FULL PAPER

Theoretical Study of Rhodium(I) Carbene Complexes: The Structural Versatility of Phosphino- Compared with Aminocarbenes

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Abstract: Density functional calculations are reported for complexes of general formula [(carbene)RhClL$_2$] featuring model phosphino- and aminocarbenes. Both the *cis* and *trans* isomers of the rhodium(I) η^1-complexes (**1–9**) were investigated, and the influence of the rhodium co-ligands (L = ethylene, phosphine, or carbon monoxide) was evaluated. In the case of phosphinocarbenes and carbon monoxide as a ligand, a somewhat unusual coordination mode was observed, in which a significant intramolecular Cl→C$_{carbene}$ interaction is present. The propensity of phosphino- and aminocarbenes to behave as four electron donors was also investigated both structurally and energetically on the related η^2-complexes **10–18**. These results as a whole emphasize the structural versatility of phosphino- compared with aminocarbene complexes.

Keywords: carbene ligands · coordination modes · density functional calculations · ligand effects · substituent effects

Introduction

Since the pioneering work of Fischer and Schrock,[1] transition-metal carbene complexes[2] have been extensively applied in stoichiometric and catalytic reactions.[3] The isolation of a broad range of metal-free singlet carbenes over the last 15 years[4,5] has stimulated further spectacular developments. In particular, *N*-heterocyclic carbenes (NHCs) that bind strongly to almost all transition metals,[6] are widely used as ligands in homogeneous catalysis, and even challenge phosphines.[7] Despite the chronologically earlier discovery of stable phosphinocarbenes (PCs) and their computationally established propensity to form complexes,[8] only four PC transition metal complexes **A–D** have been prepared by direct complexation of the corresponding free carbene (Scheme 1).[9]

Striking differences are observed between the PC and NHC coordination modes. Indeed, the η^2-coordination mode observed in most of the PC complexes[10] remains unknown for NHCs and is very rare for acyclic aminocarbenes.[11] To obtain more insight into ligand properties of PCs versus NHCs, here we report a theoretical investigation of model complexes with the general formula [(carbene)RhClL$_2$]. The influence of the L ligand (L = C$_2$H$_4$, PH$_3$, CO) on the struc-

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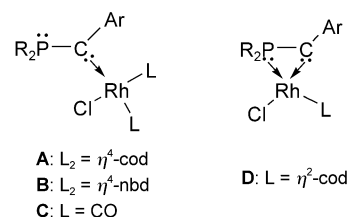Université Paul Sabatier
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Scheme 1. Structure of the η^1- and η^2-phosphinocarbene rhodium(I) complexes (**A–D**). R = *i*Pr$_2$N and Ar = 2,6-(CF$_3$)$_2$C$_6$H$_3$.

ture of the carbene complexes, and the propensity of phosphino- and aminocarbenes to behave as two- versus four-electron donors is discussed in terms of both structure and energy considerations.

Computational Details

Calculations were performed with the Gaussian 98 program,[12, 13] by using the density functional method.[14] The various structures were fully optimized with the hybrid exchange functional B3LYP.[15] This functional is built with Becke's three-parameter exchange functional, and the Lee–Yang–Parr correlation functional. The basis set retained for all calculations is CEP-31G(d). This means that the relativistically corrected effective core potentials of Stevens, Basch, and Krauss were used with a double ζ basis expansion for the valence space for all the atoms (P, N, C, Cl, Rh and H).[16] All heavy main group atoms were augmented with a single set of polarization functions as provided by Petersson et al.[17] ($\alpha_P = 0.55$, $\alpha_N = 0.8$; $\alpha_C = 0.8$; $\alpha_O = 0.8$; $\alpha_{Cl} = 0.75$). The optimized structures were confirmed as minima on the potential energy. The frequencies were calculated with analytical second derivative.

All total energies were corrected for zero-point energy (ZPE) and temperature by using unscaled density functional frequencies. The population analyses at the given optimized geometries (Wiberg bond indices) were carried out according to the Weinhold-Reed partitioning scheme.[18]

Results and Discussion

For this study, rhodium complexes were chosen as models for the experimentally characterized compounds **A**–**D**. The rhodium co-ligands L were chosen for their complementary electronic properties; alkenes such as ethylene act both as weak σ-donors and π-acceptors, PH$_3$ is essentially a σ-donor, and carbon monoxide is a strong σ-donor and π-acceptor.

For all the complexes investigated, [η^1-(R$_2$PCH)RhClL$_2$] (R = H, NH$_2$) and [η^1-(H$_2$NCH)RhClL$_2$] (L = CO, PH$_3$, C$_2$H$_4$), the rhodium adopts a more or less distorted square planar geometry with the carbene center taking up a trigonal planar environment. Both the *trans* and *cis* isomers (according to the relative positions of the two ligands L) were studied. For the *trans* isomer, a single energy minimum (*trans*) was found, the coordination planes around the rhodium and the carbene being almost coplanar. For the *cis* isomer, several energy minima have been located (*cis*, *cis'* and *cis**) (Scheme 2). They differ primarily in the position of
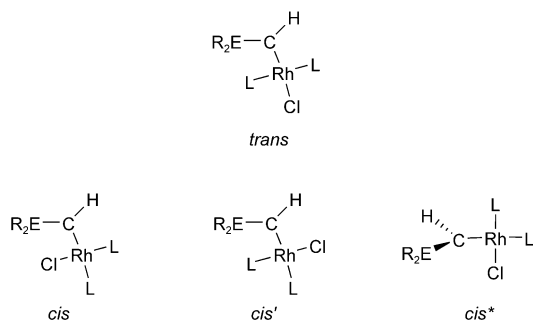
the chlorine atom and the phosphorus or nitrogen centers (*cis* : CP or CN and RhCl bonds in *syn*periplanar conformation; *cis'*: CP or CN and RhCl bonds in *anti*periplanar conformation; *cis**: CP or CN and RhCl bonds in perpendicular conformation). Since all of these energy minima present very similar structures, except *cis**, in which L = CO (as depicted), and are very close in energy (see Supporting Information), only the *cis* conformation will be taken into consideration for the *cis* isomers of all complexes in the discussions that follow. For all complexes featuring ethylene as coligands, various conformers can be anticipated, because of the relative orientation of the two olefin ligands. This aspect has not been studied in detail, and all the η^1-complexes reported feature parallel ethylene ligands.

[η^1-(H$_2$PCH)RhClL$_2$] complexes: Complexes [η^1-(carbene)RhClL$_2$] (**1–3**) that feature the parent phosphinocarbene (H$_2$PCH) were investigated first. Optimized structures of the *trans* and *cis* isomers are shown in Figure 1. The most important geometric parameters (bond lengths with related Wiberg bond indices, bond, and torsion angles), and relative energies for complexes **1–3** are listed in Table 1. As observed by Schoeller et al. for the W(CO)$_5$ fragment, the geometry of the phosphinocarbene is strongly affected upon coordination.[8a] Indeed, the PC bond is considerably lengthened (from 1.66 Å for the free carbene to 1.75–1.82 Å for complexes **1–3**), and the geometry around the phosphorus changes from trigonal planar to strongly pyramidal (the

1trans   1cis

2trans   2cis

3trans   3cis
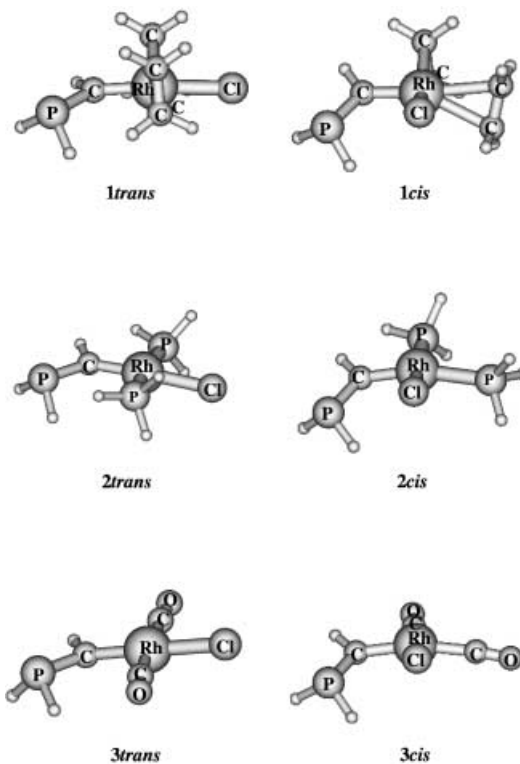
Figure 1. Structures of the *trans* and *cis* energy minima for the complexes [η^1-(H$_2$PCH)RhCl(C$_2$H$_4$)$_2$] (**1**), [η^1-(H$_2$PCH)RhCl(PH$_3$)$_2$] (**2**) and [η^1-(H$_2$PCH)RhCl(CO)$_2$] (**3**).

Scheme 2. Schematic representation of the *trans* and *cis* isomers of η^1-R$_2$ECH)RhClL$_2$ complexes. ER$_2$ = PH$_2$, P(NH$_2$)$_2$, NH$_2$ and L = C$_2$H$_4$, PH$_3$, CO.

Table 1. Geometrical parameters (bond lengths in Å and bond angles in degrees) and relative energies (kcal mol^{-1}, with zero-point vibration energy corrections) for the *trans* and *cis* isomers of the $[\eta^1$-(H$_2$PCH)RhClL$_2]$ (X = C$_2$H$_4$, PH$_3$, CO) complexes **1–3**. Wiberg Bond Indices in brackets. (see Figure 1)

	P–C	Rh–C	∡ClRhCP	Σ∡C	Σ∡P	ΔE
H$_2$PCH	1.662 (2.085)	/	/	/	360.0	/
(**1** *trans*)	1.812 (1.197)	1.893 (1.147)	−164.2	358.9	300.7	−3.1
(**1** *cis*)	1.792 (1.276)	1.881 (1.153)	−32.1	359.8	303.5	0
(**2** *trans*)	1.816 (1.180)	1.898 (1.188)	−176.3	359.9	299.7	−6.2
(**2** *cis*)	1.794 (1.276)	1.908 (1.070)	−26.3	359.9	303.9	0
(**3** *trans*)	1.794 (1.257)	1.932 (1.057)	−178.5	359.4	304.3	0.4
3 *cis*	1.755 (1.451)	1.974 (0.806)	−26.8	359.7	314.8	0
3 *cis**	1.842 (1.066)	2.059 (0.509)	115.9	350.9	294.7	−5.7

sums of the bond angles around the phosphorus for **1–3** lie in the range 300–315°).

Overall, the geometries of the *trans* and *cis* isomers are rather similar for all of complexes **1–3**. However, a somewhat peculiar structure (**3** *cis**) was located on the energy surface for the *cis* isomer with carbon monoxide, in which the PCH plane is almost perpendicular to the rhodium coordination plane (Figure 2). The carbene center is slightly pyr-
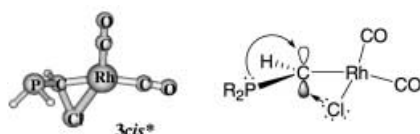

Figure 2. Structure of the energy minima **3** *cis** for $[\eta^1$-(H$_2$PCH)RhCl(CO)$_2]$.

amidalized (sum of the bond angles, **3** *cis*: 360°, **3** *cis**: 351°), and the C$_{carbene}$-Rh-Cl bond angle is considerably contracted (**3** *cis*: 91°, **3** *cis**: 49°). An elongation of the RhCl bond is apparent (**3** *cis*: 2.39 Å, **3** *cis**: 2.49 Å), while the C$_{carbene}$Cl distance is found to be significantly shortened (**3** *cis*: 3.13 Å, **3** *cis**: 1.93 Å compared with 1.76 Å for a typical C–Cl single bond). These data suggest the existence of a dative Cl→C$_{carbene}$ interaction, (note, that a similar C$_{carbene}$Cl interaction has recently been observed in a vanadium complex).[19] As a consequence of this interaction, the donation of the phosphorus lone pair to the vacant carbene orbital is reduced; this is apparent from the considerable lengthening of the PC bond (**3** *cis*: 1.76 Å, **3** *cis**: 1.84 Å).

The dominant bonding interactions in Fischer-type complexes **1–3**, arise from carbene→metal σ-donation, and metal→carbene π-back-donation[20,21] that competes with π-donation from the phosphino group[22] (Figure 3). As a result of its pronounced σ-donor character, the phosphinocarbene exerts a strong *trans* influence. Indeed, the Rh–L bonds *trans* to the carbene are significantly elongated rela-
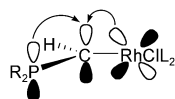

Figure 3. Schematic representation of the competition between the phosphorus lone pair donation and metal back-donation to the carbene vacant orbital.

tive to those in the *cis* positions (**1** *cis*: Rh–L$_{trans}$ 2.485 Å/ Rh–L$_{cis}$ 2.271 Å, **2** *cis*: Rh–L$_{trans}$ 2.449 Å/Rh–L$_{cis}$ 2.259 Å, **3** *cis*: Rh–L$_{trans}$ 2.007 Å/Rh–L$_{cis}$ 1.879 Å).

The geometric variations observed within the series of complexes **1–3** give further insight into the influence of the ligand L. As expected, major differences were found for the *cis* isomers, in which one of the L ligands is *trans* to the carbene. The PC and RhC bond lengths are very similar for L = C$_2$H$_4$ and PH$_3$ (**1** *cis*, **2** *cis*: PC 1.79–1.80 Å, RhC 1.88– 1.91 Å). However, for L = CO (**3** *cis*: PC 1.75 Å, RhC 1.97 Å), the PC bond is shorter, while the RhC bond is elongated. These changes are governed by the electronic properties of ligand L: the greater the π-acceptor, the lower the Rh→C$_{carbene}$ back-donation, and the greater the P→C$_{carbene}$ π-donation. The influence of these structural changes on the stability of these carbene complexes is apparent from their relative energies (Table 1). Indeed, the *trans* isomer is favored by 3–6 kcal/mol for ethylene and phosphine as co-ligands, while with carbon monoxide, the unusual structure **3** *cis** is about 6 kcal mol^{-1} more stable than **3** *trans* and **3** *cis*.

$[\eta^1$-{(H$_2$N)$_2$PCH}RhClL$_2]$ complexes: Calculations have already led us to emphasize the importance of amino substituents at phosphorus in phosphinocarbenes.[23] Therefore, analogous studies were carried out with (H$_2$N)$_2$PCH replacing the H$_2$PCH moiety. Geometric data and relative energies for complexes $[\eta^1$-{(H$_2$N)$_2$PCH}RhClL$_2]$ **4–6** are collected in Table 2.

The major structural differences, induced by the introduction of two amino substituents at the phosphorus atom, are observed on comparing **6** *cis* with **3** *cis* (L = CO). The PC bond length is much shorter, and the pyramidalization much less pronounced for the (H$_2$N)$_2$PCH relative to the H$_2$PCH coordinated carbenes. In fact, the structure of **6** *cis* is very similar to that observed experimentally for complex **B**.[9] The PC bond distance lies within the range that is typical for a PC double bond, while the phosphorus is in a trigonal planar environment. These data indicate that back-donation from the metal to the carbene center is negligible compared with the degree of donation from the phosphorus lone pair. Accordingly, the plot of the 2p$_\pi$(carbene)-centered molecular orbital of **6** *cis* revealed that the carbene vacant orbital interacts with the phosphorus lone pair, but not with metal-based orbitals (Figure 4).[24]

Interestingly the bonding situation is rather different in the related complexes **6** *trans* and **6** *cis**. The corresponding

Table 2. Geometrical parameters (bond lengths in Å and bond angles in degrees) and relative energies (kcal mol^{-1}, with zero-point vibration energy corrections) for the *trans* and *cis* isomers of the $[\eta^1\text{-}\{(H_2N)_2PCH\}RhClL_2]$ (L = C$_2$H$_4$, PH$_3$, CO) complexes **4–6**. Wiberg Bond Indices in brackets.

	P–C	Rh–C	∡ClRhCP	Σ∡C	Σ∡P	ΔE
(H$_2$N)$_2$PCH	1.622 (2.205)	/	/	/	360.0	/
$[\eta^1\text{-}\{(H_2N)_2PCH\}RhCl(C_2H_4)_2]$ **4 trans**	1.817 (1.109)	1.890 (1.159)	−167.4	356.6	315.9	−0.4
4 cis	1.774 (1.312)	1.909 (1.047)	−20.7	359.0	322.1	0
$[\eta^1\text{-}\{(H_2N)_2PCH\}RhCl(PH_3)_2]$ **5 trans**	1.821 (1.071)	1.894 (1.216)	−173.94	360.0	311.1	−8.7
5 cis	1.775 (1.299)	1.934 (0.960)	−26.8	358.8	324.0	0
$[\eta^1\text{-}\{(H_2N)_2PCH\}RhCl(CO)_2]$ **6 trans**	1.799 (1.156)	1.925 (1.097)	−177.27	359.6	317.5	12.4
6 cis	1.648 (1.812)	2.107 (0.445)	41.7	359.2	357.8	0
6 cis*	1.837 (0.999)	2.054 (0.514)	113.0	353.1	310.8	−2.2
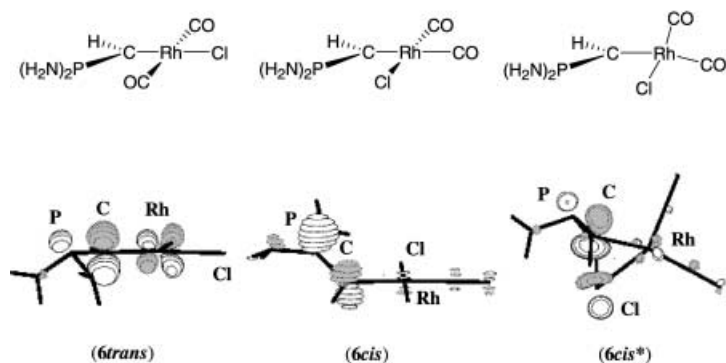
Figure 4. Plots of the $2p_\pi$(carbene)-centered molecular orbitals for structures **6 trans**, **6 cis** and **6 cis*** of complex $[\eta^1\text{-}\{(H_2N)_2PCH\}RhCl(CO)_2]$.

plots show that both phosphorus lone pair donation, and metal back-donation are involved in **6 trans**, while the carbene vacant orbital interacts with the chlorine and phosphorus lone pairs in **6 cis***. These results are corroborated by NBO population analyses, (see Supporting Information) that reveal the presence of either π_{PC} (**6 cis**), π_{CRh} (**6 trans**) or σ_{CCl} (**6 cis***) bonding interactions.

From an energetic point of view, the introduction of amino groups at phosphorus induces slightly larger energy discrepancies, except with ethylene as a co-ligand. For the strong donor ligand PH$_3$, **5 trans** is about 9 kcal mol^{-1} more stable than all the *cis* conformers, while for the strong acceptor ligand CO, the situation is completely reversed, and the *trans* isomer is approximately 12–14 kcal/mol higher in energy than all the corresponding *cis* conformers. These results demonstrate that the nature of the metal-bound ligands plays a crucial role in determining the structure of such rhodium(i) complexes.

To gain further insight into the influence of the carbene substituent, calculations were then carried out for related rhodium(i) complexes that feature the parent aminocarbene H$_2$NCH.

$[\eta^1\text{-}(H_2NCH)RhClL_2]$ complexes: Geometric data and relative energies for complexes $[\eta^1\text{-}(H_2NCH)RhClL_2]$ **7–9** are depicted and summarized in Table 3 (Figure 5). Whereas the phosphorus center was strongly pyramidalized in most of the phosphinocarbene complexes (except for **6 cis**), the nitrogen atom adopts a trigonal planar geometry in complexes **7–9**. This difference results from the lower inversion barrier of nitrogen relative to phosphorus, which leads to the higher π-donor ability of the amino relative to the phosphino group.[25] This hypothesis is corroborated by the N-C$_{carbene}$ bond distances (1.32–1.36 Å), which indicate a significant double-bond character (Wiberg bond indices for **7–9**: 1.4–1.6). The Rh-C$_{carbene}$ bond distances are slightly elongated in the aminocarbene (1.93–2.05 Å) relative to the phosphinocarbene (1.88–1.97 Å) complexes. Lastly, the absence of Cl→C$_{carbene}$ interaction in **9 cis*** is indicated by the long C-Cl distance (2.82 Å) relative to that observed in the related phosphinocarbene complexes (**3 cis***: 1.93 Å, **6 cis***: 1.96 Å).

The ligand L has only a slight effect on the structures of the aminocarbene complexes **7–9**, relative to that for the related phosphinocarbene complexes **1–3**. This is illustrated by the variations in the Wiberg bond indices for the Rh–C$_{carbene}$ bond (amino: 0.60→0.97, phosphino: 0.51→1.19), and E–C$_{carbene}$ bond (E=N: 1.39→1.63, E=P: 1.07 → 1.45). Irrespective of the electronic properties of the ligands L, back-donation from the metal center does not compete with the strong π-donation from the amino group. Accordingly, the NBO population analyses reveal the presence of π_{NC}, but not π_{CRh} interactions.

Table 3. Geometrical parameters (bond lengths in Å and bond angles in degrees) and relative energies (kcal mol^{-1}, with zero-point vibration energy corrections) for the *trans* and *cis* isomers of the $[\eta^1\text{-}(H_2NCH)RhClL_2]$ (L = C$_2$H$_4$, PH$_3$, CO) complexes **7–9** (Figure 5). Wiberg bond indices are in brackets.

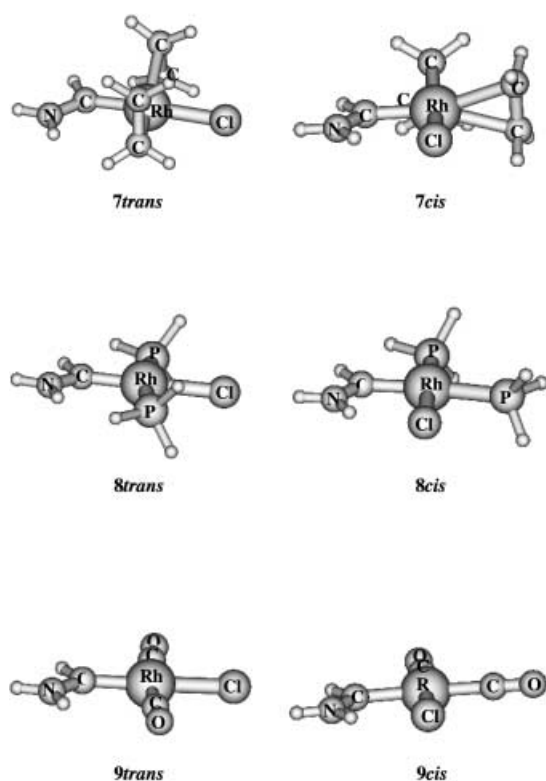|	N–C	Rh–C	∡ClRhCN	Σ∡C	Σ∡N	ΔE
H$_2$NCH	1.339 (1.570)	/	/	/	360.0	/
7 trans	1.352 (1.422)	1.927 (0.901)	−175.48	360.0	360.0	3.2
7 cis	1.330 (1.568)	1.973 (0.813)	0.78	360.0	360.0	0
8 trans	1.359 (1.387)	1.928 (0.975)	175.7	360.0	360.0	1.8
8 cis	1.335 (1.541)	1.982 (0.782)	0.43	360.0	360.0	0
9 trans	1.347 (1.451)	1.962 (0.868)	−164.4	360.0	360.0	9.5
9 cis	1.321 (1.632)	2.053 (0.597)	0.0	360.0	360.0	0
9 cis*	1.327 (1.565)	2.030 (0.559)	106.0	359.6	359.7	4.2

Figure 5. Structures of the *trans* and *cis* energy minima for the complexes [η^1-(H$_2$NCH)RhCl(C$_2$H$_4$)$_2$] (**7**), [η^1-(H$_2$NCH)RhCl(PH$_3$)$_2$] (**8**) and [η^1-(H$_2$NCH)RhCl(CO)$_2$] (**9**).

[η^2-(R$_2$PCH)RhClL$_2$] and [η^2-(H$_2$NCH)RhClL$_2$] complexes: In the η^1-complexes described above, the phosphino- and aminocarbenes act as two-electron donors that afford 16-electron [η^1-(carbene)RhClL$_2$] complexes. Due to the presence of the heteroatom lone pair in the α position to the carbene center, these carbenes can also act as four-electron donors, which result in 18-electron [η^2-(carbene)RhClL$_2$] complexes (Figure 6). The influence of both the carbene and the ligands L on such a coordination mode has been studied computationally.
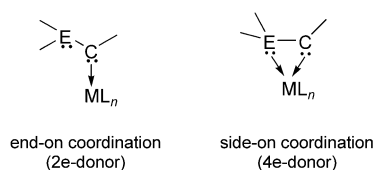

Figure 6. Schematic representations of the end-on and side-on coordination modes for amino- and phosphinocarbenes.

Irrespective of the phosphinocarbene [H$_2$PCH or (H$_2$N)$_2$PCH], or the ligand L (C$_2$H$_4$, PH$_3$ or CO), only a single energy minimum could be located in each case. The geometric data and relative energies of all of the resulting complexes **10–15** are collected in Table 4. The structures of complexes **10–12** (H$_2$PCH) and **16–18** (H$_2$NCH) are shown in Figure 7

The four ligands (carbene, Cl, and two L) adopt a slightly distorted tetrahedral arrangement around the rhodium

center.[26] The PC$_{carbene}$ and RhCl bonds are *anti*-periplanar in the ethylene complexes **10** and **13**, but almost perpendicular in the phosphine and carbon monoxide complexes **11**, **12**, **14**, and **15**. The other geometric data for all of these η^2-complexes are very similar. The PC and RhC bond lengths (PC: 1.74→1.78 Å, RhC: 1.86→1.93 Å) are at the lower limit of those observed for the corresponding η^1-complexes **1–6** (PC: 1.75→1.84 Å, RhC: 1.88 → 2.11 Å). The RhP bond lengths (2.30→2.40 Å) are in the range of those observed for Rh–PH$_3$ bonds, and are thus consistent with dative bonds. These data, as a whole, are in good agreement with those observed experimentally.[27]

From an energetic point of view, all of the 18-electron η^2-PC complexes **10–15** are only slightly higher in energy than the corresponding 16-electron η^1-complexes **1–6** (the *cis* isomer as a reference). The η^1-coordination mode is favored by 12–15 kcal mol^{-1} with ethylene and carbon monoxide, but by only 1–2 kcal mol^{-1} with phosphine as a coligand. The influence of the ligand L is easily rationalized, since the presence of strong σ-donor phosphines on the metal increases the back-donation from the metal to the carbene, and consequently reduces the P→C$_{carbene}$ π-interaction. As a result, the phosphorus lone pair is more "available" for direct coordination to the rhodium center, hence the η^2-complex is energetically more favorable than those formed with other L ligands.

The related η^2-(aminocarbene) complexes **16–18** also adopt tetrahedral geometries (Table 4). The NC bond lengths are significantly longer than those of the corresponding η^1-complexes **7–9**, lying in the range typical for single bonds. In contrast, the RhC$_{carbene}$ bonds of **16–18** are significantly shortened relative to those of **7–9**, and clearly feature some double-bond character (Wiberg bond indices: 1.16→1.32). Lastly, the RhN bond lengths (2.25–2.38 Å) are rather long.

Energetic considerations clearly highlight differences between the phosphino- and aminocarbene η^2-complexes. Indeed, the η^1-coordination mode is considerably more favored for the aminocarbene, the related η^2-structure is more than 40 kcal mol^{-1} higher in energy (Table 4). This noticeable difference between these two types of carbene probably results from both steric and electronic factors. Although phosphorus has a greater ability to accommodate small bond angles than nitrogen,[28] the greater strain of the nitrogen-containing three-membered rings can only partly explain such a difference in behavior. The major factor is again the higher π-donor ability of nitrogen relative to phosphorus.[25] This is apparent in the NBO population analyses that reveal the presence of π_{NC} interactions for all aminocarbene η^1-complexes **7–9**, while π_{PC} bonding is only observed for the phosphinocarbene η^1-complex **6**. As a result, the N→C$_{carbene}$ π-donation (η^1-complexes) is more favored than the N→Rh σ-donation (η^2-complexes), while both interactions are of similar strength for phosphorus.

These results demonstrate the propensity of phosphinocarbenes to act as two- as well as four-electron donors, while only η^1-coordination is strongly favored for aminocarbenes, in agreement with experimental data. Indeed, the η^2-coordination mode has only been observed in the case of acyclic

Table 4. Geometrical parameters (bond lengths in Å and bond angles in degrees) for the $[\eta^2\text{-}(R_2PCH)RhClL_2]$ (R = H, NH$_2$; L = C$_2$H$_4$, PH$_3$, CO) complexes **10–15**, and for the $[\eta^2\text{-}(H_2NCH)RhClL_2]$ (L = C$_2$H$_4$, PH$_3$, CO) complexes **16–18** (Figure 7). Wiberg bond indices in brackets. ΔE: energy difference (kcal mol^{-1}, with zero-point vibration energy corrections) between the η^2 complex and the corresponding η^1-complex (*cis* isomer as a reference).

	P–C	Rh–C	P–Rh	∡ClRhCP	Σ∡C	ΔE
10	1.780 (*1.182*)	1.861 (1.192)	2.392 (0.360)	−179.9	360.0	14.4
11	1.769 (1.225)	1.879 (1.078)	2.406 (0.323)	76.0	359.9	1.9
12	1.761 (1.234)	1.896 (1.015)	2.382 (0.347)	78.0	360.0	12.8
13	1.749 (1.158)	1.890 (1.120)	2.314 (0.467)	−177.4	359.9	11.9
14	1.744 (1.210)	1.908 (1.028)	2.315 (0.426)	75.8	359.9	1.4
15	1.741 (1.204)	1.926 (0.964)	2.305 (0.430)	72.8	360.0	13.0

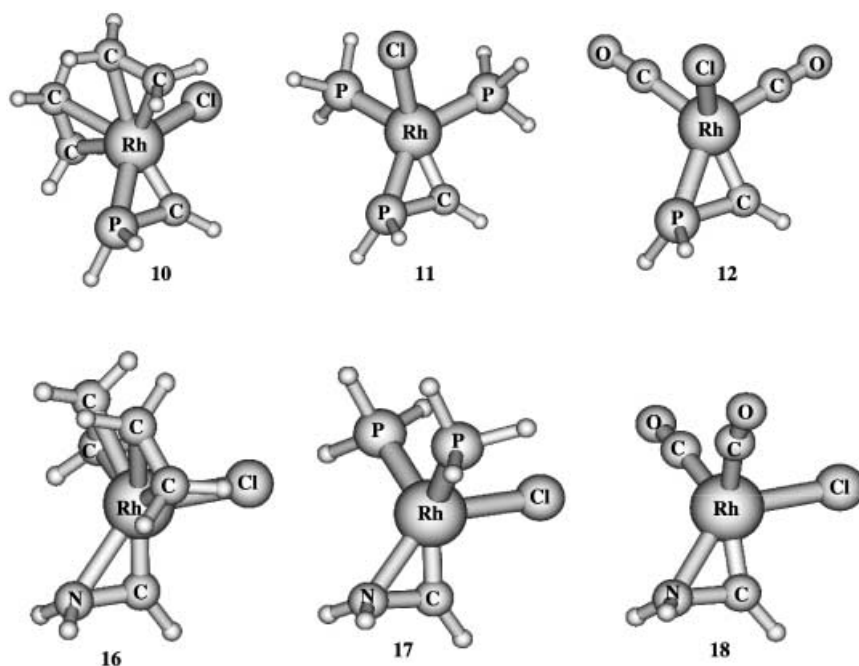|	N–C	Rh–C	N–Rh	∡ClRhCN	Σ∡C	ΔE
16	1.442 (1.058)	1.806 (1.324)	2.381 (0.202)	−179.7	360.0	42.9
17	1.439 (1.080)	1.813 (1.232)	2.282 (0.237)	−179.7	360.0	40.0
18	1.433 (1.092)	1.822 (1.157)	2.250 (0.239)	−179.8	360.0	50.0

Figure 7. Structures of the η^2-complexes of (H$_2$PCH) **10-12** and of (H$_2$NCH) **16-18**.

di(amino)carbenes,[11] in which one amino group is engaged in π-donation to the carbene center, which leaves the other available for coordination to the transition metal center.

Bonding energies of the [η^1- and η^2-(carbene)RhClL$_2$] complexes: The propensity of phosphino- and aminocarbenes to split the chloride bridges of $[Rh(\mu\text{-}Cl)L_2]_2$, and to coordinate to the resulting RhClL$_2$ fragments have been investigated quantitatively by determining the energy balance (ΔE_1) for reaction 1 in Table 5. For all the phosphino- and aminocarbene η^1-complexes, the bonding energies are calculated to be negative and very similar ($-25 \rightarrow -33$ and $-33 \rightarrow -37$ kcal mol^{-1}, respectively). The situation is rather different for the η^2-complexes. Irrespective of the nature of the ligand L, the aminocarbene is reluctant to adopt the η^2-coordination mode, as shown by the positive energy balances predicted for **16–18**. In contrast, negative ΔE_1 values are obtained for all of the η^2-(phosphinocarbene) complexes **10–15**. This coordination mode is favored by donor ligands L,

since the bonding energies are approximately twice as large for L = phosphine (ca. −30 kcal mol^{-1}) as for L = ethylene and carbon monoxide (ca. − 15 kcal mol^{-1}).

Conclusion

These results as a whole demonstrate the propensity of phosphinocarbenes to adopt various bonding modes to transition-metal centers. For [(η^1-carbene)RhClL$_2$] complexes, several bonding situations that result in important structural modifications were predicted to occur by simply varying the nature of the co-ligands L. When L is carbon monoxide, a somewhat unusual coordination mode was observed, in which there is a significant intramolecular Cl→C$_{carbene}$ interaction. For the related η^2-complexes, striking differences were predicted between phosphino- and aminocarbenes. Indeed, calculations revealed that phosphinocarbenes are much more prone to act as four-electron donors than

Table 5. Bonding energies ΔE_1 in kcal mol^{-1}, with zero-point vibration energy corrections.[a]

Compound	δ_1	Compound	δ_1
1 *cis*	−30.1	**14**	−27.8
10	−15.7	**6** *cis*	−29.6
2 *cis*	−32.7	**15**	−16.6
11	−30.8	**7** *cis*	−33.5
3 *cis*	−29.0	**16**	9.5
12	−16.2	**8** *cis*	−37.3
4 *cis*	−24.6	**17**	2.7
13	−12.8	**9** *cis*	−37.0
5 *cis*	−29.2	**18**	13.0

[a] carbene + ½ dimer → complex + ΔE_1 (1) $\Delta E_1 = E_{complex} - E_{carbene} - ½ E_{dimer}$

aminocarbenes. The higher structural flexibility of phosphino- compared with aminocarbenes has been attributed to the weaker π-donor character of the carbene phosphino substituent, and the higher ability of phosphorus to accommodate small bond angles. These properties should be of major importance for the stabilization of coordinatively, and/or electronically unsaturated catalyst "resting states" and thus, phosphinocarbenes may very well find applications as ligands for transition-metal-based catalysis.

Acknowledgement

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