation of material for publication used SHELXTL PLUS (VMS).<sup>27</sup>

**[Ru(OAc)<sub>2</sub>{(R)-1a}] (2a).** To a solution of **1a** (4.99 g, 4.83 mmol) in 100 mL of toluene was added [Ru(OAc)<sub>2</sub>(*p*-cymene)] (1.75 g, 4.95 mmol). After 96 h at 100 °C the reaction mixture was evaporated to dryness, the residue was dissolved in 70 mL of hexane, and this solution was then filtered over Celite. Concentration of the filtrates to ca. 20 mL and cooling to -20 °C for 1 h yielded a yellow-brown powder (5.12 g) in 85% yield. MS (EI): *m/e* found 1250.5 ( $M^+$ ), calcd 1250.6. IR ( $\text{cm}^{-1}$ , KBr): 1587, 1412 (COO; shoulder), 1455 (P-aryl; shoulder). <sup>31</sup>P{<sup>1</sup>H} NMR ( $\text{CDCl}_3$ , 298 K): 68.3 ppm (s). Anal. Calcd for  $\text{C}_{75}\text{H}_{102}\text{O}_6\text{P}_2\text{Ru}$ : C, 71.07; H, 8.22; P, 4.95. Found: C, 71.06; H, 7.96; P, 4.78.

**Synthesis of [Ru( $\eta^5$ -C<sub>8</sub>H<sub>11</sub>){(R)-1a}][BF<sub>4</sub>] (4).** To a solution of Ru(OAc)<sub>2</sub>(**1a**) (189 mg, 0.151 mmol) in 4 mL of CH<sub>2</sub>Cl<sub>2</sub> was added 10 equiv of 1,5-COD (185  $\mu\text{L}$ , 1.5 mmol). After 5 min 2.1 equiv of HBF<sub>4</sub>·Et<sub>2</sub>O (0.32 mmol, 43  $\mu\text{L}$  of a 7.3 M solution in diethyl ether) was added. After 4 h the reaction mixture was evaporated to dryness; the residue was washed twice with 3 mL of hexane and then redissolved in 4 mL of CH<sub>2</sub>Cl<sub>2</sub>. After washing with water (3  $\times$  4 mL) and drying over MgSO<sub>4</sub>, the solution was filtered over Celite and evaporated to dryness. Washing twice with 2 mL of hexane and drying

in vacuo afforded an orange powder in 87% yield. MS (FAB): *m/e* found 1239.7 ( $M^+$ ), calcd 1240.8. IR ( $\text{cm}^{-1}$ , KBr): 1587, 1512 ( $\eta^5$ -C<sub>8</sub>H<sub>11</sub>; m, sh), 1150–1000 (BF<sub>4</sub><sup>-</sup>; s, br). <sup>31</sup>P NMR ( $\text{CD}_2\text{Cl}_2$ , 298 K): 69.3 (d, 47) and -9.6 ppm (d, 47). <sup>19</sup>F NMR ( $\text{CD}_2\text{Cl}_2$ , 298 K): -153.7 (s, 25%, BF<sub>4</sub><sup>-</sup>) and -153.8 ppm (s, 75%, BF<sub>4</sub><sup>-</sup>). Anal. Calcd for  $\text{C}_{78}\text{H}_{107}\text{BF}_4\text{O}_2\text{P}_2\text{Ru}$ : C, 70.62; H, 8.14. Found: C, 69.86; H, 7.94.

**[Ru( $\eta^5$ -C<sub>8</sub>H<sub>11</sub>){(R)-1b}]CF<sub>3</sub>COO·CF<sub>3</sub>COOH (6).** To a solution of (R)-Pr<sup>i</sup>-MeOBIPHEP (**1b**; 1.51 g, 3.36 mmol) in 15 mL of THF was added [Ru(CF<sub>3</sub>COO)<sub>2</sub>(1,5-COD)]<sub>2</sub> (1.62 g, 1.85 mmol). After 6 h at 40 °C the yellow-brown reaction mixture was evaporated to dryness. The residue was stirred vigorously with pentane (4  $\times$  10 mL) and redissolved in 3 mL of CH<sub>2</sub>Cl<sub>2</sub>. Slow addition of 20 mL of pentane yielded an orange-brown powder (2.64 g) in 89% yield. MS (electrospray): *m/e* found 655.5 ( $M^+$ ), calcd 654.8. IR ( $\text{cm}^{-1}$ ): 1587, 1518, (sharp,  $\eta^5$ -C<sub>8</sub>H<sub>11</sub>), 1698, 1140 (CF<sub>3</sub>COO<sup>-</sup>, br), 1782, 1189 (CF<sub>3</sub>COOH, br). <sup>31</sup>P NMR ( $\text{CDCl}_3$ , 298 K): 70.8 (d, 40) and 9.2 ppm (d, 40). <sup>19</sup>F NMR ( $\text{CDCl}_3$ , 298 K): 75.96 ppm (s). Anal. Calcd for  $\text{C}_{38}\text{H}_{52}\text{F}_6\text{O}_6\text{P}_2\text{Ru}$ : C, 51.76; H, 5.94; P, 7.02. Found: C, 51.24; H, 5.95; P, 6.80.

**Acknowledgment.** P.S.P. thanks the Swiss National Science Foundation, the ETH Zurich, and F. Hoffmann-La Roche AG for financial support. We also thank F. Hoffmann-La Roche AG for a gift of BIPHEP ligands and the complex Ru(OAc)<sub>2</sub>(**1a**), as well as Johnson Matthey for the loan of precious metals. We especially thank P. Schönholzer and Dr. M. Hennig for the X-ray structure determination of **6** and Ms. E. Hoermann for excellent experimental assistance.

**Supporting Information Available:** Tables of bond lengths and angles, complete atomic coordinates, anisotropic displacement coefficients, and isotropic displacement coefficients for hydrogen atoms for **6** (9 pages). Ordering information is given on any current masthead page.

OM960812X

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