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# Bis-phosphorus stabilised carbene complexes

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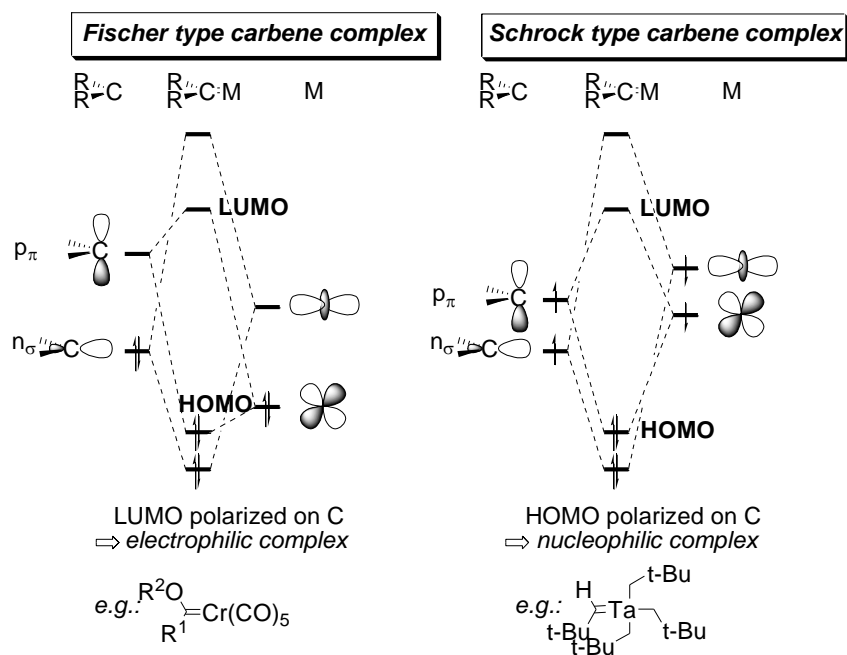
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## *1. Introduction*

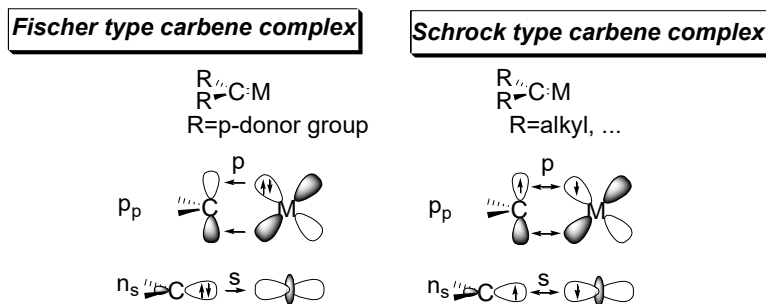
Prior to their isolation as stable species, organic carbenes have only been postulated or observed as reaction intermediates.<sup>1</sup> To achieve the stabilisation of the first free carbene, tuning of both the electronic and steric effects of substituents proved to be crucial. However, the strategy relying on the stabilisation of a carbene centre by a transition metal has been historically the most efficient way to isolate such species as carbene complexes. Over the past decades, the chemistry of these complexes has been thoroughly explored,<sup>2,3</sup> and studies have clearly demonstrated the relevance of carbene complexes in organic synthesis, in stoichiometric as well as in catalytic processes.

Pioneering works in the synthesis of carbene complexes are due to E. O. Fischer who first achieved the synthesis of pentacarbonyl(carbene)chromium complexes ( $\text{CO}_5\text{Cr}=\text{C}(\text{OMe})(\text{R})$ ) in the coordination sphere of a metal fragment.<sup>4</sup> A second class of carbene complexes was later described by R. R. Schrock in 1974, via an  $\alpha$ -elimination from a pentaalkyl tantalum(V) complex.<sup>5</sup> These two distinct families of complexes were shown to exhibit opposite reactivities, the Fischer type complexes behaving as electrophiles while the Schrock type complexes exhibit nucleophilic properties. Based on these observations, important efforts have been devoted to the theoretical study of the transition metal – carbene interaction, with the aim of describing the electronic nature of the bonding. It has been shown that the metal – carbene interaction strongly depends on the energetic gap between the carbene  $n_\sigma$  and  $p_\pi$  frontier orbitals and on the energetic gap between the metal frontier orbitals of  $\sigma$  and  $\pi$  symmetry.<sup>6</sup>



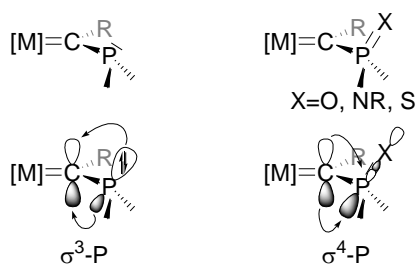
**Scheme 1**

In a Fischer type carbene complex, the carbon atom usually bears  $\pi$ -donor substituents ( $\text{R} = \text{OR}', \text{NR}'_2, \dots$ ) that destabilise the carbene vacant  $p_\pi$  orbital. In these complexes the LUMO is polarised towards the carbene centre which therefore presents an electrophilic character (Scheme 1). On the contrary, in Schrock type carbene species, the carbon atom usually bears alkyl substituents, and the complexes are therefore named alkylidene. In these complexes,  $n_\sigma$  and  $p_\pi$  frontier orbitals are thus close in energy. In this case the HOMO is polarised towards the carbon atom and the complex exhibits a nucleophilic character. To summarize, in a Fischer type carbene complex, the donation of the carbene  $n_\sigma$  lone pair to a metal vacant orbital accounts for the metal – carbon  $\sigma$ -bond and the metal carbon  $\pi$ -bond results from the back-donation from a metal orbital to the carbene vacant  $p_\pi$  orbital. On the other hand, a Schrock type carbene complex is best described by the interaction between two triplet fragments leading to the establishment of a covalent metal carbon double bond (Scheme 2).



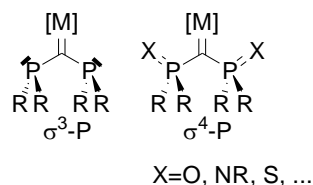
**Scheme 2**

In general, the stabilisation of the carbene centre in a complex can be provided either by the metal fragment or by the substituents on the carbon atom. The relative extent of these stabilising interactions regulates the double bond character in the M=C interaction and governs the reactivity of the carbene centre. The synthesis of new carbene complexes that present various substitution schemes is therefore of great interest to promote new reactivities. To that purpose, the introduction of phosphorus containing groups can be foreseen to be rewarding. First and foremost, the chemistry of phosphorus based functions has been well developed for more than 25 years, and now takes advantage of powerful synthetic tools. More importantly, the phosphorus atom can adopt various coordination numbers that dramatically affect its electronic properties. Indeed, a  $\sigma^3$ -P atom possesses a lone pair that can interact with a carbene centre by destabilising its vacant  $p_\pi$  orbital. On the contrary a  $\sigma^4$ -P group presents low lying  $\sigma^*$  orbitals which can be involved in delocalising electronic density in the carbene  $p_\pi$  orbital by negative hyperconjugation (Scheme 3).



**Scheme 3**

The aim of the present perspective is to gather the main conclusions that have come out of recent works devoted to the study of carbene complexes bearing two phosphorus groups ( $\sigma^3$ -P and  $\sigma^4$ -P) on the carbon atom and outline the more promising directions to explore (Scheme 4).

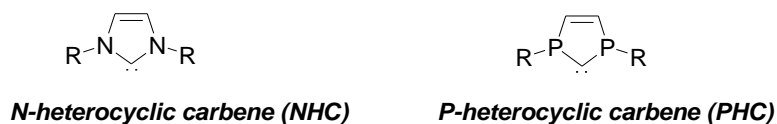


**Scheme 4**

## 2. Carbene complexes substituted by two donor $\sigma^3$ -P moieties

### 2.1 Synthesis and reactivity

The search for carbene complexes stabilised by two phosphanyl groups has motivated many studies. Indeed, this class of complexes includes the phosphorus analogues of the well-known complexes bearing an N-heterocyclic carbene (NHC) (Scheme 5).<sup>7</sup>



**Scheme 5**

NHC ligands have met with great success because of their stability and their easy and versatile synthesis.<sup>2,3</sup> They have been shown to act as almost pure, strong  $\sigma$ -donor ligands, and have found many applications both in coordination chemistry and in homogenous catalysis.<sup>3,8</sup> Interestingly, early theoretical studies have pointed to a lower stability of their P-counterparts, namely P-heterocyclic carbenes (PHCs). Indeed the geometries optimised for the parent NHC (**A**) and PHCs (**B** and **C**) present different features (Figure 1). On the first hand, the nitrogen centres of **A** are in a perfectly planar environment revealing a strong interaction between the N lone pairs and the carbene vacant  $p_\pi$  orbital (N-C=1.37 Å).<sup>9</sup> On the other hand, the P atoms in the parent PHCs remain pyramidal ( $\Sigma\alpha(\text{P})=336^\circ$ ) and both *rac* and *meso* diastereomers are stable (**B** and **C**, respectively).<sup>10</sup> This observation is in agreement with a higher inversion barrier for a phosphine (30-35 kcal/mol) compared to an amine (about 5 kcal/mol). Thus, although P is inherently as good a  $\pi$  donor as N,<sup>10c</sup> the difficulty in achieving planarity results in a weaker overlap with the vacant  $p_\pi$  orbital at C. Overall, in the calculated structures, the P lone pairs participate to the stabilisation of the carbene centre (as shown by the short P-C bonds at 1.72 Å), but the PHC ligand **B** is less stable than **A**, as attested by the very large difference in the energy for the dimerisation of NHCs and PHCs. Indeed, for the parent compounds, the Gibbs free energy for the dimerisation is 0.9 kcal/mol for NHC and -103.2 kcal/mol for PHC.

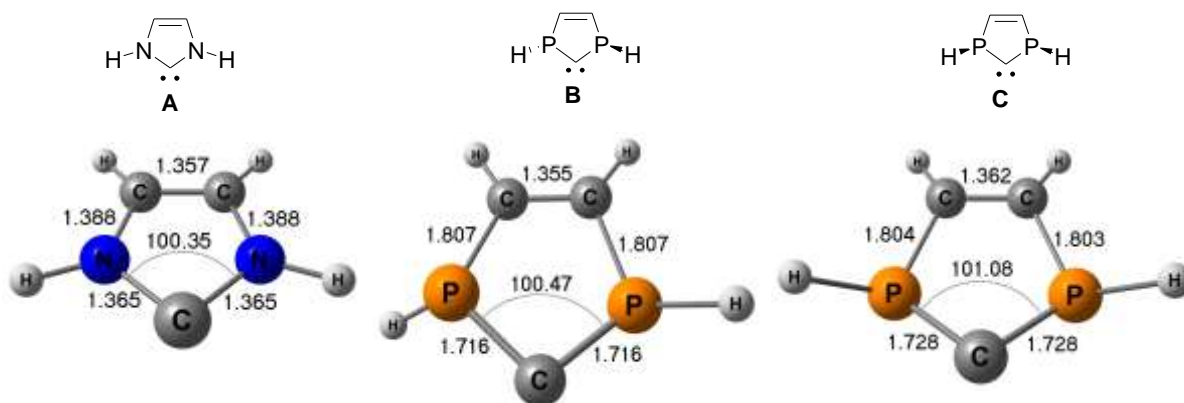
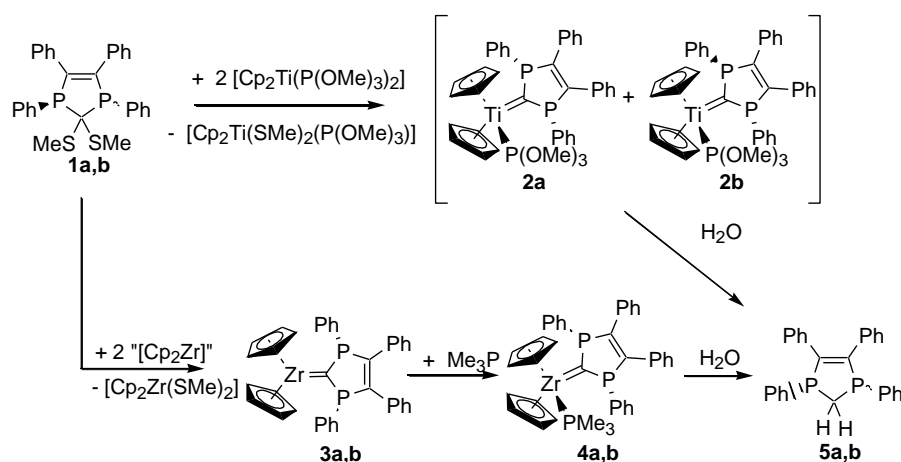


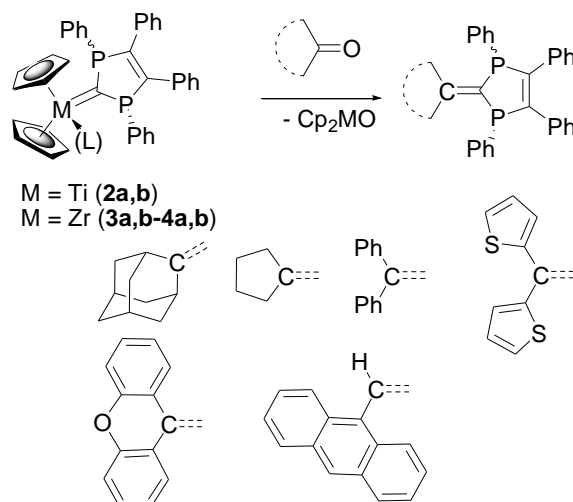
Figure 1

According to these theoretical results, two directions might be envisaged to access complexes with a coordinated PHC. A valuable approach involves the use of a stable PHC precursor that would decompose in the coordination sphere of a transition metal, leading to a complex whose PHC stabilisation is completed by the metal fragment. Another strategy would consist in increasing the effective  $\pi$ -donor ability of the  $\sigma^3$ -P atoms by lowering their inversion barriers, in order to stabilise the free PHC ligand, prior to its coordination to a metal precursor. The two approaches have been successfully explored in the last few years. In 2004, we described the first complexes of a PHC ligand.<sup>11</sup> The 2,2-dimethylthioacetal of the 1,3,4,5-tetraphenyl-1,3-diphosholene **1a** (*meso*) and **1b** (*rac*) was chosen as a carbene precursor and their reduction was performed by two equivalents of  $[\text{Ti}^{\text{II}}\text{Cp}_2(\text{P}(\text{OMe})_3)_2]$  complex. The corresponding carbene complexes **2a,b** were obtained in a 4:1 ratio (Scheme 6). Unfortunately, complexes **2a,b** exhibit a short life-time and decomposition rapidly occurs in THF at room temperature (no  $^{31}\text{P}$  NMR signal remained after 12 hours standing at  $25^\circ\text{C}$ ).



Scheme 6

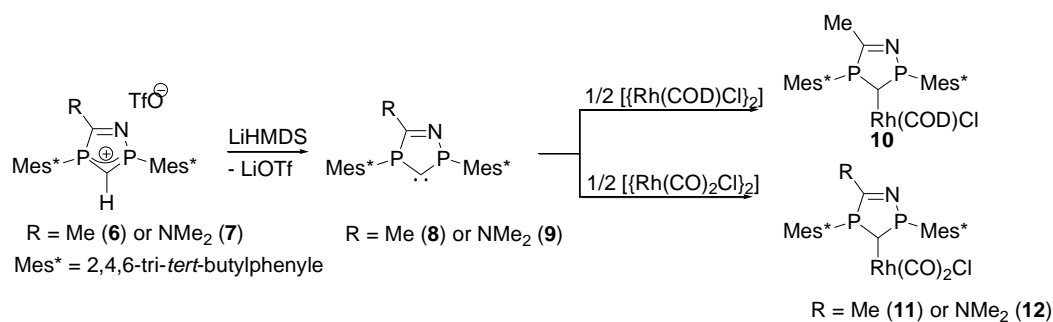
To ensure better stability to the formed carbene complexes, zirconocene was used instead of titanocene, since a stronger metal-carbon bond was expected. Reaction of **1a,b** with the transient complex  $[\text{ZrCp}_2]$  in THF at room temperature cleanly yielded complexes **3a,b** in a 4:1 ratio according to  $^{31}\text{P}$  NMR spectroscopy (Scheme 6). Contrary to their titanium counterparts, **3a,b** proved to be stable in solution for at least a week in THF at room temperature but were found to be unstable in the absence of solvent. Formation of **3a,b** was unambiguously established by addition of  $\text{PMe}_3$  to the zirconium centre to yield complexes **4a,b** that were fully characterized by multinuclear NMR spectroscopy. The  $^{13}\text{C}$  NMR signal for the carbene centre in **4a** is characterized by an  $\text{AX}_2\text{Y}$  spin system at 220 ppm with a large  $^1J_{\text{CP}}=87.3$  Hz coupling constant ( $^2J_{\text{CP}}=11.5$  Hz). This chemical shift falls in the range of data reported for zirconium carbene complexes.<sup>12</sup> The reactivity of carbene complexes **2-4a,b** was explored. These complexes proved to be highly sensitive towards hydrolysis, leading to the complete formation of 1,3-diphosphenes **5a,b** in the presence of water. This reactivity not only establishes the cleavage of the two carbon – sulphur bonds of the precursor **1a,b** but also the nucleophilic character of the resulting carbene complexes. This was further assessed by trapping **2-4a,b** with aldehydes and ketones. Thus, complexes **4a,b** react cleanly with sterically encumbered compounds (such as 2-adamantanone) or aromatic derivatives to yield 1,3-diphosphafulvenes (Scheme 7), which were shown later to be good precursors of the diphosphafulvenium radical cations.<sup>13</sup>



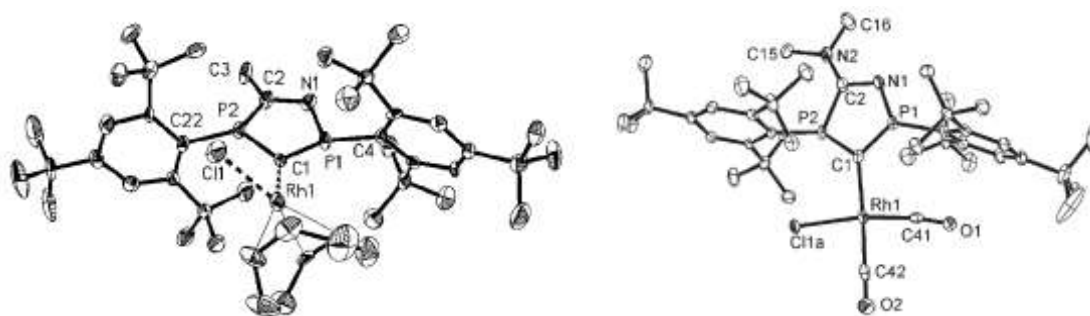
**Scheme 7**

In 2005, Bertrand and co-workers successfully employed the second strategy to access complexes featuring a PHC ligand.<sup>14</sup> Reasoning that bulky substituents would favour a planar configuration on the P atoms and thus increase the effective  $\pi$ -donor ability of the phosphorus, they prepared the 1,3-diphosphenium cations **6** and **7**. Deprotonation of these

species led to the formation of PHCs **8** and **9** which proved stable at room temperature in the solid state. In solution, **8** undergoes a [3+2] retrocycloaddition to afford acetonitrile and the corresponding 1,3-diphosphaallene. Diphosphino carbene **8** finally possesses a half-life of 5 h at 16°C in THF whereas no retrocycloaddition is observed for **9** after 24 h at 25°C in THF. The X-ray crystal structure of **8** confirmed the almost planar environment of the phosphorus centres, induced by the bulky Mes\* (Mes\*=2,4,6-tris(*tert*-butyl)phenyl) groups. The steric hindrance appeared to be a key factor to ensure the stability of the free carbenes. Indeed, the use of less sterically demanding as *tert*-Butyl groups in place of Mes\* was attempted but met with failure as the corresponding conjugate acid, precursor of the PHC, could not be obtained.<sup>15</sup> The two free PHCs (**8** and **9**) were used as ligand to obtain new rhodium(I) carbene complexes (**10-12**). Complexes **10-12** have been fully characterized by multinuclear NMR spectroscopy and the X-ray structures for both **10** and **12** have been recorded (see below).



**Scheme 8**



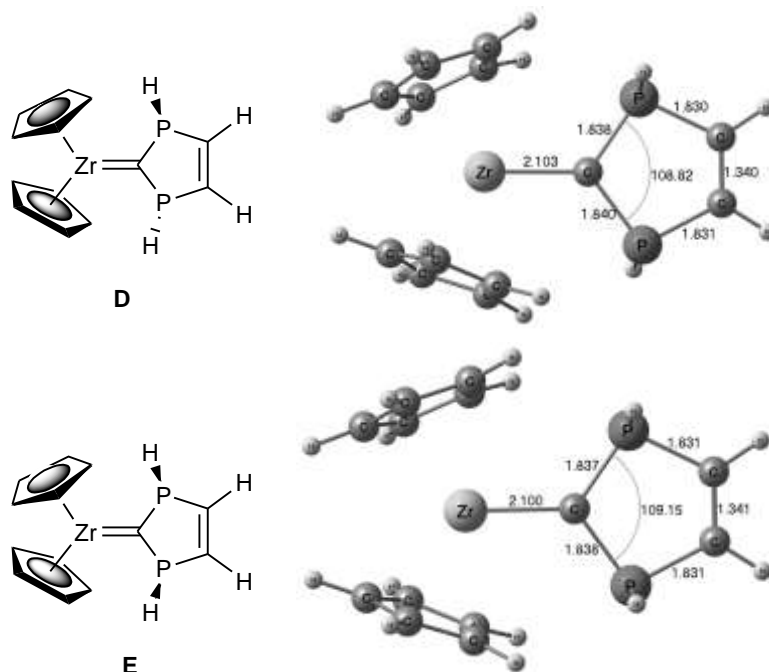
**Figure 2 : Ortep plot of complex 10 (left) and 12 (right) copyright Wiley 2005 and 2007.**

To date, the reactivity of complexes **10-12** has not been described but the stability of **10** in dichloromethane, as well as in air, points to a weak if any nucleophilic character. Moreover, the stability of the carbene centre being provided almost only by the two  $\pi$ -donor phosphorus substituents ( $\sigma^3$ -P) of the ligand, the complexes are best described as Fischer type complexes and an electrophilic character of these complexes is to be expected.

## 2.2 Electronic Structure



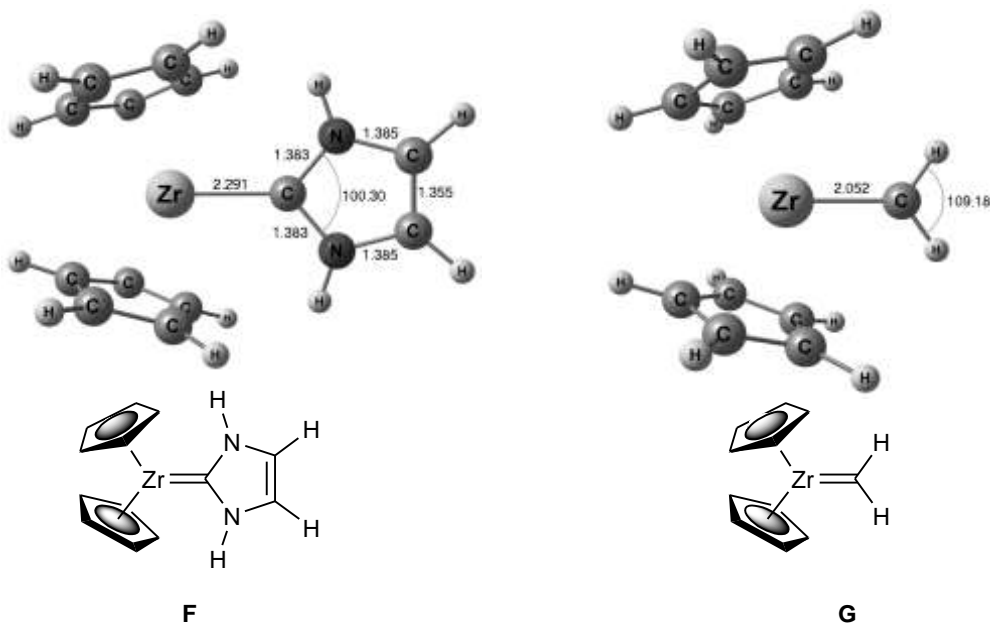
According to the experimental data, two distinct electronic situations are in play in complexes **2-4** and **10-11**. To circumvent the lack of X-ray structure for **2-4** and get further insights into their electronic structure, model complexes **D** and **E** (parent models of **3a** and **3b**) have been studied by means of DFT calculations. The geometry of the complexes is reported in Figure 3.



**Figure 3 : Model complexes D and E and their optimised geometry**

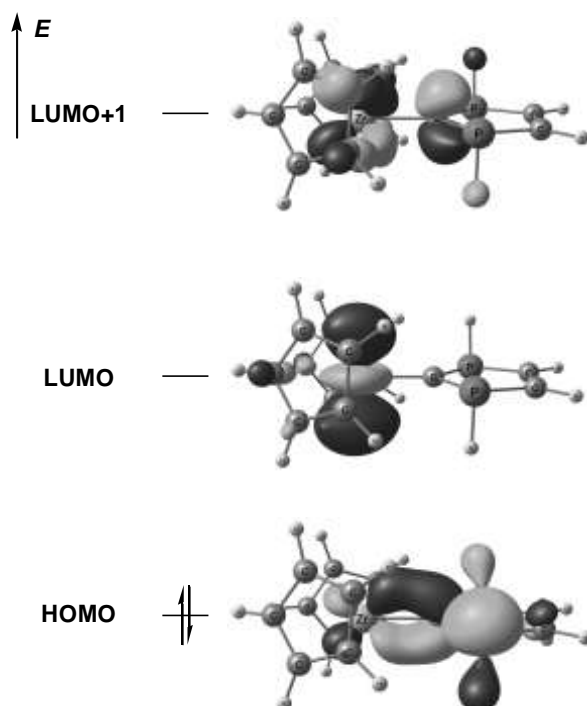
Both **D** and **E** are characterized by a strong Zr-C interaction evidenced by a short Zr-C bond (2.10 Å), which is to compare with that in zirconium alkyl complexes (Zr-C: 2.38 Å) and zirconium alkylidene complexes (2.14 Å). Moreover, the P-C bonds are longer in complexes **D** and **E** than in free PHC ligand (1.84 Å in **D** vs 1.72 Å in **B**) indicating a weak participation of phosphorus atoms in the stabilisation of the carbene centre in complexes **D** and **E**. This is further confirmed by the geometry of these atoms; whereas they tend to adopt a planar geometry in the free ligand ( $\Sigma\alpha(\text{P})=336^\circ$  in **B**), a tetrahedral environment is noted in the complexes ( $\Sigma\alpha(\text{P})=297^\circ$  in **D**).  $\sigma^3\text{-P}$  centres therefore behave as phosphines in **D** and **E** and possess inversion barriers much higher than the one computed for the corresponding free ligands ( $\Delta E_{\text{ZPE}}=22.3$  kcal/mol for **D** vs 2.1 kcal/mol for **B**). This energy profile is consistent with the observation of both diastereoisomers **4a** and **4b** in solution at room temperature. All these data point to a stabilisation of the carbene centre mostly by the metal fragment in **D** and **E**.<sup>16</sup>

Interestingly, a comparison was made between the electronic situation in complex **D** and that of its nitrogen analogue (**F**) and the alkylidene complex  $\text{Cp}_2\text{Zr}=\text{CH}_2$  (**G**) (Figure 4). As mentioned above, NHCs behave as pure  $\sigma$ -donor ligands, because of a high-lying  $p_\pi$  carbene orbital due to a strong stabilisation by the nitrogen lone pairs. On the contrary, in **G**, the stabilisation can not be ensured by the substituents on the carbon atom and must be provided by the metal. Comparing the Zr-C bond distances in **D**, **F** and **G** is diagnostic: whereas both **D** and **G** exhibit a strong Zr-C interaction (2.10 and 2.05 Å respectively), a long Zr-C bond length is calculated in **F** (2.29 Å). Furthermore the metric parameters of the imidazol-2-ylidene ring in **F** are very close to that of the free ligand **A**. N-C bonds remain short (1.38 Å) and the nitrogen atoms planar upon coordination to the zirconocene fragment, suggesting a low participation of the metal to the stabilisation of the carbene centre.



**Figure 4 : Model complexes F and G and their optimised geometry**

A precise description of the bonding situation in **D** may be done by examination of its frontier molecular orbitals (Fig. 15).



**Figure 5: Bonding Scheme in D.**

The LUMO consists in a non-bonding metal orbital ( $d_{z^2}$ ). The HOMO describes a bonding  $\pi$  interaction between the carbene  $p_\pi$  orbital and the metal  $d_{xz}$  orbital. The corresponding antibonding  $\pi^*_{Zr=C}$  orbital is vacant and represented by the LUMO+1 of the complex. To be more precise, the HOMO is polarised towards the carbon atom (67.3%) and reveals a high occupancy of the carbene  $p_\pi$  orbital in the complex (which is the equivalent of the  $p_\pi$  orbital of the PHC **B**). This electronic transfer (from the metal to the ligand) accounts well for a lower participation of the  $\sigma^3$ -P atoms to the stabilization of the carbene centre (lengthening of the P-C bonds upon coordination, pyramidal environment at the P centres). On the whole, 1.14 electrons are transferred from the metal fragment to the LUFO of the PHC ligand in **D**. The same calculation indicates that the carbene  $p_\pi$  orbital is occupied by 1.00 electron in **G** and only 0.01 electron in **F**. The NHC complex **F** and the PHC complex **D** finally possess very different bonding schemes. In **F** no  $Zr=C$  double bond character is involved, whereas **D** and **G** are typical Schrock type carbene complexes, with a true metal – carbon double bond.<sup>11</sup>

Complexes **10** and **12** have been characterized by X-ray diffraction analysis. Both structures revealed phosphorus centres in a quasi-planar environment ( $\Sigma\alpha(P)=339-359^\circ$ ) pointing to a strong stabilisation of the carbene centre by the P lone pairs. This is confirmed by short P-C bonds in the complexes comparable with those observed in the free ligands (respectively 1.71 and 1.69 Å). As a consequence, the metal fragment only slightly participates to the stabilisation of the ligand and a long Rh-C bond distance is observed (2.064(8) for **10** and 2.111(3) for **12**). These features were corroborated by the very low

values of the carbonyl stretching frequencies measured in complexes **11** and **12** (2059, 1985 and 2062, 1981  $\text{cm}^{-1}$  respectively), which indicate a strong  $\sigma$ -donor and a very low  $\pi$ -acceptor ability of the PHCs **8** and **9**. In fact, the basicity of these carbenes appears comparable to that of the more basic NHCs. Therefore, as a conclusion, the electronic situation in complexes **2-4** and **10-12** featuring both vicinal  $\sigma^3$ -P substituents, is radically different: the stabilisation of the carbene centre is mainly brought by the metal in **2-4**, whereas it is ensured by the bulky phosphorus moieties in **10-12**. This explains why these two types of complexes exhibit very different reactivities, **4a,b** being nucleophilic as revealed by hydrolysis and trapping with carbonyl derivatives, whereas **10** presents a weak if any nucleophilic character (no reaction with water, chlorinated solvents and air).

### ***3. Carbene complexes substituted by two donor $\sigma^4$ -P moieties***

As mentioned in the introduction, a  $\sigma^4$ -P group presents low lying  $\sigma^*$  orbitals which would be able to stabilise the coordinated carbene  $p_\pi$  orbital by negative hyperconjugation. But, since these functional groups act as  $\pi$  accepting moieties, they may not stabilise the carbene in its free state. Therefore, three strategies have been devised to get round this point. They are all based on the decomposition of a suitable precursor in the coordination sphere of a metal centre. The first relies on the use of stable geminal dianions, and the second is based on the synthesis of a carbenoid species. This latter method has been reported for the first time in 2007. Lastly, the geminal double deprotonation of a “methylene” ligand in the coordination sphere of a metal centre may also be carried out. In the presentation of the carbene complexes obtained by any one of these methods, we will restrict ourselves to the cases where a M-C double bond is present, at least formally. Therefore, the complexes in which the carbon centre acts as a bridging ligand between two metal centres are excluded.

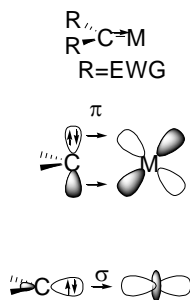
#### *3.1 Precursors*

##### *3.1.1 Geminal dianion*

###### *3.1.1.1 Synthesis*

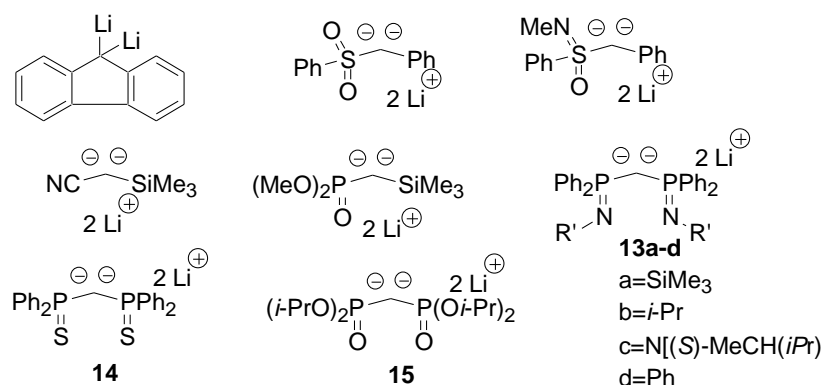
The basic principle for the use of geminal dianions to synthesise carbene complexes is presented in the following scheme. The  $\sigma$  interaction results from the donation of the lone  $n_\sigma$  lone pair at carbon into an empty orbital at the metal. The  $\pi$  interaction is specific of these fragments and results from the donation of the second lone pair. Overall, up to four electrons

may be given by the geminal dianion into orbitals of suitable symmetries and energies at the metal centre (Scheme 9).



**Scheme 9 : Bonding scheme the coordinated dianions**

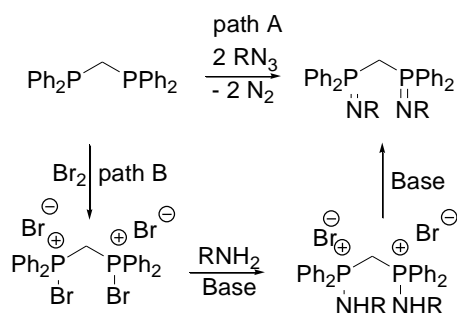
Here, as in the case of Fischer type carbene complexes, the amount of the latter  $\pi$  interaction will strongly depend on the competitive stabilisation by the R groups at the carbon center. Although nearly ten substituents have been shown to be competent to stabilise geminal dianions,<sup>17</sup> only two of these species (R = PPh<sub>2</sub>NR', PPh<sub>2</sub>S) have been used as precursors for carbene complexes of transition metals.<sup>18</sup>



**Scheme 10: Examples of dianions**

The geminal dianions are extremely sensitive and reactive species, which readily abstract protons from various sources (solvent, etc...) to form the less reactive monoanions. In fact, some of these species are only obtained in low yields after crystallisation from crude mixtures containing large excesses of the base used for the double deprotonation. For example, the sulfoximine derivative was crystallised out from the crude mixture containing excess *n*-BuLi, which was partially hydrolysed to form Li<sub>2</sub>O, incorporated in the 3D structure.<sup>17e</sup> Following this work, Müller and co-workers succeeded in the partial transmetalation of the Li<sub>2</sub>-dianion to the mixed Li-Ti-dianion species.<sup>19</sup> The real beginning of the use of the geminal dianions in coordination chemistry dates back from 1999, when the

groups of Stephan and Cavell reported independently the high yield synthesis and isolation of the bis(iminophosphorane) derivative **13a** ( $R' = \text{SiMe}_3$ ).<sup>20,21</sup> The neutral starting material was obtained using the very straightforward Staudinger synthesis from two commercial reagents: bis(diphenylphosphino)methane (dppm) and  $\text{Me}_3\text{SiN}_3$ .<sup>22</sup> Cavell and co-workers studied in depth the coordination chemistry of these species and their results will be presented further on. As clearly shown in the bonding scheme 9, modifying the electronic and the steric requirements of the stabilising substituents at the carbon centre could lead to significant changes in the reactivity of the carbene complex. Thus, an easy access to a range of iminophosphorane was desirable. If the Staudinger method seems at first glance very appealing (only  $\text{N}_2$  is formed as by product), it requires an access to azides (path A), which is not only somewhat restricted, but also some of them may be explosive. This methodology is efficient to synthesise bis(iminophosphoranes) bearing TMS,<sup>23</sup>  $\text{P}(\text{X})(\text{OR})_2$ ,<sup>24</sup> and sterically hindered aryl groups.<sup>25</sup> Aiming at varying both the electronics and sterics of bis(iminophosphoranyl)methaniides, we have recently developed a general methodology relying on the Kirsanov reaction between primary amines and the bis(phosphonium) bromide derivated from dppm (path B).<sup>26</sup> The modification of the nitrogen substituent using this methodology, in particular the access to chiral derivatives, is thus readily achieved. Moreover, the bis(aminophosphonium) intermediate salts are stable to both air and moisture. The air and moisture sensitive, neutral bis(iminophosphoranes) are then obtained by double deprotonation (Scheme 2, path B).



**Scheme 11: Two synthetic ways to bis(iminophosphoranes)**

Further deprotonation to the dianion requires the use of two more equivalents of a strong base. In 2004, we reported on the quantitative synthesis of the dianion of the bis(diphenylthiophosphinoyl)methane, and of the bisphosphonate using a similar strategy.<sup>27</sup> Experimentally, the conditions required for the efficient production of the dianions differ greatly with the nature of the phosphorus group. Indeed, although **14** can be synthesised

within 1 hour at room temperature, **13** requires more than 3 days and the complete formation of **15** is only achieved after 10 days. In the latter case, addition of TMEDA accelerated the reaction which then was complete within 3 days, whereas it has no effect on the synthesis of **13**. Even more surprising, addition of TMEDA in the reaction to form the dianion **14** prevented its formation as the monoanion precipitated from the mixture. It thus appears that the development of efficient procedures for the synthesis of other dianionic derivatives would require a precise optimisation of the reaction conditions. In this sense, using phosphorus derivatives is a tremendous advantage as the reactions may be readily followed by  $^{31}\text{P}$  NMR spectroscopy.

When soluble enough in organic solvents, dianions were characterised by multinuclear NMR spectroscopies, and present comparable spectra. In  $^{31}\text{P}$  NMR spectroscopy, a singlet at 23 ppm is observed for **14** and in the range 12-20 ppm for **13a-c**. In the  $^{13}\text{C}$  NMR, the PCP carbon appears as a triplet at very high field: 30 ppm ( $J = 41$  Hz) for **14**<sup>27</sup> and 15 ppm ( $J = 23$  Hz) for **13c**.<sup>26</sup> As **13b,d** are too insoluble to perform full NMR characterizations, indirect evidence of their formation was given by hydrolysis with  $\text{D}_2\text{O}$  giving the corresponding bis-deuterated bis(iminophosphoranes). As mentioned above, the X-Ray structures of dianions **13a,c** and **14** were resolved (Fig. 6). The bis(iminophosphorane)diide)methane ligands **13a,c** adopt both a dimeric structure which is organized around an  $\text{C}_2\text{Li}_4$  octahedron, each lithium atom being coordinated by the two dianionic carbon atoms.<sup>20,21,26</sup> The structure of dianion **14** is remarkably different since it crystallised as a dimer in which the two dianionic carbon atoms are bridged by two lithium, while the two other ones bridge two sulphur centres.<sup>27</sup> In fact, a second structure for compound **14** could be obtained from another set of solvents. It exhibited a different state of aggregation, which was investigated by variable temperature experiments.<sup>27</sup>

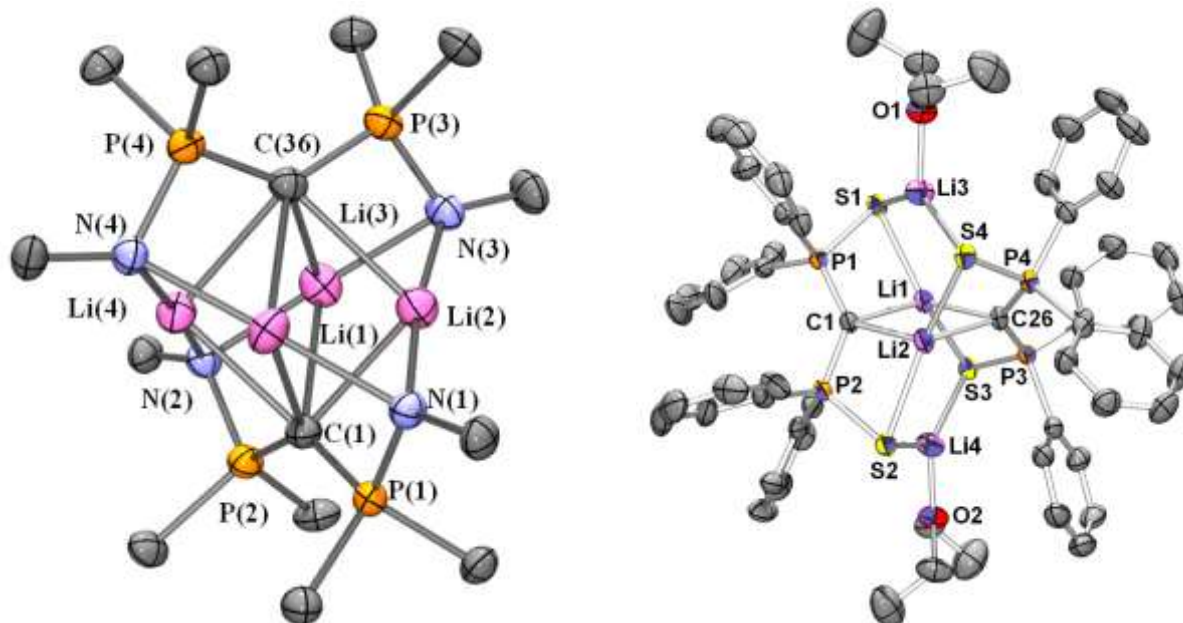


Figure 6: Molecular structure of compound **13c** (left), only the carbon atom of the MeCH(*i*-Pr) group linked to nitrogen and the ipso carbon atom of the phenyl groups have been represented for clarity, and **14** (right). Ellipsoids are drawn and 50% probability level.

### 3.1.1.2 Electronic structure

To get further insight into the electronic structure on dianions **13-15**, DFT calculations were performed (B3PW91/6-31+G\* level of theory) on parent models labelled **H**, **I** and **J** (fig. 7).<sup>27,28</sup>

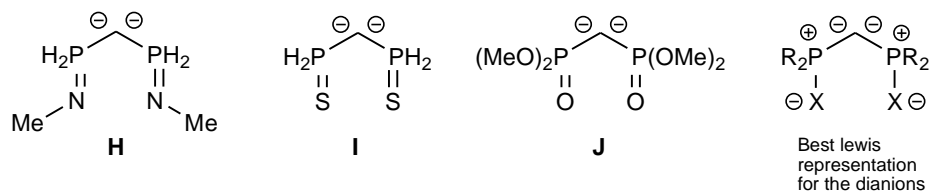


Figure 7 : Model dianions **H**, **I** and **J** and Lewis description

The optimised geometries for the dimers are in excellent agreement with the X-ray crystal structures. In particular, both the very short P-C bonds (1.68 and 1.69 Å on average in **H** and **I** respectively) and the P-X bonds are very well reproduced. The lack of Li...Li and C...C interactions is also noted (2.542 Å and 3.527 Å respectively for the sulphur derivative) and confirmed by Wiberg bond indexes calculated as 0.00. NBO analysis performed on **H**, **I** and **J** indicates that the dianionic species **13**, **14** and **15** are best described by the Lewis structure drawn in figure 7. Indeed, the central carbon atom bears two non equivalent lone pairs strongly stabilised by negative hyperconjugation (*i.e.* donation to the vicinal antibonding P-R and P-X bonds). These hyperconjugation interactions preferentially stabilise the best donor orbitals (*i.e.* LP(C), LP meaning lone

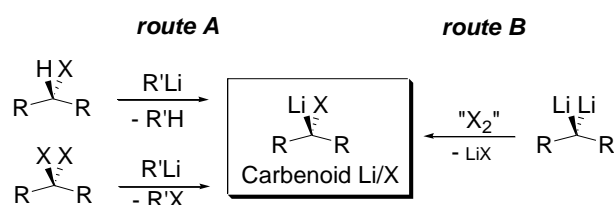


pair) which in turns results in a decreased stabilisation of the X-substituent lone pairs (LP(S) or LP(N) or LP(O)) and thus in an increased negative charge at the X centres (concomitant with an elongation of the P-X bonds). Finally, delocalisation forms that involve P-X or P-C double bonds are not accurate to describe the stability of such systems since they would involve a  $p\pi-d\pi$  bonding scheme abandoned for over 10 years.<sup>29</sup>

### 3.1.2 Carbenoid

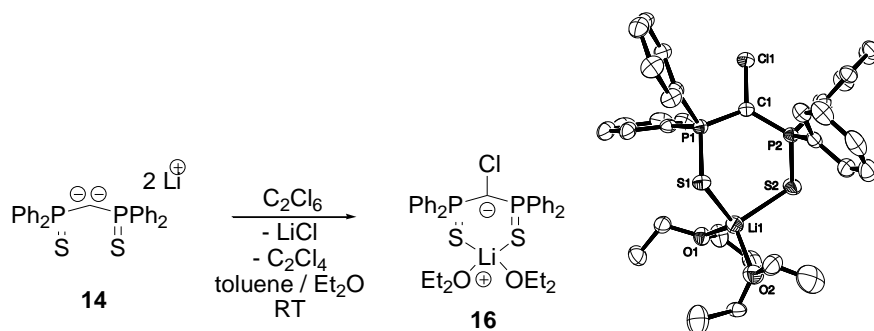
#### 3.1.2.1 Synthesis

As shown above, the  $\sigma^4$ -P functional groups act as powerful  $\pi$  accepting moieties and as a consequence, may not stabilise the carbene in its free state. From another standpoint, carbenoid species have proven in many instances their close relation in terms of reactivity with free carbenes. Most famous are the Zn carbenoids (Simmons-Smith reaction) for their uses in the cyclopropanation reaction of alkenes.<sup>30</sup> Late 2006, we reasoned that the two thiophosphinoyl substituents might stabilise, at least transiently, carbenoid species. The common very low temperature carbenoid syntheses rely on either the deprotonation of an  $\alpha$  halogenoalkane or the Li-halogen exchange from a  $\alpha$  dihalogenoalkane (scheme 12, route A).<sup>31</sup> Formally, these two routes can be viewed as the reduction of the carbon centre. With this strategy, the most stable Li-halogen carbenoid species, reported by Niecke et al, decomposes above  $-10^\circ\text{C}$ .<sup>32</sup>



**Scheme 12 : Synthetic strategies to carbenoid**

Starting from dianion **14**, a very reduced species, the controlled oxidation (route B) was attempted. Reacting **14** with hexachloroethane, a mild oxidant, allowed the isolation of a single new product **16** (Scheme 13). Noteworthy, this carbenoid is stable not only at room temperature but up to  $60^\circ\text{C}$ . Compound **16** was fully characterized by NMR spectroscopy and X-ray crystallography.<sup>33</sup>



**Scheme 13 : Synthesis of carbenoid 16**

Analysis of metric parameter reveals that the C-Cl bond (1.781(2) Å) is strong as in the corresponding neutral species obtained by hydrolysis. For typical carbenoids, the  $^{13}\text{C}$  NMR signal of the Li/X carbenoid ( $\text{R}_2\text{CLiX}$ ) centre is deshielded compared to the hydrogenated species ( $\text{R}_2\text{CHX}$ ). This downfield shift, closely related to the magnitude of paramagnetic contribution of the antibonding  $\sigma^*_{\text{C-Cl}}$  orbital to the chemical shift, has been attributed to a weakening of the carbon-halogen bond upon metalation. In the present case, the carbenoid **16** is upfield shifted compared to the hydrolysed derivative, this is in agreement with the C-Cl bond length in compound **16**.

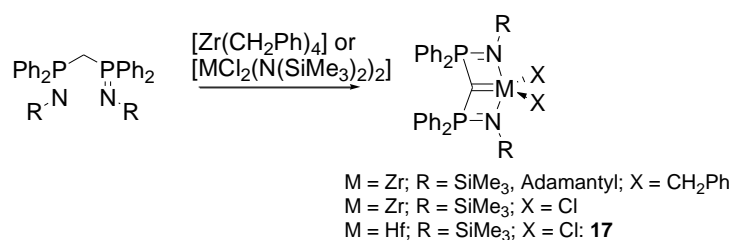
### 3.1.2.2 Electronic structure

In order to fully understand the unprecedented stability of this compound, its electronic structure was studied.<sup>33</sup> Analysis of the carbon hybridization state indicates that the carbon atom possesses a pure 2p lone pair. As for the dianion, this lone pair is very efficiently stabilised by negative hyperconjugation into the  $\sigma^*$  P-C and P-S antibonding orbitals. As a consequence, the carbon s character in the C-Cl bond remains high and the carbon atom directs a hybrid orbital with 21.9% s-character towards the chloride atom (18.6% in the hydrolysed compound). The DFT calculations therefore corroborate the experimental findings on the unusual strength of the C-Cl bond. To conclude, the stability of carbenoid **16** comes from i) the coordination of the lithium cation by the thiophosphinoyl arms and ii) the stabilisation of the carbon lone pair in a pure p orbital, which leads to a rather strong C-Cl bond.

## 3.2 Coordination to electron-deficient metal centers

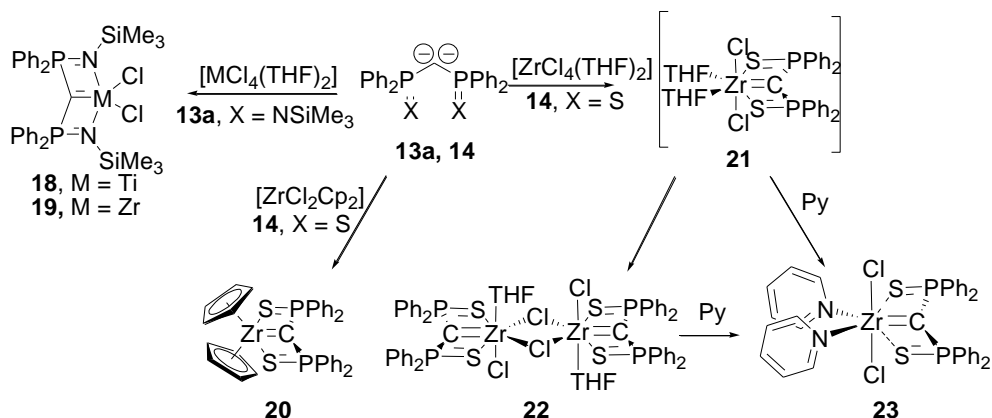
### 3.2.1 Coordination to Group IV metal centers

R. Cavell stated that “*the discovery of the first complex of this series was unexpected and serendipitous*”.<sup>17b</sup> Indeed, the transmetallation of the silyl moiety of the neutral bis(iminophosphorane) with  $\text{TiCl}_4$  was attempted. But, this only led to the formation of the simple adduct. Then, the more reactive zirconium bis amide  $[\text{ZrCl}_2(\text{N}(\text{SiMe}_3)_2)_2]$  was used leading to the *in situ* double deprotonation of the bis-iminophosphorane at relatively high temperatures (refluxing toluene). This group developed on this reactivity with other precursors bearing basic ligands, such as tetrabenzylzirconium  $[\text{Zr}(\text{CH}_2\text{Ph})_4]$  and  $[\text{HfCl}_2(\text{N}(\text{SiMe}_3)_2)_2]$  (Scheme 14).<sup>34</sup>



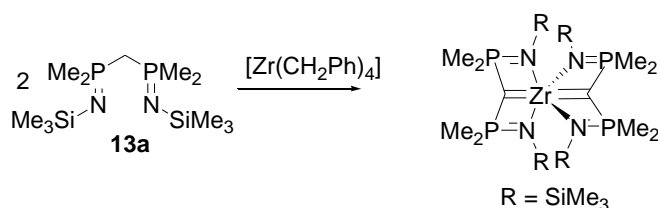
**Scheme 14 : Preparation of carbene complexes starting from neutral bis(iminophosphoranes)**

The coordination of geminal dianion to electron-deficient metal centers represents another straightforward route to carbene complexes, the  $\text{M}=\text{C}$  bond arising from the donation of the two carbon lone pairs to the acceptor metal fragment. Indeed, reaction of dianion **13a** with  $[\text{MCl}_4(\text{THF})_2]$  ( $\text{M} = \text{Zr}, \text{Ti}$ ) yielded **18** and **19**, the first stable carbene complexes of group IV metals which do not incorporate Cp ligands.<sup>35</sup> Similarly, coordination of bis(thiophosphinoyl) dianion **14** to  $[\text{ZrCp}_2\text{Cl}_2]$  and  $[\text{ZrCl}_4(\text{THF})_2]$ , led to complex **20** and **21** respectively.<sup>36</sup> The latter is converted within two hours to complex **22**. Its X-Ray crystal structure shows a dimeric structure with two chloride atoms bridging two  $[\text{ZrCl}(\text{THF})(\text{SCS})]$  units. Such dimer was never observed with bis(iminophosphorane) derivatives, probably due to a better steric protection of the metallic center in **13a** because of the trimethylsilyl groups born by the nitrogen atoms. Upon addition of an excess pyridine, complex **21** is cleanly converted to **23**, which was characterized by multi-nuclear NMR and X-Ray analysis (scheme 15). Zr-C bond distances in complexes **21-23** were found at 2.251(2), 2.180(3), and 2.172(2) Å respectively.



**Scheme 15: Titanium and Zirconium carbene complexes**

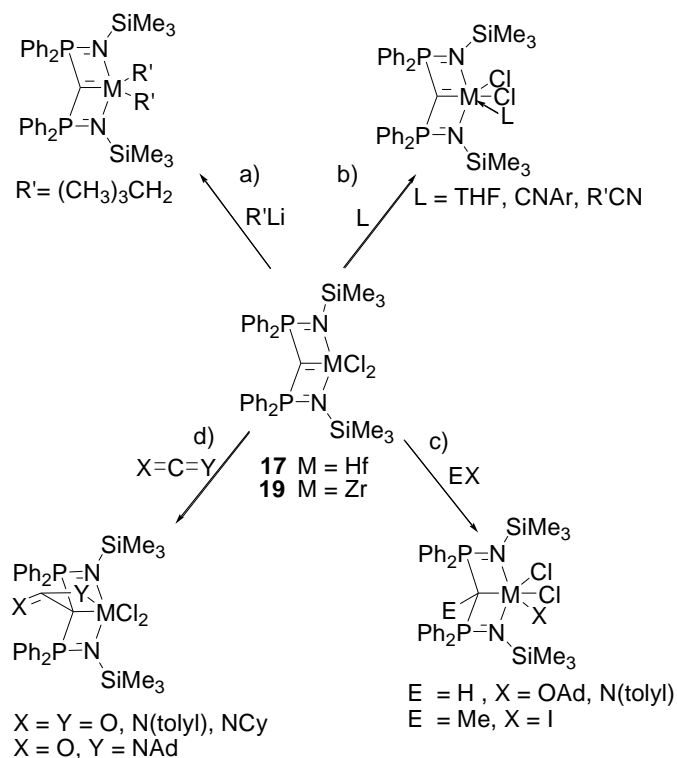
As mentioned above, carbene complexes can also arise from the reaction between neutral bis(iminophosphoranes) and chosen metal precursors bearing basic ligands, such as tetrabenzylzirconium  $[\text{Zr}(\text{CH}_2\text{Ph})_4]$  and  $[\text{HfCl}_2(\text{N}(\text{SiMe}_3)_2)_2]$  (Scheme 13).<sup>34</sup> The same reaction conducted with two equivalents of the ligand  $\text{CH}_2(\text{Me}_2\text{P}=\text{N}(\text{SiMe}_3)_2)$  and  $[\text{Zr}(\text{CH}_2\text{Ph})_4]$  allow the isolation of a bis carbene complex (Scheme 16). Nevertheless, ligands bearing other substituents on the phosphorus atom such as a cyclohexyl or a phenyl group do not exhibit the same reactivity.<sup>37</sup>



**Scheme 16 : Synthesis of zirconium bis-carbene complexes**

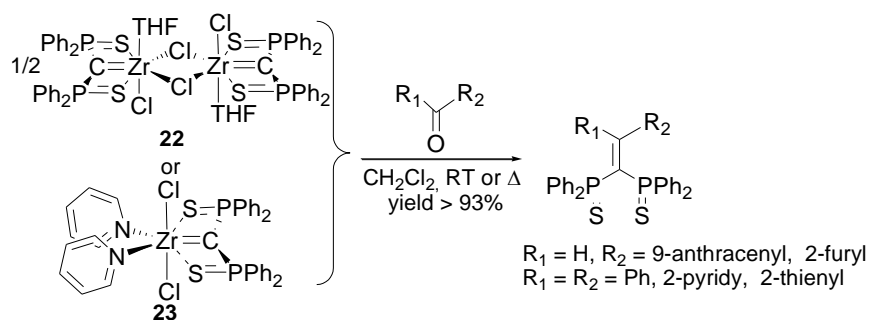
The reactivity of these group(IV) carbene complexes **17** and **19** was investigated.<sup>23</sup> Reaction with nucleophiles such as alkyllithium led to the substitution of the chloride ligands (Scheme 17, a). In presence of a two electron donor ligand L (THF, RCN or RNC), Lewis-base adducts were obtained (Scheme 17, b). When reacted with reactive electrophiles (heteroallenes derivatives) such as isocyanates, carbon dioxide or carbodiimide, the complexes did not show the expected insertion into the  $\text{M}=\text{C}$  bond. Rather, the [2+2] cycloaddition on the  $\text{M}=\text{C}$  was observed leading to the heterometallacyclobutane derivative (Scheme 17, c). The carbene double bond was also involved in reaction with proton donors

such as aromatic amines, phenols, aliphatic alcohols or methyl iodide leading to the 1,2 addition product (Scheme 17, d).



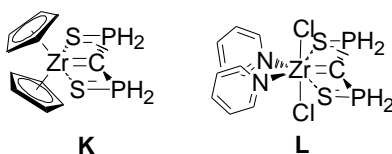
**Scheme 17 : Nucleophilic reactivity of Zr and Hf carbene complexes**

Our group studied the reactivity of (SCS) carbene complexes **20**, **22**, and **23** towards aldehydes and ketones. Despite being electron rich, complex **20** proved to be unreactive towards these electrophiles. This lack of reactivity, surprising at first glance, can be ascribed to the electronic saturation (formally 20 VE) of the metal centre. In this complex, the coordination of the oxygen atom of the carbonyl derivative is precluded, and as a consequence, this may imply that the reaction of the carbene complexes require coordination prior to addition. Accordingly, complexes **22** and **23** were found to be highly reactive towards aldehydes and ketones affording the corresponding geminal bis(diphenylthiophosfinoyl)olefins (scheme 18).



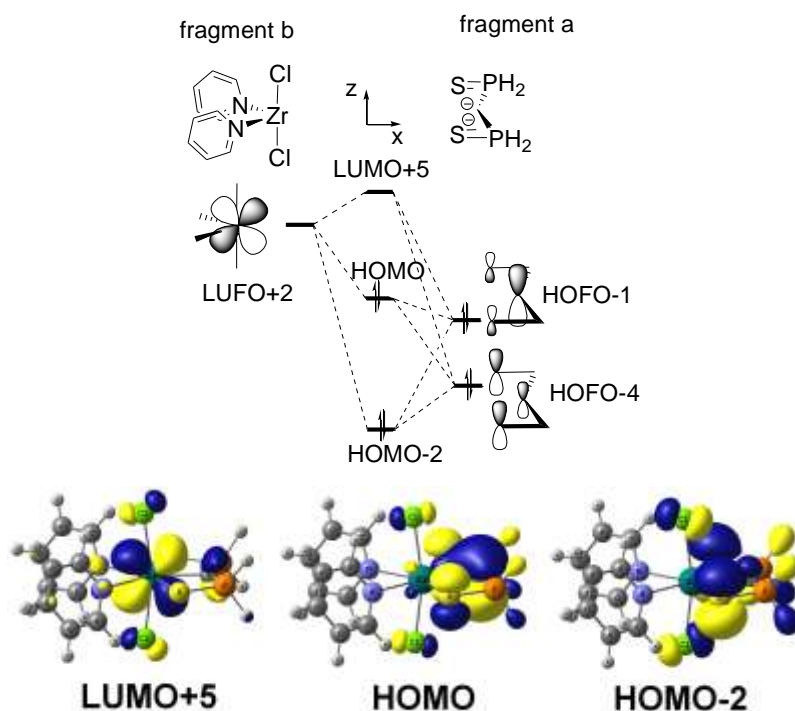
**Scheme 18 : Reactivity of (SCS) carbene complexes with aldehydes and ketones**

All these results with both (SCS) and (NCN) carbene complexes clearly evidence a polarization of the M=C bond with a nucleophilic carbon and an electrophilic metal center. To shed some light on the electronic structures of complexes **20** and **23**, DFT calculations were carried out on the B3LYP level of theory using the 6-31+G\* (for C, H, P) and LANL2DZ (for Zr) basis sets.<sup>36</sup> Optimisations conducted on models **K** and **L** in which the phenyl groups at phosphorus were replaced by hydrogen atoms (fig. 8), were found in excellent agreement with the geometries of the real complexes (X-ray structures).



**Figure 8: Model complexes K and L**

As a representative example, the analysis of complex **L** is presented here. To analyse the Zr=C double bond character, a MO diagram describing the  $\pi$ -interactions was built by decomposing the complex into two fragments, the dianionic ligand **14** (fragment a) and the 10 VE fragment “Py<sub>2</sub>ZrCl<sub>2</sub>” (fragment b) (fig. 9). Interactions between the two fragments were analysed using the AOMIX program developed by Gorelsky.<sup>38</sup> The HOFOa-1 and HOFOa-4 interact with the vacant LUFOb+2 metal orbital. The HOMO and the HOMO-2 which describe the  $\pi$ -interaction in **L** feature an important contribution of the ligand and only a weak contribution of the metal orbital. This is confirmed by the value of the Wiberg bond index of the Zr-C bond in **L** (0.80).



**Figure 9:** Simplified MO diagram of the  $\pi$ -interaction between dianionic ligand 14 (modelised by fragment a) and the  $[\text{ZrCl}_2(\text{py})_2]^{2+}$  fragment (fragment b) in model complex L.

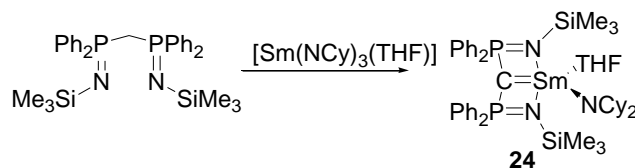
In conclusion, analysis of the electronic structures of Zr carbene complexes **K** and **L** reveals that the carbon metal bond has a low double bond character and a low bond order. In the free geminal dianion, the electron withdrawing groups (EWG) strongly stabilise the two carbon lone pairs by negative hyperconjugation (very short PC bonds with bond order of about 1).<sup>39</sup> In the corresponding complexes, the same stabilisation occurs so that the carbon  $p_\pi$  orbital is rather low in energy. This lone pair at carbon may overlap with a metal orbital of appropriate symmetry. This  $\pi$ -donation, responsible for the double bond character, also depends to a great extent on the difference in energy between the MOs involved. The calculations corroborate that the carbenic centre in these complexes bears a significant negative charge and a nucleophilic character.

### 3.2.2 Coordination to lanthanides

The case of lanthanide carbene complexes is quite an interesting one. Indeed, the classical scheme for an interaction resulting in a multiple bond between Ln and C would require first a sigma interaction between a filled orbital at the carbon and an empty orbital at Ln. Then, a back donation between a filled orbital at the metal and an empty orbital at the carbon is needed. However, in the case of Ln, such back donation is not possible as the d orbitals are empty and the f type orbitals are strongly shielded and do not participate in

bonding interactions.<sup>40</sup> Not surprisingly then, the only known examples of carbene complexes, prior to the use of the ligands presented in this review, were reported with N-heterocyclic ligands, which do not need any back donation from the metal centre. Indeed, in these cases, the Ln-C bond is typical of a single bond.<sup>41</sup> The pertinent question is therefore twofold: is it possible to synthesise another type of carbene complexes, and if so, what would be the nature of the bonding? Noteworthy, on a closely related problem, Gordon and co-workers recently showed that empty lanthanide d orbitals are involved in the stabilisation of lanthanide imido complexes *via*  $\sigma$  and  $\pi$ -donation from the imido ligand to the metal fragment.<sup>42</sup>

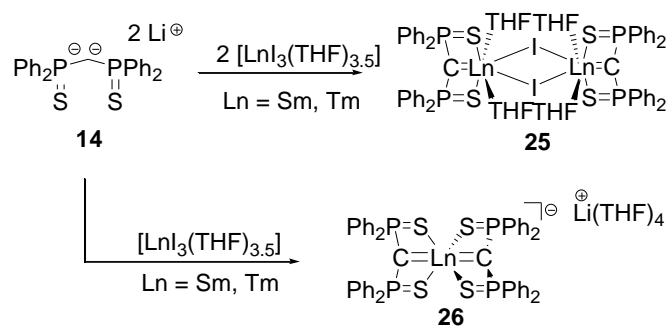
As coordination of geminal (NCN) or (SCS) dianions to electron-deficient transition metals proved to be successful to prepare carbene complexes, this strategy was extended to lanthanides. In a first approach, Cavell and coll.<sup>43</sup> utilised their efficient method: the *in situ* deprotonation of a neutral bis(iminophosphorane). The synthesis of samarium carbene **24** by reaction of  $[\text{Sm}(\text{NCy}_2)_3(\text{THF})]$  with bis(iminophosphorane) **13a** was achieved (Scheme 19). The formation of this paramagnetic complex was evidenced by the presence of a broad singlet at 43.3 ppm in  $^{31}\text{P}$  NMR, and its structure was confirmed by X-Ray analysis.



**Scheme 19: Samarium (NCN) carbene complex**

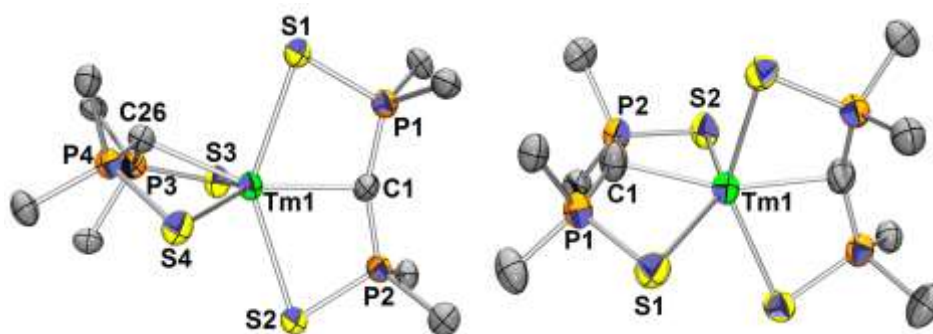
Besides, we reported the synthesis of both samarium and thullium (SCS) carbene complexes using the “geminal dianion method” between **14** and  $[\text{LnI}_3(\text{THF})_{3.5}]$  ( $\text{Ln} = \text{Sm}, \text{Tm}$ , scheme 20).<sup>44</sup> The synthesis of carbene complexes of an “early” lanthanide and “late” lanthanide was achieved to probe the effect of the size of the lanthanide on the coordination number of the complex, as it is well known that the number of coordination in lanthanide chemistry is mainly governed by steric factors. Reaction between **14** and “ $\text{LnI}_3$ ” in a 1:1 ratio led quantitatively to the formation of a iodine bridged dimer **25**, unlike in the bis(iminophosphorane) case, most certainly for steric reasons. The formation of the samarium complex **25** was accompanied by the appearance of a broad singlet at 50.8 ppm in  $^{31}\text{P}$  NMR. The recorded X-Ray structure of both samarium and thullium complexes showed that they are both seven coordinate complexes with two THF molecules coordinated to the metal centre.





**Scheme 20: Samarium (SCS) carbene complexes**

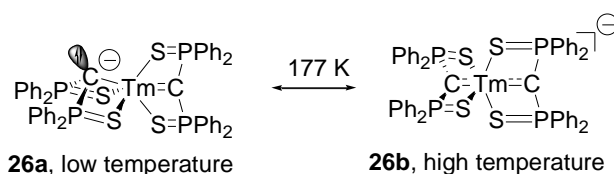
The Sm-C bond length in the (SCS) complex **25** (2.36 Å on average) is much shorter than the corresponding one in the (NCN) complex **24** (2.467(4) Å). A significant difference between these two complexes resides in the planarity at the carbenic carbon centre in **25** ( $\Sigma$  angles = 360°) whereas it is pyramidal in **24**. The planarity found in the bis(thiophosphinoyl) derivative is the most favourable case for the desired interaction between the second lone pair at carbon with an empty d orbital at the lanthanide. Then, the first homoleptic carbene complexes of both Sm and Tm in the lanthanide series could be synthesised via the substitution of the three iodine ligands of the same lanthanide precursors. In both cases, an ordered phase transition in the crystal was observed at low temperature, which allowed us to obtain two different structures for each species (fig. 10). In the Tm case, this transition occurs at 177K and the two structures are presented below.



**Figure 10 : X-Ray crystal structures of thulium complexes 26a at 150 K (two molecules in unit cell, left) and at 230 K (26b, one molecule in unit cell, right).**

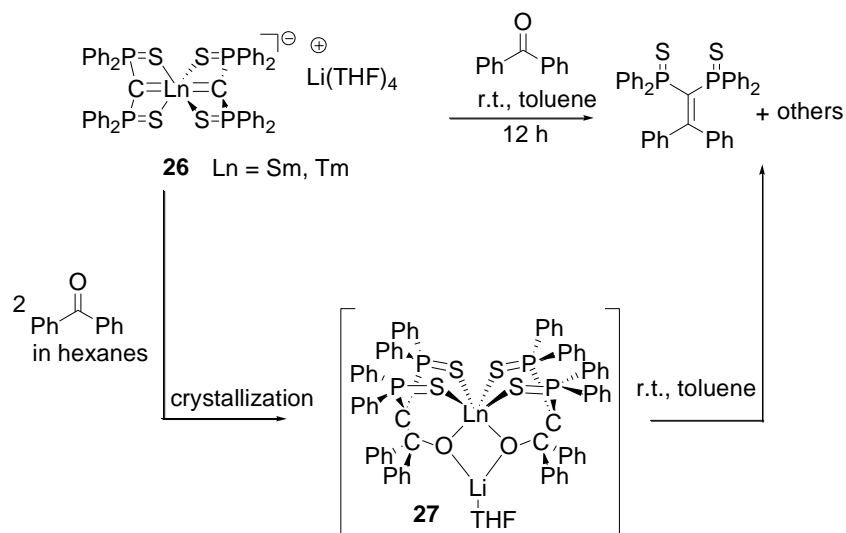
Quite interestingly, in the low temperature form **26a**, the two carbene moieties are geometrically different. In one carbene fragment, the carbon is tetrahedral with  $\Sigma$  angles = 332° (av.), with the corresponding Tm-C bond distance of 2.42 Å (av.) typical of a single bond. In the second carbenic fragment, the geometry at the carbon atom is strictly planar ( $\Sigma$  angles = 360° av.) and a shorter Tm-C bond distance of 2.38 Å (av.) is measured. These

geometrical parameters corroborate the results of the mono carbene complex, and are in favour of a double bond character for the C=Tm bond. Therefore, as shown in scheme 21, in this structure, a strongly localised electron distribution is observed. The overall charge is mainly located on the tetrahedral carbon atom, which clearly exhibits a significant  $sp^3$  character. In this complex, one carbene fragment behaves as a two electron X-type ligand, while the other donates four electrons to stabilise the thulium(III) centre.



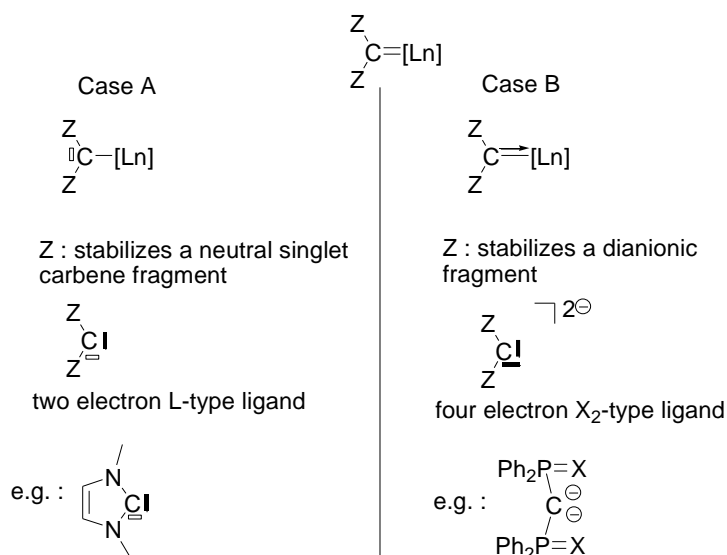
**Scheme 21: structural transition in thulium complex 26**

At 230 K, another structure was observed for complex **26**. In this form (**26b**), the two carbene moieties are identical (related by a  $C_2$  axis). Moreover, the Tm1-C1 bond distance of 2.368(3) Å is similar to the Tm1-C1 bond length in **26** (2.38 Å), and most interestingly, the geometry at both carbon atoms is here nearly planar ( $\Sigma$ angles = 351.9°) suggesting the coordination of formally two four electron donor ligands. Taken together, these data can be attributed to a delocalisation of the anionic charge over the two carbon and the thulium atoms, as shown on scheme 21, thereby indicating that a  $\pi$  overlap develops between these three atoms. Precise DFT calculations are clearly needed in order to fully describe the bonding interaction in these species, and quantify the amount of  $\pi$  donation from the carbon centre to the lanthanide empty d orbitals. In terms of reactivity, as the metal precursor is electron-deficient, behaviour similar to the Schrock-type complexes of group IV was anticipated.



**Scheme 22: Reactivity of thulium and samarium carbene complexes**

Indeed, both thulium and samarium complexes **25** reacted fast with benzophenone to yield the corresponding tetra-substituted olefin (Scheme 22). The same reaction conducted with **26** was slower, which allowed the observation of several reaction intermediates. One of them, **27**, crystallised as it formed when a slow diffusion of a saturated hexanes solution of benzophenone was added into a toluene solution of complex **26**. This complex is an open metallaoxetane intermediate similar to the one postulated in the Wittig reaction. Once dissolved in toluene, this complex disappears in solution to give the tetra-substituted olefin, proving it to be an intermediate in the reaction. These experiments demonstrated the nucleophilic character of complexes **25** and **26** and clearly establish the carbenic nature of the lanthanide-carbon bond. Finally, with these new types of carbene complexes, two cases are thus to be discussed depending on their ability to stabilise the metal-free carbene fragment (Fig. 12).



**Figure 11: Bonding aspects**

On the one hand, the carbene ligand behaves as a two electron donor ligand and has to be stabilised in its free form as a neutral singlet carbene (Fig. 11, case A). This formally corresponds to the well-known transition metal Fischer carbene complexes, in which the stability of the carbene centre is partly provided by  $\pi$ -donor substituents so that little back donation is required from the metal. Thus, little or no double bond character is found between the metal and the carbene fragment. On the other hand, in transition metal Schrock-type carbene complexes, the carbenic moiety is a non-stabilised alkylidene ligand whose stabilisation is mainly brought about by the metal fragment and leads to short metal carbon bond distances. These complexes usually exhibit a significant double bond character. This situation cannot be directly transposed to the lanthanide complexes since the metal is not able to stabilise the carbenic centre by back donation. The stability must thus be ensured by the substituents at the carbon atom. This leads to a second case where the stable form of the metal-free carbene fragment is a dianionic ligand which behaves as a four electron  $X_2$ -type ligand (Fig. 11). The complexes presented here illustrate this second class of lanthanide carbene complexes.

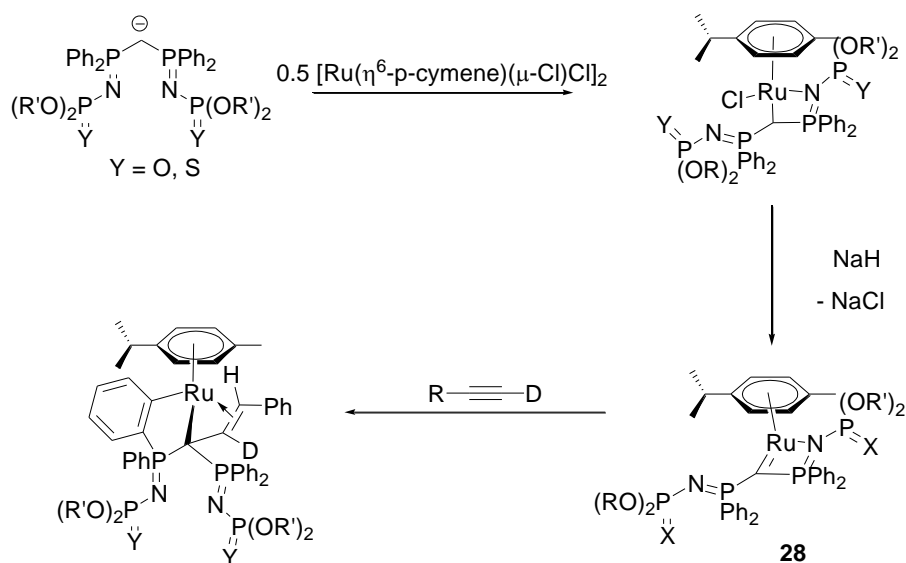
### 3.3 Coordination to electron-rich metal centres

To the opposite side of the d block are found the electron rich metal centres. It was shown above, that carbene complexes for which the carbon centre is stabilised by two  $\sigma^4$ -P groups possess a strong nucleophilic character when bound to electron poor metal centres. Namely, the HOMO of the complex is mainly localised on the carbon centre, as for typical Schrock type carbene complexes. The main goal in the use of electron rich metal centres was

thus to see whether it would be possible to observe the opposite electrophilic reactivity, typical of Fischer type carbenes.

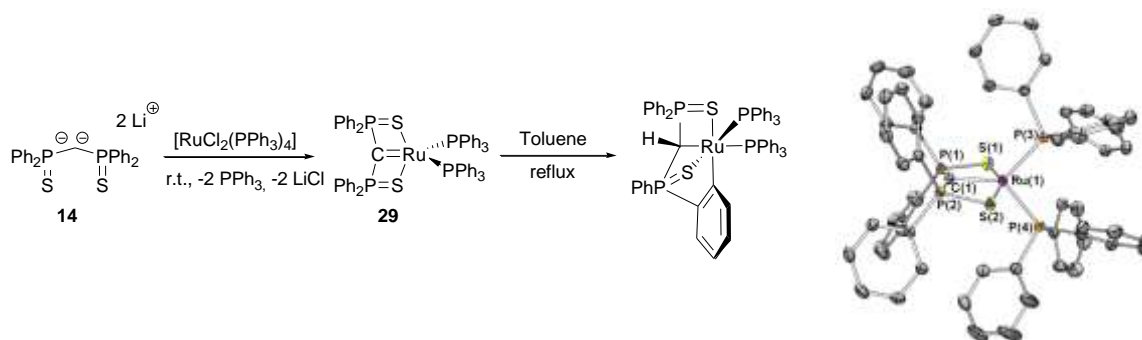
### 3.3.1 Coordination to Ru

Cadierno, Gimeno and co-workers have studied in detail ruthenium carbene complexes obtained via the deprotonation of bis(iminophosphorabyl)methanide in the coordination sphere of the metal.<sup>24b</sup> (Scheme 23). The starting neutral ligand was obtained via the Staudinger method from dppm and a commercial azide. The starting neutral ligand was obtained via the Staudinger method from dppm and a commercial azide.



**Scheme 23 : (NCN) carbene complex**

Complex **28** is coordinatively unsaturated, with a short Ru-C bond. DFT calculations show the HOMO of the complex being mainly a  $\pi$  interaction between the Ru and the C centres, and a  $\pi^*$  interaction between the Ru and the N centres.<sup>24</sup> This complex was shown to be quite reactive, in particular towards terminal alkynes. This reaction resulted in the formation of an orthometallated species which had incorporated the alkyne fragment. Deuterium labelling studies were carried out in order to see the fate of the terminal hydrogen of the alkynes. The authors proposed a mechanism involving the decoordination of the N atom prior to coordination of the alkyne. We have also used the dianion **14** in the reaction with a Ru(II) precursor bearing labile phosphine ligands. It resulted in the formation of the expected carbene complex, as evidenced by the X-Ray structure (Scheme 24).<sup>45</sup>

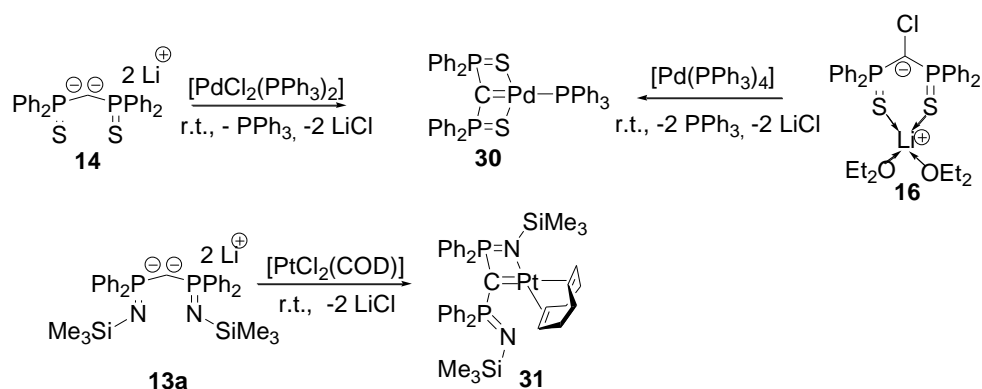


**Scheme 24: (SCS) ruthenium carbene complex**

The Ru-C bond length in **29** is quite long at 2.053(2) Å, much longer than in **28** (1.952 Å), suggesting a weak double bond character. This was further confirmed by means of DFT calculations. Unlike in the other carbene complexes, the HOMO in this case describes an antibonding  $\pi^*$  orbital between the ruthenium centre and the sulphur lone pairs, with little participation of the carbon centre. The LUMO corresponds to an antibonding  $\pi^*$  interaction between the formally  $p_\pi$  orbital at the carbon atom and the metal centred  $d_{xy}$  orbital, quite typical of electrophilic Fischer type carbene complexes (vide infra, scheme 26 A). However, this ruthenium complex is a coordinatively saturated 18 VE species, which proved quite reluctant to react with either nucleophiles or electrophiles. Its reactivity was doped by a thermal activation, leading to an orthometallation (Scheme 24). This process was fully rationalised by DFT calculations. These calculations revealed that the first step which requires a high energetic barrier involves the decooordination of one ancillary phosphinosulphide ligand. The second step involves the insertion of the Ru centre in the C-H bond of one phenyl group of the released phosphinosulphide ligand and finally the third step is migration of the hydride onto the carbenic carbon atom. Reoordination of the ancillary phosphinosulphide ligand completes the overall exothermic process.

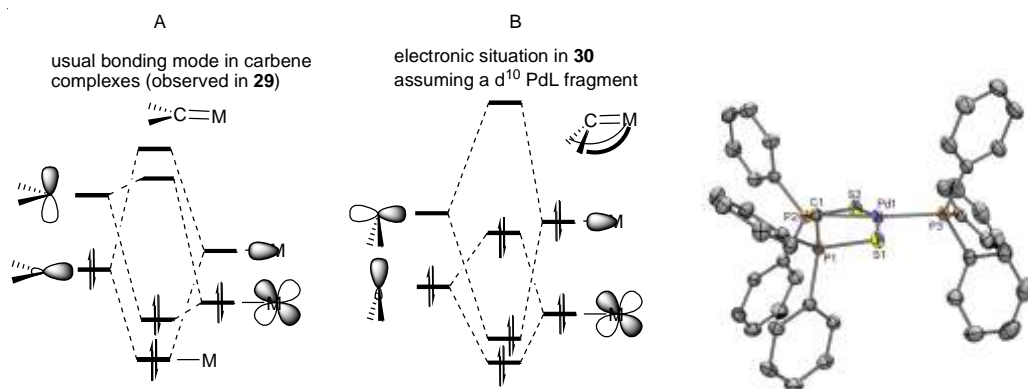
### 3.4.2 Coordination to group X metal centres

The coordination of dianions to these metal centres were studied quite simultaneously by Cavell for Pt,<sup>46</sup> and by us on Pd.<sup>47</sup> It is interesting to note that the coordination of dianion of the bis(iminophosphorane) is bidentate whereas it is tridentate in the case of our bis(thiophosphinoyl) derivative (Scheme 25).



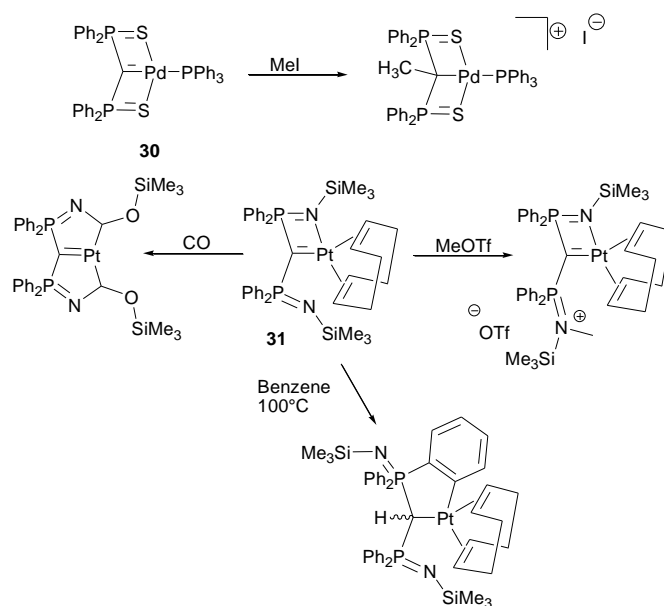
**Scheme 25: (SCS) and (NCN) palladium and platinum complexes**

Most interestingly, we showed very recently, that the same Pd complex may be formed by the reaction of the carbenoid species with a Pd(0) precursor.<sup>33</sup> This illustrated for the first time the use of a carbenoid as a precursor in the synthesis of a transition metal carbene complex. The mechanism of this process was shown to involve a  $\text{S}_{\text{N}}2$  step in which the electron rich Pd(0) center cleaves the C-Cl bond. This transformation also shows that it is, at least in principal, not important which species brings the electrons to the final complex. Reacting either the dianion with a Pd(II) precursor, or the neutral species with a Pd(0) precursor gave the same complex. The kinetics and the mechanism may be different, but the outcome is similar. The X-ray crystal structure of complex **30** pointed two unusual features (Scheme 26). Firstly, the Pd-C bond is long, typical of a single bond, and secondly, the Pd centre which adopts a square-planar geometry, is located in a quasi-perpendicular plane to the carbene fragment. DFT calculations allowed rationalising both features. It may be summarised by the following simplified orbital diagram. In fact, in this complex, assuming the Pd(0) + carbene (neutral SCS) fragmentation, it is obvious that the metal fragment of  $d^{10}$  configuration points its  $\sigma$  lone pair to the carbene vacant  $p_{\pi}$  orbital. Two electrons have to be placed in a  $\pi^*$  orbital, and therefore the  $\pi$  interaction does not lead to any bonding character between the Pd and C centres. Finally, two nonbonding electron pairs are found on Pd and C, which suggests a nucleophilic character (Scheme 26 B).<sup>47</sup>



**Scheme 26 : X-Ray crystal structures and MO description of the M=C bonding in the palladium complex 30.**

In terms of reactivity, we could show that the nucleophilic character of the Pd complex is in fact rather weak. It did not react with water, dichloromethane (crystallising solvent), but reacted with stronger electrophiles such as MeI to form a new C-C bond.<sup>47</sup> Cavell and co-workers reported the C-H insertion in one of the phenyl rings of the backbone of the platinum complex **31** when heated in benzene at 100°C.<sup>46</sup> In general this complex showed a ligand centred reactivity, which is not surprising as the non coordinated iminophosphorane ligands are highly sensitive species to Lewis acids. To this typical reactivity is added the N-SiMe<sub>3</sub> reactivity. Taking this to their advantage, the authors realised the double CO insertion leading to a tris carbene complex (Scheme 27).<sup>48</sup>

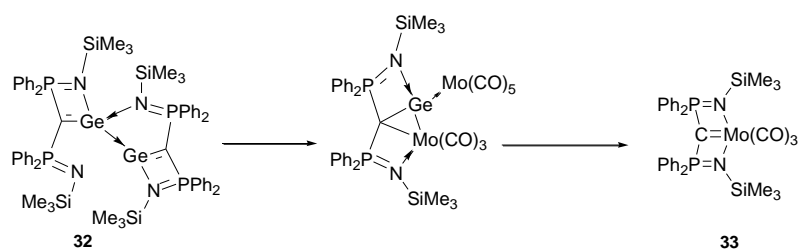


**Scheme 27: Reactivity of palladium and platinum carbene complex 30 and 31**



### 3.4 Miscellaneous metal centres

To complete this overview on the reactivity of (NCN) complexes, the work of Leung and co-workers concerning the use of a related bis(germavinylidene) **32** in the synthesis of the Mo(0) complex **33** has to be mentioned. Formally, this may be seen as a transmetallation process. They have isolated the intermediate bimetallic species (Scheme 28).<sup>49</sup>

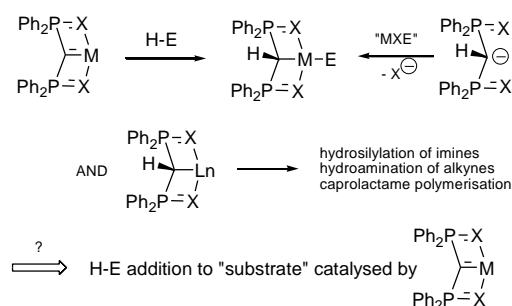


Scheme 28 : Synthesis of molybdenum complex **33**

## 4. Conclusion and perspectives

The amount of results gathered over the very short period, less than a decade, since the beginning of the use of phosphorus stabilised “carbene fragments” is quite impressive. In this article, we have presented the two different strategies devised, which rely on the various coordination numbers accessible to the phosphorus atom:  $\sigma^3$ -P and  $\sigma^4$ -P. The electronic properties of these moieties are opposite: a  $\sigma^3$ -P atom possesses a lone pair and therefore will act as a  $\pi$  donor, whereas a  $\sigma^4$ -phosphorus fragment presents low lying  $\sigma^*$  orbitals and therefore will act as a  $\pi$  acceptor. Only two results have been obtained involving the “PHC ligands”, using different strategies. Nevertheless, these show that the chemical behaviour of the carbene may be tuned from nucleophilic to electrophilic by changing the substituents at P and the metal centre. Many more data are available on the use of  $\sigma^4$ -phosphorus moieties as carbene stabilising fragments. Two main strategies have emerged. The first relies on the use of a neutral ligand doubly deprotonated at the same carbon centre in the coordination sphere of the metal centre. This approach proved quite efficient with the highly electropositive metal centres (group 4). A more versatile method consists in using a stable geminal dianion. Indeed, it allowed the synthesis of carbene complexes ranging from electron poor (lanthanides, early transition metal centres) to electron rich metal centres (group 8 and 10). More recently, the synthesis of a carbenoid species, deriving from the dianion **14**, has opened new ways to carbene complexes. The reactivity of the carbene fragment was in the vast majority of the complexes nucleophilic, as in typical Schrock type complexes. In particular, it has allowed the synthesis various alkene derivatives, later used in the isolation of stable radical species.<sup>13</sup> In

some instances, the carbene fragment was quite unreactive, and the ligand could thus be used as an innocent ligand. As the extent of stabilisation of the dianion greatly depends on the phosphorus substituents, new reactivities may be observed simply by changing the PCP backbone. Finally, the nucleophilic character may be used in their reaction with an electrophile EH to form *in situ* the addition product, which is the same product as the one resulting from the reaction of the monoanion with a “M(E)X” metallic fragment.<sup>50</sup> In particular, catalytic processes have been developed by the group of Roesky and co-workers in the case of lanthanide derivatives, such as intramolecular hydroamination of alkynes, hydrosilylation of imines and  $\epsilon$ -caprolactone polymerisation.<sup>51</sup> Therefore, as the separated processes are all known, the search for catalytic processes relying on the use of these carbene complexes as catalytic precursors appears as the next logical step.



**Scheme 29 : perspectives in the use of bis-phosphorus stabilised carbene complexes**

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