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Schrock type transition metal complex formation of push–pull substituted phosphanyl-carbenes, a quantum chemical investigation by density-functional methods

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Abstract

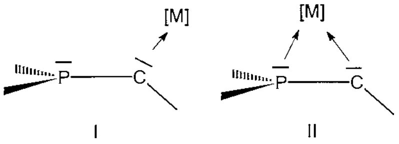
The formation of coordination compounds of phosphanyl carbenes with a transition metal in a high oxidation state (Schrock type) is evaluated by density functional theory. In the Schrock type carbene complexes the transition metal–carbon bond possesses a multiple bond character. If one of the ligands at the carbene center possesses a leaving ability, e.g. as the diaminophosphenium unit, a facile distortion to a new type of an anionic metallaalkylidene donor-acceptor complex with a diaminophosphenium cation is predicted. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Schrock type; Diaminophosphenium unit; Donor-acceptor complex

1. Introduction

The formation of transition metal complexes with phosphanylcarbenes as a 2-electron donor, type **I**, or as a 4-electron donor, type **II**, is now a well established matter in chemistry [1–5]. The pendant to the original Fischer type complexes $[M] = W(CO)_5$ (late transition metals in low oxidation states) are the Schrock type complexes (transition metal in high oxidation states), which are known to form stronger metal–carbon bonds than the Fischer type complexes. The bonding nature of carbene complexes has been analyzed in a variety of quantum chemical calculations [6–13]. Most noticeable, following the pioneering concept of Taylor and Hall [6] and Carter and Goddard [7], the metal–carbon bond can be considered as a mutual donor-acceptor interaction of two closed shell (singlet) fragments or alternatively of two triplet fragments. The former type of interaction holds true for the Fischer type carbenes in which a d^6-transition metal fragment ($[M] = ML_5$, $M = Cr$, Mo, W; $L = CO$) coordinates while for the latter transition metals in higher oxidation states (of the metal fragment) are bound to the carbene carbon. The concept was also verified recently for phosphimidene complexes [14,15] since an electrophilic (ML_5, $M = Cr$, Mo, W; $L = CO$) [14,16,17] and nucleophilic ($M = Zr$, $(L) = CP_2$) [18–20] behavior at the PR end was observed (Scheme 1).

Phosphanylcarbenes, on the other hand, in addition to η^1-coordination form 4 electron donor coordination, type **II**. The η^2-coordination compounds can be synthe-sized by various procedures and were lucidly discussed in a recent review [21]. Transition metal complexes of alkyl- and aryl-phosphanylcarbenes are known for the Fischer type as well as for the Schrock type.



Scheme 1.

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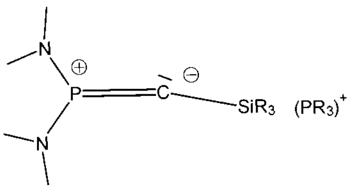

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Scheme 2.

Interestingly, the well known push–pull carbene **1** is reluctant to transition metal complex formation (Scheme 2). Up to now corresponding complexes have not been reported. A recent quantum chemical study [22] has addressed this problem. The Fischer type complexes in general require for their existence electronegative substitutents (e.g. amino groups) attached to the central carbon atom. On the other hand electronegative ligands at a carbene tend to sharpen the valence angle at the central carbon atom [23,24]. In other words these carbenes already have the appropriate bent conformation for complexation, and the preparation energy [25] required to add a transition metal fragment, is minimal. In contrast the push–pull carbene structures [26,27] are almost linear, as also substantiated by quantum chemical calculations [28–31], and the energy required to form bent carbene structures for complexation is substantial and diminishes the metal–carbon bond energies [22]. Thus this type of transition metal complex with a $M(CO)_5$ ($M = Cr, Mo, W$) fragment possesses a smaller overall tendency to form stable coordination compounds (e.g. as compared with aminocarbene complexes). The quantum chemical calculations reveal for the Fischer type carbene complexes bond orders between the metals and the carbene carbon less than a single bond [22]. In other words in the Fischer type complexes with η^1-coordination the transition metal is weakly bound to the carbene carbon.

On the contrary it is known for the Schrock type carbene complexes that the resulting metal–carbon bonds are essentially stronger and are between a single and a double bond [6,13]. As a further consequence the Fischer type carbene complexes show an electrophilic behavior while the Schrock type carbenes reveal nucleophilic behavior at the carbene (phosphinidene [15]) center. However, a strong covalent metal–carbon bond character requires the transition metal in a higher oxidation state.

Since the [M]–C bond strengths of the Schrock type are larger than for the Fischer type carbene complexes one may question whether corresponding coordination compounds may exist for the push–pull substituted carbenes, **1**. This aspect will be discussed in the present publication, on the basis of quantum chemical calculations at density functional level. In more detail, it will be shown that η^1-coordination with transition metals of the Schrock type induces in the push–pull carbenes a strong bond stretching of the PC bond with concomitant formation of a donor-acceptor complex of a phosphenium cation and a metallaalkylidene anion.

2. Theoretical

All calculations were performed with the GAUSSIAN-98 suit of programs [32]. The various structures were fully optimized at the B3LYP level. This method is built with Becke's three-parameter exchange functional [33] and the Lee–Yang–Parr correlation functional [34]. As basis sets we used the relativistically corrected effective core potentials of Stevens, Basch and Krauss [35] with a double-ζ basis expansion for the valence space (B3LYP/SBK(d)). All heavy main group atoms were augmented with a single set of polarization functions as suggested by Schmidt et al. [36]. The energy optimizations were conducted by analytically determined nuclear coordinate gradients. All of the investigated structures were characterized by vibrational analysis within the harmonic approximation. The force constants within the harmonic approximation were derived from analytically computed second-order nuclear coordinate gradients. The population analyses at the given optimized geometries were carried out within the Weinhold–Reed partitioning scheme [37]. Further analysis of the electron distributions of the various structures were performed on the basis of the 'atoms in molecules' method of Bader [38].

Density functional as well as MCSCF calculations yield for WCl_4 a triplet ground state. The best description for the energy lowest triplet and singlet states is given at the MCSCF level with subsequent multi-reference correction. The MCSCF optimization (CAS(2,5), i.e. two electrons in the space of five d-orbitals) of the singlet ($WCl = 2.286$ Å, $< ClWCl = 1.05.1, 118.6°$, D_{2d} symmetry, $^1A_1$ state) results with respect to the triplet ($WCl = 2.291$ Å, $< ClWCl = 109.5°$, $^3B_2$ state) an energic disadvantage of the former over the latter by 23.8 kcal mol^{-1}. This value reduces to 20.0 kcal mol^{-1} when additional correction for dynamical electron correlation is (at the OVB-MP2 [39] level) considered. [Within the ligand field of T_d symmetry the two highest occupied molecular orbitals are of e symmetry [40]. Consequently the energy lowest states are given by the cross-product $e \otimes e$, leading to A_1 and B_2 configurations within the lower D_{2d} symmetry group. The energy lowest triplet state, which is of interest in the following discussion, is $^3B_2$]. At the density functional level the singlet–triplet separations in favor to the triplet are essentially smaller [41].

3. Results and discussion

3.1. Qualitative considerations on carbenes

First we will briefly summarize the substituent effects on the various types of carbenes, as determined from all-valence electron quantum chemical calculations at the density functional level (B3LYP/6-31g(d,p)) [31]. Amino- and phosphino-carbenes in general possess singlet ground states [28] as evaluated in detail elsewhere [30,31]. The substituent effects which govern the singlet–triplet separation in carbenes are determined by the inductive (I) and conjugative (mesomeric, M) acting substituents attached to the central carbon. Electropositive substituents (+I) at carbon tend to open its valence angle and hence promote a triplet ground state, electronegative substituents act opposite [23,24].

The amino group (+M, −I), with respect to the neighboring carbon, causes a strongly bent carbene structure with a considerable singlet–triplet (ΔE_{S-T}) energy separation (Fig. 1, top). A trifluoromethyl group (CF_3), replacing the hydrogen causes an increase of ΔE_{S-T}. It is the consequence of a −I and a (weak) −M effect of this substituent [31]. On the other hand a silyl group acts in a different manner (+I, weak −M with respect to its neighboring carbon). The valence angle at carbon strongly increases and ΔE_{S-T} lowers (Fig. 1, bottom). The effect of silyl substitution on the electronic states of carbenes is well documented [42]. Inductive and mesomeric effects are in favor of a reduced singlet–triplet energy separation. On the other hand the phosphino group (Fig. 2, top) is a poorer π-donor (than the amino group), its inductive effect is comparable to the neighboring carbon, resulting in a smaller singlet–triplet energy separation. Again the introduction of a silyl group opens the valence angle at carbon with concomitant lowering of ΔE_{S-T}, but to a lesser extent. For comparison, the electron withdrawing effect of fluorine (strong −I, weak +M) in CF_2 is in strong favor of a singlet ground state. It possesses a sharp $<$FCF angle and a sizable singlet–triplet energy separation (54.1 [31], 56.6 [43] kcal mol^{-1}).

The matter is different for the bisaminophosphino carbene (Fig. 2, bottom). Here p-electrons are withdrawn towards the electronegative nitrogens, the PC bond gains more s-character, and is shortened. As a consequence the alternative phosphaacetylene structure [26,28] with a linear ligand arrangement at the carbon is pronounced. The π-electron withdrawing silyl group is here particularly effective in stabilizing of this limiting structure. These push–pull type carbenes are almost linear in the singlet and in the triplet state. We may note here that the magnitudes of the singlet–triplet energy separations depend on the shape of the chosen functional [44], nevertheless the predicted trends for the substituent effects should be correctly reproduced.

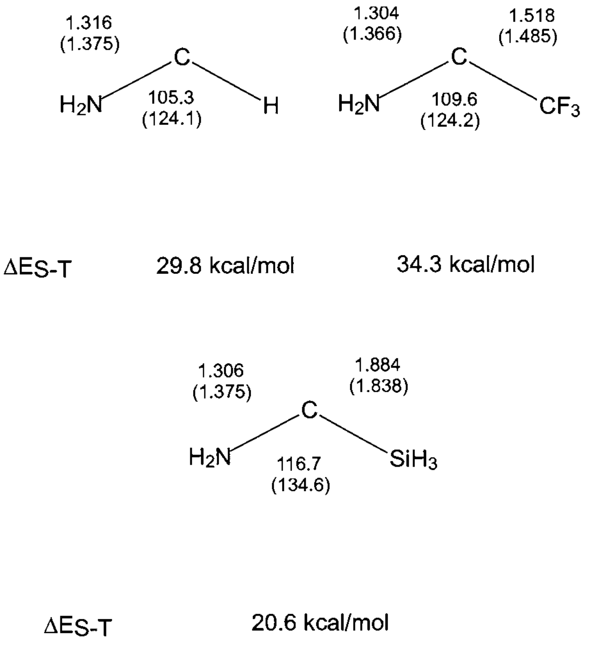


Fig. 1. Most important bonding parameters (bond lengths are measured in (Å) and bond angles in (°)) of singlet and triplet (values in parentheses) carbenes and singlet–triplet energy separations (ΔE_{S-T}, in kcal mol^{-1}) of amino-carbenes, as determined from all valence electron correlations at density functional level [31].

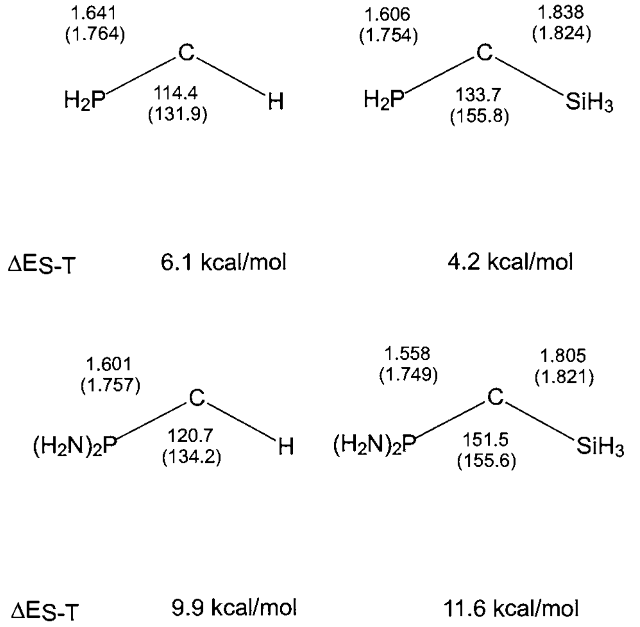


Fig. 2. Phosphino-substituted carbenes.

It has been shown that the push–pull carbenes possess very low inversion barriers at the central carbon [30], thus these structures are very flexible. Even more, the calculated equilibrium geometries are strongly dependent on the basis sets and methods chosen for the quantum chemical level (see Section 4). In practice the bonding situation of these carbenes is even more complicated. In order to protect the structures kinetically the phosphinocarbenes are substituted with bulky groups which effect the equilibrium structures of these carbenes. Corresponding calculations to this aspect will be presented at the end of this publication.

3.2. Schrock type carbenes, η^1-coordination

A typical metal fragment of Schrock type is WCl_4. The transition metal is in the (formal) oxidation state + IV and the fragment possesses a triplet ground state (see Section 2). A variety of carbene complexes with this fragment were evaluated with the DFT calculations. The considerations include the parent methylene, amino- and various phosphino-substituted carbenes. The results of the investigations are summarized in Table 1. The metal–carbon distances are essentially shorter than in the corresponding Fischer type complexes [22] and the Wiberg bond indices (values in parentheses) indicate a double-bond character. In other words these transition metal complexes are best described as metalla-alkylidenes, in accordance with previous considerations [5,13]. A peculiar structure possesses the push–pull substituted carbenes of the Bertrand type, $(H_2N)_2PCR$ ($R = SiH_3$, $PH_3^{(+)}$). They reveal a short M–C bond, as compared with the other carbenes and also a strong double character (Wiberg bond indices). A corresponding 'stick and ball' plot [45] for this type of structure is shown in Fig. 3(A).

The phosphorus atoms are strongly pyramidalized $\Sigma < (P)$ ($R = SiH_3$ 311.0°, $PH_3^{(+)}$ 311.9°) and the P–C distances are rather large ($R = SiH_3$, $PH_3^{(+)}$ 1.824, 1.856 Å) essentially larger than a PC single bond. More details about the unusual electronic bonding situation are provided by the NBO analysis. The Wiberg bond indices for the PC bonds evidence a fractional character, thus indicating a donor-acceptor interaction of a diaminophosphenium cation with an anionic metalla-alkylidene. The overall bonding situation can be written in the following limiting structure **2** (Scheme 3). The population analysis is in full support of this assertion, e.g., for $R = SiH_3 + 0.659$ el are located in the phosphenium unit and the PC bond index is 0.571. Furthermore the results are also confirmed by an inspection of the Laplacian of the electron density distributions for $R = SiH_3$ (Fig. 3(B)). The negative charge is concentrated at the carbon atom, and a lone pair is pointing from carbon to the phosphorus.

The full departure of the phosphenium unit would lead to the formation of an anionic carbyne complex. Such structures are experimentally traced [46–49] and were characterized recently by quantum chemical calculations [13]. At our DFT level we obtain for $[HCWCl_4]^{(-)}$ a MC distance of 1.747 Å with a Wiberg bond index of 2.493, thus indicating a triple bond character between W and C. The MC distances in the metal-complexes are 1.824 Å ($R = SiH_3$) and 1.856 Å ($R = PH_3^{(+)}$), intermediate between the η^1-complexes of the other phosphanyl-carbenes (see Table 1) and the metalla-carbyne structure. The M–C bond energies, ΔE (Table 1, in kcal mol^{-1}, with zero-point vibrational energy corrections) are derived according to Eq. (1).

$$^3[WCl_4] + {}^3[\text{carbene}] \rightarrow {}^1[WCl_4\text{–carbene}] + \Delta E \qquad (1)$$

At times they are calculated from the triplet states. For the determination of the energy quantities according to Eq. (1) we have calculated the equilibrium singlet states for the various carbene structures at the effective core potential level and the ΔE_{S-T} values were taken from the previous contribution [31]. For the hitherto unknown cases, these were supplemented by additional quantum chemical calculations, at the same computational level given previously (B3LYP/631g(d,p)).

Table 1

Transition metal–carbon distances (Å) for R^1R^2C–WCl_4, singlet–triplet energy separations of carbenes and bond energies of various substituted carbenes R^1R^2C, at B3LYP/SBK(d) level [a]

R^1	R^2	r (M–C) (Å)	ΔE_{S-T} [b,c]	ΔE [b]
H	H	1.874 (1.815)	−11.2 [b]	69.5 (73.3) [e]
NH_2	H	1.940 (1.351)	29.8 [d]	13.8
NH_2	SiH_3	1.925 (1.410)	20.6 [d]	25.1
NH_2	NH_2	1.993 (1.130)	51.1 [d]	−22.3
PH_2	H	1.879 (1.631)	6.5 [b]	61.6
PH_2	SiH_3	1.863 (1.684)	4.3 [b]	60.4
$P(NH_2)_2$	H	1.854 (1.752)	9.9 [b]	51.0
PF_2	SiH_3	1.860 (1.723)	−2.3 [d]	71.1
$P(NH_2)_2$	SiH_3	1.823 (1.912)	11.1 [b]	49.1
$P(NH_2)_2$	PH_3	1.856 (1.757)	26.1 [b]	9.9

[a] Wiberg bond indices (M–C) are in parentheses.

[b] Relative energies (with zero-point vibrational energy corrections) in kcal mol^{-1}.

[c] Values for singlet–triplet energy separations are taken from Ref. [31].

[d] This work, same quantum chemical level (B3LYP/6-31g(d,p)) as given in Ref. [31].

[e] Ref. [13].

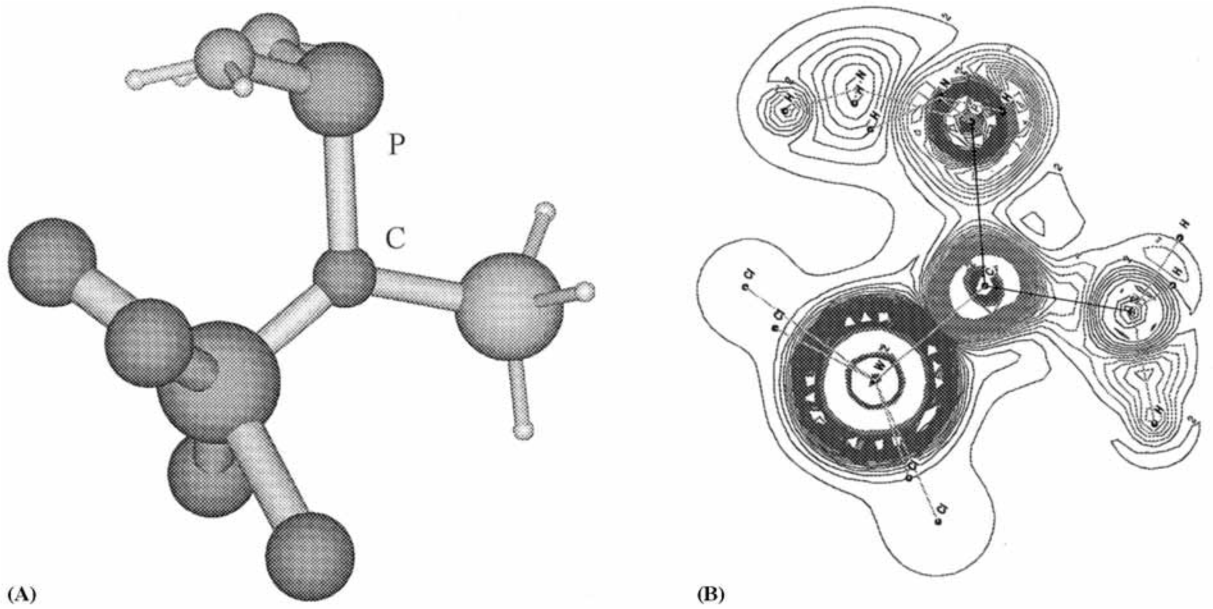
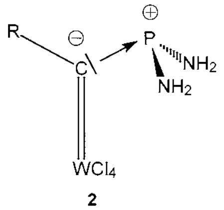


Fig. 3. Stick and ball plots of the silyl (A) derivative, (B) is Laplacian of the electron density of (A).

The resulting MC bonds reveal a strong variation in bond energies. Most strongly bound is the methylene-WCL_4 complex, in agreement with previous [13] considerations. Carbenes with a pronounced singlet ground state (e.g., R^1, $R^2 = NH_2$) have only small M–C bond energies. This trend is further corroborated for the cationic push–pull carbenes (e.g. $R^1 = P(NH_2)_2$, $R^2 = PH_3^{(+)}$); there the carbons are linear ($< R^1CR^2 \sim 180°$). Hence the formation of the Schrock type complexes is inhibited by (a) the large singlet–triplet separation and (b) the large distortion energy required to bend the valencies at carbon, in order to make transition metal complexation likely. [We note that for the carbenes with strong pronounced singlet stabilities the transition metal complexes can equally well be considered from singlet–singlet fragment coupling]. The calculations indicate that the phosphinocarbenes with a small singlet–triplet energy separation (e.g., $R^1 = PH_2$, $R^2 = H$, SiH_3) should possess strong MC bonds. Our findings are also supported by the experimental investigations on various tantalum complexes [26] on phosphanylcarbenes. The calculations predict considerable stable Schrock type complexes for the push–pull carbene with $R^1 = P(NH_2)_2$, $R^2 = SiH_3$, the stability is less pronounced for the phosphonium derivative ($R^2 = PH_3^{(+)}$).

The presented considerations keep track of η^1-coordiation. However it is known that η^2-coordinated species exist equally as well. Consequently we further investigated corresponding ring systems for the push–pull carbenes, **3**, as well as the isomeric structures, **4**. The latter refers to a carbyne transition metal complex, the substituent R (SiH_3, $PH_3^{(+)}$) is shifted towards the phosphorus. The ring structures **3** are not stable entities on the electronic hypersurface, the species rearrange without activation energy to the η^1-structure **2**. Structures **4** are stable, but higher in energy than the donor-acceptor complex (3.8 kcal mol^{-1} for $R = SiH_3$ and 13.2 kcal mol^{-1} for $R = PH_3^{(+)}$) (Scheme 4).

We are well aware of the fact that in the actual experiment the carbene structures are superimposed by a strong steric congestion exerted by the bulky substituents. Also the definition of the Schrock type carbene complex is less clearcut than that of a Fischer type carbene complex. The high oxidation state of the transition metal can be achieved by early transition metals which are fairly electropositive and/or late transition metals surrounded by electronegative ligands. For the cases presented here we have taken the WCl_4 fragment where the transition metal oxidation state can be considered formally as + IV. At



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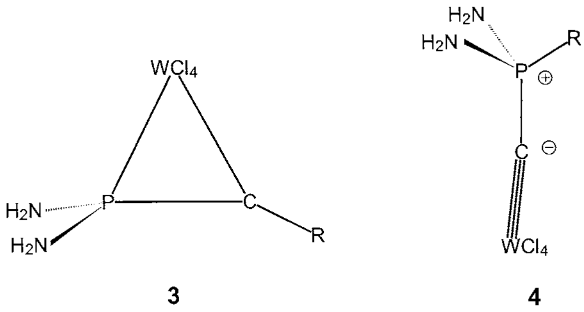
Scheme 3.



Scheme 4.

Table 2
Method dependence of equilibrium geometry of the push–pull carbene $(H_2N)_2CSiH_3$ (singlet) [a,b]

Method	CSi	<PCSi	PC
RHF/6-31g(d)	1.798	180.0	1.518
B3LYP/6-31g(d)	1.805	151.5	1.558
MP2/6-31g(d)	1.817	140.8	1.569
B3LYP/6-311+g(d,p)	1.813	145.3	1.561
MP2/6-311+g(d,p)	1.821	138.3	1.570
B3LYP/6-311+g(2df, 1p)	1.807	142.9	1.556
B3LYP/SBK(d)	1.837	133.1	1.590
MP2/SBK(d)	1.849	127.3	1.600

[a] Bond lengths are measured in (Å) and bond angles in (°).

[b] Sum of angles at phosphorus at all levels of sophistication is 360°.

least our investigations predict certain tendencies which govern the stabilities of the Schrock type carbene complexes.

4. Appendix

The inversion at the carbon center has been studied recently [30], revealing a low energy barrier for the push–pull carbene $R^1 = P(NH_2)_2$, $R^2 = SiH_3$. Here we emphasize that the actual angle at the central carbon is the result of a subtle balance of π-conjugation of the phosphino-unit with the p-orbital at carbon, and concomitant bending at this atom. The same structure was evaluated with various basis sets and electron correlated levels, RHF, B3LYP and MP2. The results for the most relevant bonding parameters are summarized in Table 2.

The various procedures yield a rather large variation of the <PCSi angles. With shortening of the PC bond a phosphaacetylene structure [28] is enhanced and the central carbon atom becomes a linear environment of ligands. A linear regression of PC bond lengths versus <PCSi angles yields a regression coefficient $r = -0.961$, it indicates the inherent problem of the quantum chemical treatment of this molecular structure. In general at the RHF the phosphaacetylene geometry (linear carbon, short PC bond) is overemphasized while the MP2 calculations pronounce the opposite trend, a bent carbene structure comes to the fore. It is the consequence of a weak PC-π-bonding with a strong electron correlation contribution. For all cases a strong coupling of the PC bond lengths with the <PCSi angle is observed. With this we mean that bending the carbon causes lengthening of the PC bond and the deformation potential is extremely weak. This matter has already been previously discussed in a different [30] context.

Another aspect deserved mentioning here, it is the effect of substituents on the equilibrium geometry of the carbene. Hitherto the quantum chemical calculations are restricted to a consideration of the parent system (H-substitution at the terminal carbene positions). Only one study deals with the full substitution [29], but the considerations are restricted to the RHF treatment. Since the actual structure strongly depends on the electron correlation treatment, it is obvious that the results are susceptible to electron correlation effects. In order to further analyze this aspect we performed density functional calculations on a variety of substituted push–pull carbenes, given overall the same computational level (B3LYP/6-31g*). Plots of the various structures are summarized in Fig. 4, the relevant bonding parameters are collected in Table 3.

It is obvious that the bulky substituents exert considerable effects on the resulting equilibrium geometries. Alkyl groups at the carbon (methyl, *t*-butyl)

Table 3
Bonding parameters of substituted push–pull carbenes **1** [a,b]

Compound	R^1	R^2	PC	$<PCR^2$	Σ <P [c]
1a	H	CH_3	1.586	138.8	358.7
1b	CH_3	$C(CH_3)_3$	1.592	140.7	359.3
1c	i-prop	$C(CH_3)_3$	1.601	104.6	360.0
1d	H	SiH_3	1.558	151.5	360.0
1e	CH_3	$Si(CH_3)_3$	1.566	154.7	360.0
1f	i-prop	$Si(CH_3)_3$	1.559	177.6	360.0
1g	t-but	$Si(CH_3)_3$	1.562	170.3	360.0

[a] Bond lengths are measured in (Å) and bond angles in (°).

[b] $R^1(R^2)$ are substituents at the nitrogens (carbon) (at B3LYP/6-31g(d) level).

[c] Sum of angles at phosphorus.

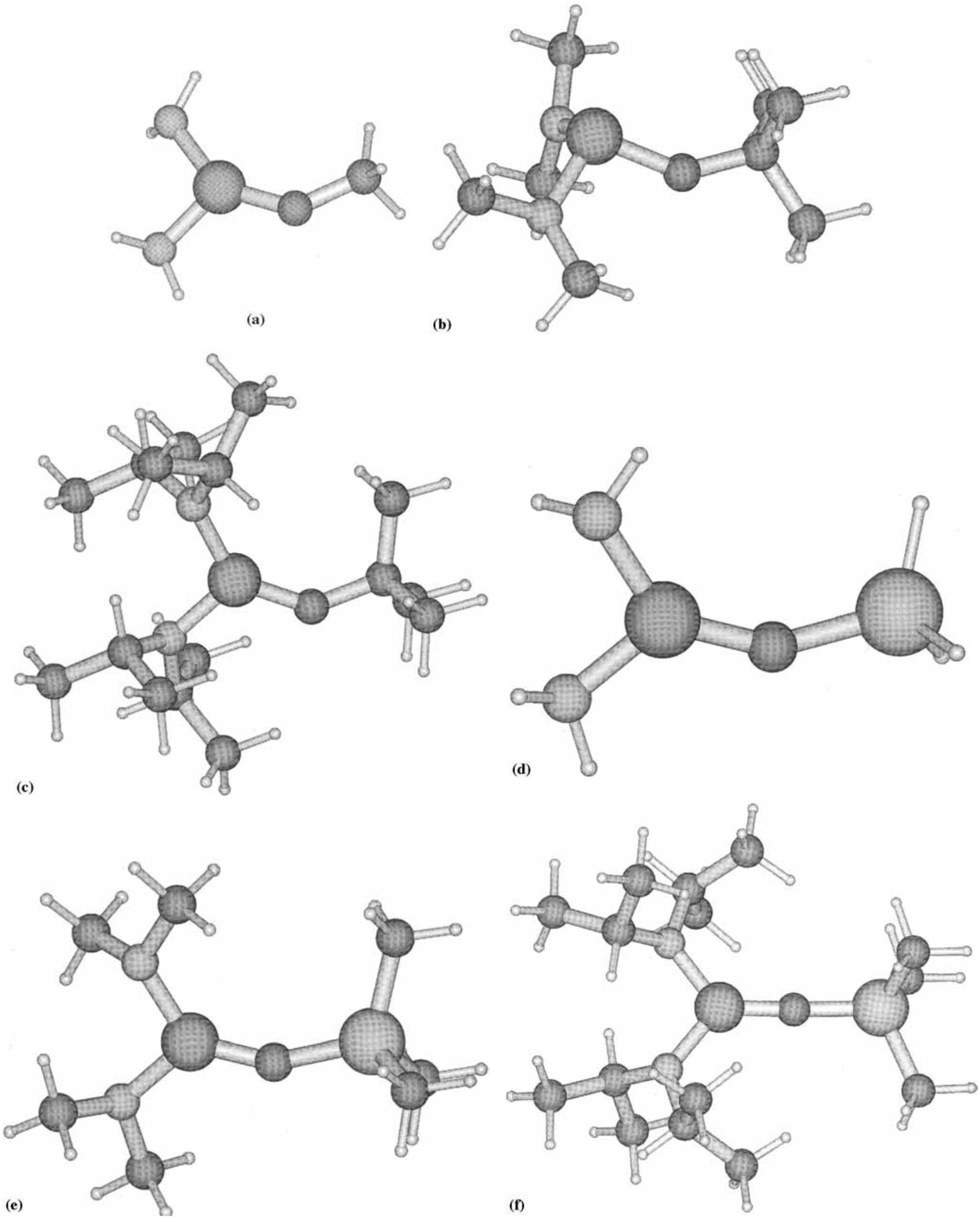


Fig. 4. Plots of various push–pull carbenes, B3LYP/6-31g* fully optimized, $(R^1_2N)_2PCR^2$, R^1/R^2 = H/Me **1a**, Me/*t*-but **1b**, *i*-prop/*t*-but **1c**, H/SiH_3 **1d**, Me/$SiMe_3$ **1e**, *i*-prop/$SiMe_3$ **1f**, *t*-but/$SiMe_3$ **1g**.

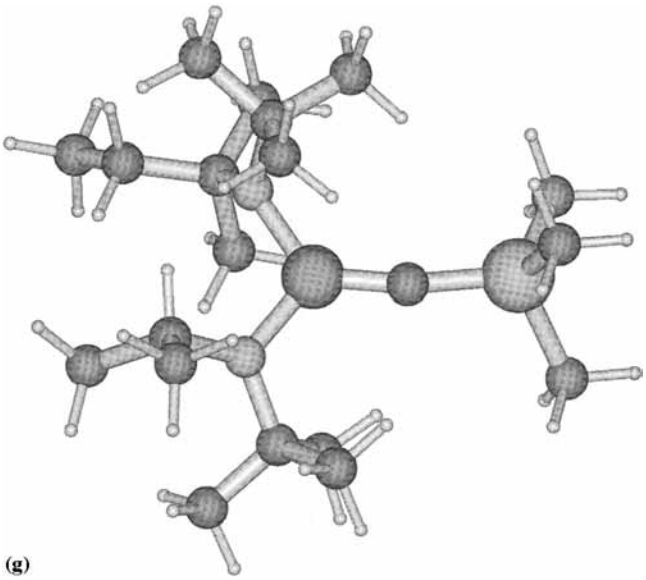


Fig. 4. (*Continued*)

enforce a stronger bending of the carbon with concomitant lengthening of the PC bond. A silyl, group (silyl, trimethylsilyl) at carbon yields an opening of the $<\mathrm{PCR}^2$ angle and shortening of the PC bond. The plots also indicate that the carbene structures are sterically strongly encumbered for attack by a transition metal fragment.

Acknowledgements

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