

On the ligand properties of the P- versus the N-heterocyclic carbene for a Grubbs catalyst in olefin metathesis

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Abstract

The 1,4-diphospha-2-azol-5-ylidene is a homologue to the Ender's type carbene. It is a possible candidate for a ligand in the metathesis reaction of olefins. Based on density functional calculations the differences between the electronic structures of both systems are evaluated. The NHC (N-heterocyclic carbene) possesses a larger singlet–triplet energy separation than the PHC (P-heterocyclic carbene) analogue. Thus the latter exerts a larger Lewis acidity than the former. In comparison with, the donor-ability (σ -basicity) in both systems is similar. As a consequence for the PHC carbene a Ru-fragment as a ligand for catalysis is stronger bound. This causes in the olefin metathesis a lower dissociation energy (compared to the NHC analogue) with respect to the formation of the catalyst active 14el species. As a consequence, the olefin will be weaker bound as well. This can be overcome by attaching sterically demanding substituents such as mesityl or super-mesityl to the phosphorus atoms. They induce mutual steric hindrance with concomitant increase of the S–T separation of the free carbene. Thus the Lewis acidity of the carbene is reduced. On this basis for the PHC's with larger S–T energy separations the dissociation energy of the phosphine fragment is raised and the adding olefin fragment will be stronger bound to the transition metal. While these effects describe the electronic situation in the reactive species, steric effects at the ligand carbene mediate the stabilities of the individual intermediates in the metathesis reaction by exertion of inter- and intra-ligand repulsion.

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1. Introduction

Olefin metathesis is a fundamental reaction for the formation of a plethora of carbon–carbon double bond systems [1–4]. The diversity in this field is best represented by the “first generation”, **I**, and “second generation”, **II**, catalysts, where for the latter a N-heterocyclic carbene (NHC) replaces one phosphane group [5–9] (Scheme 1).

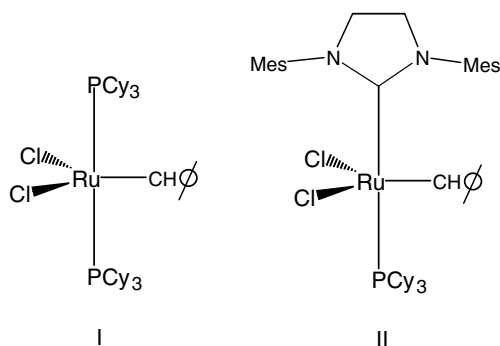
The increased reactivity of the “second-generation” catalysts, **II**, with respect to the former, **I**, was originally explained by an enhanced *trans* effect of the phosphane on the dissociation step which was concluded from

extensive in situ kinetic studies [10,11]. These solution phase studies were also supported by gas-phase experiments on **I** [12,13] and on **II** [14]. In principle, the basic mechanism for the olefin metathesis was predicted some time ago by Hérisson and Chauvin [15]. The details of the mechanism are now well substantiated by an intense effort of experimental [10–24] studies. We may note here that very effective ruthenium carbene catalysts have also been presented in cationic [25] and other systems [26–29].

The detailed mechanism of olefin metathesis catalyzed by ruthenium carbene complexes has been enlightened by intense computational studies [9,13,25,30–44]. The majority of these studies deals with a truncated model system, with PH_3 instead of PCy_3 (tri-cyclohexylphosphine) as a ligand. Only recent quantum chemical studies cover the detailed substituent effects which are

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Scheme 1.

in action at the carbene catalysts [44,40,45]. The most likely mechanism for the olefin metathesis with a Grubbs-type ruthenium carbene complex which is nowadays accepted is summarized in Fig. 1.

The reaction is initiated from **A** with the removal of a phosphine ligand under formation of an electron unsaturated 14e⁻ species **B**. It refers to an endothermic process and is thus initiated by heat. In a second step an olefin is added to yield **C** which further undergoes reaction to a metallacyclobutane species **D**. The olefin addition is exothermic and it is the necessary condition for the occurrence of the metathesis reaction. The reactions are reversible and cause further formation of the metathesis reaction to **E** and **F**. The reaction is quenched by addition of a phosphine. The turn-over-number (TON) determines largely the activity of the catalyst. If the energy barrier between **C** and **D** is

small the TON is large. There are also other aspects which determine the quality of a catalyst, such as synthetic availability, resistance against solvents, etc. The dissociative mechanism depicted in Fig. 1 is now generally accepted. It is based on the concept that an electronically unsaturated intermediate **B** is formed. Individual intermediates could be traced, such as the recently observed ruthenacyclobutane species [46]. Fast initiating improvements on the metathesis event have been devised as well [47]. The proposed reaction mechanism finds strong support by quantum chemical calculations [41]. These also make an associative mechanism for olefin addition to the catalyst **A** fairly unlikely (not shown here in Fig. 1). It would require an olefin *cis*-addition to an equatorial position of the catalyst which at least for the bulky substituents at the nitrogens is sterically demanding.

The most common ligand for L is at present the family of N-heterocyclic carbenes (NHCs) [48,49], of which **1** is the most prominent ligand for a Grubbs catalyst (Scheme 2). A higher element homologue to this is the recently synthesized P-heterocyclic carbene (PHC) species **2c** [50], the relative to Ender's carbene [49] **3**. In order to protect **2c** kinetically the phosphorus atoms are substituted by bulky super-mesityl [Mes* = 2,4,6-tri(*tert*-butyl)phenyl] groups. The fact that **2c** is now experimentally accessible [51] arose our interest to a detailed study of the electronic properties of this new type of carbene, as a potential ligand for catalysts.

In the present quantum chemical study we compare the properties of this PHC ligand with those of the NHC ligand as a suitable candidate in the olefin metathesis reaction. We have investigated the dissociative mechanism for this reaction. It is the most relevant part of the hypersurface for this reaction.

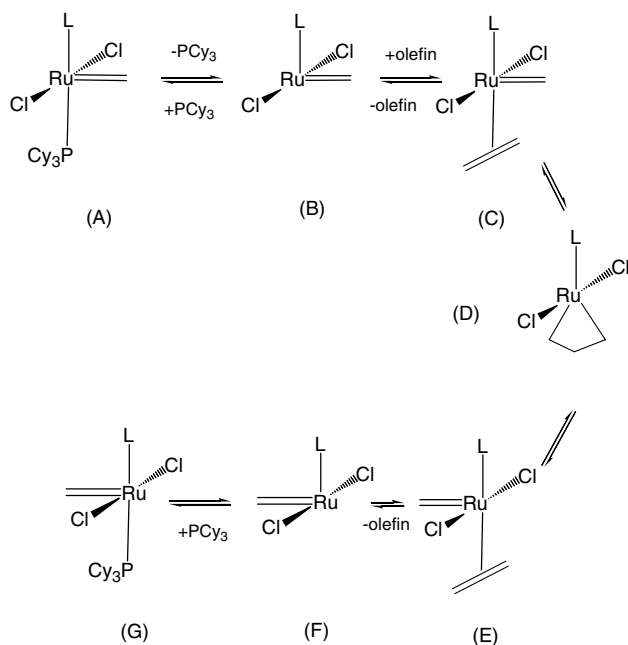
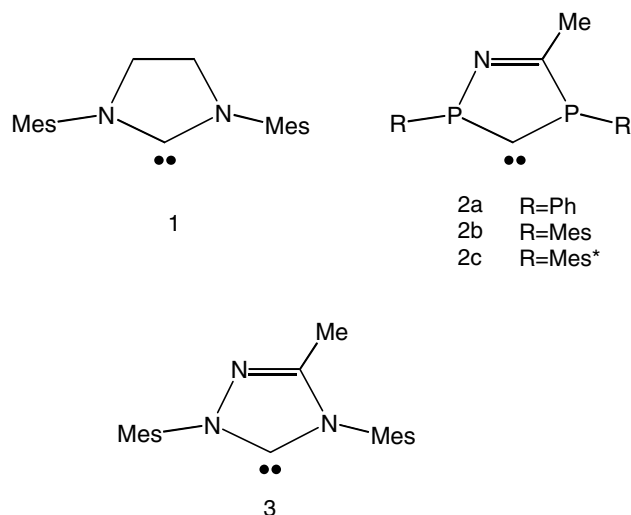


Fig. 1. Dissociative mechanism for olefin metathesis by Grubbs-type ruthenium carbene complexes.



Scheme 2.

2. Results and discussion

2.1. The free carbenes

It is informative to study first the electronic properties of the free carbenes **2a–c** in comparison with **3**. In the NHC carbene the replacement of the nitrogen by phosphorus atoms causes a strong decrease in the singlet–triplet (S–T) energy separation [52]. The lone pairs at P are less capable for π -donation into the vacant p-orbital at the carbene unit than those at N. Furthermore, the tendency for trigonal phosphorus to pyramidalize is per se larger than for trigonal nitrogen. Thus the essential difference of a phosphorus versus a nitrogen substituted cyclic carbene is in particular determined by these two effects. As will be shown in the following discussion this has considerable consequences for the electronic properties of a substituted ligands **2a–c**. The singlet and to more extent the triplet is pyramidalized at the phosphorus atoms. The bonding situation is revealed by the equilibrium geometries of both states for the parent system **2** (R = H) (Scheme 3); the values (bond lengths in Angströms, bond angles in degrees) refer to a singlet (S) [top] or a triplet (T) [bottom].

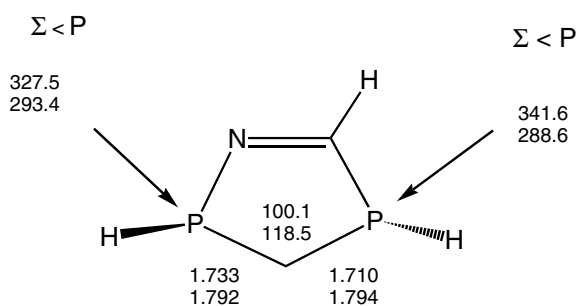
As expected, in the singlet the phosphorus atoms are less pyramidalized as compared with the triplet. It is witnessed by the sum of bond angles around the phosphorus atoms. Concomitantly, the PC distances are shorter in the singlet than in the triplet. In addition, the valence angle at the carbene carbon is more widened in the triplet versus the singlet. Full planarization of the phosphorus atoms is of energetic disadvantage to both electronic

states. However, it is less for the singlet as compared to the triplet. The S–T energy difference results for parent **2** (R = H) to 22.1 kcal/mol (ZPE correction included). A fully planar singlet structure is 8.4 kcal/mol less stable than the equilibrium geometry. For the triplet the corresponding difference results to 58.2 kcal/mol. In other words, if one assigns to a first order these values to the double inversion process at the phosphorus atoms the barrier is fairly small within the singlet and large for the triplet. Since the singlet is much less pyramidalized than the triplet appropriate substituents at the phosphorus atoms exert considerable steric hindrance, in particular for the triplet state. This indicates that bulky substituents which enforce further planarization at the phosphorus atoms will sizably increase the S–T separation for the P-carbene.

In order to put these arguments on firmer ground we performed quantum chemical calculations on a variety of sterically encumbered carbenes **2a–c**. For the substituents at the phosphorus atoms we have chosen R(P) = methyl, phenyl, mesityl (Mes = 2,4,6-tri-methylphenyl) and super-mesityl (Mes* = 2,4,6-tri-(*tert*-butyl)phenyl). The results of the investigations are summarized in Table 1.

Plots of the corresponding carbene conformations in their energy lowest singlet states are given in Fig. 2 (for relevant bonding parameters see Table 1).

Accordingly, the bulky substituents at the phosphorus atoms tend to adopt a bisected orientation with respect to the plane of the five-membered ring. It becomes more pronounced in the order Ph < Mes < Mes*. At the same time the S–T separation in the carbene is increased. Since a small S–T separation refers to an energy low lying LUMO and on the other hand a large S–T value parallels a strong nucleophilicity of the carbene [53], the relation of electrophilicity versus nucleophilicity of the carbene is tuned by the sterical congestion of the substituents at P. From the carbenes listed in Table 1 **2a–c** possess similar HOMO energies, as identified from the Kohn-Sham orbital energies. RHF calculations (at the RI-BP86 geometries) yield lower energies, however they are also alike for **2a–c**. The levelling of the HOMO is to a first order determined by an inductive effect exerted by the neighbour atoms. The LUMO is π -conjugated with its neighbours and thus stronger tuned by mesomeric interaction [54]. As will be seen in the following discussion



Scheme 3.

Table 1

S–T energy differences and bonding parameters of different phosphorus atoms substituted **2**, given by the RI-BP86/SV(P) level

R(P)	S–T (kcal/mol)	C–P(N) (Å)	C–P(C) (Å)	$\Sigma \angle P(N)$ (°)	$\Sigma \angle P(C)$ (°)	$-E_a^b$
Me	25.4 (24.9) ^a	1.734	1.702	330.3	346.5	5.2 (8.5)
Ph (2a)	26.7 (25.9) ^a	1.711	1.718	341.2	341.4	5.3 (7.8)
Mes (2b)	30.3 (29.9) ^a	1.710	1.724	343.4	340.3	5.1 (7.8)
Mes* (2c)	41.3	1.705	1.721	350.7	352.0	5.0 (7.6)

^a Values in parentheses are with zero-point vibrational energy corrections.

^b Kohn-Sham HOMO energies in eV (1 au = 27.211 eV), in parentheses are values from RHF calculations at the RI-BP86 optimized geometries.

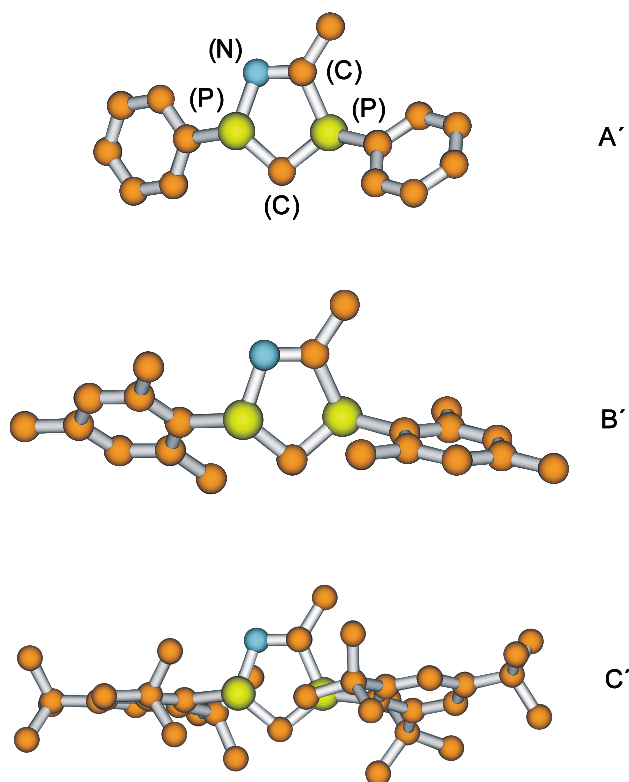


Fig. 2. Plots of the singlet states of PHC carbenes; from top to bottom R(P) = Ph, Mes, Mes*. Hydrogens are omitted for clarity.

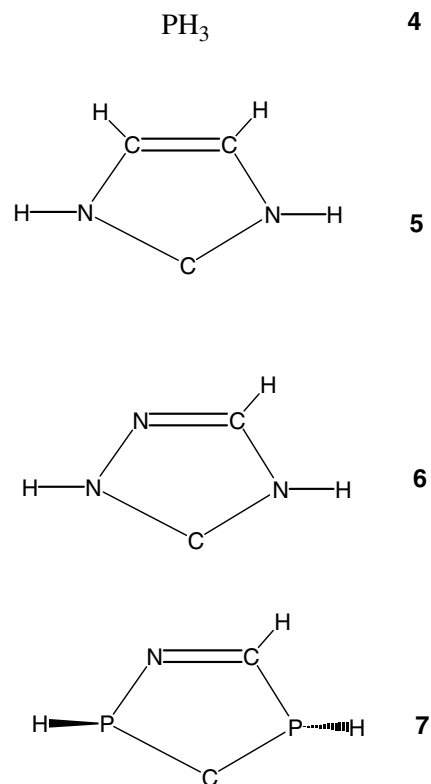
these aspects are of essential importance for the construction of a corresponding ruthenium catalyst.

2.2. The ruthenium catalysts of parent systems

In this section, we will evaluate the different stationary points of the metathesis reaction as a function of the ligand attached to **2**. It is informative to study first the reaction for the parent compounds. In the experiment such model catalysts do not exist, but their consideration provides valuable information on the electronic effects operating these catalytic systems. In the later section, we will then focus on the fully substituted species. For the calculations of the various stationary points for the parent compounds on the catalytic cycles ligands **4–7** were chosen for consideration (Scheme 4).

The relevant stationary points for the catalytic cycle were determined for the catalyst **A**, the 14 electron species **B**, the olefin complex **C**, and the metallacyclobutane **D**, (see also Fig. 1). The most important bond lengths which were obtained by energy optimization (RI-BP86/SV(P)) and are summarized in Fig. 3. Bonding parameters for the L–Ru-bonds obtained with the RI-MP2 approximation are added in parentheses.

It can be seen that the ligands **4–6** exert similar properties on the various geometrical facets of the intermediary species in the catalytic cycle. In particular for the NHCs **5** and **6** the bonding parameters for the axial



Scheme 4.

bonds are similar within the species **A–D**. However a slight difference results for **4** as a ligand. In all intermediates it is weaker bound than the NHCs. In the experimental reality, however, the parent ligand system can serve only as a first guide to the understanding of the metathesis reaction, since it is known that substituents play a considerable role in stabilizing the different intermediates [24,40,44,45]. A full substitution pattern of the PHCs will be evaluated in a later section of this publication.

A remarkable difference is also obtained for the parent PHC, **7**. The relevant different bonding parameters for this series of structures are marked in italics. Already in the precursor catalyst **A** the C–Ru distance is shortened by 0.1 Å, as compared with the nitrogen congener **6**. This trend continues to the 14e[−] species **B**. Such a bond shrinking is also witnessed in the olefin complex **C** and the metallacyclobutane, **D**. Striking is also for L = **7** in **C** the essentially shorter Ru–C bond (to the carbene carbon). This gives credit to believe that **7** as a ligand in the metathesis reaction is more strongly bound to the metal center than its corresponding nitrogen analogue **6**.

Since the Ru–C bond is strongly attributed by electron correlation, its outcome by the quantum chemical calculations depends on the chosen density functional level. For further investigation of this aspect we have repeated the structure optimizations at: (a) the B3LYP

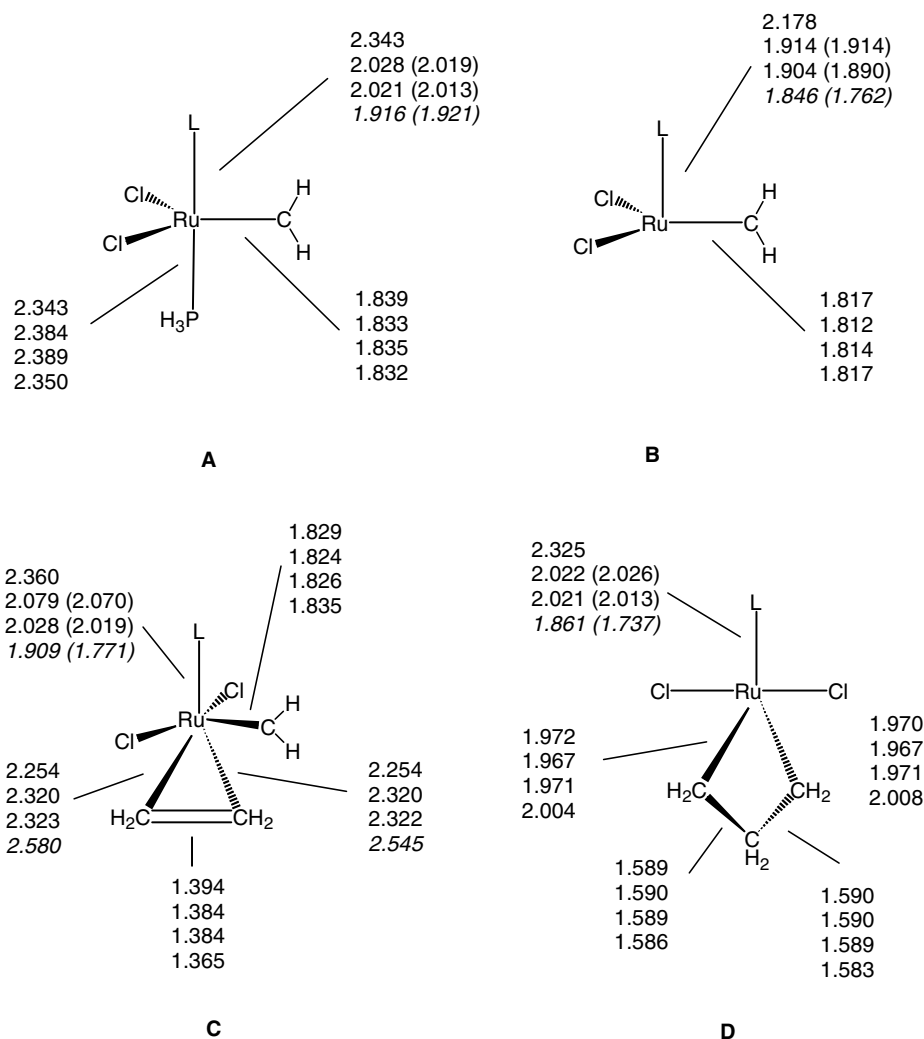
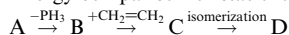


Fig. 3. Geometrical parameters for intermediates **A–D** with ligands **4–7** (from top to bottom); bond lengths are in Angström units, bond angles are in degrees.

Table 2

Energy comparison of stationary points for ligands **4–7**



Ligand	ΔE (kcal/mol) ^a				ΔG (kcal/mol) ^b			
	A	B	C	D	A	B	C	D
4	-19.2	0.0	-14.2	-6.3	-8.9	0.0	-3.2	4.3
5	-16.4	0.0	-9.3	-14.4	-5.7	0.0	2.4	-3.4
6	-16.5	0.0	-13.0	-12.2	-5.9	0.0	-1.4	-0.5
7	-7.2	0.0	-1.8	-7.8	2.9	0.0	6.7	5.1

^a Energies with zero-point vibrational energy correction.

^b Free energy at 298 °K.

level and (b) the RI-MP2 method [62]. The difference in bond lengths results to 2–3 pm and the Ru–C distances are generally shorter at the RI-MP2 level (Fig. 3, values in parentheses).

To complete this picture we will record here the energy values (RI-BP86) obtained for the different spe-

cies. A collection of data is given in Table 2. We list here the reaction energies, corrected by zero-point energies (within the harmonic approximation) and the free energies computed for the gas phase at room temperature.

The 14eI intermediate **B** is in the consideration of energy balances for all cases the reference point. Consider

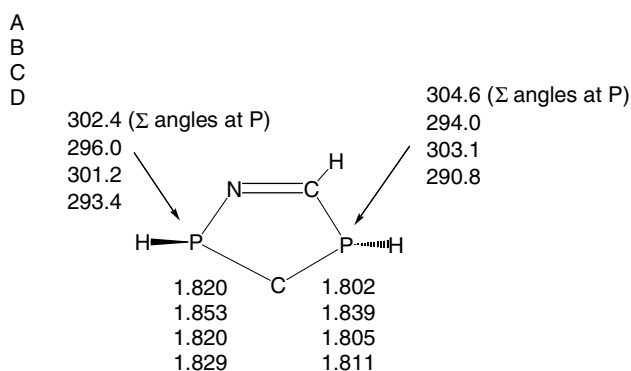
first the total energies. Phosphine or olefin addition is at times an exothermic process. The energy values for **C** and **D** are given with reference to **B** plus ethene and those for **A** in reference to **B** plus phosphine. Consequently for **4** as a ligand **L** intermediate **D** results sizable less stable than intermediate **C**. For the NHC **6** both intermediates are of comparable stability. The bonding situation is again essentially different for the P-heterocyclic carbene **7**. The olefin is only loosely bound to the metal (see Fig. 3) and the resulting bond energy is fairly small. In comparison with, **D** is more stable than **C**. Our investigations take only axial olefin addition into considerations. This approach is disadvantaged [41] for **4**, but preferred for the more bulky systems **5–7**.

A computation of the thermodynamic quantities (ΔG at room temperature, gas phase) yields a somewhat different picture (see Table 2). In comparison with the electronic energies (ΔE values) the inclusion of entropy contributions makes the energy differences between the different species much smaller. Even more, for the weakly bound adducts of **7** the energy balances become endothermic. In contrast to the results for the gas phase, the experiments are usually carried out in solution. In solution translations and rotations are hindered by molecular tumbling in solvent–solute interactions. Since smaller molecules have fewer vibrational normal modes, they also have proportionally larger contributions from translational and rotational entropy. Hence, the data given in Table 2 represent an overestimate of the reaction free energies for associate reactions (i.e., are too positive), and an underestimate for dissociative reactions (i.e., they are too negative).

What is the reason for the different stabilities of the 14el species **B** for the P-heterocyclic carbene in relation to **A**, **C** and **D**? A hint is provided by an inspection of the geometrical environment of the carbene unit as a function of the different species **A–D**. It is illustrated in Scheme 5.

The sum of angles reaches a minimum for the species **B** which is considered to be the intermediate driving the

from top to bottom



Scheme 5.

metathesis reaction. A stronger pyramidalization at the phosphorus atoms brings a triplet state to the fore. As a further consequence the Ru–C bond gains covalent bond character. Tentatively, one can state that the P-heterocyclic carbene does mimic the behaviour of a Schrock-type carbene complex [55] since the ligand **L** is stronger bound to the metal as compared with the corresponding N-heterocyclic carbene as a ligand. Our analysis is in accord with previous considerations [56,57] which indicate stronger covalent bond formation for electron unsaturated transition metal fragments by triplet–triplet coupling [56] of two mutually interacting fragments.

Our investigations on the N-heterocyclic carbene as a ligand in the olefin metathesis reaction is in line with previous detailed investigations [41] which cover the associate as well as the dissociate reaction mechanism. A further refinement of the transition states interconnecting **C** and **D** was not attempted. We may relate the reader to a dynamical study of the metathesis reaction [58] where the equilibrium between both species over tiny energy barriers was discussed. We will not further record in detail our findings on a *cis*-oriented **2** ($R = H$). In essence it reveals a slightly larger Lewis acidity than its *trans*-isomer, but is prohibited in the experimental reality by bulky substituents at the phosphorus atoms. As will be shown in the following section, for a more quantitative view of the reaction electronic as well as steric effects have to be included in the considerations.

2.3. Ruthenium catalysts for the substituted carbenes

In the last section of this publication, we will present the results for the sterically demanding P-heterocyclic carbenes. We have again chosen for the computational studies different derivatives of the Bertrand's carbene [50] **2c**, this system is well characterized and synthetically easily accessible. According to the aforementioned consideration the PHC possesses an S–T energy difference which is smaller than in the NHC, but the magnitude is depending on the substituents attached to the phosphorus atoms. In other words, sizable bulky substituents cause an almost planar environment at phosphorus and attenuate a ligand property more alike a NHC ligand. On the other hand, less bulky substituents **R** give rise to a strong bond formation for the 14el intermediate.

Our analysis is based on the results of density functional calculations. They are known to suffer from the deficiency to account properly for dispersive interactions [59]. On the other hand, these may become of importance for the stabilization of sterically encumbered structures. Nevertheless, the RI-BP86 method is at present the only method of choice for quantum chemical studies of large structures.

With this shortcoming on density functionals in mind we have calculated the corresponding intermediates

A–D for ligands **2a–c** (R(P) = Ph, Mes and Mes*). As a departing phosphine ligand we have chosen tri-cyclohexylphosphine, in order to keep our model most closely to the hitherto known catalysts. For completeness we have included in our considerations corresponding results of the various stationary points on the metathesis reaction of the “second generation catalyst” **II**. The results of the quantum chemical investigations on the geometries of the various intermediates are summarized first for the latter in Fig. 4.

For the catalyst again a strong axial relationship between bond lengths becomes apparent. The release of PCy₃ (Cy = *cyc*-Hex) from **A** to **B** causes a shortening of the C–Ru bond which is lengthened by further addition of ethene (in **C**), or subsequent metallacyclobutane formation (**D**). Albeit these trends are also apparent in the parent systems (see Fig. 3) the absolute values for the bond lengths are different. We attribute the slightly longer Ru–C bonds in **A** as compared with **5** and **6** to the steric hindrance exerted by the bulky mesityl substituents attached to the nitrogen atoms and the neighbouring phenyl group. Another difference stems from the phosphine unit which is different in **A** (Fig. 4) versus **4A–7A** (Fig. 3). The different nucleophilicity of the phosphine unit causes a different bonding to the 14el species **B**.

We will now continue our report with the results for the PHCs. As representative examples we have chosen here the ligands **2a–c**. As already recorded in Table 1, with increasing bulkiness of the substituents the phosphorus atoms become almost trigonal planar and the S–T energy separation is increased. Considering only

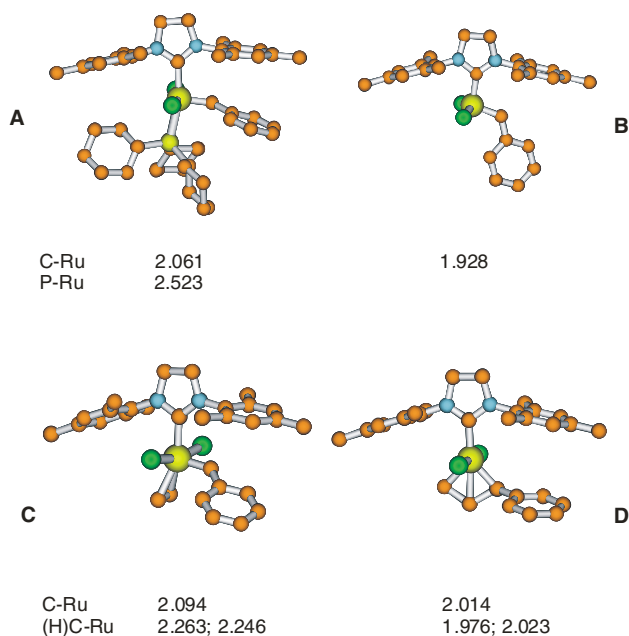


Fig. 4. Stationary points **A–D** (bond lengths in Angströms, bond angles in degrees) for **II**. Hydrogens are omitted for clarity. The carbene unit at Ru is the CH(Ph) fragment.

the electronic effects for ligand fixation of the olefin or phosphine, in the 14el intermediate **B** the Ru–L bond should become more tightened in the order R(P) = Mes* < Mes < Ph. The most important bonding parameters for catalyst **A** (carbenes **2a** and **2c**) for the two extreme cases R = Ph [left] and Mes* [right] are shown in Fig. 5.

An energetic comparison of the various intermediates (energy minimum structures) for the ligands **2a–c** is summarized in Table 3. The relationship of the axial bonds as a function of the S–T energy separation is well seen here. The Mes substituted **2b** takes up an intermediate position between both extremes, **2a** and **2c**. For

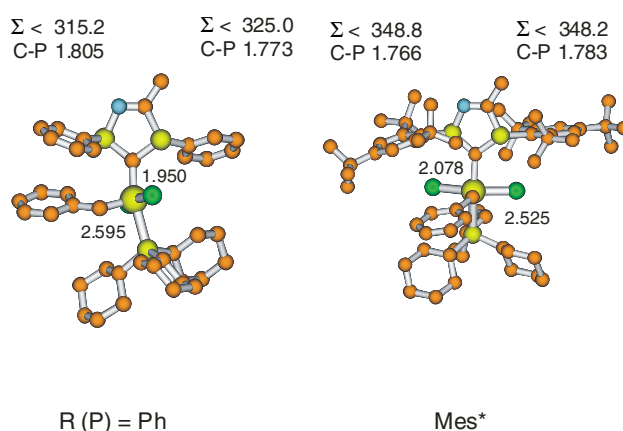


Fig. 5. Geometries (bond lengths in Angströms, bond angles in degrees) of **A** (carbenes **2a** and **2c**). Hydrogens are omitted for clarity.

Table 3
Geometry parameters and relative energies of stationary points for **2a–c** (Scheme 2)

Ligand	Compound	C–Ru ^a (Å)	Ru–C ^b (Å)	ΔE (kcal/mol) ^c
2a (R = Ph)	A	1.950	2.595 ^d	–10.5
	B	1.853		0.0
	C	1.922	2.497; 2.346	–1.7
	D	1.912	2.061; 1.982	–7.8
2b (R = Mes)	A	1.967	2.561 ^d	–9.1 [–13.7] ^e
	B	1.873		0.0 [0.0] ^e
	C	1.936	2.264; 2.437	–0.7 [–7.2] ^e
	D	1.909	1.989; 2.041	–8.9 [–13.9] ^e
2c (R = Mes*)	A	2.078	2.525 ^d	–6.0
	B	1.894		0.0
	C	–	–	–
	D	1.962	1.978; 2.042	–9.4

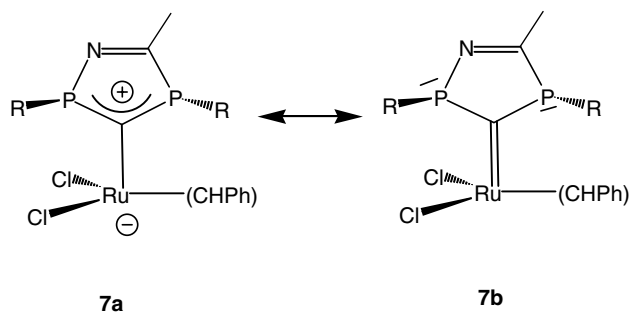
^a C(carbene)–Ru distance.

^b C(ethene)–Ru distance(s).

^c Relative energies with respect to **B**.

^d Ru–P(Cy)₃ distance.

^e Values in brackets are calculated for the corresponding derivatives of **II**.



Scheme 6.

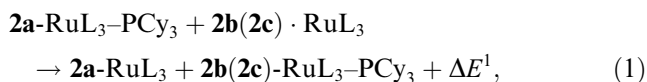
R(P) = Mes* we could not locate an olefin complex **C**, it rearranges without energy barrier to **D**.

The sterically bulky substituents R(P) lengthen the (axial) Ru–C bond, via interligand repulsion between the PHC and the phenyl group at the Ru-center. A slight bond lengthening is also observed for catalyst **A**. In **A**, the PCy₃ ligand is most strongly bound for R(P) = Ph and least bound for Mes*.

One can view the 14el intermediate **B** as a resonance of two canonical structures, **7a** and **7b**, in which the latter is formed by coupling of a triplet carbene with a triplet transition metal fragment (“triplet–triplet” coupling [56,57]) (Scheme 6).

In **7a** a dipolar character is emphasized while in **7b** the two unpaired electrons at the carbene center are used for double bond formation towards the electronically unsaturated transition metal fragment. Shrinking the Ru–C bond brings the TM-fragment in closer proximity to the ligands at P and induces sterical hindrance. It is in agreement with the computational results on **2a–c** (R = Ph, Mes, Mes*). These effects, the tuning of the stability and hence the reactivity of the intermediate 14el species **B** is absent for the NHC carbene. There the singlet and triplet states adopt a planar environment at nitrogen. We may differentiate the varying steric demand in “intra-ligand” (bulky substituents at phosphorus) and “inter-ligand” repulsion (hindrance between the ligand L and the ruthenium fragment).

In order to analyze this aspect in more detail, we have studied the following group transfer reaction (1),



where RuL₃ is Ru(=CHPh)Cl₂.

It corresponds to the transfer of the phosphine PCy₃ from the catalysts with **2a–2b** (or **2c**). The following values for ΔE¹ were obtained: **2b** 1.4, **2c** 4.5 kcal/mol. This indicates that **A** is relatively less stable towards the formation of **B** for the sterically most demanding **2c** ligand, which is reflected in the corresponding Ru–P bond lengths.

The vibrational analyses for the optimized structures were not possible, due to their large size. We also note

that the CHPh fragment at the transition metal was always calculated in *cis*-orientation to the ring nitrogen. There exist also *trans*-isomers. Further studies on a selected variety of structures (not presented here) reveal more conformations of similar energy (≤0.5 kcal/mol, ΔE). There is no further point in discussing this aspect, the structures of the catalysts and their intermediates are very flexible. For completeness we also include here the energetic results for the type **II** catalyst which are added in Table 2 in parentheses. In comparison with the corresponding PHC ligand **2b** (R = Mes) the PCy₃ in **II** is stronger bound and also the exothermic energy values for olefin addition to **B** and the subsequent rearrangement to the metallacyclobutane **C** result somewhat larger.

3. Conclusions

The results of our computational study can be summarized as follows:

- (1) The P-heterocyclic carbenes exert smaller S–T energy separations as compared to their N-heterocyclic counterparts. The magnitudes of the S–T energy values depend on the actual substituents attached to the phosphorus atoms. Sterically demanding substituents such as the Mes* group cause a trigonal environment at the phosphorus atoms. This is of stronger advantage to a singlet rather than a triplet state and the S–T energy separation will be increased. The concept of flattening phosphorus centers with sterically demanding substituents has been discussed previously in a different context by Nyulaszi et al. [60,61].
- (2) In the olefin metathesis cycle a small S–T energy separation is of advantage to the 14el species which is the key intermediate for the initiation of the catalyst cycle. If it is very stable, the initiation temperature will be low. Consequently, the P-heterocyclic carbene as a ligand in the intermediate 14el transition metal fragment is more strongly bound than the N-heterocyclic carbene. These electronic effects are superimposed by steric effects which tend to become important for bulky substituents attached to the phosphorus atoms.
- (3) As a further consequence of the larger stability of the 14el fragment the olefin coordination becomes less favourable, on the other hand the rearrangement towards the metallacyclobutane intermediate becomes more facile.
- (4) For the sterically severely congested catalyst systems one can differentiate between inter- and intra-ligand steric hindrances which effect the relative stabilities of the intermediate species. For the PHCs as ligands both effects are operative.

Our investigations indicate that the P-heterocyclic carbene is an interesting candidate as a ligand for the olefin metathesis reaction. The considerations presented here should be of importance to other catalytic processes as well, where a NHC ligand is involved. Hence, we think that our recognitions may be far reaching for the understanding of these processes. Nevertheless, we are aware of the fact that its suitability for the experiment requires additional qualities on a catalyst, e.g., stability in solvents, air etc. So a final proof of our model has to be given by experiment.

4. Theoretical section

All of the quantum chemical calculations were performed with the TURBOMOLE 5.7 suite of program systems [62]. Some of the calculations were also performed with the G03 set of programs [63]. As basis sets we used the SV(P) basis [64] whose quality is comparable to the 6–31g(d) basis set of Pople et al. [65]. For ruthenium we employed the effective core potential derived from the Stuttgart–Dresden group [66]. All structures were fully energy optimized, i.e., with respect to C_1 symmetry. For 4–7, we characterized the stationary points by vibrational analysis within the harmonic approximation. This was performed analytically [67].

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