

Review

Stable non-N-heterocyclic carbenes (non-NHC): recent progress

Yves Canac, Michele Soleilhavoup, Salvador Conejero, Guy Bertrand *

UCR-CNRS Joint Research Chemistry Laboratory (UMR 2282), Department of Chemistry, University of California, Riverside, CA 92521-0403, USA

Received 3 October 2003; accepted 6 February 2004

Available online 5 March 2004

Abstract

This account summarizes the results that have been obtained by our group since 2000 in the area of stable singlet acyclic carbenes. It includes aryl- and alkyl-(phosphino)carbenes, aryl(amino)carbenes, and (amino)(phosphino)carbenes. Our most recent achievements, the transformation of stable carbenes into other stable carbenes are also discussed, along with preliminary results concerning the ligand properties of these species.

© 2004 Elsevier B.V. All rights reserved.

Keyword: Carbene

1. Introduction

In 2000, we published a review summarizing the literature results concerning stable carbenes, their transition metal complexes as well as the catalytic properties of the latter [1]. At that time, apart from some 50 N-heterocyclic carbenes (NHCs) of types **A** [2], **B** [3] and **C** [4], and (phosphino)(silyl)carbenes **D** [5], only four other carbenes **E** [6], **F** [7], **G** [8], and **H** [9] (Fig. 1) were structurally characterized, all of them bearing two heteroatom substituents.

Recently, spectacular results have been obtained in the catalysis arena using stable NHCs, as new types of ligand for transition metal catalysis [10]. These achievements have been made possible because of the availability of stable NHCs. Indeed, it is important to remember that NHC–transition complexes have been known since 1968 [11] and their organometallic chemistry was investigated by Lappert in the sixties [12]. Herrmann recently wrote [10a], “NHCs are not just phosphine mimics, there is increasing experimental evidence that NHC–metal catalysts surpass their phosphine-based counterparts in both

activity and scope of application”. Additionally, NHCs are more strongly bound to the metal (thus avoiding the necessity for the use of excess ligand), the catalysts are less sensitive to air and moisture, and have proved remarkably resistant to oxidation [13]. The efficiency of NHC ligands **A–C** in catalysis is largely due to their strong σ -donor property, which can be superior to that of the best phosphine donor ligands [14].

Importantly, Herrmann recently reported [15] that (i) even though the free non-NHC **F** is more sensitive than the NHCs, the stability toward air and moisture of the corresponding metal complexes is similar to that of complexes bearing NHC ligands; (ii) the carbene ligand **F** induces even higher electron density at the metal center than the saturated NHC **B**. To date, **F** is the most basic known carbene ligand.

During the last three years, our group has prepared a variety of new types of stable non-NHCs that includes monoheteroatom-substituted carbenes, which might well become excellent ligands for transition metal catalysts. This account summarizes these results.

2. Results and discussion

2.1. Structure of (phosphino)(silyl)carbenes

In 2000, more than a decade after our discovery of the first stable carbene [5a], we finally succeeded in

* Corresponding author. Present address: UCR/CNRS Joint Research Laboratory, Department of Chemistry, University of California, Riverside, CA 92521-0403, USA. Tel.: +1-909-787-2719; fax: +1-909-787-2725.

E-mail addresses: gbertran@chimie.ups-tlse.fr, gbertran@mail.ucr.edu (G. Bertrand).

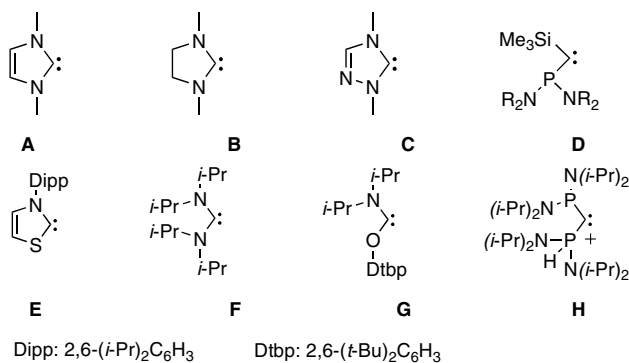
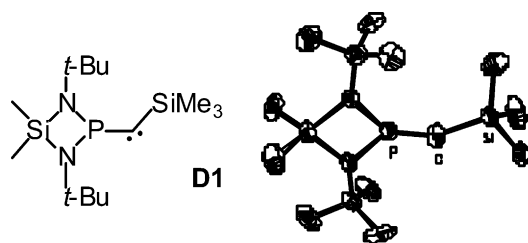
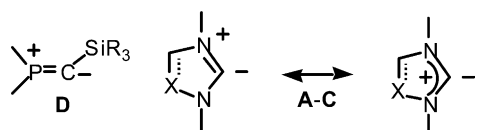


Fig. 1. Stable carbenes known before 2000.

obtaining single crystals of a (phosphino)(silyl)carbene [16]. An X-ray diffraction study (Fig. 2) combined with an electron localization function (ELF) analysis of the carbene **D1** allowed us to conclude that (phosphino)(silyl)carbenes **D** are best described by a phosphorus vinyl ylide structure with a lone pair at carbon (Fig. 3).

In fact, the electronic structure of **D** is not fundamentally different from that of NHCs **A–C** (Fig. 3), in which both nitrogen lone pairs interact with the vacant carbene orbital giving rise to a four- π -electron three-center system. It can even be added, that because of the reluctance of phosphorus to participate in π -donation, which forces it to become planar [17], the formally vacant orbital of the carbene center of **D** is more available than that of NHCs. This is the reason why phosphino carbenes **D** can engage in cyclopropanation reactions [18] and even react with Lewis bases [19], which is not the case for NHCs **A–C**.

At that time, some carbene chemists argued that the nature of the stable carbenes was strongly influenced by the interaction of the two heteroatom substituents with the carbene centre and therefore they were somewhat different from their transient cousins. Thus, we started a

Fig. 2. Molecular structure of carbene **D1**.Fig. 3. Electronic structure of carbenes **A–C** and **D**.

program aiming to the synthesis of stable carbenes with only one heteroatom substituent.

2.2. Stable carbenes with only one heteroatom substituent

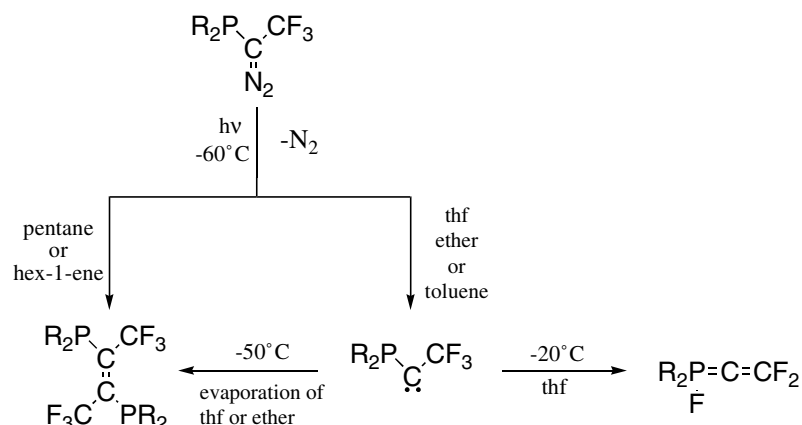
In 2000, we reported the preparation of a (phosphino)(trifluoromethyl)carbene [20]. Its chemical behavior exactly matches that of its transient congeners, even subtle effects observed with transient carbenes can be reproduced. For example, Jones [21a], Moss [21b,21c], and Goodman [21d] showed that transient singlet carbenes (such as chlorocarbenes) interact weakly with aromatics, but not with simple olefins. This interaction led to an extension of the benzylchlorocarbene lifetime from 23 ns (isooctane) to 285 ns (benzene) [21c]. Similarly, we found that photolysis of the diazo precursor in hex-1-ene at -60 °C led to the carbene dimer, while in toluene we obtained the carbene, which is stable up to -30 °C for weeks (Scheme 1).

In order to increase the stability of this type of carbene, the small, σ -attracting CF₃ group was replaced by the bulky 2,6-bis(trifluoromethyl)phenyl group, which is both a σ - and a π -attractor. Carbene **I** appeared to be stable for weeks at room temperature both in solution and in the solid state (mp: 68–70 °C). The molecular structure of **I** (Fig. 4) shows that the phosphorus atom is in a planar environment and the P–C_{carbene} bond length [1.54 Å] is short, as expected because of the donation of the phosphorus lone pair into the vacant carbene orbital. The aromatic ring is perpendicular to the C_{carbene}PNN plan allowing the delocalization of the carbene lone pair into the ring, which is apparent from the very large angle at the carbene centre [162°]. Clearly, the aryl group acts as an electron-withdrawing group and helps in the stabilization of the carbene center. In other words, carbene **I** has to be considered as a push–pull carbene.

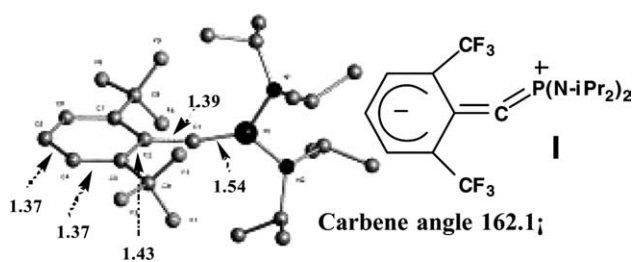
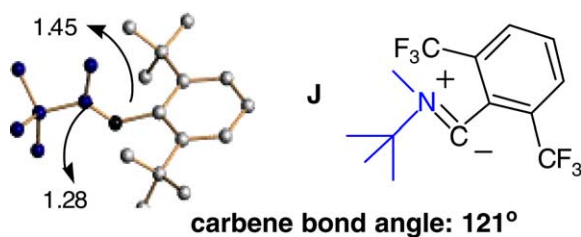
The isolation of **I** was of importance since it demonstrated for the first time that monoheteroatom-substituted carbenes could be stable, indefinitely, at room temperature.

The next step was to investigate whether a single electronically active substituent is sufficient to isolate a carbene. In 2001, we were able to isolate several (amino)(aryl)carbenes **J**, which were also stable at room temperature in solution and in the solid state (mp: 16 °C) [22] (Fig. 5).

It is interesting to compare the molecular structures of **J** (Fig. 5) with that of the push–pull (phosphino)(aryl)carbene **I** (Fig. 4) and push–push diamino-carbenes **F**. For **J** the nitrogen atom is in a planar environment and the N–C_{carbene} bond length (1.28 Å) is even shorter than that observed for acyclic diamino-carbenes **F** (1.37 Å), which indicates a stronger donation of the nitrogen lone pair into the vacant carbene orbital. In marked contrast with the cumulenec system **I**, the



Scheme 1. Photolysis of (phosphino)(trifluoromethyl)diazomethane, fate of the carbene.

Fig. 4. Molecular structure of carbene **I**.Fig. 5. Molecular structure of carbene **J**.

$C_{\text{carbene}}-C_{\text{aro}}$ bond distance is long (**J**: 1.45 Å ; **I**: 1.39 Å) and the carbene bond angle rather acute (**J**: 121° ; **I**: 162°). These data clearly indicate that the potentially π -acceptor 2,6-bis(trifluoromethyl)phenyl group does not interact with the carbene lone pair of **J** and is therefore *spectator*.

By the end of 2001, all of the known stable singlet carbenes followed, to some extent, Pauling's predictions [23] that the substituents should preserve the electro-neutrality of the carbene center (Fig. 6). This is obvious for push-pull carbenes **D**, **H** and **I**, in which the carbene bears both a π -donating and a π -withdrawing substituent. NHCarbenes **A–C**, **E**, **G** and acyclic diamino-carbene **F** have two π -donor substituents, and are sometimes referred to as push-push carbenes, but the amino- and alkoxy- groups also act as strong σ -electron

withdrawing substituents. Lastly, carbene **J** features a spectator substituent and an amino group, which is again both a π -donor and σ -attractor.

This raises the question: Is electron donation sufficient to stabilize a carbene, as shown for **K** and **L** (Fig. 6)? The answer is again yes. In 2002, we have shown that the (mesityl) (phosphino)carbene **K** (mp: 148°C) can be isolated, although it features a π - and σ -donor phosphino group and a spectator substituent [24]. Indeed, the $P1C1C2$ angle [148.7(2)°] is significantly smaller than in **I** [162.1(3)°] and the $C1C2$ bond length [1.438(3) Å] is in the range typical for $C(sp^2)-C(sp^2)$ single bonds, and as expected is longer than that observed for the push-pull system **I** [1.390(4) Å] (Fig. 7).

Even more interesting, the corresponding (methyl)(phosphino)carbene **L** was characterized spectroscopically at -85 °C [24]. Despite the poor steric protection and the potential to undergo 1,2-hydrogen

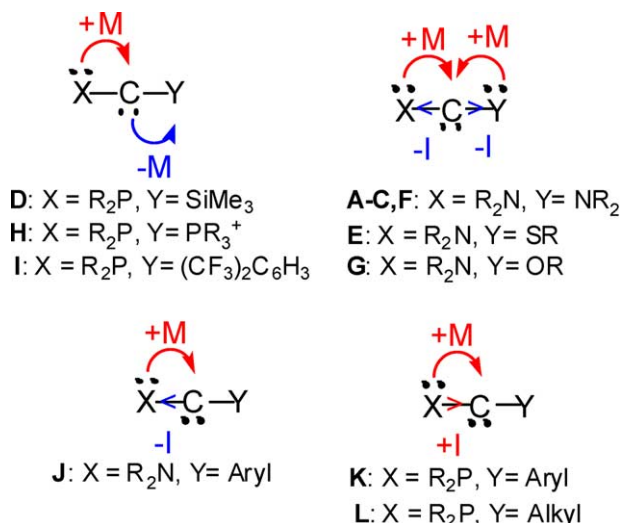
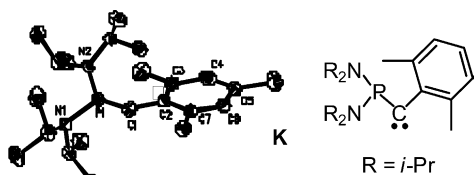
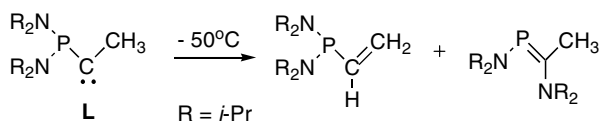


Fig. 6. Different modes of stabilization of carbene center.

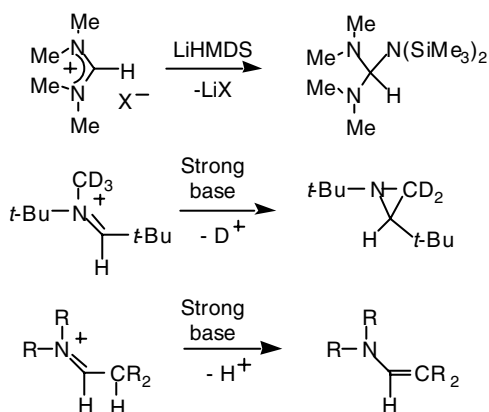
Fig. 7. Molecular structure of carbene **K**.Scheme 2. Rearrangements of carbene **L**.

shifts [25], this methylcarbene could be observed by ^{31}P NMR up to $-50\text{ }^\circ\text{C}$ ($t_{1/2} \sim 10\text{ min}$ at $-50\text{ }^\circ\text{C}$), where it quickly isomerises, into the corresponding alkene and phosphalkene (Scheme 2).

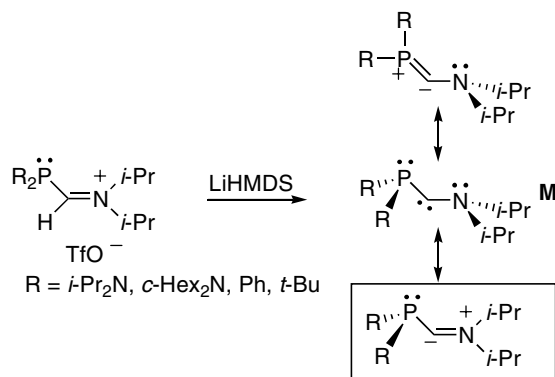
Since simple phosphino carbenes such as **K** and **L** are stable or at least persistent, it was of primary interest to know if mono-amino carbenes bearing a σ -donor group, as a second substituent, would also be stable. So far, the most general method for the preparation of stable carbenes involves deprotonation of appropriate precursors by strong bases. However, it appears that for unhindered formamidinium ions [26], as well as for alkyl substituted iminium salts [27] [precursors of (alkyl)(amino)carbenes] competitive reactions take place (Scheme 3).

2.3. (Amino)(phosphino)carbenes

Since the synthetic routes which were known did not allow for the preparation of (alkyl)(amino)carbenes, we approached this problem by synthesizing the (amino)(phosphino)carbene **M** [28]. Note, that this was also a way to discover which, between R_2P and R_2N



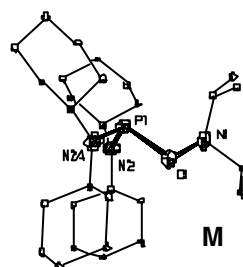
Scheme 3. Competitive reactions versus deprotonation of iminium salts.

Scheme 4. Synthesis and electronic structure of carbene **M**.

substituents, is better for stabilizing the carbene center (Scheme 4).

Carbenes **M** were generated cleanly at $-78\text{ }^\circ\text{C}$ by deprotonation of the corresponding phosphino iminium salts with the lithium salt of hexamethyldisilylazane, and were initially characterized by multinuclear NMR spectroscopy. The main feature of the NMR spectra of **M** is the very low field values of the ^{13}C chemical shifts of the carbene carbon atom (δ : 320–348 ppm, J_{PC} : 22–101 Hz). These signals are even further down field than those observed for the known diaminocarbenes (210–300 ppm) and in a totally different region from those for phosphinocarbenes (100 and 145 ppm) [1]. In all cases the ^1H NMR spectra highlighted the presence of two different isopropyl groups on the nitrogen atom bound to the carbene center, which indicates the absence of free rotation about the C–N bond [29]. All these NMR data strongly suggest that only the amino substituent interacts with the carbene center, the phosphino group remaining merely a spectator substituent. This was confirmed by an X-ray diffraction study of **M** ($\text{R} = c\text{-Hex}_2\text{N}$) (Fig. 8).

The pyramidalization of the phosphorus atom (sum of bond angles = 304.5°) and the long P1–C1 bond length (1.856 Å), which is in the range associated with P–C single bonds, together demonstrate that the phosphino group is indeed a spectator substituent. In agreement with this statement, is the orientation of the phosphorus lone pair, which is perpendicular to the

Fig. 8. Molecular structure of carbene **M**.

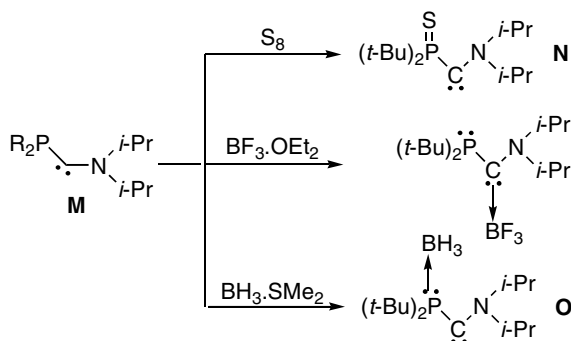
(formally empty) π orbital on the carbene center. As expected, the nitrogen atom is in a planar environment (sum of bond angles = 359.6°), and the N1–C1 bond length (1.296 Å) is short. Finally, the carbene bond angle is acute (116.5°), as anticipated for a carbene stabilized by an amino group, and not broad as for carbenes stabilized by a phosphino group [1].

From these data, it can be stated that an amino group is much more efficient for stabilizing a carbene center than a phosphino group. Therefore from the experimental data described above, it is clear that a broad range of stable mono-amino carbenes will be easily available.

2.4. From stable carbenes to stable carbenes

We then wanted to check whether the spectator substituent of a carbene could be used as a second functional group. In other words, is it possible to perform chemical transformations at the periphery of these types of molecule without affecting what has been considered for many years as the prototype of reactive intermediates, namely the carbene center. For this study [28], we chose the (amino)(phosphino)carbenes **M**, the phosphino group being the second functional group of the molecule.

Elemental sulfur, BF_3 and BH_3 react with both phosphines and aminocarbenes [30], and therefore competitive reactions could occur in the case of (amino)(phosphino)carbenes **M**. Interestingly, at -30°C , a clean and quick reaction occurs when sulfur was added to a thf solution of **M** affording the corresponding (amino)(thiophosphoranyl)carbene **N** (Scheme 5), which is stable in solution at room temperature for a few days. The carbenic structure of **N** was apparent from the low field ^{13}C signal at 322 ppm ($^1J_{\text{PC}} = 108.1$ Hz). Highly regioselective reactions were also observed using Lewis acids. Treatment of a thf solution of **M** with one equivalent of $\text{BF}_3 \cdot \text{OEt}_2$ led to the quantitative formation of the carbene complex, which has been characterized by NMR spectroscopy. The ^{11}B and ^{19}F NMR signals appear as quartets ($^1J_{\text{BF}} = 43$ Hz) without any



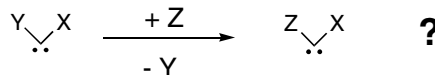
Scheme 5. Reactivity of carbene **M**.

coupling with phosphorus, demonstrating the selective interaction of BF_3 with the carbene center. In contrast, the softer Lewis acid BH_3 interacts selectively with the phosphorus lone pair to afford the carbene **O**. The structure of this new carbene **O**, which is also perfectly stable at room temperature (mp: 100–102 °C), was confirmed by an X-ray diffraction study [28]. Compared to **M**, a slightly wider bond angle at the carbene center (123.0°) is observed, while the P–C_{carbene} (1.831 Å) and C_{carbene}–N (1.293 Å) bond lengths remain in the range expected for a single and double bond, respectively. These results gave a first indication that, starting from a single stable carbene, numerous new stable carbenes can be prepared.

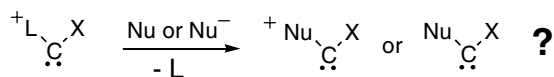
The substitution reaction (taken in a broad sense), is certainly the best process to prepare a variety of derivatives starting from a single precursor. Is it thus possible to perform substitution reactions at a carbene center and therefore to obtain a library of carbenes from a single precursor (Scheme 6)? Obviously, the starting carbene has to be stable, which implies that X should be an amino or a phosphino group.

Whatever the mechanism involved, the properties of the leaving group play a key role. For nucleophilic substitution, the leaving group ability is inversely related to base strength and therefore weakly nucleophilic anions and neutral entities are by far the best. However, the leaving group Y has to bring some steric protection, which probably eliminates the possible use of halogen or other weak nucleophilic anions such as trifluoromethane sulfonate. In contrast several bulky neutral leaving groups would be excellent candidates. Moreover, the conversion of a neutral nucleofuge into a cationic one confers a dramatically increased electrophilicity to the substrate. This effect is predominantly electrostatic in origin, the so-called field effect [31]. In the last twenty years, this approach has led to spectacular achievements. For example, starting from alkynyl-(phenyl)iodonium species, diverse functionalized alkynes including previously unknown acetylenic carboxylates, sulfonates, and phosphates have become available [32a]. Aryliodonio diazo compounds can undergo nucleophilic substitution reactions with neutral nucleophiles with retention of the very fragile diazo function [32b]. The nucleofuge is not just restricted to hypervalent iodine compounds, and the leaving ability can be tuned [32c,32d].

Thus one might ask: Is it possible to prepare onio-substituted stable carbenes and to perform nucleophilic substitution that would generate a variety of new stable carbenes (Scheme 7)?



Scheme 6. Substitution reaction at a carbene center?



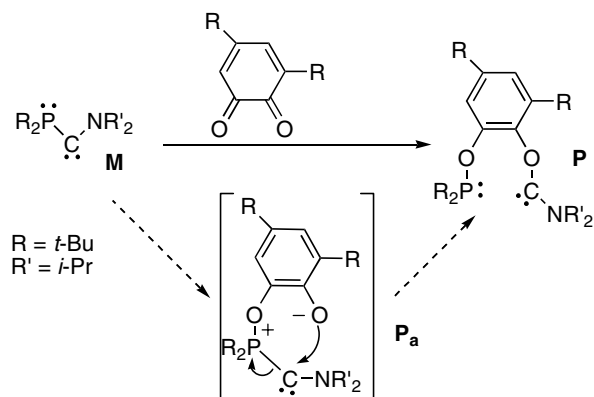
Scheme 7. Onio-substituted carbenes and substitution?

As shown in Scheme 5, (amino) (phosphino)carbene **M** reacts with elemental sulfur and BH_3 at phosphorus leading to new carbenes **N** and **O**, respectively. On the other hand, it is known that *ortho*-quinones react with phosphines to give hypervalent neutral phosphorus derivatives, in equilibrium with the corresponding phosphonium salt [33]. Therefore, in order to test a possible intramolecular nucleophilic substitution reaction at carbene, we carried out the reaction of **M** with a sterically hindered *ortho*-quinone. Indeed, if the quinone reacts with the phosphorus lone pair of **M**, as expected, we should obtain carbene **Pa** featuring both a phosphonio nucleofuge and an aryloxy nucleophile. On monitoring the reaction by ^{31}P NMR spectroscopy at $-78^\circ C$ no intermediates such as **Pa** could be detected. In contrast, we instantaneously observed the formation of the new carbene **P**, which was isolated as yellow crystals in 87% yield (Scheme 8) [34]. The ^{13}C NMR signal at 268 ppm, with no coupling with phosphorus, leaves no doubt on the carbene structure and on the formal insertion of the quinone into the phosphorus-carbene bond.

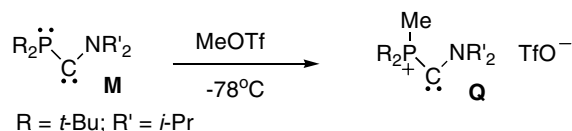
Since phosphines are known to react with a wide range of electron-poor unsaturated derivatives, the extrapolation of this reaction will allow for the synthesis of numerous carbenes.

We then investigated the possibility of an alkylation reaction on carbene **M**, which would lead to an onio-substituted carbene and would open the way for intermolecular substitution reactions. Indeed, the carbene **M** cleanly reacts at $-78^\circ C$, with methyl trifluoromethanesulfonate giving the desired carbene **Q** (Scheme 9) [34].

The new carbene **Q** is also indefinitely stable at room temperature both in solution and in the solid state (mp:



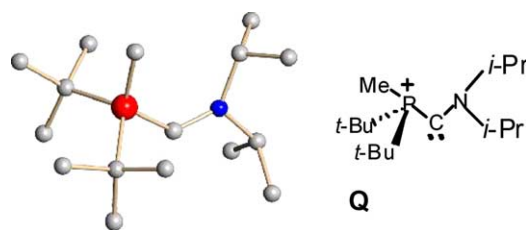
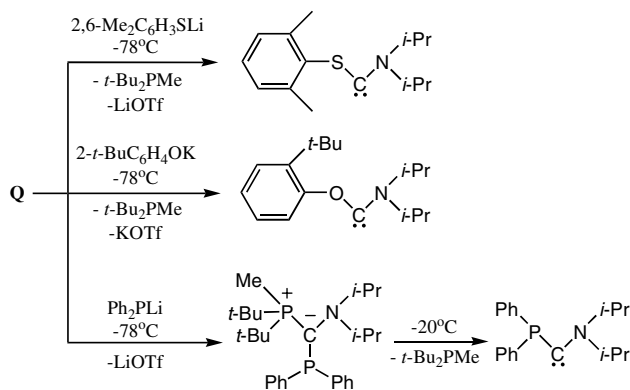
Scheme 8. Insertion of a quinone into a phosphorus-carbene bond.

Scheme 9. Synthesis of onio-carbene **Q**.

$58^\circ C$, dec.). The ^{13}C NMR signal for the carbene carbon atom appears at low field (302 ppm, d, $J_{PC} = 111.4$ Hz), suggesting that there is only a slight, if any, electronic interaction between the phosphonio group and the carbene center. This is confirmed by a single crystal X-ray diffraction study (Fig. 9), which shows a short CN bond (1.30 Å), a long PC bond (1.82 Å), and an acute angle about the carbene (122°).

In order to prove the feasibility of substitution reactions at the carbene center of **Q**, three different nucleophiles were chosen: the lithium or potassium salts of 2,6-dimethylthiophenol, 2-*tert*-butylphenol and diphenylphosphine. The reactions were carried out in tetrahydrofuran at $-78^\circ C$, and multinuclear NMR spectroscopy showed that they lead quantitatively to the expected new carbenes, along with di-*tert*-butyl(methyl)phosphine (Scheme 10). The spectroscopic data for the sulfino- and phosphino-carbene compared well with those already published [28,8], whereas the previously unknown (amino)(oxo)carbene has been fully characterized in solution.

These results are very promising, although somewhat shocking. Indeed, for carbene specialists, such substi-

Fig. 9. Molecular structure of carbene **Q**.Scheme 10. Substitution reactions at the carbene center of **Q**.

tution reactions at a carbene center, were unimaginable, even just a few years ago.

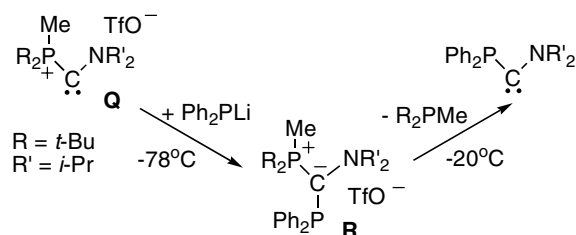
We have performed preliminary studies concerning the mechanism of these substitution reactions. Monitoring the reaction of **Q** with lithium diphenylphosphide, by ^{31}P NMR spectroscopy at -78°C , allowed for the characterization of an initial product of type **R**, namely a phosphorus ylide resulting from the addition of the phosphide to the iminium moiety (AX system, $\delta = 43$ and 1 ppm, $J_{\text{PP}} = 260$ Hz). At -20°C , elimination of the di(*t*-butyl)methylphosphine occurred, affording the amino phosphino carbene (Scheme 11).

This addition–elimination mechanism is not unexpected. Indeed, according to calculations at the HF/3–21G* level, the dissociation energy of $\text{H}_3\text{PC}(\text{H})(\text{NH}_2)$ into phosphine and aminocarbene would be 8.1 kcal/mol; for comparison, a dissociation energy of 53.2 kcal/mol has been found for $\text{H}_3\text{PC}(\text{H})(\text{CH}_3)$ [35]. It is reasonable to believe that C-substituted phosphorus ylides are destabilized by the two-center four-electron system (lone pairs at carbon and nitrogen).

2.5. Ligand properties of non-NHCs

Clearly NHCs have already proved their ability to bind metals and to give excellent catalysts. In contrast, very little is known regarding the coordination chemistry of stable non-NHCs, apart from the already mentioned work by Herrmann and co-workers [15] using the acyclic bis(diisopropylamino)carbene **F**.

Direct complexation of (phosphino)(silyl)carbenes **D** has not yet been reported, and all our attempts have failed. The apparent reluctance of carbenes **D** to act as ligands has recently been tentatively rationalized by theoretical study [36]. It was concluded that in contrast with NHCs, carbenes **D** tend to adopt widened valence angles at the central carbon, due to the electropositive character of the phosphanyl group. As a consequence, energy costly conformational changes to a bent carbene structure are required to allow metal complexation. Theoretical studies also mentioned that since the singlet–triplet separation is fairly small for phosphino carbenes [37,38], one would expect that the nature of the metallic fragment should play a crucial role in determining whether phosphinocarbene η^1 -complexes would adopt a Fischer- or a Schrock-type coordination mode. Furthermore, phosphinocarbenes



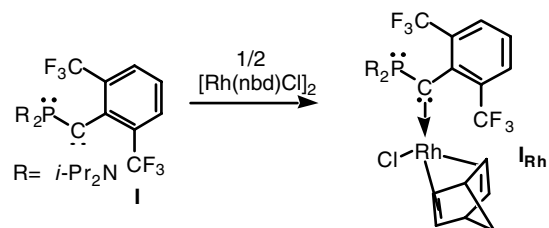
Scheme 11. Mechanism of the substitution reaction at carbene.

can potentially act as four-electron donors (side-on complexation). This may be important during catalytic processes, as the chameleon-like ability of these ligands to alter their electronic demands may very well stabilize the coordinatively and electronically unsaturated ‘resting state’ of the catalyst [38].

Our recent discovery that (aryl)(phosphino)- **I** and (amino)(phosphino)-carbenes **M** can also be isolated prompted us to investigate their ligand behavior.

Treatment of the [2,6-bis(trifluoromethyl)-phenyl](phosphino) carbene **I** with half an equivalent of $[\text{RhCl}(\text{nbd})]_2$ in toluene at -50°C immediately and quantitatively affords the corresponding carbene complex **I_{Rh}** (Scheme 12) [39]. The ^{31}P NMR chemical shift of **I_{Rh}** ($\delta +100.8$ ppm) is deshielded by 130 ppm compared to that of the free carbene **I**, and now appears in the region typically associated with methylene phosphonium salts (trigonal planar phosphorus cations) [40]. Moreover, the ^{13}C NMR chemical shift for the carbene center ($\delta 120.6$ ppm, $^1J_{\text{C-P}} = 2$ Hz, $^1J_{\text{C-Rh}} = 59$ Hz) is shielded compared to that of the free carbene ($\delta 146.1$ ppm, $^1J_{\text{C-P}} = 271$ Hz). All these data are similar to those observed for similar NHC complexes [41].

Pale yellow crystals of **I_{Rh}** (m.p.: 156°C dec.) suitable for an X-ray diffraction study (Fig. 10) were obtained by cooling a dichloromethane/pentane solution to -80°C . The carbene center adopts a trigonal planar environ-



Scheme 12. Complexation of carbene **I**.

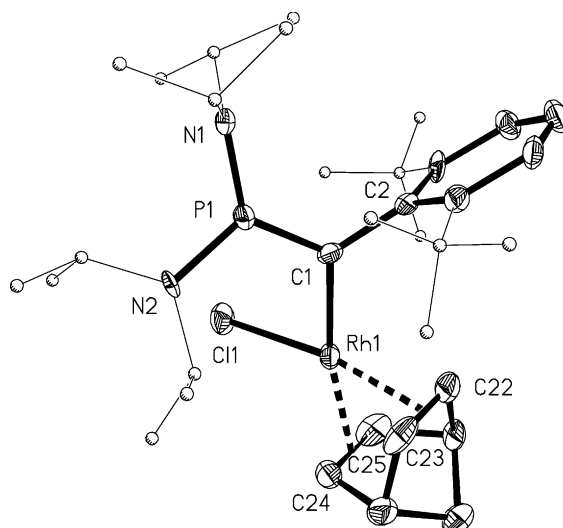
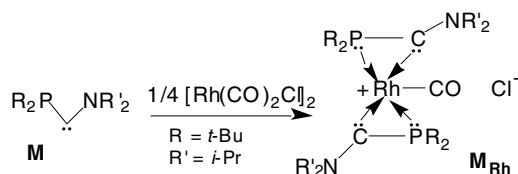


Fig. 10. Molecular structure of complex **I_{Rh}**.

ment with the plane defined by P–C_{carbene}–C2 being twisted by about 47° out of the square coordination plane around the rhodium. As predicted by Schoeller et al. [36a], coordination induces a considerable contraction of the bond angle about the carbene center (from 162° in the free carbene **I** to 119° in **I**_{Rh}). The carbene-rhodium bond distance [2.096(7) Å] is in the range typical for C–Rh single bonds, and is even slightly longer than that observed for related NHC rhodium complexes (2.00–2.04 Å). These data suggest that **I**_{Rh} is best regarded as a Fischer-type carbene complex, the carbene-metal interaction consists almost exclusively of donation of the carbene lone pair into an empty metal-based orbital. Back-donation from the metal to the carbene center is negligible compared to that from the phosphorus lone pair. Indeed, the phosphorus atom adopts a trigonal planar geometry with a P–C_{carbene} bond distance of 1.673(7) Å, which is longer than in the free carbene, 1.544(3) Å, but still very short.

Note that in the case of **I**_{Rh}, the inherent chelation of the nbd ligand prevents the formation of an η²-complex. In order to prove the possibility of such a coordination mode (important for catalysis purposes) [38] and to test the ligand behavior of other phosphinocarbenes, we reacted the (phosphino)(amino)carbenes **M** with 0.25 equivalent of [Rh(CO)₂Cl]₂. The reaction appeared to be very clean, and chiral complexes **M**_{Rh} were isolated in high yield (Scheme 13) [42]. The high field ³¹P NMR chemical shift (δ –58.6) and the large coupling constant (¹J_{PRh} = 102 Hz) clearly suggests an η²-coordination



Scheme 13. Complexation of carbene **M**.

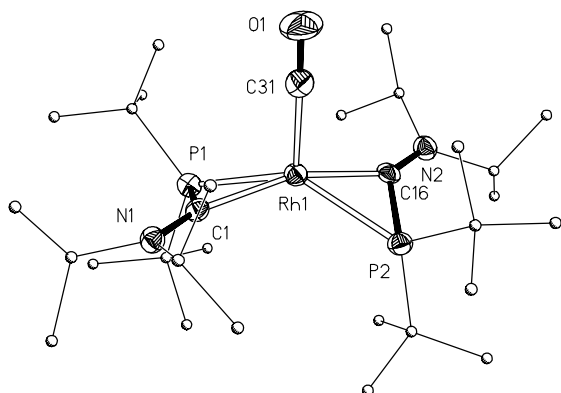


Fig. 11. Molecular structure of complex **M**_{Rh}.

mode, while the presence of two phosphinocarbenes ligands was indicated by the multiplicity of the ¹³C NMR signals for the CO and C_{carbene} nuclei (δ 201, dt, ¹J_{CRh} = 86 Hz, ²J_{CP} = 16 Hz; δ 227, dt, ¹J_{CRh} = 24 Hz, ¹J_{CP} = 23 Hz).

The structure of complex **M**_{Rh} was unambiguously established by an X-ray diffraction study (Fig. 11).

3. Conclusion and outlook

In the last years, it has been demonstrated that NHCs strongly bind transition metal centers, leading to extremely active and robust catalysts, which often outperform their phosphine-based analogues. However, the structure of NHCs can only be modified through variation in the nitrogen and carbon backbone substituents. As a consequence, the steric demands of these ligands can easily be varied using the N-substituents, but their electronic character can only be modified slightly. Indeed, the only significant variation possible is a choice between using either a saturated or an unsaturated backbone.

The results described in this account demonstrate that, in contrast to what has generally been believed, many types of carbene can be isolated. We are developing original and practical synthetic routes to various stable carbenes, with a special emphasis to those that are sufficiently flexible to allow for the preparation of a library of carbenes starting from a single precursor. The gamut of electronic effects possible should afford an excellent opportunity to better understand the mechanisms of catalysis involved and therefore to improve further the catalytic systems.

Major breakthroughs can also be expected in asymmetric catalysis. Here is a crucial area differentiating acyclic carbenes from NHCs. The NHCs have been rendered chiral by either modification at the 4 and/or 5 positions but these variations actually have not been successful in providing high asymmetric induction. The simple attachment of chiral substituents at the amine function has also met with limited success. We feel the chirality is not close enough to the reactive center in these scaffolds. The open carbenes will allow for chirality at the alpha position. This should result in high chiral induction effects.

Acknowledgements

We sincerely thank the students and postdoctoral fellows who have contributed to this research and whose names are listed in the references, with a special mention to the CNRS Research Associates of G.B., Dr. Antoine Bacciredo and Dr. Didier Bourissou. We are grateful to

the ACS/PRF (38192–AC4), the CNRS, and RHODIA for financial support of the most recent work.

References

- [1] D. Bourissou, O. Guerret, F.P. Gabbaï, G. Bertrand, *Chem. Rev.* 100 (2000) 39.
- [2] A.J. Arduengo, R.L. Harlow, M. Kline, *J. Am. Chem. Soc.* 113 (1991) 361.
- [3] A.J. Arduengo, J.R. Goerlich, W.J.A. Marshall, *J. Am. Chem. Soc.* 117 (1995) 11027.
- [4] D. Enders, K. Breuer, G. Raabe, J. Runsink, J.H. Teles, J.P. Melder, K. Ebel, S. Brode, *Angew. Chem. Int. Ed.* 34 (1995) 1021.
- [5] (a) A. Igau, H. Grutzmacher, A. Baceiredo, G. Bertrand, *J. Am. Chem. Soc.* 110 (1988) 6463;
(b) A. Igau, A. Baceiredo, A. Trinquier, G. Bertrand, *Angew. Chem. Int. Ed.* 28 (1989) 621;
(c) G. Gillette, A. Baceiredo, G. Bertrand, *Angew. Chem. Int. Ed.* 29 (1990) 1429;
(d) G. Bertrand, in: G. Bertrand (Ed.), *Carbene Chemistry: From Fleeting Intermediates to Powerful Reagents*, Marcel Dekker, New York, 2002.
- [6] A.J. Arduengo, J.R. Goerlich, W.J.A. Marshall, *Liebigs Ann.* (1997) 365.
- [7] R.W. Alder, P.R. Allen, M. Murray, G. Orpen, *Angew. Chem. Int. Ed.* 35 (1996) 1121.
- [8] R.W. Alder, C.P. Butts, M. Murray, G. Orpen, *J. Am. Chem. Soc.* 120 (1998) 11526.
- [9] M. Soleilhavoup, A. Baceiredo, O. Treutler, R. Ahlrichs, M. Nieger, G. Bertrand, *J. Am. Chem. Soc.* 114 (1992) 10959.
- [10] (a) W.A. Herrmann, *Angew. Chem. Int. Ed.* 41 (2002) 1290;
(b) L. Jafarpour, S.P. Nolan, *Adv. Organomet. Chem.* 46 (2001) 181;
(c) T.M. Trnka, R.H. Grubbs, *Acc. Chem. Res.* 34 (2001) 18.
- [11] K. Ofele, *J. Organomet. Chem.* 12 (1968) P42.
- [12] D.J. Cardin, B. Cetinkaya, M.F. Lappert, *Chem. Rev.* 72 (1972) 545.
- [13] (a) E. Peris, J.A. Loch, J. Mata, R.H. Crabtree, *Chem. Commun.* (2001) 201;
(b) M. Albrecht, J.R. Miecznikowski, A. Samuel, J.W. Faller, R.H. Crabtree, *Organometallics* 21 (2002) 3596.
- [14] I. Huang, H.J. Schanz, E.D. Stevens, S.P. Nolan, *Organometallics* 18 (1999) 2370.
- [15] (a) K. Denk, P. Sirsch, W.A. Herrmann, *J. Organomet. Chem.* 649 (2002) 219;
(b) M. Tafipolsky, M. Scherer, K. Ofele, G. Artus, B. Pedersen, W.A. Herrmann, S.G. McGrady, *J. Am. Chem. Soc.* 124 (2002) 5865.
- [16] T. Kato, H. Gornitzka, A. Baceiredo, A. Savin, G. Bertrand, *J. Am. Chem. Soc.* 122 (2000) 998.
- [17] S. Goumri, Y. Leriche, H. Gornitzka, A. Baceiredo, G. Bertrand, *Eur. J. Inorg. Chem.* (1998) 1539.
- [18] (a) J. Krysiak, T. Kato, H. Gornitzka, A. Baceiredo, M. Mikolajczyk, G. Bertrand, *J. Org. Chem.* 66 (2001) 8240;
(b) S. Goumri-Magnet, T. Kato, H. Gornitzka, A. Baceiredo, G. Bertrand, *J. Am. Chem. Soc.* 122 (2000) 4464.
- [19] S. Goumri-Magnet, O. Polischuck, H. Gornitzka, C.J. Marsden, A. Baceiredo, G. Bertrand, *Angew. Chem. Int. Ed.* 38 (1999) 3727.
- [20] C. Buron, H. Gornitzka, V. Romanenko, G. Bertrand, *Science* 288 (2000) 834.
- [21] (a) R.T. Ruck, M. Jones Jr., *Tetrahedron Lett.* 39 (1998) 2277;
(b) K. Krogh-Jespersen, S.Q. Yan, R.A. Moss, *J. Am. Chem. Soc.* 121 (1999) 6269;
(c) R.A. Moss, S. Yan, K. Krogh-Jespersen, *J. Am. Chem. Soc.* 120 (1998) 1088;
(d) M.I. Khan, J.L. Goodman, *J. Am. Chem. Soc.* 117 (1995) 6635.
- [22] S. Sole, H. Gornitzka, W.W. Schoeller, D. Bourissou, G. Bertrand, *Science* 292 (2001) 1901.
- [23] L. Pauling, *Chem. Commun.* (1980) 688.
- [24] (a) E. Despagnet, H. Gornitzka, A.B. Rozhenko, W.W. Schoeller, D. Bourissou, G. Bertrand, *Angew. Chem. Int. Ed.* 41 (2002) 2835;
(b) E. Despagnet-Ayoub, S. Sole, H. Gornitzka, A.B. Rozhenko, W.W. Schoeller, D. Bourissou, G. Bertrand, *J. Am. Chem. Soc.* 125 (2003) 124.
- [25] R. Bonneau, M.T.H. Liu, in: U.H. Brinker (Ed.), *Advances in Carbene Chemistry*, vol. 2, Jai Press, Stanford, 1998.
- [26] R. Alder, in: G. Bertrand (Ed.), *Carbene Chemistry: From Fleeting Intermediates to Powerful Reagents*, Marcel Dekker, New York, 2002, p. 153.
- [27] X. Cattoen, S. Sole, C. Pradel, H. Gornitzka, K. Miqueu, D. Bourissou, G. Bertrand, *J. Org. Chem.* 68 (2003) 911.
- [28] N. Merceron, K. Miqueu, A. Baceiredo, G. Bertrand, *J. Am. Chem. Soc.* 124 (2002) 6806.
- [29] R.W. Alder, M.E. Blake, J.M. Oliva, *J. Phys. Chem. A* 103 (1999) 11200.
- [30] (a) F.E. Hahn, L. Wittenbecher, R. Boese, D. Blaser, *Chem. Eur. J.* 5 (1999) 1931;
(b) N. Kuhn, G. Henkel, T. Kratz, J. Kreuzberg, R. Boese, A.H. Maulitz, *Chem. Ber.* 126 (1993) 913.
- [31] W. Adcock, F. Anvia, G. Butt, A. Cook, P. Duggan, C.A. Grob, S. Marriott, J. Rowe, A.M. Taagepera, R.W. Taft, R.W. Topsom, *J. Phys. Org. Chem.* 4 (1991) 3053.
- [32] (a) P.J. Stang, *Angew. Chem. Int. Ed.* 31 (1992) 274;
(b) R. Weiss, J. Seubert, F. Hampel, *Angew. Chem. Int. Ed.* 33 (1994) 1952;
(c) R. Weiss, M. Handke, S. Reichel, F. Hampel, *Z. Naturforsch.* 53b (1998) 599;
(d) R. Weiss, M. Handke, F. Hampel, *Z. Naturforsch.* 53b (1998) 916.
- [33] F. Ramirez, C.P. Smith, J.F. Pilot, A.S. Gulati, *J. Org. Chem.* 33 (1968) 3787.
- [34] N. Merceron-Saffon, A. Baceiredo, H. Gornitzka, G. Bertrand, *Science* 301 (2003) 1223.
- [35] H.J. Bestmann, A.J. Kos, K. Witsgall, P.v.R. Schleyer, *Chem. Ber.* 119 (1986) 1331.
- [36] (a) W.W. Schoeller, D. Eisner, S. Grigoleit, A.R. Rozhenko, A. Alijah, *J. Am. Chem. Soc.* 122 (2000) 10115;
(b) W.W. Schoeller, A.R. Rozhenko, A. Alijah, *J. Organomet. Chem.* 617–618 (2001) 435.
- [37] W.W. Schoeller, *Eur. J. Inorg. Chem.* (2000) 369.
- [38] S. Dovesi, E. Solari, R. Scopelliti, C. Floriani, *Angew. Chem. Int. Ed.* 38 (1999) 2388.
- [39] E. Despagnet, K. Miqueu, H. Gornitzka, P.W. Dyer, D. Bourissou, G. Bertrand, *J. Am. Chem. Soc.* 124 (2002) 11834.
- [40] O. Guerret, G. Bertrand, *Acc. Chem. Res.* 30 (1997) 486.
- [41] W.A. Herrmann, M. Elison, J. Fischer, C. Kocher, G.R.J. Artus, *Chem. Eur. J.* 2 (1996) 772.
- [42] N. Merceron-Saffon, A. Baceiredo, H. Gornitzka, G. Bertrand, unpublished work.