

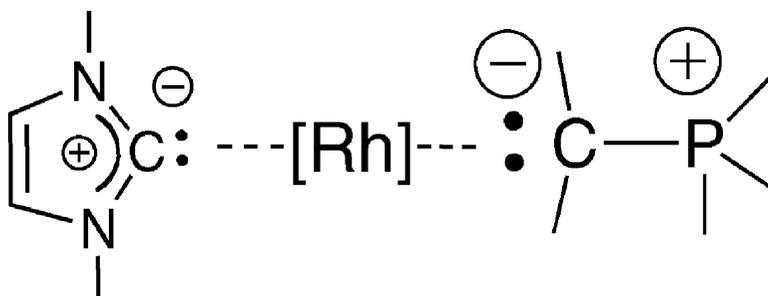
Article

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## Diaminocarbene and Phosponium Ylide Ligands: A Systematic Comparison of their Donor Character

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**Abstract:** The coordinating properties of the diaminocarbene (A) and phosponium ylide (B) ligand types have been investigated systematically through a test family of C,C-chelating ligands containing two moieties of either kind. The overall character of  $o\text{-C}_6\text{H}_4\text{A}_a\text{B}_b$  ligands ( $a + b = 2$ ) has been analyzed from the IR CO stretching frequencies of isostructural complexes  $[(\eta^2\text{-C}_6\text{H}_4\text{A}_a\text{B}_b)\text{Rh}(\text{CO})_2][\text{TfO}]$ . The test moieties  $\text{A} = \text{NC}_2\text{H}_2\text{N}^+(\text{Me})\text{C}^-$  and  $\text{B} = \text{Ph}_2\text{P}^+\text{CH}_2^-$  were first considered. While the ligands bearing at least one diaminocarbene end (AA,  $a = 2$  and AB,  $a = 1$ ) could be generated (and trapped by complexation), the bis-ylide case BB ( $a = 0$ ) proved to be awkward: treatment of the dication  $\text{C}_6\text{H}_4(\text{P}^+\text{Ph}_2\text{Me})_2$  with  $n\text{-BuLi}$  indeed lead to the Schmidbauer's carbodiphosphorane  $\text{Ph}_3\text{P}=\text{C}=\text{PPh}_2\text{Me}$ , through an unprecedented ylido-pentacoordinated phosphorane which could be fully characterized by NMR techniques. The bis-ylide ligand type  $\text{C}_6\text{H}_4\text{B}_2$  could however be generated by bridging the phosponium methyl groups by a methylene link ( $\text{B}_2 = (\text{P}^+\text{Ph}_2\text{CH}^-)_2\text{CH}_2$ ), preventing the formation of the analogous highly strained carbodiphosphorane. The three complexes  $[(\eta^2\text{-C}_6\text{H}_4\text{A}_a\text{B}_b)\text{Rh}(\text{CO})_2][\text{TfO}]$  were fully characterized, including by X-ray diffraction analysis and  $^{103}\text{Rh}$  NMR spectroscopy. Comparison of their IR spectra indicated that the  $\text{A}_2$  type bis-NHC ligand is less donating than the hybrid AB type, which is itself less donating than the  $\text{B}_2$  type bis-ylide ligand. The excellent linear variation of the  $\nu_{\text{CO}}$  frequencies vs  $a$  ( $= 0, 1, 2$ ) shows that the coordinating moieties act in a pseudoindependent way. This was confirmed by DFT calculations at the B3PW91/6-31G\*\*/LANL2DZ\*(Rh) level. It is therefore demonstrated that a phosponium ylide ligand is a stronger donor than a diaminocarbene ligand.

### Introduction

Beyond the efficiency of main group Lewis acids, the superior versatility of transition metal complexes for the activation of organic substrates, in either stoichiometric or catalytic processes, ensues from their ability to combine dual electronic properties, namely: electron acceptance (of substrate valence electron pairs) and electron donation (into the antibonding orbitals of the C–X bonds to be cleaved). For a given process, these oxymoric properties are tuned by the design of optimal “spectator” ligands exhibiting the right balance between their “electron deficiency” ( $\pi/\sigma$  accepting character) and their “electron richness” ( $\sigma/\pi$  donating character).

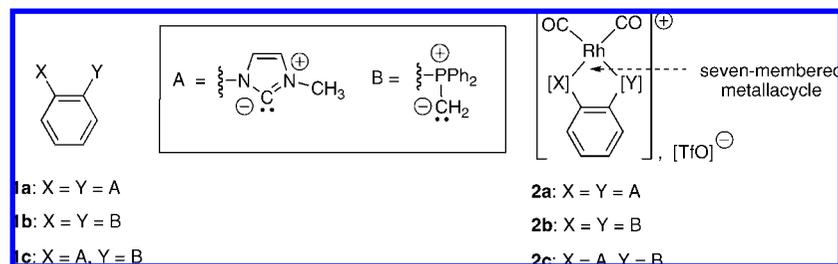
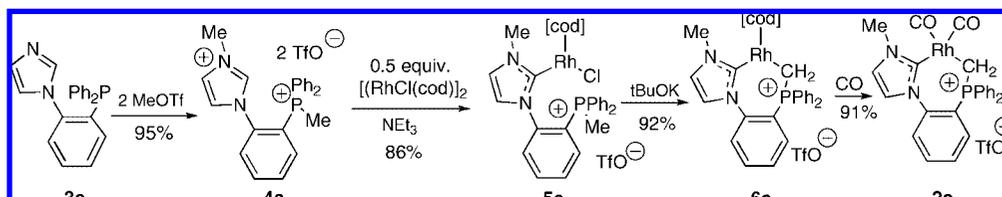
In the past decade, major advances have focused on the development of electron-rich ligands of late transition metal complexes for various challenges in catalysis, in particular C–C bond forming reactions.<sup>1</sup> Such spectator ligands are indeed interesting in two respects: (i) they tend to stabilize the Lewis acidic catalytic center, and (ii) they are prone to facilitate the slowest (limiting) steps, such as oxidative addition, transmetalation, or reductive elimination. Among them, neutral carbon

ligands today compete with the numerous types of phosphorus and nitrogen ligands.<sup>2</sup>

The carbon category has been mainly illustrated by electron-rich *unsaturated*  $sp^2\text{-C}$  ligands, namely cyclic diaminocarbenes (NHCs),<sup>3</sup> whose efficiency is generally attributed to their unique combination of strongly  $\sigma$ -donating, poorly  $\pi$ -accepting, and planar steric properties. The NHCs have thus been used to promote catalytic processes such as Pd-catalyzed cross-coupling<sup>4</sup> and Ru-catalyzed olefin metathesis,<sup>5</sup> where the stabilization of coordinatively unsaturated metal intermediates is crucial.

(1) Littke, A. F.; Fu, G. C. *Angew. Chem., Int. Ed.* **2002**, *41*, 4176. Zapf, A.; Beller, M. *Chem. Commun.* **2005**, 431. Muira, M. *Angew. Chem., Int. Ed.* **2004**, *43*, 2201.

(2) Lavallo, V.; Canac, Y.; Präsang, C.; Donnadiu, B.; Bertrand, G. *Angew. Chem., Int. Ed.* **2005**, *44*, 5705. Marrot, S.; Kato, T.; Gornitzka, H.; Baccaredo, A. *Angew. Chem., Int. Ed.* **2006**, *45*, 2598. Owen, J. S.; Labinger, J. A.; Bercaw, J. E. *J. Am. Chem. Soc.* **2004**, *126*, 8247. Gründemann, S.; Kovacevic, A.; Albrecht, M.; Faller, J. W.; Crabtree, R. H. *J. Am. Chem. Soc.* **2002**, *124*, 10473. Nakafuji, S. Y.; Kobayashi, J.; Kawashima, T. *Angew. Chem., Int. Ed.* **2008**, *47*, 1141.  
(3) Marion, N.; Díez-González, S.; Nolan, S. P. *Angew. Chem., Int. Ed.* **2007**, *46*, 2988. Pugh, D.; Danopoulos, A. A. *Coord. Chem. Rev.* **2007**, *251*, 610. Nolan, S. P. *N-Heterocyclic Carbenes in Synthesis*; Wiley-VCH: Weinheim, Germany, 2006. Kuhn, N.; Al-Sheikh, A. *Coord. Chem. Rev.* **2005**, *249*, 829. Peris, E.; Crabtree, R. H. *Coord. Chem. Rev.* **2004**, *248*, 2239. Crudden, C. M.; Allen, D. P. *Coord. Chem. Rev.* **2004**, *248*, 2247. César, V.; Bellemin-Lapponnaz, S.; Gade, L. H. *Chem. Soc. Rev.* **2004**, *33*, 619. Bourissou, D.; Guerret, O.; Gabbai, F. P.; Bertrand, G. *Chem. Rev.* **2000**, *100*, 39.  
(4) Herrmann, W. A.; Elison, M.; Fischer, J.; Köcher, C.; Artus, G. R. J. *Angew. Chem., Int. Ed.* **1995**, *34*, 2371. Kantchev, E. A. B.; O'Brien, C. J.; Organ, M. G. *Angew. Chem., Int. Ed.* **2007**, *46*, 2768.  
(5) Trnka, T. M.; Grubbs, R. H. *Acc. Chem. Res.* **2001**, *34*, 18.

**Scheme 1.** Test Family of C,C-Chelating Ligands and Rh(CO)<sub>2</sub> Complexes thereof with the Three Possible Combinations of NHC and Phosphonium Ylide Moieties**Scheme 2.** Synthesis of the NHC-Phosphonium Ylide Dicarboxylrhodium Complex **2c**

Neutral spectator carbon-centered ligands **A** are also represented by phosphonium ylides.<sup>6</sup> The catalytic properties of these saturated *sp*<sup>3</sup>-C ligands have been more punctually illustrated.<sup>6</sup> Whereas the free ylide precursor contains an almost-planar carbanion stabilized by an adjacent tetrahedral phosphonium center, the ligand exclusively acts by  $\eta^1$ -C coordination to metal centers (to the best of our knowledge, no  $\eta^2$ -C=P coordination has ever been reported). Ylides share two noticeable common features with the NHCs: (i) an intrinsic  $\alpha$ -zwitterionic character ( $^-\text{C}=\text{N}^+$ ,  $^-\text{C}-\text{P}^+$ ) resulting in a formal  $\beta$ -zwitterionic form of the coordinated unit ( $^-\text{M}-\text{C}=\text{N}^+$ ,  $^-\text{M}-\text{C}-\text{P}^+$ ) and (ii) a strong  $\sigma$ -donor vs  $\pi$ -acceptor character toward metals.

We recently reported on a novel type of strongly donating C,C-chelating ligand occurring in a stable and catalytically active NHC-phosphonium ylide complex.<sup>7</sup> At the outset, the electron-donating ability of *soft*, phosphine-like, carbene ligands was *a priori* expected to be lower than that of *harder* ylide ligands. Nevertheless, a more accurate understanding of the “electronics” of these carbon ligands is desired.

A systematic investigation is tackled from a test family of chelating C,C-ligands containing the same bridge (an *ortho*-phenylene ring) and all combinations of two representatives of the two types of ligating moiety: N-bonded N-methylimidazolylidenes (**A**) and P-bonded diphenylmethylphosphonium ylides (**B**). These ligands *o*-C<sub>6</sub>H<sub>4</sub>A<sub>a</sub>B<sub>b</sub>,  $a + b = 2$ , are denoted as **1a** ( $a = 2$ ), **1b** ( $a = 0$ ), and **1c** ( $a = 1$ ) (Scheme 1). In order to estimate the overall  $\sigma$ -donating vs  $\pi$ -accepting properties of **1a–c**, we rely on the values of the IR stretching frequencies of “conjugated” carbonyl ligands through a given metal center.

We selected a Rh(I) center (variations of the CO stretching frequencies of Rh<sup>I</sup>(CO)<sub>2</sub> complexes have been extensively studied with other ligands)<sup>8</sup> and the triflate counteranion: the test family is thus constituted by the three complexes [(Rh(CO)<sub>2</sub>( $\eta^2$ -C<sub>6</sub>H<sub>4</sub>A<sub>a</sub>B<sub>b</sub>)] [TfO],  $a + b = 2$ , denoted as **2a** ( $a = 2$ ), **2b** ( $a = 0$ ), and **2c** ( $a = 1$ ) (Scheme 1).

It must be emphasized that the hybrid ligands of the test family correspond to *minimal* steric effects from both the NHC and ylide moieties. Indeed, in the spirit of Tolman,<sup>9</sup> influence of steric effects from *any* ligand on Rh–C=O moieties (the selected observables) must basically appear sharply as the “size” of the ligand arrives at the critical value corresponding to a van der Waals contact between the ligand and a CO fragment. In the devised rigid framework (Scheme 1), the possible steric effect is brought down to a minimum: in the case of the  $^-\text{CH}_2(\text{P}^+\text{Ph}_2\text{Ar})$  ylide moiety (respectively, the CN(Ar)NMe carbene moiety), the bulkiest ArPh<sub>2</sub>P<sup>+</sup> (respectively NAr) substituent is *a priori* constrained remote from the CO fragments, and the CH<sub>2</sub> unit (respectively the CNMe unit) is as small as possible. In particular, it has been indeed claimed that nonhindered NHC ligands do not exert a steric effect on the metal center.<sup>10</sup>

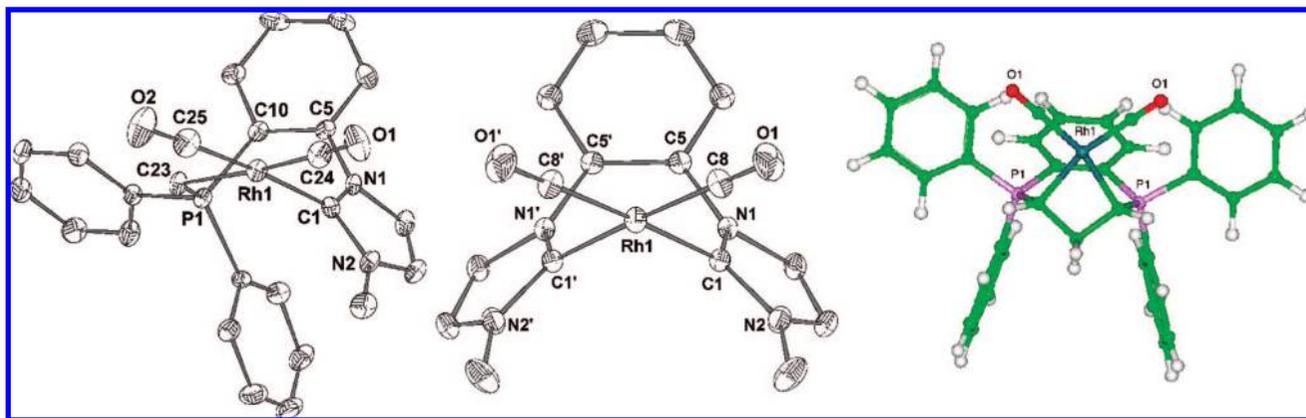
## Results and Discussion

The first target was complex **2c** containing the hybrid NHC-phosphonium ylide ligand **1c**, recently described in a palladium complex.<sup>7</sup> Treatment of the known dication **4c** (prepared by dimethylation of **3c**) with 0.5 equiv of [RhCl(cod)]<sub>2</sub> in the presence of triethylamine in acetonitrile readily afforded the phosphonocarbene complex **5c** in 86% yield as a 60/40 mixture of two stereoisomers (Scheme 2).

The occurrence of two stereoisomers of **5c** likely results from a restricted rotation about the N–aryl or/and Rh–CN<sub>2</sub> bonds.

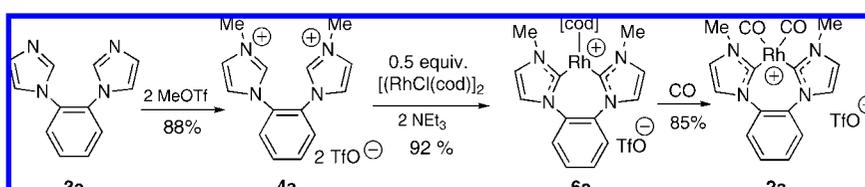
- (6) Falvello, L. R.; Ginés, J. C.; Carbó, J. J.; Lledós, A.; Navarro, R.; Soler, T.; Urriolabeitia, E. P. *Inorg. Chem.* **2006**, *45*, 6803. Vicente, J.; hicote, M. T. *Coord. Chem. Rev.* **1999**, *193–195*, 1143. Kolodizhnyi, O. I. *Tetrahedron* **1996**, *52*, 1855. Kaska, W. C.; Ostojza Starzewski, K. A. In *Ylides and Imines of Phosphorus*; Johnson, A. W., Ed.; John Wiley & Sons: New York, 1993; Chapter 14. Schmidbaur, H. *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 907. Canal, C.; Lepetit, C.; Soleilhavoup, M.; Chauvin, R. *Afinidad* **2004**, *61*, 298. Zurawinski, R.; Donnadiu, B.; Mikolajczyk, M.; Chauvin, R. *J. Organomet. Chem.* **2004**, *689*, 380. Zurawinski, R.; Donnadiu, B.; Mikolajczyk, M.; Chauvin, R. *Organometallics* **2003**, *22*, 4810. Ohta, T.; Sasayama, H.; Nakajima, O.; Kurahashi, N.; Fujii, T.; Furukawa, I. *Tetrahedron: Asymmetry* **2003**, *14*, 537.
- (7) Canac, Y.; Duhayon, C.; Chauvin, R. *Angew. Chem., Int. Ed.* **2007**, *46*, 6313.

- (8) Martin, D.; Baceiredo, A.; Gornitzka, H.; Schoeller, W. W.; Bertrand, G. *Angew. Chem., Int. Ed.* **2005**, *44*, 1700. Mayr, M.; Wurst, K.; Ongania, K.-H.; Buchmeiser, M. R. *Chem.–Eur. J.* **2004**, *10*, 1256. Herrmann, W. A.; Ofële, K.; v.; Preysing, D.; Herdtweck, E. *J. Organomet. Chem.* **2003**, *684*, 235. Enders, D.; Gielen, H.; Runsink, J.; Breuer, K.; Brode, S.; Boehn, K. *Eur. J. Inorg. Chem.* **1998**, 913.
- (9) Tolman, C. A. *Chem. Rev.* **1977**, *77*, 313.
- (10) Dorta, R.; Stevens, E. D.; Scott, N. M.; Costabile, C.; Cavallo, L.; Hoff, C. D.; Nolan, S. P. *J. Am. Chem. Soc.* **2005**, *127*, 2485. Díez-González, S.; Nolan, S. P. *Coord. Chem. Rev.* **2007**, *251*, 874.



**Figure 1.** ORTEP views of the X-ray crystal structures of complexes **2c** (left) and **2a** (middle), with thermal ellipsoids drawn at the 30% probability level, and optimized geometry of complex **2b'** (the most stable conformer) (right) at the B3PW91/6-31G\*\*/LANL2DZ\*(Rh) level of calculation.

**Scheme 3.** Synthesis of the Bis-NHC Dicarbonylrhodium Complex **2a**



The structure of **5c** was definitively confirmed by X-ray diffraction analysis of a single crystal.<sup>11</sup> Deprotonation of the methyl substituent of the phosphonium residue of **5c** with potassium *tert*-butoxide in THF gave the desired NHC-phosphonium ylide complex **6c** in 92% yield, as a single stereoisomer. Following a classical procedure, the ultimate complex **2c** was obtained in good yield (91%) by treating a solution of **6c** in THF under an atmospheric pressure of carbon monoxide. The <sup>13</sup>C NMR spectrum of the air-stable complex **2c** showed two CO signals at +184.6 and +189.6 ppm with classical <sup>103</sup>Rh–<sup>13</sup>C coupling constants ( $J_{\text{CRh}} = 59.3$  and 59.7 Hz, respectively). The structure of **2c** was unambiguously confirmed by X-ray diffraction analysis of yellow crystals deposited from CH<sub>2</sub>Cl<sub>2</sub>/Et<sub>2</sub>O.<sup>11</sup> The geometry at the Rh(I) center is square-planar, with a boat-shaped seven-membered metallacycle (Figure 1). Finally, the IR stretching frequencies of the CO ligands of **2c** in CHCl<sub>3</sub> were measured at 2088 and 2071 cm<sup>-1</sup>.

The symmetrical bis-NHC dicarbonylrhodium complex **2a** was then targeted. Dimethylation of 1,1'-(1,2-phenylene)bis(imidazole) **3a**<sup>12</sup> with 2 equiv of methyl triflate (MeOTf) in CH<sub>2</sub>Cl<sub>2</sub> gave the corresponding dication **4a** in 88% yield. Treatment of **4a** with 0.5 equiv of [RhCl(cod)]<sub>2</sub> in the presence of 2 equiv of triethylamine in acetonitrile cleanly afforded the bis-NHC chelate complex **6a** in 92% yield. Finally, bubbling CO through a THF solution of **6a** afforded the dicarbonylrhodium complex **2a** in 85% yield (Scheme 3).

By comparison with the dissymmetrical complex **2c**, the main feature of the <sup>13</sup>C NMR spectrum of **2a** is the presence of a single CO signal at +187.5 ppm ( $J_{\text{CRh}} = 57.2$  Hz), thus suggesting a symmetrical structure. An X-ray diffraction study of an air-stable single crystal of **2a** confirmed the NMR assignment (Figure 1).<sup>11</sup> The coordination geometry of **2a** is

otherwise similar to that of **2c** (quasi square-planar RhC<sub>4</sub> unit and boat-shaped seven-membered metallacycle). It must be stressed that, in both **2a** and **2c**, a minimal steric interaction between the CO fragments and the NHC/ylide ligands is supported by the absence of a significant compression of the van der Waals spheres of the CO and the closest H atoms (CH<sub>2</sub>, NCH<sub>3</sub>). The IR CO stretching frequencies of **2a** occur at 2030 and 2084 cm<sup>-1</sup> in CHCl<sub>3</sub>. As a stronger donor ligand is expected to weaken the C=O bonds and thus result in a lower wave-number of their stretching frequencies, the NHC-phosphonium ylide ligand **1c** is definitely a stronger donor than the bis-NHC ligand **1a**, at least with respect to the [Rh(CO)<sub>2</sub>][TfO] moiety.

The remaining target, the bis-phosphonium ylide complex **2b**, is *a priori* challenging for its zwitterionic rhodate nature.<sup>13</sup> All attempts to generate the desired bis-phosphonium ylide complex **2b** in a one-pot three-step procedure from diphosphonium **4b**<sup>14</sup> failed. This could be attributed to the impossibility to generate the bis-ylide **1b** from **4b** which inevitably lead to the formation of the carbodiphosphorane **8b**. Multinuclear NMR monitoring experiments indeed showed that addition of 2 equiv of *n*-butyllithium at -78 °C to a solution of **4b** in THF-*d*<sub>8</sub> resulted in the immediate formation of a cyclic five-membered ylide **7b** as a mixture of two stereoisomers (95/5). This ylidophosphorane **7b** results from the internal attack of the initially formed mono-ylide of **4b** to the adjacent phosphonium moiety (Scheme 4).

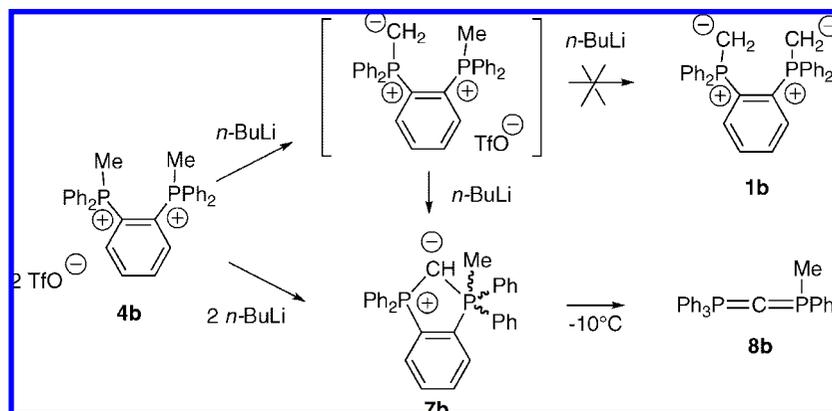
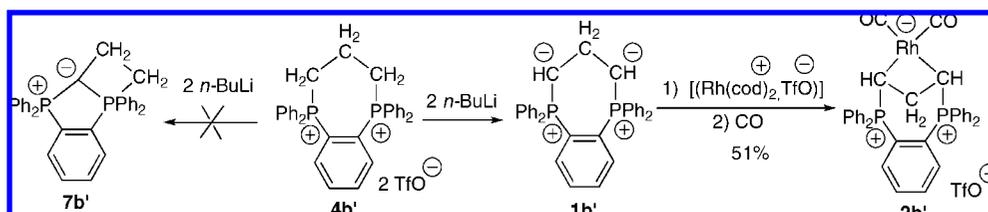
The fascinating structure of **7b** was first assigned on the basis of its <sup>31</sup>P NMR chemical shifts ( $\delta_{\text{P}} = -2.2$  and  $-100.0$  ppm;  $J_{\text{PP}} = 60.8$  Hz) which are indeed indicative of a P<sub>IV</sub>CP<sub>V</sub> sequence. The CH ylide functionality was confirmed by <sup>1</sup>H and <sup>13</sup>C NMR spectroscopy ( $\delta_{\text{CH}} = +0.64$  ppm, dd,  $J_{\text{HP(IV)}} = 22.3$ ,  $J_{\text{HP(V)}} = 13.4$  Hz;  $\delta_{\text{C}} = +15.1$  ppm, dd,  $J_{\text{CP(IV)}} = 112.7$ ,  $J_{\text{CP(V)}} = 163.6$  Hz). The presence of two stereoisomers in **7b** is explained by its trigonal bipyramidal geometry at one phos-

(11) CCDC 676873 (**5c**), 676874 (**2c**), and 676875 (**2a**) contain 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](http://www.ccdc.cam.ac.uk/data_request/cif).

(12) So, Y. H. *Macromolecules* **1992**, *25*, 516.

(13) Chauvin, R. *Eur. J. Inorg. Chem.* **2000**, 577.

(14) Schmidbaur, H.; Herr, R.; Zybail, C. E. *Chem. Ber.* **1984**, *117*, 3374.

Scheme 4. Synthesis of Carbodiphosphorane **8b** via the Elusive Ylidophosphorane **7b**Scheme 5. Synthesis of the Bis-Ylide Dicarboxylrhodium Complex **2b'**

phorus atom, the methyl substituent being located in either axial or equatorial position. Pursuing the VTP NMR monitoring by warming up the THF-*d*<sub>8</sub> solution to  $-10\text{ }^{\circ}\text{C}$ , the cyclic ylidophosphorane **7b** was shown to slowly ( $t_{1/2} \approx 12\text{ h}$ ) but quantitatively rearrange into carbodiphosphorane **8b** (Scheme 4).<sup>15</sup>

In order to avoid the formation of the ylidophosphorane of type **7b**, we decided to study the deprotonation of a cyclic diphosphonium **4b'**.<sup>16</sup> The steric demand in the analogous tricyclic ylidophosphorane **7b'** is indeed unlikely. And indeed, NMR monitoring of the deprotonation of **4b'** with 2 equiv of *n*-BuLi in THF-*d*<sub>8</sub> at low temperature, allowed for identifying the expected cyclic bis-ylide **1b'**. The <sup>31</sup>P NMR spectrum of the solution displayed a single singlet at +24.4 ppm, giving a first indication about the nature and the symmetry of the environment of the phosphorus atoms. The structure of **1b'** was confirmed by <sup>1</sup>H and <sup>13</sup>C NMR. In particular, the simultaneous presence of a triplet of triplets at  $\delta_{\text{H}} = +0.59\text{ ppm}$  ( $J_{\text{HP}} = 26.8$ ,  $J_{\text{HH}} = 3.3\text{ Hz}$ ) and of a triplet at  $\delta_{\text{C}} = +21.9\text{ ppm}$  ( $J_{\text{CP}} = 4.4\text{ Hz}$ ) was assigned to the bridging methylene group of **1b'**. The bis-ylide **1b'** was however quite unstable ( $t_{1/2} \approx 45\text{ min}$  at  $+20\text{ }^{\circ}\text{C}$ ). Both the complexation and the cod-(CO)<sub>2</sub> exchange reactions were thus performed *in situ* in a one-pot sequence. Addition of a stoichiometric amount of [Rh(cod)<sub>2</sub>][TfO] to a THF solution of the bis-ylide **1b'**, followed by treatment with an excess of CO, afforded the expected complex **2b'** in a 51% overall yield (Scheme 5). In contrast to the previous NHC complexes **2a** and **2c**, the bis-ylide complex **2b'** is unstable in the air and slowly decomposes even at low temperature under an inert atmosphere, giving a black precipitate attributable to decomplexation. This sensitivity could be simply anticipated from the two-bond formal charge separation of the zwitterionic rhodate structure, which should cancel after hydrolysis.

As observed for **1b'**, the presence of a single signal in the <sup>31</sup>P NMR spectrum ( $\delta_{\text{p}} = +41.3\text{ ppm}$ ) indicates a symmetrical structure for **2b'**. The significant shift of the <sup>31</sup>P signal (as compared to the free diylide **1b'**:  $\delta_{\text{p}} = +24.4\text{ ppm}$ ) and the observed multiplicity (d,  $J_{\text{PRh}} = 4.1\text{ Hz}$ ) are both in agreement with the ylide–rhodium complex structure of **2b'**. The presence of a Rh–CH unit was confirmed by multinuclear NMR spectroscopy and, in particular, by the high-field <sup>13</sup>C NMR signal of the metalated ylidic carbon coupled to the <sup>103</sup>Rh nucleus:  $\delta_{\text{CH}} = -7.6\text{ ppm}$  (dd,  $J_{\text{CP}} = 33.9$  and  $J_{\text{CRh}} = 13.8\text{ Hz}$ ). As in the case of the bis-NHC dicarboxylrhodium complex **2a**, the symmetry of **2b'** was confirmed by the presence of a single <sup>13</sup>CO signal at +188.5 ppm. The structure was further confirmed by ESI mass spectrometry ( $m/z = 645\text{ [M]}^+$ ), but all attempts to grow high quality single crystals were unsuccessful. Facing this difficulty, DFT calculations of complex **2b'** were undertaken at the B3PW91/6-31G\*\*/LANL2DZ\*(Rh) level (Figure 1). Taking into consideration the standard deviations of XRD analyses, this level of calculation was first validated by a reasonable agreement between the optimized and experimental geometries of the complexes **2a** and **2c** (Table 1). The calculations indeed reproduce the relative shortness of the experimental NHC–Rh bonds (*ca* 2.04 Å in **2a**, 2.07 Å in **2c**) with respect to the ylide–Rh bond (*ca* 2.16 Å in **2c**). Moreover, they are also in accord with the relative shortness of the respective *trans*-Rh–CO bonds and with the relative lengthening of the respective *trans*-RhC=O bonds (with standard deviations of *ca* 0.010 Å). Both these observations can be made consistent by ascribing a stronger  $\sigma$ -donating vs  $\pi$ -accepting character to the ylide moiety than to the NHC moiety. For the bis-ylide complex **2b'**, two minima of 6.4 kcal/mol relative energy were obtained on the potential energy surface of *C<sub>s</sub>* symmetry. Both minima display a slightly distorted square-planar arrangement at the Rh(I) center, but they differ by the conformation of the seven-membered rhodacycle, which is envelope-shaped in the

(15) Note that **8b** has been previously described starting from the same precursor **4b**; however the authors have proposed a different mechanism (see ref 14).

(16) The preparation of compound **4b'** will be published elsewhere.

**Table 1.** Selected Experimental and Calculated Structural Data of Dicarboxylrhodium Complexes<sup>a</sup>

	C <sub>ylide</sub> -Rh	C <sub>NHC</sub> -Rh	C <sub>ylide</sub> -P	C-O	Rh-CO	X-Rh-Y <sup>d</sup>	s.p. dev. <sup>b</sup>
				<b>2c:</b>			
XRD	2.155(8)	2.069(8)	1.750(7)	1.147(12) ( <i>trans</i> to NHC)	1.864(10) ( <i>trans</i> to NHC)	93.9	3.9
				1.172(12) ( <i>trans</i> to ylide)	1.850(10) ( <i>trans</i> to ylide)		
calcd	2.156	2.070	1.776	1.146 ( <i>trans</i> to NHC)	1.905 ( <i>trans</i> to NHC)	92.8	0.5
				1.149 ( <i>trans</i> to ylide)	1.888 ( <i>trans</i> to ylide)		
				<b>2a:</b>			
XRD	-	2.036(3)	-	1.117(4)	1.899(3)	82.4	0.4
calcd	-	2.066	-	1.145	1.910	82.5	3.6
				<b>2b<sup>c</sup>:</b>			
calcd	2.138	-	1.770	1.150	1.891	67.6	12.9
				<b>2b:</b>			
calcd	2.143 2.160	-	1.771	1.150 1.149	1.881 1.890	93.0	4.6

<sup>a</sup> Geometry optimizations were performed at the B3PW91/6-31G\*\*/LANL2DZ\*(Rh) level, under C<sub>s</sub> symmetry constraint when possible. Bond lengths are in Å, and valence angles in degrees. <sup>b</sup> Deviation (in degrees) from a planar RhC<sub>4</sub> arrangement (angle between OC-Rh-CO and X-Rh-Y planes). <sup>c</sup> Structural data for the most stable conformer. <sup>d</sup> X, Y = A and/or B (see Scheme 1).

less stable isomer and boat-shaped in the most stable one (like in **2a** and **2c**) (Figure 1).<sup>17</sup>

For a direct comparison in the test family, the initially targeted bis-ylide complex **2b** was calculated (Table 1). Beyond the difference in ylide-Rh-ylide angle and square-planar deviation, the structure found for **2b** is quite comparable with that of the methylene-bridged homologue **2b'**. The methylene bridge of **2b'** thus exerts a secondary perturbation, and this complex can indeed be regarded as relevant within the test family.

The NMR chemical shifts of the two conformers of **2b'** were also calculated at the B3PW91/6-31+G\*\*/LANL2DZ\*(Rh) level using the GIAO formalism.<sup>17</sup> The most stable conformer gives the best agreement with the experimental values, especially for all <sup>1</sup>H, <sup>31</sup>P, and <sup>13</sup>C nuclei remote from the rhodium atom (e.g., for the ylidic unit:  $\delta^{31}\text{P}(\text{exp}) = 41.30$  ppm,  $\delta^{31}\text{P}(\text{calcd}) = 43.25$  ppm;  $\delta^1\text{H}(\text{exp}) = 1.73$  ppm,  $\delta^1\text{H}(\text{calcd}) = 2.05$  ppm;  $\delta^{13}\text{C}(\text{exp}) = -7.60$  ppm,  $\delta^{13}\text{C}(\text{calcd}) = 7.37$  ppm). This excellent agreement gives further support to the structural assignment both in the solid state and in solution.

The carbonyl IR stretching absorptions of **2b'** (in CHCl<sub>3</sub> solution) occur at lower frequencies ( $\nu_{\text{CO}}$ : 1984, 2051 cm<sup>-1</sup>) than those of complexes **2c** ( $\nu_{\text{CO}}$ : 2008, 2071 cm<sup>-1</sup>) and **2a** ( $\nu_{\text{CO}}$ : 2030, 2084 cm<sup>-1</sup>). These successive shifts unambiguously indicate that substitution of a NHC moiety for a phosphonium ylide moiety systematically increases the donor character of the C,C-chelating ligand. This variation is consistent with the variation of the formal charge at the rhodium atom: +1 in **2a**, 0 in **2c**, -1 in **2b'**, the formal oxidation state of the metal (Rh(I)) and the overall charge of the complexes (+1) remaining the same (with the same counteranion, TfO<sup>-</sup>).

Nolan et al. recently discussed the electronic parameter of NHC ligands on the basis of the experimental and DFT-calculated  $\nu_{\text{CO}}$  frequencies in the [(NHC)Ir(CO)<sub>2</sub>Cl] complexes.<sup>18</sup> In the same spirit, the  $\nu_{\text{CO}}$  frequencies of **2a**, **2c**, and **2b'** were calculated at the DFT level and compared with the  $\nu_{\text{CO}}$  values calculated for related dicarbonylrhodium(I) complexes containing other P,P-, P,C-, and C,C-chelated ligands based on the same 1,2-phenylene bridge: the bis-diphenylphosphine complex **9**, the diphenylphosphine-NHC complex **10**,

the bis-abnormal NHC complex **11**, and the initially targeted bis-ylide complex **2b** (Table 2).

For the known complexes, a good agreement between experimental and calculated values is obtained, with a systematic gap of  $\Delta_{\text{av.}(\text{calcd-exp})} \approx 106\text{--}107$  cm<sup>-1</sup>. These results confirm the exceptionally high donor character of the phosphonium ylide moieties. Across the series, the bis-phosphine ligand of **9** is the least donating, while the bis-ylide ligand of **2b'** is the most donating. The latter is even a better donor than the bis-abnormal NHC ligand of **11**.<sup>19</sup> Interestingly, the same difference in the average  $\nu_{\text{CO}}$  values is observed when substituting an NHC moiety for a phosphonium ylide moiety:  $\Delta_{\text{av.}\nu_{\text{CO}}}(\mathbf{2a} \rightarrow \mathbf{2c}) = 16.7$  cm<sup>-1</sup> and  $\Delta_{\text{av.}\nu_{\text{CO}}}(\mathbf{2c} \rightarrow \mathbf{2b}) = 15.7$  cm<sup>-1</sup>.

The complex **12** is deduced from **2c** by removing the rigid phenylene bridge, the separated methylene triphenylphosphorane, and the *N*-1,3-dimethyl-imidazolylidene ligands being coordinated in *cis*-position. The averaged calculated  $\nu_{\text{CO}}$  values (2143.5 cm<sup>-1</sup> for **12** and 2146.2 cm<sup>-1</sup> for **2c**) indicate that the electronic communication, if any, between the phosphonium ylide and the NHC units has no influence on the donor ability of the units. This result validates *a posteriori* the choice of the test family: the phenylene bridge just acts as an insulating rigid link, allowing the *cis*-coordinating units of **2c** to be pseudoindependent.

The <sup>103</sup>Rh NMR spectrum of the complexes has also been recorded. It is observed that an increase of the basicity of the ligand (i.e., a decrease of the  $\nu_{\text{CO}}$  value) results in an increase of the  $\delta^{103}\text{Rh}$  value (**2a**, +542 ppm; **2c**, +731 ppm; and **2b'**, +983 ppm). Although intriguing at first sight (*if* the influence of the gross diatropic electronic effect was predominant, the nucleus should be shielded by increasing the local electron density), this trend is consistent with previously reported specific tendencies of other square-planar Rh(I) complexes<sup>20</sup> (by contrast, the intuitive trend applies to Rh(II) complexes<sup>20</sup>).

## Conclusion

In summary, we described the synthesis of C,C-chelated rhodium complexes with NHC and phosphonium ylide moieties. On the way to bis-ylide complexes, original ylidophosphorane and bis-ylide were evidenced. Direct comparisons between *sp*<sup>2</sup> and *sp*<sup>3</sup>-C ligands in dicarbonylrhodium complexes unambigu-

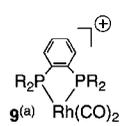
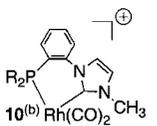
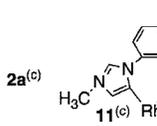
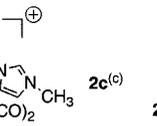
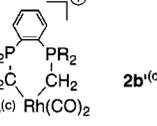
(17) The calculated structure of the less stable conformer of **2b'** and the calculated NMR chemical shifts of both conformers of **2b'** are given in the Supporting Information.

(18) Kelly, R. A.; Clavier, H.; Giudice, S.; Scott, N. M.; Stevens, E. D.; Bordner, J.; Samardjiev, I.; Hoff, C. D.; Cavallo, L.; Nolan, S. P. *Organometallics* **2008**, *27*, 202.

(19) Arnold, P. L.; Pearson, S. *Coord. Chem. Rev.* **2007**, *251*, 596.

(20) Bonnaire, R.; Davoust, D.; Platzer, N. *Org. Magn. Reson.* **1984**, *22*, 80. Varshavsky, Y. S.; Cherkasova, T. G.; Podkorytov, I. S.; Lyssenko, K. A.; Nikol'skii, A. B. *J. Organomet. Chem.* **2003**, *665*, 156.

**Table 2.** Experimental and Calculated IR CO Stretching Frequencies (cm<sup>-1</sup>) for Complexes **2a**, **2b**, **2b'**, **2c**, **9**, **10**, and **11**<sup>d</sup>

							
$\nu_{\text{CO}}(\text{exp})$	–	–	2030 2084	–	2008 2071	–	1984 2051
av. (exp)	–	–	2057	–	2039.5	–	2017.5
$\nu_{\text{CO}}(\text{calcd})$	2148.1 2186.0	2145.0 2184.4	2142.1 2183.7	2125.5 2170.3	2121.0 2171.4	2104.0 2157.0	2099.0 2150.0
av. (calcd)	2167.1	2164.7	2162.9	2147.9	2146.2	2130.5	2124.5
$\Delta\text{av. (calcd-exp)}$	–	–	105.9	–	106.7	–	107.0

<sup>a</sup> Five-membered rhodacycle. <sup>b</sup> Six-membered rhodacycle. <sup>c</sup> Seven-membered rhodacycle. <sup>d</sup> Calculations were performed at the B3PW91/6-31G\*\*/LANL2DZ\*(Rh) level.

ously demonstrated that a phosphonium ylide is more donating than an NHC. Applications of these extremely electron-rich ligands in homogeneous catalysis are now under investigation.

## Experimental Section

**General Remarks.** THF and diethyl ether were dried and distilled over sodium/benzophenone, pentane, dichloromethane, and acetonitrile over P<sub>2</sub>O<sub>5</sub>. All other reagents were used as commercially available. All reactions were carried out under an argon atmosphere, using Schlenk and vacuum line techniques. Column chromatography was carried out on silica gel (60 Å, C.C 70–200 μm). The following analytical instruments were used. <sup>1</sup>H, <sup>13</sup>C, <sup>31</sup>P, and <sup>103</sup>Rh NMR: Bruker ARX 250, DPX 300, or AV 500. X-Ray diffraction: Iqds STOE. Mass spectrometry: Quadrupolar Nermag R10-10H. Elemental analyses: Perkin-Elmer 2400 CHN (flash combustion and detection by catharometry). NMR chemical shifts  $\delta$  are in ppm, with positive values to high frequency relative to the tetramethylsilane reference for <sup>1</sup>H and <sup>13</sup>C and to H<sub>3</sub>PO<sub>4</sub> for <sup>31</sup>P. <sup>103</sup>Rh chemical shifts are given to a high frequency of  $\Xi(^{103}\text{Rh}) = 3.16$  MHz.

**Synthesis of 5c.** A mixture of  $[\{\text{RhCl}(\text{cod})\}_2]$  (0.34 g, 0.7 mmol), dication **4c** (0.92 g, 1.4 mmol), and NEt<sub>3</sub> (0.22 mL, 1.5 mmol) was dissolved in CH<sub>3</sub>CN (20 mL) and stirred at room temperature for 2 h. After evaporation of the solvent, the crude residue was washed with water (20 mL). Then the organic layer was extracted with CH<sub>2</sub>Cl<sub>2</sub> (20 mL) and dried with anhydrous MgSO<sub>4</sub>. After evaporation of the solvent, **5c** was obtained as a yellow oil (0.91 g, 86%). Recrystallization of **5c** at –20 °C from CH<sub>2</sub>Cl<sub>2</sub>/toluene gave yellow crystals as a mixture (60/40) of two stereoisomers (mp 134–136 °C). NMR assignment: <sup>a</sup>minor isomer (40%), <sup>b</sup>major isomer (60%): <sup>31</sup>P{<sup>1</sup>H} NMR (CDCl<sub>3</sub>, 25 °C):  $\delta = +21.2^{\text{a}}$ ;  $+22.0^{\text{b}}$ ; <sup>1</sup>H NMR (CDCl<sub>3</sub>, 25 °C):  $\delta = 1.40^{\text{a}}$  (m, 0.6H, CH<sub>2</sub>cod),  $1.53^{\text{a}}$  (m, 0.6H, CH<sub>2</sub>cod),  $1.65\text{--}2.40^{\text{a,b}}$  (m, 11H, CH<sub>2</sub>cod),  $2.01^{\text{a}}$  (d,  $J_{\text{HP}} = 12.9$  Hz, 1.8H, CH<sub>3</sub>P),  $2.44^{\text{b}}$  (d,  $J_{\text{HP}} = 14.2$  Hz, 3H, CH<sub>3</sub>P),  $2.55^{\text{a}}$  (m, 0.6H, CH<sub>2</sub>cod),  $3.25^{\text{b}}$  (m, 1H, CH<sub>cod</sub>),  $3.38^{\text{b}}$  (m, 1H, CH<sub>cod</sub>),  $3.43^{\text{a}}$  (m, 0.6H, CH<sub>cod</sub>),  $4.05^{\text{a}}$  (s, 1.8H, CH<sub>3</sub>),  $4.09^{\text{b}}$  (s, 3H, CH<sub>3</sub>),  $4.48^{\text{b}}$  (m, 1H, CH<sub>cod</sub>),  $4.76^{\text{b}}$  (m, 1H, CH<sub>cod</sub>),  $4.82^{\text{a}}$  (m, 1.2H, CH<sub>cod</sub>),  $6.10^{\text{a}}$  (s, 0.6H, H<sub>ar</sub>),  $6.30^{\text{b}}$  (d,  $J_{\text{HH}} = 1.70$  Hz, 1H, H<sub>ar</sub>),  $6.96^{\text{a}}$  (s, 0.6H, H<sub>ar</sub>),  $7.14^{\text{b}}$  (d,  $J_{\text{HH}} = 1.70$  Hz, 1H, H<sub>ar</sub>),  $7.20\text{--}7.25^{\text{a,b}}$  (m, 2.2H, H<sub>ar</sub>),  $7.33^{\text{a}}$  (m, 0.6H, H<sub>ar</sub>),  $7.40\text{--}7.80^{\text{a,b}}$  (m, 17H, H<sub>ar</sub>),  $7.96\text{--}8.05^{\text{a,b}}$  (m, 2.6H, H<sub>ar</sub>),  $8.74^{\text{a}}$  (m, 0.6H, CH<sub>cod</sub>); <sup>13</sup>C{<sup>1</sup>H} NMR (CDCl<sub>3</sub>, 25 °C):  $\delta = 7.7^{\text{b}}$  (d,  $J_{\text{CP}} = 55.0$  Hz, CH<sub>3</sub>P),  $7.8^{\text{a}}$  (d,  $J_{\text{CP}} = 57.5$  Hz, CH<sub>3</sub>P),  $27.9^{\text{a}}$  (s, CH<sub>2</sub>cod),  $28.3^{\text{b}}$  (s, CH<sub>2</sub>cod),  $28.4^{\text{b}}$  (s, CH<sub>2</sub>cod),  $28.8^{\text{a}}$

(s, CH<sub>2</sub>cod),  $31.6^{\text{a}}$  (s, CH<sub>2</sub>cod),  $32.4^{\text{b}}$  (s, CH<sub>2</sub>cod),  $32.7^{\text{b}}$  (s, CH<sub>2</sub>cod),  $33.6^{\text{a}}$  (s, CH<sub>2</sub>cod),  $38.4^{\text{a}}$  (s, CH<sub>3</sub>N),  $38.5^{\text{b}}$  (s, CH<sub>3</sub>N),  $67.2^{\text{a}}$  (d,  $J_{\text{CRh}} = 12.3$  Hz, CH<sub>cod</sub>),  $67.3^{\text{a}}$  (d,  $J_{\text{CRh}} = 11.9$  Hz, CH<sub>cod</sub>),  $69.5^{\text{b}}$  (d,  $J_{\text{CRh}} = 13.9$  Hz, CH<sub>cod</sub>),  $70.1^{\text{b}}$  (d,  $J_{\text{CRh}} = 14.3$  Hz, CH<sub>cod</sub>),  $98.6^{\text{a}}$  (m, CH<sub>cod</sub>),  $99.1^{\text{a,b}}$  (m, CH<sub>cod</sub>),  $115.4^{\text{a}}$  (d,  $J_{\text{CP}} = 84.5$  Hz, C<sub>ar</sub>),  $117.9^{\text{a}}$  (d,  $J_{\text{CP}} = 88.6$  Hz, C<sub>ar</sub>),  $118.5^{\text{b}}$  (d,  $J_{\text{CP}} = 88.1$  Hz, C<sub>ar</sub>),  $118.9^{\text{b}}$  (d,  $J_{\text{CP}} = 87.1$  Hz, C<sub>ar</sub>),  $119.9^{\text{a}}$  (d,  $J_{\text{CP}} = 94.5$  Hz, C<sub>ar</sub>),  $120.8$  (q,  $J_{\text{CF}} = 321.1$  Hz, CF<sub>3</sub>SO<sub>3</sub><sup>-</sup>),  $121.2^{\text{b}}$  (d,  $J_{\text{CP}} = 90.6$  Hz, C<sub>ar</sub>),  $122.0^{\text{a}}$  (s, CH<sub>ar</sub>),  $123.2^{\text{b}}$  (s, CH<sub>ar</sub>),  $124.8^{\text{b}}$  (s, CH<sub>ar</sub>),  $125.0^{\text{a}}$  (s, CH<sub>ar</sub>),  $130.2^{\text{b}}$  (d,  $J_{\text{CP}} = 13.1$  Hz, CH<sub>ar</sub>),  $130.5$  (d,  $J_{\text{CP}} = 12.6$  Hz, CH<sub>ar</sub>),  $130.6$  (d,  $J_{\text{CP}} = 12.0$  Hz, CH<sub>ar</sub>),  $130.7$  (d,  $J_{\text{CP}} = 13.3$  Hz, CH<sub>ar</sub>),  $130.8$  (d,  $J_{\text{CP}} = 13.0$  Hz, CH<sub>ar</sub>),  $131.1$  (d,  $J_{\text{CP}} = 13.1$  Hz, CH<sub>ar</sub>),  $131.6$  (d,  $J_{\text{CP}} = 7.3$  Hz, CH<sub>ar</sub>),  $132.5$  (d,  $J_{\text{CP}} = 10.6$  Hz, CH<sub>ar</sub>),  $132.7$  (d,  $J_{\text{CP}} = 10.3$  Hz, CH<sub>ar</sub>),  $132.8$  (d,  $J_{\text{CP}} = 6.8$  Hz, CH<sub>ar</sub>),  $133.0$  (d,  $J_{\text{CP}} = 10.9$  Hz, CH<sub>ar</sub>),  $133.6$  (d,  $J_{\text{CP}} = 6.7$  Hz, CH<sub>ar</sub>),  $134.9$  (s, CH<sub>ar</sub>),  $135.5$  (s, CH<sub>ar</sub>),  $136.0$  (d,  $J_{\text{CP}} = 8.0$  Hz, CH<sub>ar</sub>),  $136.2$  (d,  $J_{\text{CP}} = 9.1$  Hz, CH<sub>ar</sub>),  $142.8^{\text{b}}$  (d,  $J_{\text{CP}} = 3.5$  Hz, C<sub>ar</sub>),  $143.3^{\text{a}}$  (s, C<sub>ar</sub>),  $183.7^{\text{b}}$  (d,  $J_{\text{CRh}} = 52.1$  Hz, NCN),  $184.8^{\text{a}}$  (d,  $J_{\text{CRh}} = 51.4$  Hz, NCN); MS(ES<sup>+</sup>):  $m/z$ : 603 [M<sup>+</sup>]; HRMS (ES<sup>+</sup>) calcd for C<sub>31</sub>H<sub>34</sub>N<sub>2</sub>ClPRh 603.1203; found, 603.1190. Anal. Calcd for C<sub>32</sub>H<sub>34</sub>N<sub>2</sub>ClPRhF<sub>3</sub>SO<sub>3</sub>: C, 51.04; H, 4.55; N, 3.72. Found: C, 50.41; H, 4.76; N, 3.43.

**Synthesis of 6c.** A 1/1 mixture of *t*-BuOK and complex **5c** (0.72 g, 1.0 mmol) was cooled to –78 °C, and THF (20 mL) was added. The suspension was warmed to room temperature and stirred for 1 h. After evaporation of the solvent, extraction of the residue with CH<sub>2</sub>Cl<sub>2</sub> (20 mL) afforded **6c** as a yellow oil (0.63 g, 92%). <sup>31</sup>P{<sup>1</sup>H} NMR (CD<sub>3</sub>CN, 25 °C):  $\delta = +30.8$  (d,  $J_{\text{PRh}} = 2.1$ ); <sup>1</sup>H NMR (CD<sub>3</sub>CN, 25 °C):  $\delta = 1.21\text{--}2.57$  (m, 10H, CH<sub>2</sub>cod, CH<sub>2</sub>P),  $3.40$  (m, 1H, CH<sub>cod</sub>),  $3.50$  (m, 1H, CH<sub>cod</sub>),  $3.73$  (s, 3H, CH<sub>3</sub>),  $4.37$  (m, 1H, CH<sub>cod</sub>),  $4.80$  (m, 1H, CH<sub>cod</sub>),  $6.55$  (d,  $J_{\text{HH}} = 1.70$  Hz, 1H, H<sub>ar</sub>),  $7.03$  (d,  $J_{\text{HH}} = 1.70$  Hz, 1H, H<sub>ar</sub>),  $7.33\text{--}7.96$  (m, 14H, H<sub>ar</sub>); <sup>13</sup>C{<sup>1</sup>H} NMR (CD<sub>3</sub>CN, 25 °C):  $\delta = -3.3$  (dd,  $J_{\text{CP}} = 32.1$  Hz,  $J_{\text{CRh}} = 25.4$  Hz, CH<sub>2</sub>P),  $27.9$  (s, CH<sub>2</sub>cod),  $29.2$  (s, CH<sub>2</sub>cod),  $32.1$  (s, CH<sub>2</sub>cod),  $33.0$  (s, CH<sub>2</sub>cod),  $37.2$  (s, CH<sub>3</sub>N),  $77.3$  (d,  $J_{\text{CRh}} = 8.7$  Hz, CH<sub>cod</sub>),  $82.1$  (d,  $J_{\text{CRh}} = 9.5$  Hz, CH<sub>cod</sub>),  $91.7$  (d,  $J_{\text{CRh}} = 6.9$  Hz, CH<sub>cod</sub>),  $93.0$  (d,  $J_{\text{CRh}} = 7.3$  Hz, CH<sub>cod</sub>),  $122.2$  (d,  $J_{\text{CP}} = 85.3$  Hz, C<sub>ar</sub>),  $121.2$  (q,  $J_{\text{CF}} = 319.6$  Hz, CF<sub>3</sub>SO<sub>3</sub><sup>-</sup>),  $122.8$  (s, CH<sub>ar</sub>),  $124.2$  (s, CH<sub>ar</sub>),  $125.8$  (d,  $J_{\text{CP}} = 98.6$  Hz, C<sub>ar</sub>),  $126.8$  (d,  $J_{\text{CP}} = 67.9$  Hz, C<sub>ar</sub>),  $127.4$  (d,  $J_{\text{CP}} = 6.5$  Hz, CH<sub>ar</sub>),  $128.3$  (d,  $J_{\text{CP}} = 12.2$  Hz, CH<sub>ar</sub>),  $129.1$  (d,  $J_{\text{CP}} = 11.8$  Hz, CH<sub>ar</sub>),  $129.5$  (d,  $J_{\text{CP}} = 10.8$  Hz, CH<sub>ar</sub>),  $130.6$  (d,  $J_{\text{CP}} = 9.1$  Hz, CH<sub>ar</sub>),  $132.6$  (d,  $J_{\text{CP}} = 9.0$  Hz, CH<sub>ar</sub>),  $132.7$  (s, CH<sub>ar</sub>),  $133.0$  (s, CH<sub>ar</sub>),  $134.3$  (d,  $J_{\text{CP}} = 9.4$  Hz, CH<sub>ar</sub>),  $134.6$  (s, CH<sub>ar</sub>),  $143.1$  (s,

$C_{ar}$ , 186.0 (dd,  $J_{CRh} = 52.2$  Hz,  $J_{CP} = 3.9$  Hz, NCN); MS( $ES^+$ ):  $m/z$ : 567 [ $M^+$ ].

**Synthesis of 2c.** Carbon monoxide was bubbled (1 h) at room temperature through a solution of complex **6c** (0.25 g, 0.35 mmol) in THF (40 mL). After evaporation of the solvent under vacuum, purification by chromatography on silica gel ( $CH_2Cl_2$ /acetone) gave **2c** as a yellow solid residue (0.21 g, 91%). Recrystallization at  $-20$  °C from  $CH_2Cl_2/Et_2O$  afforded yellow crystals (mp 206–208 °C).  $^{31}P\{^1H\}$  NMR ( $CDCl_3$ , 25 °C):  $\delta = +33.2$  (d,  $J_{PRh} = 3.9$  Hz);  $^1H$  NMR ( $CDCl_3$ , 25 °C):  $\delta = 1.55$  (ddd,  $J_{HH} = 13.9$  Hz,  $J = 12.0$  Hz,  $J = 2.1$  Hz, 1H,  $CH_2P$ ), 1.94 (ddd,  $J_{HH} = 13.9$  Hz,  $J = 11.3$  Hz,  $J = 2.9$  Hz, 1H,  $CH_2P$ ), 3.71 (s, 3H,  $CH_3$ ), 6.86 (d,  $J_{HH} = 1.93$  Hz, 1H,  $H_{ar}$ ), 7.24 (m, 1H,  $H_{ar}$ ), 7.40–7.78 (m, 13H,  $H_{ar}$ ); 7.93 (m, 1H,  $H_{ar}$ );  $^{13}C\{^1H\}$  NMR ( $CD_3CN$ , 25 °C):  $\delta = -5.3$  (dd,  $J_{CP} = 38.1$  Hz,  $J_{CRh} = 20.9$  Hz,  $CH_2P$ ), 38.1 (s,  $CH_3N$ ), 121.2 (q,  $J_{CF} = 319.6$ ,  $CF_3SO_3^-$ ), 121.6 (d,  $J_{CP} = 88.3$  Hz,  $C_{ar}$ ), 122.7 (d,  $J_{CP} = 92.6$  Hz,  $C_{ar}$ ), 124.7 (s,  $CH_{ar}$ ), 125.0 (s,  $CH_{ar}$ ), 125.4 (d,  $J_{CP} = 84.5$  Hz,  $C_{ar}$ ), 128.1 (d,  $J_{CP} = 6.4$  Hz,  $CH_{ar}$ ), 129.3 (d,  $J_{CP} = 12.6$  Hz,  $CH_{ar}$ ), 129.4 (d,  $J_{CP} = 15.1$  Hz,  $CH_{ar}$ ), 129.7 (d,  $J_{CP} = 11.5$  Hz,  $CH_{ar}$ ), 130.7 (d,  $J_{CP} = 9.4$  Hz,  $CH_{ar}$ ), 132.8 (d,  $J_{CP} = 9.3$  Hz,  $CH_{ar}$ ), 133.2 (s,  $CH_{ar}$ ), 133.6 (s,  $CH_{ar}$ ), 135.2 (d,  $J_{CP} = 9.2$  Hz,  $CH_{ar}$ ), 135.6 (s,  $CH_{ar}$ ), 141.9 (s,  $C_{ar}$ ), 175.3 (dd,  $J_{CRh} = 44.6$  Hz,  $J_{CP} = 9.8$  Hz, NCN), 184.6 (d,  $J_{CRh} = 59.7$  Hz, CO), 189.6 (d,  $J_{CRh} = 59.3$  Hz, CO);  $^{103}Rh$  NMR ( $CD_3CN$ , 25 °C):  $\delta = +731$ ; MS( $ES^+$ ):  $m/z$ : 515 [ $M^+$ ]; HRMS ( $ES^+$ ) calcd for  $C_{25}H_{21}N_2O_2PRh$ , 515.0396; found, 515.0364.

**Synthesis of 4a.** Methyl trifluoromethanesulfonate (0.57 mL, 5.1 mmol), was added at  $-78$  °C to a  $CH_2Cl_2$  solution (20 mL) of **3a** (0.53 g, 2.5 mmol). Then the suspension was warmed to room temperature and stirred for 12 h. After filtration, the solid residue was washed with additional  $CH_2Cl_2$  (40 mL) affording **4a** (1.19 g, 88%) as a white microcrystalline solid (mp 163–165 °C).  $^1H$  NMR ( $CD_3CN$ , 25 °C):  $\delta = 3.95$  (s, 6H,  $CH_3$ ), 7.46–7.55 (m, 4H,  $H_{ar}$ ), 7.79–7.92 (m, 4H,  $H_{ar}$ ), 8.89 (s, 2H, CH);  $^{13}C\{^1H\}$  NMR ( $CD_3CN$ , 25 °C):  $\delta = 36.5$  (s,  $CH_3$ ), 121.0 (q,  $J_{CF} = 320.8$  Hz,  $CF_3SO_3^-$ ), 123.3 (s,  $CH_{ar}$ ), 124.8 (s,  $CH_{ar}$ ), 128.5 (s,  $CH_{ar}$ ), 129.9 (s,  $C_{ar}$ ), 132.6 (s,  $CH_{ar}$ ), 137.8 (s, CH); MS(FAB $^+$ ):  $m/z$ : 389 [ $M - CF_3SO_3^-$ ]; HRMS ( $ES^+$ ) calcd for  $C_{15}H_{16}N_4F_3SO_3$ , 389.0895; found, 389.0907. Anal. Calcd for  $C_{15}H_{16}N_4F_3S_2O_6$ : C, 35.69; H, 3.00; N, 10.41. Found: C, 35.97; H, 2.66; N, 10.38.

**Synthesis of 6a.** A mixture of  $\{[RhCl(cod)]_2\}$  (0.77 g, 1.6 mmol), dication **4a** (1.68 g, 3.1 mmol), and  $NEt_3$  (0.87 mL, 6.2 mmol) was dissolved in  $CH_3CN$  (40 mL) and stirred at 40 °C for 12 h. After evaporation of the solvent, the crude residue was washed with water (20 mL). Then the organic layer was extracted with  $CH_2Cl_2$  (20 mL) and dried with anhydrous  $MgSO_4$ . After washing with  $Et_2O$  (20 mL), **6a** (1.72 g, 92%) was obtained as a beige powder (mp 204–206 °C).  $^1H$  NMR ( $CD_3CN$ , 25 °C):  $\delta = 1.44$ –1.59 (m, 2H,  $CH_{2cod}$ ), 1.76–1.99 (m, 2H,  $CH_{2cod}$ ), 2.11–2.26 (m, 2H,  $CH_{2cod}$ ), 2.38–2.52 (m, 2H,  $CH_{2cod}$ ), 3.88 (s, 6H,  $CH_3$ ), 4.33 (m, 2H,  $CH_{cod}$ ), 4.60 (m, 2H,  $CH_{cod}$ ), 7.21 (d,  $J_{HH} = 1.9$  Hz, 2H,  $H_{ar}$ ), 7.37 (d,  $J_{HH} = 1.9$  Hz, 2H,  $H_{ar}$ ), 7.63–7.72 (m, 4H,  $H_{ar}$ );  $^{13}C\{^1H\}$  NMR ( $CD_3CN$ , 25 °C):  $\delta = 29.8$  ( $CH_{2cod}$ ), 30.1 ( $CH_{2cod}$ ), 37.2 (s,  $CH_3$ ), 87.4 (d,  $J_{CRh} = 7.3$  Hz,  $CH_{cod}$ ), 91.6 (d,  $J_{CRh} = 8.2$  Hz,  $CH_{cod}$ ), 121.2 (q,  $J_{CF} = 320.8$  Hz,  $CF_3SO_3^-$ ), 122.8 (s,  $CH_{ar}$ ), 123.6 (s,  $CH_{ar}$ ), 126.6 (s,  $CH_{ar}$ ), 129.5 (s,  $CH_{ar}$ ), 135.1 (s,  $C_{ar}$ ), 184.0 (d,  $J_{CRh} = 52.2$  Hz, NCN); MS( $ES^+$ ):  $m/z$ : 449 [ $M^+$ ].

**Synthesis of 2a.** Carbon monoxide was bubbled (1 h) at room temperature through a solution of complex **6a** (1.51 g, 2.5 mmol) in THF (40 mL). After evaporation of the solvent, and washing with  $Et_2O$  (20 mL), **2a** was obtained as a yellow solid (1.17 g, 85%). Recrystallization at  $-20$  °C from  $CH_2Cl_2$  gave yellow crystals (mp 174–176 °C).  $^1H$  NMR ( $CD_3CN$ , 25 °C):  $\delta = 3.90$  (s, 6H,  $CH_3$ ), 7.37 (d,  $J_{HH} = 1.9$  Hz, 2H,  $H_{ar}$ ), 7.46 (d,  $J_{HH} = 1.9$  Hz, 2H,  $H_{ar}$ ), 7.62–7.74 (m, 4H,  $H_{ar}$ );  $^{13}C\{^1H\}$  NMR ( $CD_3CN$ , 25 °C):  $\delta = 38.3$  (s,  $CH_3$ ), 121.2 (q,  $J_{CF} = 320.8$  Hz,  $CF_3SO_3^-$ ), 124.3 (s,  $CH_{ar}$ ), 124.6 (s,  $CH_{ar}$ ), 127.3 (s,  $CH_{ar}$ ), 130.2 (s,  $CH_{ar}$ ), 133.0 (s,  $C_{ar}$ ), 174.1 (d,  $J_{CRh} = 44.0$  Hz, NCN), 187.5 (d,  $J_{CRh} = 57.2$

Hz, CO);  $^{103}Rh$  NMR ( $CD_3CN$ , 25 °C):  $\delta = +542$ ; MS( $ES^+$ ):  $m/z$ : 397 [ $M^+$ ]; HRMS ( $ES^+$ ) calcd for  $C_{16}H_{14}N_4O_2Rh$ , 397.0172; found, 397.0242.

**Synthesis of 7b.** Butyllithium (2.5 M, 0.11 mL, 0.27 mmol) was added to a solution of diphosphonium **4b** (0.10 g, 0.13 mmol) in THF- $d_8$  (1 mL) at  $-78$  °C in an NMR tube. Monitoring the reaction by low temperature NMR allowed the characterization of ylide **7b** as a mixture of stereoisomers (95/5). According to NMR spectroscopy, at  $-10$  °C, ylide **7b** was quantitatively converted to carbodiphosphorane **8b** ( $t_{1/2} \approx 12$  h). Major isomer (95%):  $^{31}P\{^1H\}$  NMR (THF- $d_8$ ,  $-10$  °C):  $\delta = -2.2$  (d,  $J = 60.8$  Hz,  $P^+$ ),  $-100.0$  (d,  $J = 60.8$  Hz,  $P$ );  $^1H$  NMR (THF- $d_8$ ,  $-10$  °C):  $\delta = 0.64$  (dd,  $J_{HP^+} = 22.3$  Hz,  $J_{HP} = 13.4$  Hz, 1H, PCHP), 2.37 (d,  $J_{HP} = 12.0$  Hz, 3H,  $CH_3P$ ), 6.86–6.88 (m, 2H,  $H_{ar}$ ), 6.94 (t,  $J = 7.4$  Hz, 2H,  $H_{ar}$ ); 7.02–7.16 (m, 5H,  $H_{ar}$ ), 7.24 (m, 1H,  $H_{ar}$ ), 7.32–7.76 (m, 10H,  $H_{ar}$ ), 7.87 (dd,  $J_{HH} = 8.1$  Hz,  $J_{HP^+} = 12.5$ , 4H,  $H_{ar}$ );  $^{13}C\{^1H\}$  NMR (THF- $d_8$ ,  $-10$  °C):  $\delta = 15.1$  (dd,  $J_{CP^+} = 112.7$  Hz,  $J_{CP} = 163.6$  Hz, PCHP), 23.2 (d,  $J_{CP} = 20.7$  Hz,  $CH_3P$ ), 123.6 (dd,  $J_{CP^+} = 90.4$  Hz,  $J_{CP} = 10.8$  Hz,  $C_{ar}$ ), 123.8 (s,  $CH_{ar}$ ), 125.3 (d,  $J_{CP^+} = 11.0$  Hz,  $CH_{ar}$ ), 126.1 (d,  $J_{CP} = 5.1$  Hz,  $CH_{ar}$ ), 126.5 (d,  $J_{CP} = 2.5$  Hz,  $CH_{ar}$ ), 127.3 (d,  $J_{CP^+} = 11.3$  Hz,  $CH_{ar}$ ), 127.9 (d,  $J_{CP^+} = 12.0$  Hz,  $CH_{ar}$ ), 128.5 (d,  $J_{CP^+} = 11.8$  Hz,  $CH_{ar}$ ), 128.6 (d,  $J_{CP^+} = 11.8$  Hz,  $CH_{ar}$ ), 129.0 (d,  $J_{CP^+} = 2.4$  Hz,  $CH_{ar}$ ), 129.7 (d,  $J_{CP} = 5.4$  Hz,  $CH_{ar}$ ), 129.8 (s,  $CH_{ar}$ ), 130.1 (d,  $J_{CP} = 9.5$  Hz,  $C_{ar}$ ), 131.1 (d,  $J_{CP^+} = 2.8$  Hz,  $CH_{ar}$ ), 131.3 (d,  $J_{CP^+} = 2.7$  Hz,  $CH_{ar}$ ), 131.5 (dd,  $J_{CP^+} = 16.3$  Hz,  $J_{CP} = 4.9$  Hz,  $CH_{ar}$ ), 132.1 (d,  $J_{CP^+} = 10.5$  Hz,  $CH_{ar}$ ), 132.2 (d,  $J_{CP^+} = 10.2$  Hz,  $CH_{ar}$ ), 133.3 (d,  $J_{CP^+} = 83.3$  Hz,  $C_{ar}$ ), 142.7 (d,  $J_{CP} = 128.8$  Hz,  $C_{ar}$ ), 168.4 (dd,  $J_{CP^+} = 15.2$  Hz,  $J_{CP} = 10.6$  Hz,  $C_{ar}$ ), 174.8 (dd,  $J_{CP^+} = 10.7$  Hz,  $J_{CP} = 3.4$  Hz,  $C_{ar}$ ). Minor isomer (5%):  $^{31}P\{^1H\}$  NMR (THF- $d_8$ ,  $-10$  °C):  $\delta = -0.6$  (d,  $J = 57.7$  Hz,  $P^+$ ),  $-95.6$  (d,  $J = 57.7$  Hz,  $P$ ).

**Synthesis of 1b'.** Butyllithium (2.5 M, 0.16 mL, 0.40 mmol) was added to a solution of diphosphonium **4b'** (0.15 g, 0.19 mmol) in THF- $d_8$  (2 mL) at  $-78$  °C in an NMR tube. Monitoring the reaction by low temperature NMR allowed the characterization of bis-ylide **1b'**.  $^{31}P\{^1H\}$  NMR (THF- $d_8$ ,  $-40$  °C):  $\delta = +24.45$ ;  $^1H$  NMR (THF- $d_8$ ,  $-40$  °C):  $\delta = 0.59$  (tt,  $J_{HP} = 26.8$  Hz,  $J_{HH} = 3.3$  Hz, 2H,  $CH_2$ ), 2.59 (broad t,  $J_{HP} = 22.7$  Hz, 2H, CH), 7.09–7.14 (m, 2H,  $H_{ar}$ ), 7.28–7.30 (m, 2H,  $H_{ar}$ ), 7.35–7.50 (m, 20H,  $H_{ar}$ );  $^{13}C\{^1H\}$  NMR (THF- $d_8$ ,  $-40$  °C):  $\delta = 21.9$  (t,  $J_{CP} = 4.4$  Hz,  $CH_2$ ), 24.4 (broad d,  $J_{CP} = 117.0$  Hz, CH), 127.6 (m,  $CH_{ar}$ ), 128.3 (m,  $CH_{ar}$ ), 130.0 (s,  $CH_{ar}$ ), 131.5 (broad s,  $CH_{ar}$ ), 133.5 (t,  $J_{CP} = 10.4$  Hz,  $CH_{ar}$ ), 140.4 (dd,  $J_{CP} = 86.7$  Hz,  $J_{CP} = 12.3$  Hz,  $C_{ar}$ ), 141.1 (d,  $J_{CP} = 29.9$  Hz,  $C_{ar}$ ).

**Synthesis of 2b'.** To a solution of diphosphonium **4b'** (0.89 g, 1.13 mmol) in THF (40 mL) at  $-78$  °C was added butyllithium (2.5 M, 0.95 mL, 2.38 mmol). The suspension was warmed to  $-40$  °C and stirred for 30 min. After addition of a solution of cationic rhodium complex (0.58 g, 1.24 mmol) in THF (20 mL) at  $-40$  °C, the solution was stirred for 1 h. After warming up to room temperature, carbon monoxide was bubbled during 30 min. After filtration, the solvent was evaporated under vacuum. The remaining residue was washed with pentane (40 mL) and then extracted with  $CH_2Cl_2$  (60 mL) affording **2b'** as a brown solid (0.54 g, 51%).  $^{31}P\{^1H\}$  NMR ( $CDCl_3$ , 25 °C):  $\delta = +41.3$  (d,  $J_{PRh} = 4.1$  Hz);  $^1H$  NMR ( $CDCl_3$ , 25 °C):  $\delta = 1.72$ –1.74 (m, 2H, CH), 3.32 (broad td,  $J_{HP} = 24.7$  Hz,  $J_{HH} = 13.4$  Hz, 1H,  $CH_2$ ), 3.80–3.96 (m, 1H,  $CH_2$ ), 7.14–7.18 (m, 4H,  $H_{ar}$ ), 7.45–7.78 (m, 18H,  $H_{ar}$ ); 7.97–8.00 (m, 2H,  $H_{ar}$ );  $^{13}C\{^1H\}$  NMR ( $CDCl_3$ , 25 °C):  $\delta = -7.6$  (dd,  $J_{CP} = 33.9$  Hz,  $J_{CRh} = 13.8$  Hz, CH), 29.3 (broad s,  $CH_2$ ), 118.5 (d,  $J_{CP} = 57.9$  Hz,  $C_{ar}$ ), 120.7 (q,  $J_{CF} = 320.8$  Hz,  $CF_3SO_3^-$ ), 124.0 (d,  $J_{CP} = 75.5$  Hz,  $C_{ar}$ ), 129.6 (d,  $J_{CP} = 10.1$  Hz,  $CH_{ar}$ ), 130.2 (d,  $J_{CP} = 8.8$  Hz,  $CH_{ar}$ ), 133.3 (d,  $J_{CP} = 6.3$  Hz,  $CH_{ar}$ ), 133.4 (d,  $J_{CP} = 7.5$  Hz,  $CH_{ar}$ ), 133.6 (d,  $J_{CP} = 7.5$  Hz,  $CH_{ar}$ ), 133.8 ( $CH_{ar}$ ), 134.3 ( $CH_{ar}$ ), 137.9 (t,  $J_{CP} = 8.2$  Hz,  $CH_{ar}$ ), 188.5 (d,  $J_{CRh} = 64.2$  Hz, CO);  $^{103}Rh$  NMR ( $CD_3CN$ , 25 °C):  $\delta = +983$ ; MS( $ES^+$ ):  $m/z$ :

645 [M<sup>+</sup>]; HRMS (ES<sup>+</sup>) calcd for C<sub>35</sub>H<sub>28</sub>O<sub>2</sub>P<sub>2</sub>Rh, 645.0620; found, 645.0632.

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**Supporting Information Available:** X-ray crystallographic data for complexes **2a**, **2c**, and **5c** (CIF) as well as computational details (calculated structure of the less stable conformer of **2b'**, calculated NMR chemical shifts of both conformers of **2b'**, symmetry, Cartesian coordinates, number of imaginary vibrational frequencies (NImag), total energies (a.u.) of rhodium complexes **2a–c**, **9–11**). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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