Structural Investigation in Solution of a Series of Five-Coordinate Bisphosphanylaryl Ruthenium(II) Complexes

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Keywords: Ruthenium / NMR spectroscopy / NOESY / P ligands / Monoanionic terdentate *P,C,P′*-bisphosphanylaryl ligand

The structure of the ruthenium(II) complexes [RuCl{$C_6H_2(CH_2PPh_2)_2$-2,6-R-4}(PPh_3)] [R = H (**1**), Ph (**2**) or Br (**3**)] was investigated in solution using two-dimensional NMR techniques (^{1}H-^{1}H-, ^{13}C-^{1}H- and ^{31}P-^{1}H-correlation NMR spectroscopy and ^{1}H NOESY). The ^{1}H and ^{13}C NMR spectra of the complexes **1**–**3** were similar and could be completely assigned. The results of the NOESY study indicated that these complexes have a distorted square-pyramidal geometry in solution as was established for the parent complex R = H in the solid state by an X-ray crystal structure determination. The strategies used for the interpretation of the ^{1}H, ^{13}C and ^{31}P NMR spectra of these compounds and the resulting assignments form the basis for future in situ studies involving these complexes in catalytic processes.

Introduction

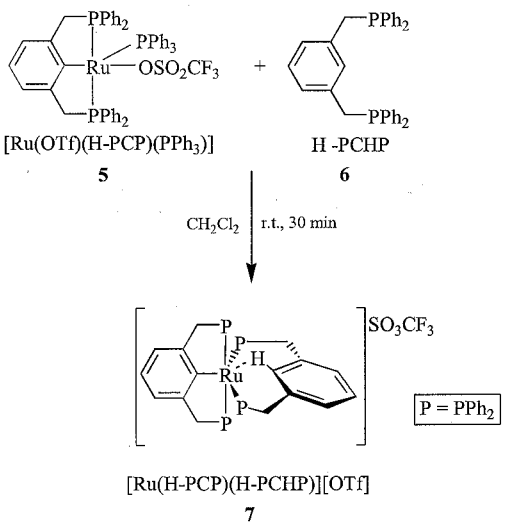
During the last two decades a new class of organometallic species has emerged containing the metal in a terdentate monoanionic framework. In these compounds, the ligand binds to the metal through two heteroatoms (e.g. N, P, S) and an anionic carbon atom usually from an aryl fragment. Examples of this type of complexes, containing a bis-orthochelating amine[1] or phosphane,[2,3] aryl monoanion (commonly known as a "pincer" ligand) bound to a ruthenium(II) center, are presented in Scheme 1.

[RuCl(R-PCP)PPh_3] R = H, **1**; Ph, **2**; Br, **3**

[RuCl(H-NCN)PPh_3] **4**

Scheme 1. Schematic representation of Ru−PCP and −NCN complexes

Examining the reaction behavior of these compounds revealed that [Ru(OSO_2CF_3)(H−PCP)(PPh_3)] (**5**) reacted with the parent arene $C_6H_4(CH_2PPh_2)_2$-1,3 (H−PCHP, **6**) to give **7** (see Scheme 2). In **7**, which was structurally characterized by X-ray diffraction, a neutral H−PCHP ligand is η^3-*P,H,P′* ligated to the bis-orthochelated bisphosphanylaryl ruthenium cation. Complexes like **7**, containing an aromatic C−H group coordinated to a metal center (i.e., an agostic contact),[4] are rare and are thought to be intermediates in processes leading to the formation of a metal−carbon bond (cyclometalation).[5−7]



[Ru(OTf)(H-PCP)(PPh_3)] **5**

H-PCHP **6**

[Ru(H-PCP)(H-PCHP)][OTf] **7**

Scheme 2. Formation of ruthenium complex **7**, containing an aryl C−H···Ru interaction

Attempts to study the structure of **7** in solution by NMR spectroscopy were hampered by a complex resonance pattern and fluxional behavior. Interpretation of the ^{1}H, ^{13}C and ^{31}P NMR patterns of **7** was further frustrated by the lack of a detailed assignment of the ^{1}H and ^{13}C NMR spectra in complexes where the PCP-type ligand had phenyl groups attached to the phosphorus atoms,[8] mainly those with geometries other than square-planar.[2,3,5,9,10] In particular, a detailed understanding of the binding mode of the H−PCHP ligand in **7** requires an accurate assignment of the aromatic region of the ^{1}H and ^{13}C NMR spectra of related complexes such as **1**−**3**. Furthermore, these PCP metal complexes have an increasing importance as novel catalysts[8b,8c,11−13] as well as materials with interesting new physico-chemical properties.[14] A detailed knowledge of the

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NMR spectroscopic features of these compounds, i.e., coupling network, chemical shift and relative spatial positioning of the various nuclei, mainly the ones closer to the metal center, can play an important role in further investigations of reactivity, bonding, structure-energy relationships and in the understanding of the intimate steps of catalytic processes involving these pincer ruthenium complexes. Therefore, we set out to study in detail the NMR spectra of the [RuCl(R−PCP)PPh_3] compounds **1−3**.

Due to the presence of several aromatic rings, an obvious and nontrivial problem in compounds **1−3** is to distinguish the resonances belonging exclusively to one particular type of aromatic group. The structures of these complexes in solution were studied by ^1H, ^{13}C and ^{31}P NMR spectroscopy with the application of two-dimensional techniques (^1H-^1H-COSY, ^{13}C-^1H-COSY and ^{31}P-^1H-COSY) to allow full assignment of the ^1H and ^{13}C resonances, in particular those in the aromatic regions. Furthermore, a study of the three-dimensional structure in solution was performed by applying standard NOE techniques (^1H-NOESY). More importantly, these assignments were performed without any sort of chemical modification of the complexes studied, like, for instance, replacement of hydrogen atoms by deuterium or fluorine or NMR "silent" nuclei.

Results

The structure of [RuCl(H−PCP)(PPh_3)] (**1**) in the solid state has been determined by X-ray diffraction.[15] The local geometry around the Ru^{II} center in **1** has been described as distorted square-pyramidal (see Figure 1). The PPh_3 ligand occupies the apical position, while the other two phosphorus centers, together with the chlorine and C_{ipso} atom, form the base of the square-pyramidal arrangement. As a result, the complex has a mirror-type arrangement of the two fused five-membered chelate rings. The phosphorus center in each of the puckered chelate rings has one phenyl group equatorially and one axially (i.e., opposite to the apical PPh_3 ligand) orientated.

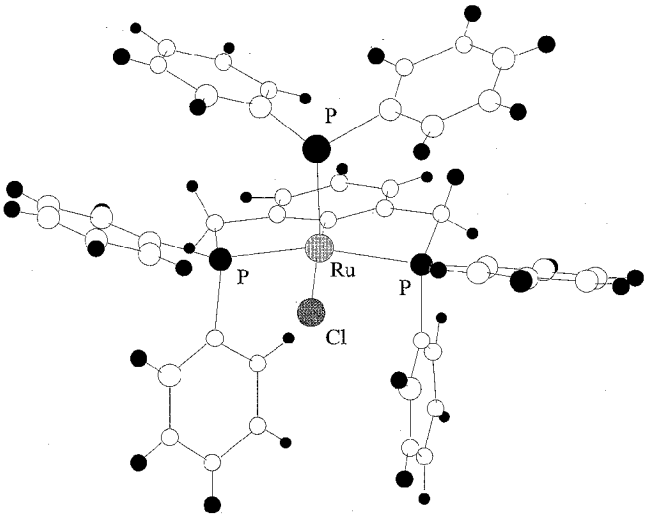


Figure 1. The molecular geometry of [RuCl(H−PCP)(PPh_3)] (**1**) in the solid state;[15] one phenyl ring from the PPh_3 ligand is omitted for clarity; the mirror-type arrangement (apparent mirror-plane) through the C_{ipso}−Ru−Cl is clearly visible

As a common feature, the ^1H NMR spectra of **1−3** contain a set of doublets of virtual triplets for the diastereotopic benzylic protons (for instance, see the abscissa in Figure 2[16]). Moreover, the $^{31}P\{^1H\}$ NMR spectra of these compounds consist of a doublet and a lower field triplet ($^2J_{pp} \approx 30$ Hz) for the R−PCP and PPh_3 phosphorus nuclei, respectively. In the $^{13}C\{^1H\}$ NMR spectra a small $^2J_{C_{ipso}-PPh_3}$ coupling constant of about 15−20 Hz is observed. These observations establish the *trans*-positioning of the R−PCP phosphorus atoms and the *cis*-arrangement of the R−PCP and PPh_3 phosphorus atoms, and suggest that the square-pyramidal structure of **1** found in the solid state exists in solution as well.

As the complexes **1−3** gave very similar results in the NMR analysis, compound **1** will be used as a representative compound for the following discussion.

^{31}P-^1H Correlation Spectroscopy (^{31}P-^1H-COSY)

The ^{31}P-^1H-COSY NMR spectra of a solution of **1** in CD_2Cl_2 allowed us to readily locate all P−Ph *ortho* protons, see Figure 2.[16] Only three cross-peaks (therefore, only three types of *ortho* protons) were observed in the aromatic region of the ^1H NMR spectrum, one for the PPh_3 ligand and the other two for the H−PCP ligand. This indicates that the four phenyl rings from the H−PCP ligand are divided into two sets of diastereotopic phenyl groups (hereafter labeled as Ph-a and Ph-b) which later could be assigned to the equatorial and axial phenyl groups, respectively (see ^1H NOESY experiments), whereas the phenyl rings of the PPh_3 ligand are equivalent. These findings imply that there is no restricted rotation about any P−Ph bond or about the Ru−PPh_3 bond. Also, no Ru−P bond dissociation-association process is operative on the NMR time scale at room temperature. Consequently, under these conditions there is a *pseudo*-molecular symmetry plane containing the C_{ipso}−Ru−P(PPh_3) atoms.

^1H-^1H Correlation Spectroscopy

In the ^1H-^1H-COSY spectrum of the ruthenium complexes **1−3** the location of protons H-3,5 (see Figure 3)[16] could easily be determined due to a cross-peak between these protons and one set of benzylic protons. The related $^4J_{HH}$ indirect coupling between these protons in the one-dimensional 300 MHz ^1H spectrum could not be observed. Interestingly, this behavior is quite general and is not restricted to cyclometalated R−PCP-type ligands. A similar phenomenon was also observed in a ^1H-^1H-COSY analysis involving related nitrogen-based ligands and can be explained by analogy with allylic systems:[17a,18a] the smaller the torsional angle between the benzyl C−H bond and the axis of the arene π-orbitals, the larger is the four-bond coupling. Therefore, the presence of this cross-peak brings interesting structural consequences because it suggests that these benzylic protons are occupying a *pseudo*-axial posi-

tion in the two fused five-membered chelate rings in relation to the ruthenium coordination plane. This idea was later confirmed by a ^{1}H NOESY experiment (see below), and it has become quite important in the structural analysis of [RuCl(H−PCP)PPh$_3$] in which the H−PCP ligand has one of the benzylic protons of each methylene carbon atom replaced by a methyl or ethyl group (i.e., the ligand has two chiral centers in the molecule).[24]

The multiplet at lowest field in the ^{1}H NMR spectrum (between δ = 7.80−7.90 for **1**), showing cross-peaks with the R−PCP phosphorus atoms in Figure 2,[16] integrates to four protons and it was observed by ^{13}C-^{1}H-COSY analysis (Figure 4)[16] to have a cross-peak with only one type of aromatic carbon atom. Therefore, it can be safely assigned as the resonance due to the four *ortho* Ph-a protons. This multiplet shows a cross-peak in the ^{1}H-^{1}H-COSY (Figure 3)[16] with protons located in a second multiplet at δ = 7.30−7.50. The nonexistence of any other cross-peak involving these two regions of the ^{1}H-^{1}H-COSY spectrum allows us to conclude that the *meta* and *para* protons of the Ph-a are overlapping and located in the multiplet at δ = 7.30−7.50.

^{13}C-^{1}H Correlation Spectroscopy

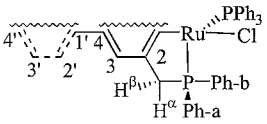
Entering the information gathered so far into normal- and long-range ^{13}C-^{1}H-correlation NMR spectra {and using the assignments of the ^{13}C{^{1}H} NMR spectrum of [RuCl(H-NCN)(PPh$_3$)] (**4**)},[1] it was possible to locate all C−H resonances as well as most of the quaternary carbons (C$_{quat}$) in the ^{1}H and ^{13}C NMR spectra of **1**−**3**. In particular, all proton and carbon resonances of the parent complexes **1** and **2** could be assigned (see Figure 4[16] for **1**). Only in the case of compound **3** could the C$_{quat}$ of the Ph-a rings not be located. Table 1 summarizes all ^{1}H and ^{13}C NMR spectroscopic data and assignments for complexes **1**−**3**.

The presence of an apparent molecular symmetry plane involving C$_{ipso}$−Ru−P(PPh$_3$)−Cl is even clearer in these ^{13}C-^{1}H-COSY NMR spectra. For instance, Figure 4[16] shows that the *ortho*-protons and -carbons of the PPh$_3$ ligand are chemically equivalent (i.e., they have identical chemical shifts) and the same conclusion can be drawn for the *meta* and *para* nuclei. Furthermore, each phenyl group of the −PPh$_2$ fragment has an individual set of resonances related to either Ph-a or Ph-b. However, the *ortho* (or *meta* or *para*) Ph-a protons and carbons appear as single resonances. The same conclusion is valid for the Ph-b group. The *ortho* and *meta* carbon nuclei as well as the C$_{quat}$ of the Ph-a and Ph-b rings give distinct *pseudo*-triplets which is the expected pattern for carbons connected to a *trans* phosphorus atom.[17b,19]

NOE Analysis

More precise information about the three-dimensional structure of species **1**−**3** in solution can be obtained from

Table 1. ^{1}H (300 MHz) and ^{13}C NMR (75 MHz) data of compounds **1**, **2** and **3** in CD_2Cl_2 (relative to internal tetramethylsilane)

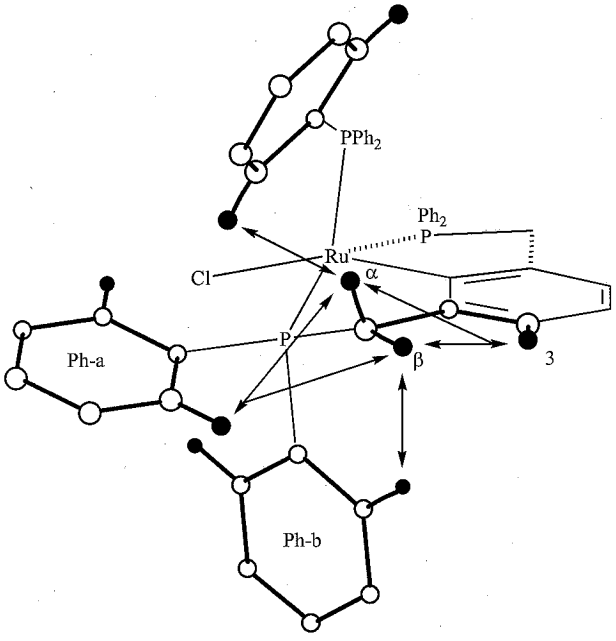


		^{1}H (δ, mult., $^2J_{HH}$, $^{vt}J_{HP}$ Hz)			^{13}C (δ, mult., J_{CP} Hz)		
		1[a]	**2**	**3**[b]	**1**	**2**	**3**
Benzylic	C−H$^{\alpha}$[c]	2.36 (bd, 16)	2.48 (bd, 16)	2.37 (bd, 16)	39.19 (vt, 15)	39.27 (vt, 16)	39.08 (vt, 15)
Groups	C−H$^{\beta}$	3.48 (dvt, 16, 6)	3.56 (dvt, 16, 6)	3.45 (dvt, 16, 6)			
	C$_{ipso}$	−	−	−	172.53 (d, 17)	173.30 (d, 16)	172.77 (d, 17)
Xylylene	C-2,6	−	−	−	151.20 (vt, 8)	151.66 (vt, 9)	152.97 (vt, 9)
Ring	C−H-3,5	6.96	7.31	7.13	123.34 (vt, 9)	121.66 (vt, 9)	125.73 (vt, 9)
	C−(R)-4	6.81	−	−	122.11 (s)	135.02 (s)	115.95 (s)
	ortho	7.84 (m)	7.88 (m)	7.85 (m)	133.15 (vt, 6)	133.11 (vt, 6)	133.10 (vt, 5)
Ph-a	*meta*	7.38	7.40	7.39	128.71 (vt, 5)	128.75 (vt, 5)	128.75 (vt, 4)
	para	7.42	7.45	7.44	130.18 (s)	130.23 (s)	130.32 (s)
	C$_{quat}$	−	−	−	134.76 (vt)	134.82	[d]
	ortho	7.11	7.18	7.11	132.81 (vt, 6)	132.84 (vt, 6)	132.71 (vt, 5)
Ph-b	*meta*	6.93	6.94	6.95	128.31 (vt, 4)	128.37 (vt, 4)	128.41 (vt, 4)
	para	7.09−7.14	7.09−7.10	7.12−7.15	129.27−129.31 (s)	129.39 (s)	129.45−129.50 (s)
	C$_{quat}$	−	−	−	136.07 (vt, 17)	135.90 (vt, 16)	[d]
	ortho	7.05	7.10	7.08	134.47 (d, 10)	134.46 (d, 10)	134.39 (d, 10)
PPh$_3$	*meta*	6.83	6.83	6.86	127.29 (d, 10)	127.29 (d, 10)	127.39 (d, 10)
	para	7.09−7.14	7.14	7.12−7.15	129.27−129.31 (s)	129.35 (s)	129.45−129.50 (s)
	C$_{quat}$	−	−	−	136.69 (dvt, ^1J = 51, ^{vt}J = 2−3)	136.55 (dm, 51)	136.35 (d, 52)
	1′	−	−	−	−	141.98 (s)	−
[b]	2′	−	7.70	−	−	126.68 (s)	−
	3′	−	7.44	−	−	128.82 (s)	−
	4′	−	7.30	−	−	126.76 (s)	−

[a] s = singlet, d = doublet, m = multiplet, b = broad and vt = virtual triplet. Non reported multiplicities are related to resonances only detected indirectly by two-dimensional techniques. − [b] See Figure at head of Table. − [c] Splittings due to the virtual triplet not resolved. − [d] One C$_{quat}$ is at δ = 134.03 and overlaps with PPh$_3$ *ortho* carbons. The other is at δ = 135.50 (vt, $^{vt}J_{CP}$ = 17 Hz). It was not possible to determine to which phenyl ring they were related to.

phase-sensitive ^{1}H NOESY measurements. The intensity of cross-peaks originating from dipolar interactions is very sensitive to the distance between the participating nuclei and they are often too weak to be detected when this distance is larger than 3 Å.[18b] A series of ^{1}H NOESY spectra was recorded. The interactions between benzylic and aromatic protons proved to be an excellent structural probe. Figure 5[16] shows this region for compound **1**. Only the benzylic protons at $\delta = 2.36$ (H^{α}) show a cross-peak with the *ortho* PPh_3 protons. This indicates that the PPh_3 ligand is in the apical position, as is observed in the solid state (Figure 1). The high-field chemical shift of H^{α} is then probably caused by a magnetic anisotropic effect originating from the PPh_3 ligand.

NOE correlation signals involving the aromatic protons H-3,5 and both benzylic protons H^{α} and H^{β} are also observed. However, the different intensities of these cross-peaks reveal that H^{β} is closer to protons H-3,5 than H^{α}. This is a clear reflection of the puckering occurring in the two fused five-membered chelate rings. The benzylic protons are not bisecting the xylylene plane. In order to be closer to H-3,5, H^{β} must be in a nearly periplanar conformation with the xylylene plane. H^{α}, on the other hand, is directed toward an *anti*-planar conformation with the same plane (Scheme 3). As a consequence, the H−PCP phosphorus atoms that are occupying the flip of an envelope conformation assumed by each one of the two fused rings, are pointing away from the PPh_3 ligand.



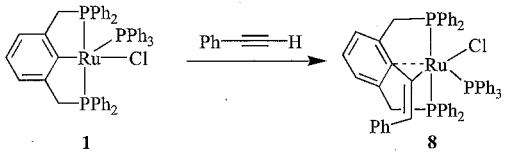
Scheme 3. Spatial interactions involving the benzylic protons in **1**

Protons H^{α} and H^{β} interact almost equally with the *ortho* protons of the Ph-a ring placing the $P-C_{quat}$ bond of Ph-a in an approximately coplanar situation with the plane formed by the $P-CH_2-C$-2 (or -6) bonds. On the other hand, the (weak) interaction between the *ortho* Ph-b protons and the H^{β} protons is consistent with a *pseudo*-axial position of the former.

The same features observed in the NOESY spectrum of **1** were also present in the spectra of complexes **2** and **3**, showing that the presence of different substituents in the *para* position relative to the metal center (H, Ph or Br for **1**, **2** or **3**, respectively) does not affect the geometry around the metal. An analysis of the NOESY spectra also showed that the structures in solution of these complexes are very similar to that found in the solid state for complex **1**.

Discussion

In the case of the unsaturated ruthenium complex $[RuCl_2(PPh_3)_3]$ it has been found in the solid state that one of the *ortho* phenyl protons is directed toward the empty coordination site, blocking this position.[20] The NMR analysis performed with complexes **1**−**3** (and the solid structure of **1** as well) did not reveal any equivalent feature. On the contrary, all Ph-a and Ph-b rings in these complexes are freely rotating and do not exhibit any preferred configuration other than being equatorial or axial, respectively. This suggests that the vacant site *trans* to the PPh_3 ligand is relatively available for the coordination of nucleophilic species. Indeed, a facile reaction between **1** and 4-phenylpyridine (4-PhPy) producing the 18-electron complex [RuCl(H−PCP)(PPh_3)L] (L = 4-PhPy) has been reported.[15] Furthermore, species in which L is either a coordinated phenyl acetylene molecule or a vinylidene substituent [L = PhC(H)=C=] are thought to be involved in the formation of ruthenium complex **8** in the reaction of **1** with phenyl acetylene (Scheme 4).[10]



Scheme 4. Reaction of **1** with phenylacetylene yielding vinylidine-substituted ruthenium complex **8**

Dissociation of PPh_3 is a common phenomenon in ruthenium complexes such as $[RuCl_2(PPh_3)_n]$ ($n = 3$ or 4).[21] However, despite the fact that the PPh_3 ligand in **1**−**3** is easily replaced by two-electron donor ligands (e.g. CO,[15] PMe_3,[15] R−PCHP[23,25]), solutions of the pure complexes did not reveal the presence of any free PPh_3. Furthermore, if intra- or intermolecular processes were operative leading to PPh_3 exchange, they would cause an interchange between the Ph-a and Ph-b protons, as well as between the benzylic protons H^{α} and H^{β}. Nevertheless, cross-peaks indicating fluxional processes were not present in any of the ^{1}H NOESY spectra recorded. Therefore, the replacement of PPh_3 in complexes **1**−**3** by the two-electron donor ligands mentioned above is most likely the result of dissociation of the PPh_3 from saturated species of these complexes.

The chemical shift of the C_{ipso} in complexes of the R−NCN ligand is sensitive toward the type of R substituent.[22] Taking the H−NCN complex as reference (i.e., R = H), downfield shifts greater than 1 ppm in the $\delta_{C_{ipso}}$ of com-

plexes containing electron-withdrawing R groups and the converse effect (i.e., upfield shifts) when electron-donating groups were present. Similar behavior was recently observed in palladium complexes of the pyridine PCP-type ligand [$C_5H_2N(CH_2PPh_2)_2$-3,5] upon coordination of Lewis acidic species to the pyridine nitrogen atom.[9c] In the case of the complexes reported here, the electronic effect of the bromo and phenyl *para* substituents on the C_{ipso} chemical shift is negligible (see Table 1) and probably reflects the buffer effect exerted by π-acidic phosphorus groups on the overall electron density of the complexes.

Conclusion

The results of the present study are currently being applied for the assignment and the understanding of more complex structures containing free and anionic PCP-type ligands, such as compound **7**,[23] ruthenium complexes containing chiral H−PCP type ligands[24] as well as other PCP-metal complexes which have recently been published. The results of these studies will be published shortly.

Experimental Section

Complexes **1, 2**[2] and **3**[25] were prepared according to literature procedures. All manipulations were performed under a dry nitrogen atmosphere using standard Schlenk techniques. Typically, ca. 30 mg of complex was dissolved in 0.7 mL of CD_2Cl_2 and then transferred to a 5 mm NMR tube provided with a glass stopper. Chemical shifts are in ppm relative to $(CH_3)_4Si$ (^1H and ^{13}C NMR spectra) or H_3PO_4 85% (^{31}P NMR spectra). CD_2Cl_2 was degassed prior to use (four times) using the freeze-pump-thaw methodology and then stored under nitrogen over molecular sieves 4 Å. ^1H, $^{13}C\{^1H\}$ and $^{31}P\{^1H\}$ NMR spectra were recorded at 298 K on a Varian Unity Inova 300 MHz spectrometer using standard pulse sequences. Except in the case of the NOESY measurements, all other two-dimensional experiments were performed in a nonphase-sensitive mode. The second pulse in the ^1H-^1H-COSY experiment was set to 45°. Normal-range ^{13}C-^1H-COSY NMR spectra were recorded considering $^1J_{HC} = 140$ Hz and for the long-range experiment the appropriate delays were adjusted for $^nJ_{HC} = 8$ Hz. T_1 times for complexes **1−3** were in the range 0.4−1.5 s. NOESY spectra were recorded with mixing times of 0.5, 1.0 and 1.5 s with a relaxation delay of 2.0 s.

1: ^1H NMR (CD_2Cl_2, 300 MHz): δ = 2.36 (bd, $^2J_{HH}$ = 16 Hz, 2 H, CH_2), 3.48 (dvt, $^2J_{HH}$ = 16 Hz, $^{vt}J_{HP}$ = 6 Hz, CH_2), 6.81 (H-4), 6.83 (*m*-PPh_3), 6.93 (*m*-Ph-b), 6.96 (H-3,5), 7.05 (*o*-PPh_3), 7.09−7.14 (*p*-Ph-b, *p*-PPh_3), 7.11 (*o*-Ph-b), 7.38 (*m*-Ph-a), 7.42 (*p*-Ph-a), 7.84 (m, *o*-Ph-a). − $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 75 MHz): δ = 39.19 (vt, $^{vt}J_{CP}$ = 15 Hz, CH_2), 122.11 (s, C-4), 123.34 (vt, $^{vt}J_{CP}$ = 9 Hz, C-3,5), 127.29 (d, $^3J_{CP}$ = 10 Hz, *m*-PPh_3), 128.31 (vt, $^{vt}J_{CP}$ = 4 Hz, *m*-Ph-b), 128.71 (vt, $^{vt}J_{CP}$ = 5 Hz, *m*-Ph-a), 129.27−129.31 (s, *p*-Ph-b, *p*-PPh_3), 130.18 (s, *p*-Ph-a), 132.81 (vt, $^{vt}J_{CP}$ = 6 Hz, *o*-Ph-b), 133.15 (vt, $^{vt}J_{CP}$ = 6 Hz, *o*-Ph-a), 134.47 (d, $^2J_{CP}$ = 10 Hz, *o*-PPh_3), 134.76 (vt, C_{quat} PPh-a), 136.07 (vt, $^{vt}J_{CP}$ = 17 Hz, C_{quat} PPh-b), 136.69 (dvt, $^1J_{CP}$ = 51 Hz, $^{vt}J_{CP}$ = 2−3 Hz, C_{quat} PPh_3), 151.20 (vt, $^{vt}J_{CP}$ = 8 Hz, C-2,6), 172.53 (d, $^2J_{CP}$ = 17 Hz, C_{ipso}).

2: ^1H NMR (CD_2Cl_2, 300 MHz): δ = 2.48 (bd, $^2J_{HH}$ = 16 Hz, 2 H, CH_2), 3.56 (dvt, $^2J_{HH}$ = 16 Hz, $^{vt}J_{HP}$ = 6 Hz, CH_2), 6.83 (*m*-PPh_3), 6.94 (*m*-Ph-b), 7.09−7.10 (*p*-Ph-b), 7.10 (*o*-PPh_3), 7.14 (*p*-PPh_3), 7.18 (*o*-Ph-b), 7.30 (4′), 7.31 (H-3,5), 7.40 (*m*-Ph-a), 7.44 (3′), 7.45 (*p*-Ph-a), 7.70 (2′), 7.88 (m, *o*-Ph-a). − $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 75 MHz): δ = 39.27 (vt, $^{vt}J_{CP}$ = 16 Hz, CH_2), 121.66 (vt, $^{vt}J_{CP}$ = 9 Hz, C-3,5), 126.68 (s, 2′), 126.76 (s, 4′), 127.29 (d, $^3J_{CP}$ = 10 Hz, *m*-PPh_3), 128.37 (vt, $^{vt}J_{CP}$ = 4 Hz, *m*-Ph-b), 128.75 (vt, $^{vt}J_{CP}$ = 5 Hz, *m*-Ph-a), 128.82 (s, 3′), 129.35 (s, *p*-PPh_3), 129.39 (s, *p*-Ph-b), 130.23 (s, *p*-Ph-a), 132.84 (vt, $^{vt}J_{CP}$ = 6 Hz, *o*-Ph-b), 133.11 (vt, $^{vt}J_{CP}$ = 6 Hz), 134.46 (d, 10), 134.82, 135.02 (s), 135.90 (vt, $^{vt}J_{CP}$ = 16 Hz), 136.55 (dm, 51), 141.98 (s), 151.66 (vt, $^{vt}J_{CP}$ = 9 Hz), 173.30 (d, $^2J_{CP}$ = 16 Hz, C_{ipso}).

3: ^1H NMR (CD_2Cl_2, 300 MHz): δ = 2.37 (bd, $^2J_{HH}$ = 16 Hz, 2 H, CH_2), 3.45 (dvt, $^2J_{HH}$ = 16 Hz, $^2J_{HP}$ = 6 Hz, 2 H, CH_2), 6.86 (m, 6 H, *m*-PPh_3), 6.95 (m, 4 H, *m*-PPh_2), 7.08 (m, 6 H, *o*-PPh_3), 7.11 (m, 4 H, *o*-PPh_2), 7.12−7.15 (m, 5 H, *p*-PPh_2 and *p*-PPh_3), 7.13 (2 H, CH-3,5), 7.39 (m, 4 H, *m*-PPh_2), 7.44 (m, 2 H, *p*-PPh_2), 7.85 (m, 4 H, *o*-PPh_2). − $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 75 MHz): δ = 39.08 (vt, $^{vt}J_{CP}$ = 15 Hz, CH_2), 115.95 (s, C−Br), 125.73 (vt, $^{vt}J_{CP}$ = 9 Hz, C-3,5) 127.39 (d, $^3J_{CP}$ = 10 Hz, *m*-PPh_3), 128.41 (vt, $^{vt}J_{CP}$ = 4 Hz, *m*-PPh_2), 128.75 (vt, $^{vt}J_{CP}$ = 4 Hz, *m*-PPh_2), 129.45−129.50 (two singlets, *p*-PPh_3 and *p*-PPh_2), 130.32 (s, *p*-PPh_2), 132.71 (vt, $^{vt}J_{CP}$ = 5 Hz, *o*-PPh_2), 133.10 (vt, $^{vt}J_{CP}$ = 5 Hz, *o*-PPh_2), 134.03 (m, C_{quat}-PPh_2), 134.39 (d, $^2J_{CP}$ = 10 Hz, *o*-PPh_3), 135.50 (vt, $^{vt}J_{CP}$ = 17 Hz, C_{quat}-PPh_2), 136.35 (d, $^1J_{CP}$ = 52 Hz, C_{quat}−PPh_3), 152.97 (vt, $^{vt}J_{CP}$ = 9 Hz, C-2,6), 172.77 (d, $^2J_{CP}$ = 17 Hz, Ru−C_{ipso}). − $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 121 MHz): δ = 36.74 (d, 2P, Br−PCP), 80.62 (t, $^2J_{PP}$ = 32 Hz, 1P, PPh_3).

Acknowledgments

This work was financially supported by the Conselho Nacional de Desenvolvimento Científico e Tecnológico (CNPq), Brazil, and the Council for Chemical Sciences of the Netherlands Organization for Scientific Research (CW-NWO).

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Received December 27, 1999
[I99478]