Bonding aspects of P-heterocyclic carbene transition metal complexes. A computational assessment

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Abstract

Gradient-corrected (BP86) density-functional calculations were used to study the chemical bond between transition-metal complexes and N- and P-heterocyclic carbenes EHC (EHC = imidazolin-2-ylidene; 1,3-dimethylimidazolin-2-ylidene; 1,3-dihydro-1,3-diphosphol-2-ylidene; 1,3-dimethyl-1,3-diphosphol-2-ylidene). Forty two complexes of the type $[M] \leftarrow EHC$, $[M] = CuCl$, $AgCl$, $AuCl$, $BeCl^+$, Cu^+, Ag^+, Au^+, have been studied. Both electrostatic contributions as well as π-back-donation are of special importance for the $[M] \leftarrow EHC$ bond. The metal–ligand bond strengths are comparable for NHC and PHC complexes. Whereas the former undergo stronger electrostatic interactions, the latter show a higher degree of π-bonding. When considering NHC and PHC as ligands for transition-metal-based catalysts, the results of the present study suggest that PHC both compete with NHC – in terms of metal-to-ligand bond strength – as well as complement NHC – in terms of the nature of the metal–ligand bond.
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1. Introduction

With the isolation of a stable cyclic diamino carbene in the form of an imidazol-2-ylidene derivative [1], and with subsequent generalization of the structural motif and extension of this new class of compounds [2], Arduengo and co-workers [3] have brought to conclusion Wanzlick's quest for stable carbenes actively pursued during the 1960s. This work has revived an area of chemical research that has received growing attention over the last 10 years [4]. Soon after the initial report of the first N-heterocyclic carbenes (NHC), syntheses and characterizations of two-coordinate homoleptic bis-NHC adducts of gold [5], silver, copper [6], nickel and platinum [7] were described, and in the years following the extended and successful use of NHC ligands in

transition-metal (TM) chemistry introduced a new and powerful concept in organometallic catalysis [8–10].

Although the majority of catalytic processes that utilize TM-NHC complexes are based on transition metals from groups 8, 9 and 10, linear coinage-metal-NHC compounds have been successfully employed in catalytic transformations as well [11,12], and the synthesis and structural characterization of N-heterocyclic gold(I) complexes has recently been reported [13–15]. The synthesis, structure and reactivity of silver(I) N-heterocyclic carbenes is the topic of a current review article [16].

A detailed understanding of the salient features of the TM–NHC bond is key to rational catalyst design, the important features being thermochemistry as well as the nature of the chemical bond. With respect to the first aspect, quantum chemical computations often provide good approximations for bond strength values, but it is the experimental determination of thermodynamic properties that results in definite and unquestionable values. With respect to the second aspect, information on type and

characteristic of chemical bonding is primarily obtained from theoretical analyses, but experimental charge-density studies provide valuable insights into the nature of the chemical bond.

When it comes to thermodynamics of the TM–NHC bond, calorimetric studies of Cp*RuCl complexes [17] and a detailed steric and electronic investigation of (NHC)Ni(CO)$_3$ complexes [18] led to an assessment of TM–NHC bond energies, and these results allowed a direct comparison between the N-heterocyclic carbene ligand and classical phosphines. Taking into consideration the strength of the M–L bond, it was found that bonds to NHC ligands are slightly stronger than those to tertiary phosphines. A theoretical investigation of a number of Cr(CO)$_5$L complexes is in line with the experimental results, and the nucleophilicity of the ligand L decreases when going from amino carbenes to tertiary phosphines [19]. The nature of the chemical bond in Cr(CO)$_5$NHC complexes has also been the subject of a combined experimental and theoretical charge-density study, in which the extent of electron delocalization was investigated [20].

The seminal theoretical studies of N-heterocyclic carbenes that appeared five years after Arduengo's initial report dealt with the issues of charge distributions and aromaticity [21,22], and supported the general picture of bonding properties of the NHC ligand that evolved during the first years of TM-NHC chemistry. Imidazol-2-ylidene binds to a transition metal center through σ-donation only [23], a notion that was further corroborated by calculations on TM complexes of the type ClM ← NHC, M = Cu, Ag, Au [24]. However, a significant amount of π-interaction between group 11 metals and NHC ligands was recently proposed on the basis of structural data [25,26]. This proposal was further supported in theoretical calculations and the π-back-bonding interactions for a diaminocarbene model compound was estimated to contribute to approximately 15–30% of the complexes overall orbital interaction energy [27]. In a newly computational study, in which the bonding in ClM ← (NHC) complexes is reinvestigated [28], Frenking and co-workers estimate that the orbital interaction part of the bonding has about 20% π back-bonding, but they carry the bond analysis one step further. The authors state that the metal–carbene bonds are mainly held together by classical electrostatic attraction, which contributes at least to 65% of the binding interactions.

The unusual stability of NHC compounds as well as their bonding properties as ligands in TM complexes are in part due to the ability of nitrogen to act as a π-donor, which decreases the electron deficiency at the adjacent carbene center. This observation together with the notion that the inherent π-donor capabilities of the heavier elements are as large or even larger than their second row homologues [29] renewed interest in phosphorus stabilized carbenes in general, and in P-heterocyclic carbenes (PHC) in particular. PHC complexes are interesting candidates to compete with or complement NHC as ligands for organometallic catalysis.

The ongoing search for phosphorous stabilized carbenes is supported by theoretical calculations, which not only provide insight into the chemical bonding of these hitherto unknown compounds, but which also suggest design strategies and identify desirable structural elements [30–34]. A major step was made when stable amino(phosphino) carbenes (**I**) could be isolated and characterized [35]. This work lead to the conclusion that a carbene moiety has to be considered as an ordinary functional group. Ligand properties of phosphino carbenes have been investigated in a computational study and this new class of ligands displays a high degree of structural versatility when compared to aminocarbenes, which in turn might be utilized in tuning the properties and reactivity of carbene TM complexes [36]. A stable P-heterocyclic carbene (**II**) has lately been reported by Bertrand and co-workers [37]. The authors not only describe the synthesis and crystal structure of this new stable class of carbenes, but also discuss different rhodium complexes formed with this new type of heterocyclic carbene.
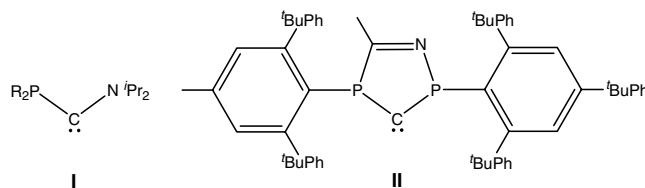
In the present work, we will examine the nature of PHC-M complexes compared to their nitrogen homologues. The emphasis will be on a *qualitative* assessment of the nature of the [M] ← PHC bond, rather than on highly accurate, *quantitative* determination of bond energy values. Density-functional theory (DFT) in combination with suitable bond analysis schemes constitutes the method of choice when establishment of trends in chemical bonding is sought, and we will present a concise account of our theoretical approach before discussing our findings in detail.

2. Computational methodology

2.1. General procedure

Gradient-corrected density-functional calculations were based on the local density approximation with Slater exchange [38] and treatment of correlation according to Vosko et al. [39]. Gradient corrections for exchange and correlation were those proposed by Becke [40] and Perdew [41], respectively. All calculations have been performed with the Amsterdam Density Functional suite of programs, ADF version 2004.01 [42–45]. The valence electrons of Au, Ag, Cu and Be were described with ADF basis set V (triple-ζ STO plus two polarization functions), and for remaining atoms ADF basis set IV (triple-ζ STO plus one polarization function) was chosen. Electrons of the core shells (1s2s2p3s3p3d4s4p4d4f for Au, 1s2s2p3s3p3d for Ag;

1s2s2p for Cu, P; 1s for N, C, Be) have been treated within the frozen core approximation. For compounds containing elements of periods 5 or 6, relativistic effects have been incorporated based on the zero-order regular approximation [46,47].

2.2. Bond analysis

We analyze the bonding energy in $[M] \leftarrow$ PHC and $[M] \leftarrow$ PHC complexes according to the general energy decomposition scheme for the study of metal–ligand interactions as devised by Ziegler [48]. Here, we consider the interaction of two fragments [M] and NHC or PHC, respectively, which both posses the local equilibrium geometry of the final molecule, and which both have an electronic structure suitable for bond formation. The energy associated with this process is referred to as the bond snapping energy, BE_{snap} [49]. Although the bond snapping energy, BE_{snap}, does not always correlates with bond dissociation enthalpies, since reorganization and relaxation of the fragments are not taken into account, the bond snapping energy, BE_{snap}, is closely related to bond enthalpy terms, which in turn provide a good approximation to bond strength values [50].

The bond snapping energy, BE_{snap}, can be decomposed into two main components, namely steric interaction ΔE^0 and the orbital interaction ΔE_{int}:

$$BE_{snap} = -[\Delta E^0 + \Delta E_{int}]. \tag{1}$$

The steric interaction term ΔE^0 can further be split into an electrostatic interaction term ΔE_{elstat} and a Pauli repulsion term ΔE^{Pauli}, which is directly related to the two-orbital three or four electron interactions between occupied orbitals on both interacting fragments

$$\Delta E^0 = \Delta E_{elstat} + \Delta E^{Pauli}, \tag{2}$$

whereas ΔE_{elstat} constitutes a stabilizing contribution to BE_{snap}, ΔE^{Pauli} constitutes a destabilizing contribution, and it is the relative size of electrostatic interaction and Pauli repulsion that determines the overall character of the steric interaction term. The important contribution of electrostatic interaction for chemical bonding becomes evident in cases where ΔE^0 represents an attractive, rather than a repulsive, interaction, and other partitioning schemes have been suggested to more clearly emphasize the relative importance of ΔE_{elstat} [28,51]. However, we shall adapt the partitioning scheme as outlined in Eq. (1), and we refer the reader to the literature for a detailed discussion of the energy decomposition analysis employed in the present work [52].

3. Results and discussion

We have optimized the geometries of six heterocyclic carbenes EHC, E = N, P, of 36 transition-metal carbene complexes $[TM] \leftarrow$ EHC, $[TM]$ = CuCl, AgCl, AuCl, Cu^+, Ag^+, Au^+, and of six main group metal carbene adducts $[M] \leftarrow$ EHC, $[M] = BeCl^+$ (Scheme 1).
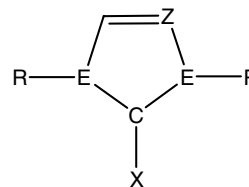
Scheme 1.

The labeling scheme for the investigated compounds is summarized in Table 1. On occasion and when the context remains clear, we will refer to carbenes **1** to **6** as [NH], [NMe], [PH], [PMe], [P′H] and [P′Me], respectively. Compounds containing carbenes **1** and **2** adopt C_{2v} symmetry, whereas compounds containing carbenes **3** and **4** adopt C_2 symmetry.

The cationic coinage-metal complexes have been included in the present study, since such compounds are likely to represent the active species in catalytic carbene transfer reactions [12]. Beryllium complexes have been investigated before as model for carbenes that act as pure σ-donor ligands [53]. In this work, the bonding situation in beryllium-carbene complexes such as $[BeCl(CH_2)]^+$ has been analyzed [53], and it was concluded that the dominant factor which determines the chemical stability of carbenes and carbene complexes is the population of the carbon $p(\pi)$ orbital. This stabilizing interaction can either be provided internally by conjugative π-interaction between the carbenic carbon atom and adjacent heteroatoms such as nitrogen, or externally by π-back-donation from a TM center in case of carbene complexes. The question arises how PHC compounds compare to the well known NHC compounds in terms of internal and external π-stabilization of the carbenic C-atom. Furthermore, the synthesis and structure of the ionic beryllium-carbene complex [BeCl$(2)_3$]$^+$ has been reported [54]. The large charge-to-radius ratio makes beryllium one of the hardest known Lewis acids, and the authors point out that the character of its compounds is mainly influenced by this property. Thus, the interaction of NHC and PHC compounds with the $[BeCl]^+$ fragment serves as a prototypical test case for evaluation of the relative importance of electrostatic inte-ractions.

Table 1
Labeling scheme for the compounds studied

	E = N, Z = CH		E = P, Z = CH		E = P, Z = N	
	R = H	R = Me	R = H	R = Me	R = H	R = Me
X = None	**1**	**2**	**3**	**4**	**5**	**6**
X = CuCl	**1a**	**2a**	**3a**	**4a**	**5a**	**6a**
X = AgCl	**1b**	**2b**	**3b**	**4b**	**5b**	**6b**
X = AuCl	**1c**	**2c**	**3c**	**4c**	**5c**	**6c**
X = Cu$^+$	**1d**	**2d**	**3d**	**4d**	**5d**	**6d**
X = Ag$^+$	**1e**	**2e**	**3e**	**4e**	**5e**	**6e**
X = Au$^+$	**1f**	**2f**	**3f**	**4f**	**5f**	**6f**
X = BeCl$^+$	**1g**	**2g**	**3g**	**4g**	**5g**	**6g**

3.1. Electronic structure of NHC and PHC

The electronic structure of carbene complexes in general, and of NHC and PHC compounds in particular is well understood; N- and P-heterocyclic carbenes possess singlet ground states [21,22,30,37,55,56]. A molecular orbital (MO) analysis based on Kohn–Sham (KS) orbitals provides valuable insight into the electronic structure of heterocyclic carbenes. KS-orbitals derived from DF calculations are often successfully employed in a qualitative manner in MO arguments, and it has been convincingly argued that these seem to be the orbitals a qualitative, chemical analysis needs [57]. We refer the reader to the literature for a detailed assessment of the properties of KS-orbitals in comparison to orbitals derived from other theoretical approaches [58].

The frontier KS-orbital diagram depicted in Fig. 1 shows shape and relative energies orbitals of carbenes **1**, **3**, and **5** relevant for interaction with transition-metal fragments thus for possible external π-stabilization.

The HOMO (1a$_1$ for **1**, 1a for **3**, 3a for **5**) is suitable for bond formation with a TM fragment via σ-donation. The interaction of the empty carbenoid p-orbital with occupied p-orbitals at the adjacent heteroatoms results in an E–C–E bonding and occupied π-orbital responsible for carbenic stabilization (1b$_1$ for **1**, 1b for **3** 1a for **5**) and in an E–C–E antibonding and empty π-orbital available for back-donation (2b$_1$ for **1**, 2b for **3** 4a for **5**). This E–C interaction is stronger for nitrogen as it is for phosphorus, and the antibonding orbitals for **3** and **5** are at lower energies than their nitrogen based counterpart in **1**. As a result, the HOMO–LUMO gap decreases from 4.9 to 2.6 eV when going from NHC to PHC compounds. Whereas for **3** and **5** the orbitals 2b and 4a represent the LUMO, the LUMO for **1** is orbital 1a$_2$, and antibonding π-orbital with no contributions from the carbenic carbon. However, the orbital 2b$_1$ represents the LUMO + 1 and is close in energy to 1a$_2$. Whereas for **1** and **3** the orbitals 1b$_1$ and 1b correspond to the HOMO − 1, the orbital 1a of complex **5** is to be classified as HOMO − 2. Here, the HOMO − 1 is a nitrogen lone pair orbital. As observed for the orbital pair LUMO/LUMO + 1, the HOMO − 2 too is close in energy to the HOMO − 1 so that the qualitative frontier orbital picture is comparable for all three carbenes **1**, **3**, and **5**. We further note that the relative energy of the HOMO decreases by about 1 eV, when going from N- to the P-heterocyclic carbenes. The general trends outlined for carbenes **1**, **3**, and **5** apply to other, related carbenes as well. The key point of this brief frontier orbital analysis is the fact that P-heterocyclic carbenes have orbitals ready for π-back-bonding at lower energies, and in cases where π-back-dona-tion is of importance for the [M]–EHC bond we might expect that PHC undergo a stronger π-type interaction than NHC. This observation is paralleled by the change in singlet–triplet (ST) separation when going from NHC to PHC systems. It has been reported that the ST-gap drops from 331 kJ/mol for compound **1** to only 88 kJ/mol for compound **3** [37].
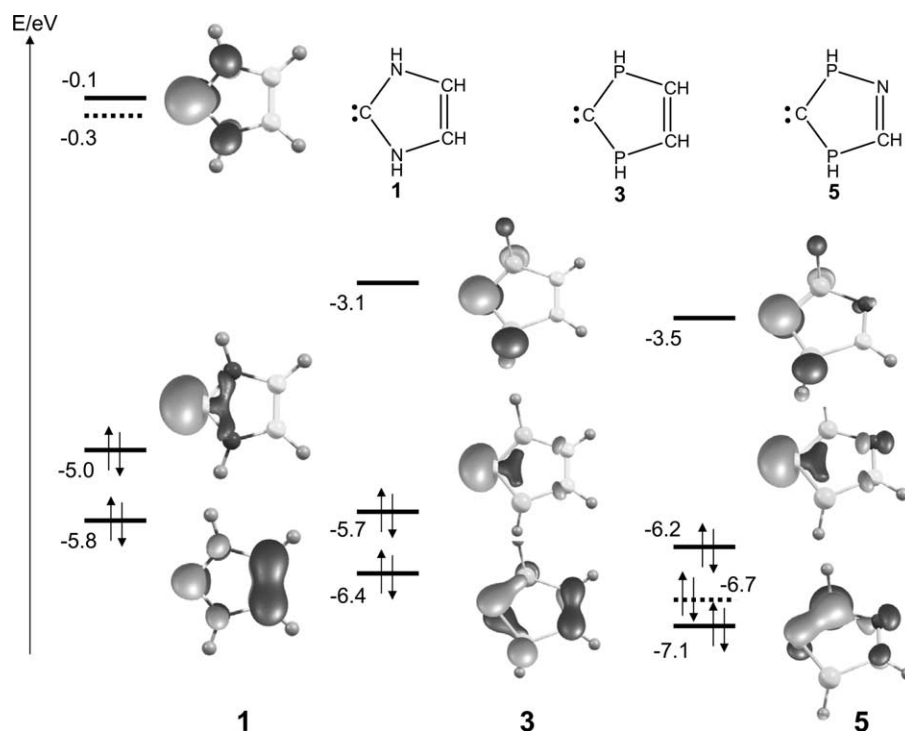

Fig. 1. Frontier KS-orbital diagram for carbenes **1**, **3**, and **5**. For energy levels drawn as broken lines, no corresponding pictorial representation of the orbital is given.

3.2. Geometries

Representative geometries for complexes **1c**, **4f**, and for carbene **6** are displayed in Fig. 2 and illustrate the characteristic features of heterocyclic carbenes and of [M]–NHC and [M]–PHC complexes.

As already mentioned, [M]–NHC complexes as well as the NHC ligands **1** and **2** adopt C_{2v} symmetry with planar coordination around nitrogen, whereas PHC carbenes **3** and **4** and their [M]–PHC complexes adopt C_2 symmetry, with pyramidalization of the phosphorus atoms and a slight tilting of the five-membered ring. For carbene **4**, the non-planar geometry around phosphorus has been explained in the theoretical study by Schoeller and co-workers, who trace this effect to the strong tendency for pyramidalization of trigonal phosphorus, which is in part due to the fact that phosphorus has a tendency to suffer from orbital non-hybridazation [34]. Two geometric arrangements possessing pyramidal P-atoms are conceivable, one structure displaying *anti*-pyramidalization and adopting C_2 symmetry, the other displaying *syn*-pyramidalization and adopt-

ing C_s symmetry. Schoeller and co-workers found that the singlet ground states are characterized by *anti*-pyramidalization and C_2 symmetry. All structures of PHC complexes investigated in this work display five-membered heterocyclic rings with *anti*-pyramidalization.

The structure of carbene **6** features two different phosphorus atoms with different degree of pyramidalization, a structural element that is also found for the related carbene **5**. We refer to the two different P-atoms adjacent to a double-bond carbon and to nitrogen as P_C and P_N, respectively. The sum of the three bond angles around the phosphorus atom $\sum\theta_P$ is often taken as measure for pyramidalization. The distinct pyramidalization of the two different phosphorus centers is a prominent feature of carbene **II**, and DFT calculations on this compound as well as on related model compounds **IIa** and **IIb** reveal the structural elements that determine the distortion from planarity [37]. The results for different PHC are collected in Fig. 3.

As argued before, $\sum\theta_P$ increases significantly as the steric demand of the substituents at the phosphorus atom increases. This in turn has implications for the electronic structure of the heterocyclic carbenes. Stronger pyramidalization around P causes a larger singlet–triplet energy gap as well as an increase of the HOMO orbital energies [37]. We note that the P_N atoms have the stronger tendency for pyramidalization.

The most significant geometric parameter for $[M] \leftarrow$ EHC complexes is the $C_{carbene}$ to M_{TM} bond distance d_{CTM}, and optimized bond length values for complexes under investigation have been compiled in Fig. 4.

The cationic beryllium complexes form by far the shortest metal to ligand bonds, and the bond-lengths for complexes of group 11 metals follow the expected trend $Cu < Au < Ag$, a manifestation of relativistic bond-length contraction [59]. For complexes of copper and gold, we find that the cationic complexes display slightly shorter bond-lengths d, whereas for the silver compounds, the opposite trend is observed. As we shall see, all cationic complexes form stronger $TM^+ \leftarrow$ EHC bonds than their neutral ClTM $\leftarrow$ EHC counterparts, and for the cationic silver complexes, the presumption that shorter bonds are
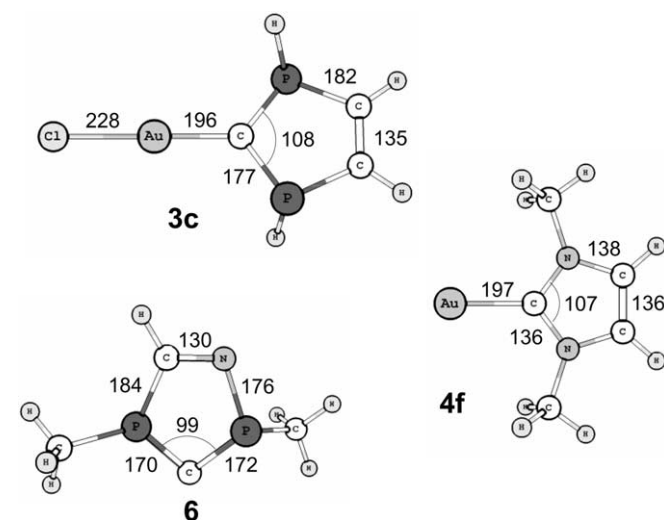

Fig. 2. Optimized BP86 geometries for compounds **3c**, **4f**, and **6**. Selected bond distances and bond angles are given in pm and degree, respectively.
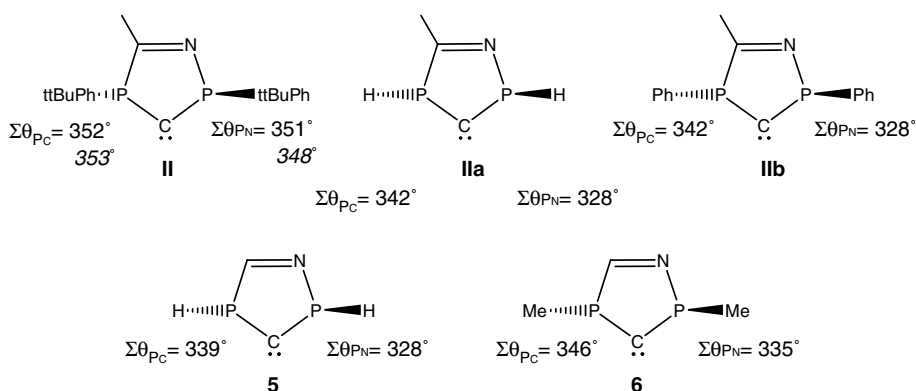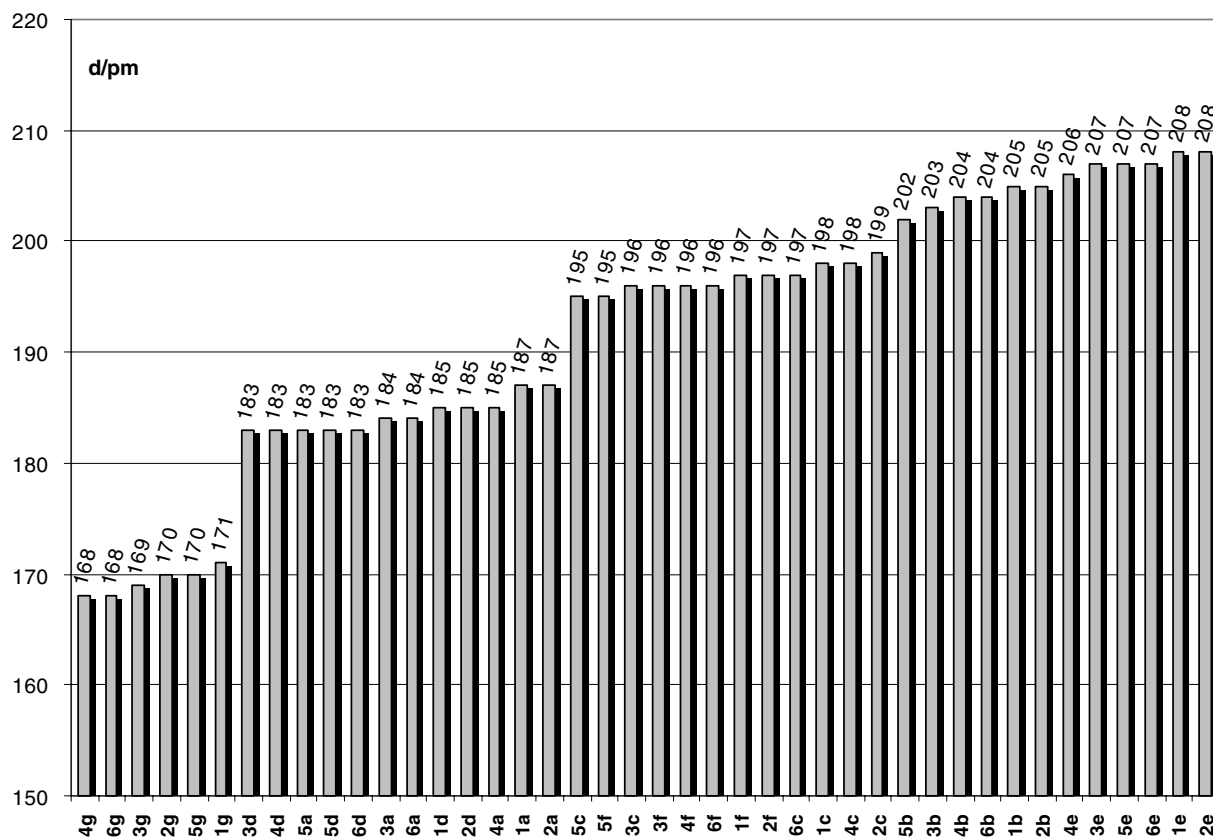

Fig. 3. *Anti*-pyramidalization for P-heterocyclic carbenes (DFT and experimental values (in *italics*) for **II**, **IIa**, **IIb** from Ref. [37]).

Fig. 4. Bond distances d_{CTM} (in pm) for optimized $[M] \leftarrow$ EHC complexes.

stronger bonds – at the heart of many interpretations of molecular structure – does not seem applicable. For certain transition metal complexes, experimental results clearly suggesting that longer bonds can indeed be stronger bonds have been reported [60], and the phenomenon of breakdown of bond length–bond strength correlation has been theoretically analyzed [61]. Since an in-depth analysis of this interesting fact is out of the scope of the present work, we refer the reader to the literature for further details. We point out that a similar trend was found for related phosphine complexes M^+-PR_3 and ClM-PR_3 (M = Ag, Au; R = H, Me) [62].

We conclude this section with a brief comparison of calculated bond distances with data obtained from crystal structure determination for selected compounds, as well as with optimized geometries from selected previous computational studies. The relevant data are presented in Table 2.

The calculations by Frenking and co-workers on complexes **1a**, **1b**, **1c** also utilize the BP86 functional, but use a triple-ζ STO basis augemented by two polarization functions as well as relativistic corrections throughout, and do not employ a frozen core. As a result, the Cu–C and Cu–Cl distances reported by Frenking and coworkers [28] are about 3 pm shorter, whereas for silver and gold complexes

Table 2
Bond lengths (in pm) for ClM-NHC complexes (Scheme 1: X = ClM, E = N, Z = CH; M = Cu, Ag, Au) from experiment and theory

| | BP86 | | | B3LYP | X-ray | |
	R = H[a]	R = H[b]	R = Me[b]	R = Me[c]	R = 2,6-(iPr)$_2$C$_6$H$_3$	R = Mesithyl
d(Cu–C)	184.3	187	187	–	188.1(7)[d]	–
d(Cu–Cl)	207.7	210	210	–	210.6(2)[d]	–
d(Ag–C)	205.6	205	205	211.7	–	205.6(7)[e]
d(Ag–Cl)	229.0	229	229	239.3	–	231.4(2)[e]
d(Au–C)	205.6	198	199	–	194.2(3)[e]	–
d(Au–Cl)	227.5	228	229	–	226.98(11)[e]	–

[a] Ref. [28].
[b] This work.
[c] Ref. [63].
[d] Ref. [64].
[e] Ref. [15].

both sets of BP86 calculations essentially result in same bond distances. Bond distances obtained from B3LYP calculations [63] for complex **1e** are significantly longer than the BP86 values. Our calculations are in good agreement with experimental data for copper and silver complexes. For the gold complexes, we find a larger deviation in the metal–ligand separation, but a good agreement for the Au–Cl distance. This comparison of structural data for NHC complexes suggests that the chosen computational approach can be expected to yield reliable results for PHC complexes as well.

3.3. Bond energy analysis

For the model complexes studied in this work, bond snapping energies, BE_{snap}, have been obtained based on the bond forming reaction between a transition metal fragment [M] and a heterocyclic carbene EHC

$$[M] + EHC \rightarrow [M] \leftarrow EHC. \qquad (3)$$
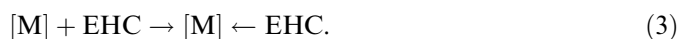
In order to facilitate the bond energy analysis, a graphical comparison of BE_{snap} values is given in Fig. 5.

From Fig. 5, the following general trends become evident: The strongest [M]–EHC bonds are found for the beryllium complexes, and cationic metal complexes form stronger bonds than their neutral counterparts. For complexes of group 11 metals, the strength of the overall bonding interaction decreases in the order Au > Cu > Ag. EHC with H substitution of the heteroatom form weaker bonds

compared to the Me-substituted complexes, and N-heterocyclic carbenes form stronger bonds than P-heterocyclic carbenes.

Based on our analysis, we can identify four distinct factors that influence the strength of the [M]–EHC bond: (i) Charge variation has by far the greatest effect on the metal-to-ligand bond strength. Cationic complexes form bonds that are stronger by about 120–250 kJ/mol when compared to their neutral counterparts. This gain in bond strength increases for different metals in the order Ag < Cu < Au. Thus, of all the coinage-metal complexes considered, the complexes with the gold(I) cation form the strongest bonds. (ii) When comparing different transition metal centers, one has to differentiate between neutral and cationic complexes. For the neutral complexes, variation of the transition metal center causes an increase in bond strength in increments of about 50 kJ/mol according to the order Ag < Cu < Au. The bond strength increments amount to about 100 kJ/mol for cationic compounds. Compared to [Au$^+$] complexes, bonds to the beryllium fragment [ClBe$^+$] are even stronger by about 30 kJ/mol in changes in BE_{snap} in the order of 50 kJ/mol. (iii) The substitution at the heteroatom of the heterocyclic carbene also exerts an influence on the [M]–EHC bond strength. Here we compare pairs of complexes [NH]/[NMe], [PH]/[PMe], and [P'H]/[P'Me]. Again, we have to consider neutral and cationic complexes differently. For cationic NHC, carbenes carrying methyl groups at N form bonds to transition-metal fragments that are between 25 and 35 kJ/mol stronger than their H-substituted homologues. The increase in bond
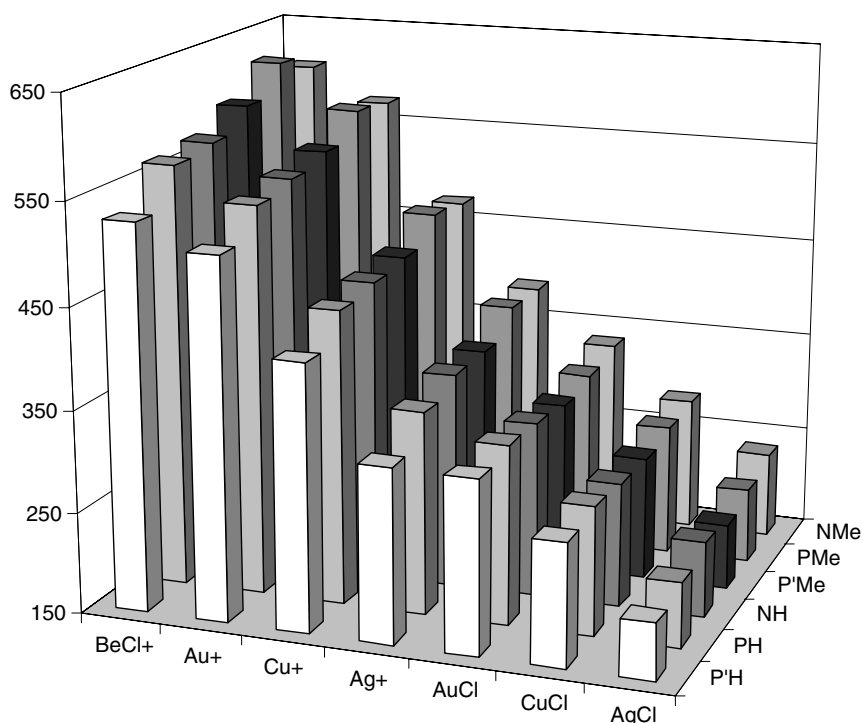

Fig. 5. Bond snapping energies BE_{snap} (in kJ/mol) for [M] ← EHC complexes.

strength decreases for neutral systems, and amounts to about 10 kJ/mol. Turning to cationic PHC, [PMe] and [P'Me] bonds with metal fragments are about 40–60 kJ/mol stronger than those of [PH] and [P'H]. For the neutral systems, however, the bonds of carbenes [PMe] and [P'Me] are only slightly stronger (AgCl), about the same strength (CuCl), or even slightly weaker (AuCl). (iv) With respect to the nature of the heterocyclic carbene, no clear trends emerge, and the effects are rather subtle. We can state that N-carbenes **1** and **2** as well as P-carbenes **3** and **4** form stronger bonds than P'-carbenes **5** and **6**. Comparing [NH] and [NMe] complexes with those of [PH] and [PMe], we find that BE_{snap} values are close within 10 kJ/mol, and that the relative strengths of [M]–NHC and [M]–PHC is influenced by nature of the transition metal and substitution pattern at the carbene.

Having established general trends for BE_{snap} values, we will now analyze the nature of the [M]–EHC bond in terms of steric and orbital interactions. The steric interaction ΔE^0 comprises Pauli repulsion as well as electrostatic attraction, and the fact that for almost all of the complexes investigated in the present study the term ΔE^0 constitutes an overall stabilizing bond interaction, clearly emphasizes the importance of electrostatic interaction. Thus, for most of the complexes, both ΔE^0 and ΔE_{int} contribute to stabilization of the bond between transition metal and carbene. The question remains which of these interactions is dominant, and in Fig. 6, the percentage contributions of orbital interaction $\%\Delta E_{int}$ to the bond snapping energy BE_{snap} are displayed.

All complexes have a sizeable ΔE_{int} contribution, ranging from 55% up to above 100%. We note that in cases, when $\%\Delta E_{int}$ exceeds a value of 100%, the steric interaction term is no longer stabilizing, but destabilizing. The influence of ΔE_{int} increases with increasing atomic number of the metal, Be < Cu, < Ag < Au, and as expected, cationic complexes show somewhat smaller $\%\Delta E_{int}$ values. At the same time, the bonding contribution of ΔE^0 and therefore the size of ΔE_{elstat} decreases, in accord with an increased shielding of the atomic nucleus. Comparing N-heterocyclic carbenes and P-heterocyclic carbenes, we find that for the latter orbital interactions are more pronounced. This also implies that electrostatic interaction is more important for NHC complexes than it is for PHC compounds.

The last point we want to address in our bond analysis is a σ- and π-partitioning of the orbital interaction. If a molecule possesses symmetry, ΔE_{int} can be broken down into contributions from orbitals of different irreducible representations [48]. As already mentioned, complexes with N-heterocyclic carbenes are of C_{2v} symmetry, whereas complexes with P-heterocyclic carbenes have C_2 symmetry. Relevant symmetry elements and choice of coordinate system for the symmetric complexes are illustrated in Scheme 2.

The symmetry element that both point groups have in common is a twofold axis of rotation, and we can differentiate between orbitals that are symmetric (a in C_2, a_1 and a_2 in C_{2v},) and orbitals that are antisymmetric (b in C_2, b_1 and b_2 in C_{2v}) with respect to this rotation. The concept of symmetry partitioning relates strongly to the idea of σ and π
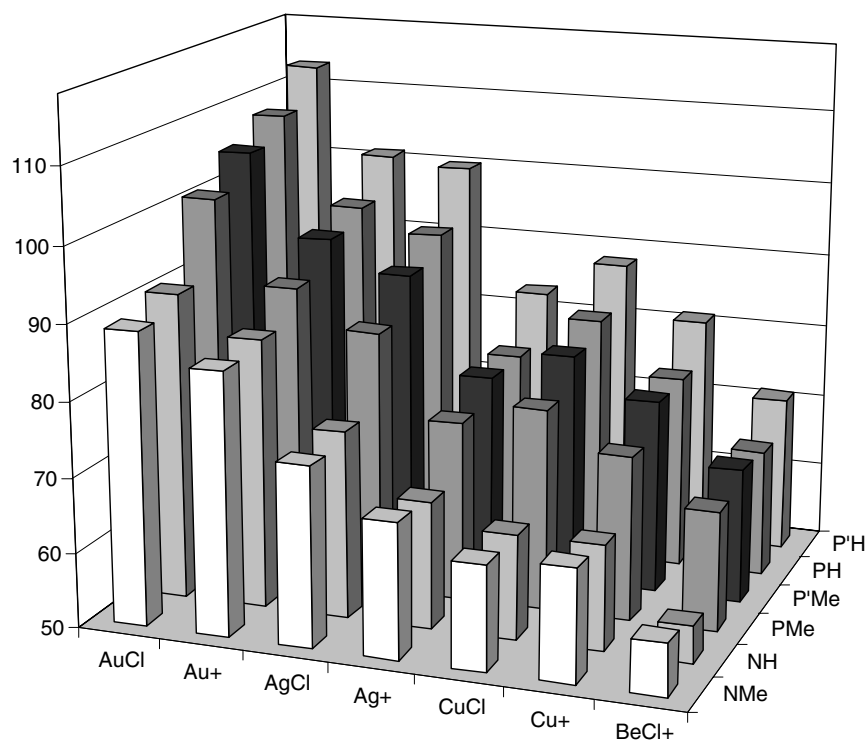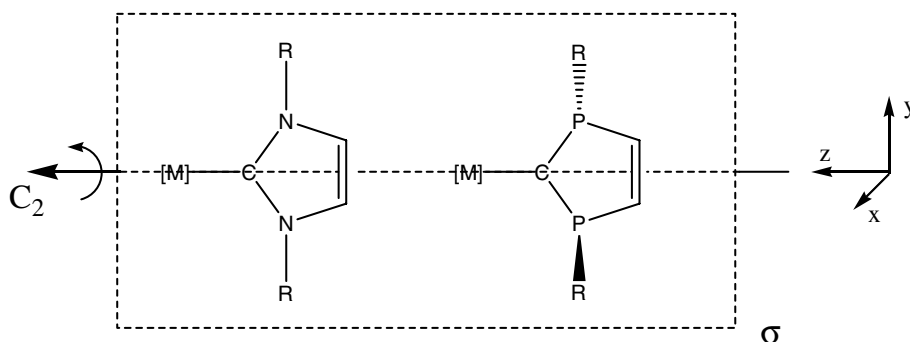

Fig. 6. Relative contribution of the orbital interaction ΔE^{int} to the bond snapping energy BE_{snap} (in %).

Scheme 2.

bonding, and allows us to define intrinsic σ- and π-bond strengths, $D_{\sigma,int}$ and $D_{\pi,int}$, respectively. The intrinsic bond strength values are solely defined based on orbital interaction ΔE_{int}, Eq. (4), and do not take into account any steric repulsion.

$$\Delta E_{int} = -[D_{\sigma,int} + D_{\pi,int}]. \tag{4}$$

Orbitals belonging to irreducible representations a, a_1 and a_2 contribute to $D_{\sigma,int}$, whereas orbitals belonging to irreducible representations b, b_1 and b_2 contribute to $D_{\pi,int}$. Since the main contribution to $D_{\pi,int}$ stems from back-bonding into the carbenic p_{π} orbital, whose nodal plane coincides with the plane of the E–C–E framework of the

five-membered ring, we will separately consider the $\Delta E_{int}(b_1)$ contributions for systems with C_{2v} symmetry. One might refer to $-\Delta E_{int}(b_1)$ as major component of the intrinsic π-bond strengths $D_{\pi,int}$. With our choice of coordinate system, the carbenic p_{π} orbital in NHC available for back-bonding belongs to the irreducible representation b_1.

Relative contributions of $D_{\pi,int}$ to the orbital interaction ΔE_{int} are presented in Fig. 7.

For NHC complexes, $D_{\pi,int}$ amounts to 25–35% of the orbital interaction energy. Considering the $-\Delta E_{int}(b_1)$ contribution, we can say that back-bonding accounts for at least 15–25% of ΔE_{int}. These results are in good agreement with the analysis presented by Meyer and co-workers [27].
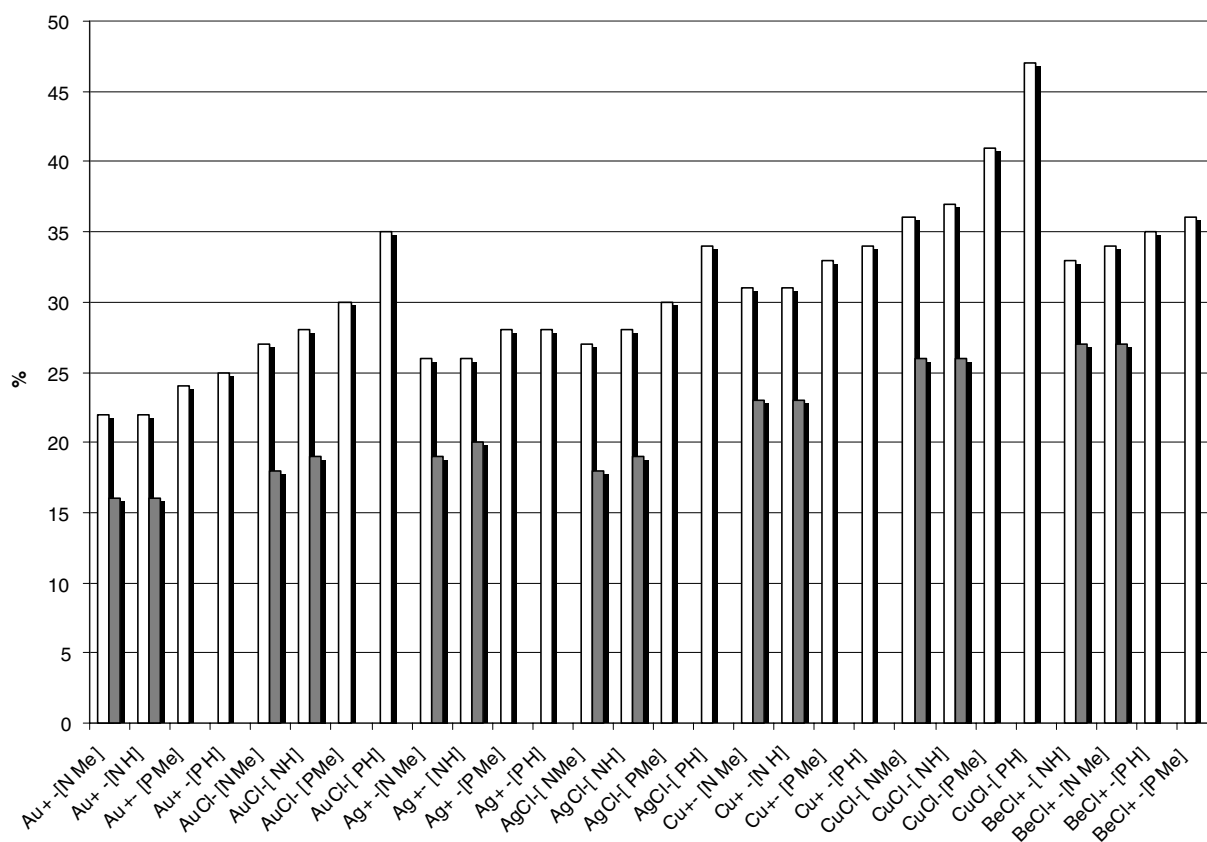

Fig. 7. Absolute contribution of $D_{\pi,int}$ (white bars) and $-\Delta E_{int}(b_1)$ (dark bars) to the orbital interaction ΔE_{int} (in %).

Turning to PHC complexes, the $D_{\pi,int}$ contribution increases up to 45%. As anticipated before, PHC undergo stronger back-bonding interaction with a TM center than NHC. In general, the relative contribution of $D_{\pi,int}$ increases according to the order Au < Ag < Cu.

The neutral complexes display stronger π-contributions than their cationic counterparts, and even the bond to the [BeCl$^+$] fragment is calculated to have a sizeable portion of π-bonding character. These trends can be explained by considering relevant bonding orbitals. A detailed and in-depth fragment orbital analysis of the M–NHC bond has been presented by Meyer and co-workers [27], and we restrict ourselves to a concise description of the orbital responsible for back-bonding interaction. Schematic orbital representations are given in Scheme 3.

Although cationic beryllium does not possess occupied orbitals suitable for donation to the carbenic p_π orbital, the presence of chlorine lone pair orbitals contribute to the Be–Cl bond and populate orbitals at the metal center that further donate electron density to the carbene ligand. For [ClM] fragments, repulsive interaction between occupied d-orbitals at the metal and occupied p-orbitals at chlorine is reduced when electron density is donated from the metal to the carbene ligand. This reduction of repulsive interaction is the driving force for enhanced π back-donation in [ClTM] systems compared to their cationic counterparts.

It is instructive to compare the bonding situation in [M]–EHC complexes with systems for which a σ-donation/π-back-donation bonding scheme is well established. Fischer-type carbenes serve as good reference compounds, and for complexes (CO)$_5$M=CH$_2$, the $D_{\pi,int}$ contribution amounts to 43%, 46%, 49%, and 31% for M = Cr, Mo, W, Mn$^+$, respectively [65]. NHC in general undergo weaker π-bonding interaction than the prototypical Fischer carbenes, but the $D_{\pi,in}$ contribution for PHC is comparable to the case of Fischer-type complexes. This conclusion is further corroborated by the fact that π-bonding in Fischer type complexes depends strongly on the nature of the carbene ligand [66]. For example, the relative π-contributions

drops to about 20% for the alkoxy-carbene compound (CO)$_5$Cr=C(OMe)Me. The similarity in bonding between complexes with N-heterocyclic carbene ligands and classical Fischer carbene complexes has also been emphasized by Frenking and co-workers [28].

The present bonding analysis underlines the notion that heterocyclic carbenes are indeed capable of π-bonding with transition-metal centers. Although PHC undergo stronger π-interactions than NHC, the present work in view of previous studies suggest that the nature of [M]–EHC bond is to a large part dominated by the orbital make-up of the transition metal fragment, and that variation in EHC changes strength, but not character of the metal-to-ligand π-bond.

4. Conclusion

The present study suggests that PHC form bonds with transition metal centers in strength comparable to those of NHC. However, the nature of the [M]–EHC bond is distinctly different for N-heterocyclic and P-heterocyclic carbenes. PHC are more likely to undergo stronger π-bonding interaction when compared with NHC. Although electrostatic interaction is of crucial importance for the [M]–EHC bond, this effect is more pronounced for NHC than for PHC. The pyramidalization of phosphorus further influences the metal to carbene bond strength, and it can be expected that an increase in pyramidalization leads to an increase in bond strength. However, this change is not a dominant bonding effect. Substituent variation at phosphorus not only influences the degree of pyramidalization but might introduce other modifications in the electronic structure, all of which need to be evaluated together on a comparable basis.

The development of stable P-heterocyclic carbenes is in part stimulated by the search for compounds that "can compete with and/or complement NHC as ligands for transition-metal-based catalysts" [37]. The results of the present study suggest that PHC both compete with NHC – in terms of metal to ligand bond strength – as well as complement NHC – in terms of the nature of the metal–ligand bond.

Appendix A. Supplementary data

Tables comprising detailed energy decomposition analysis and symmetry decomposition of orbital interactions. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2005.07.112.
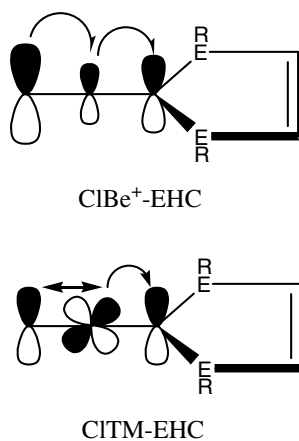
Scheme 3.

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