On the Electronic Properties of Substituted Phosphanylcarbenes

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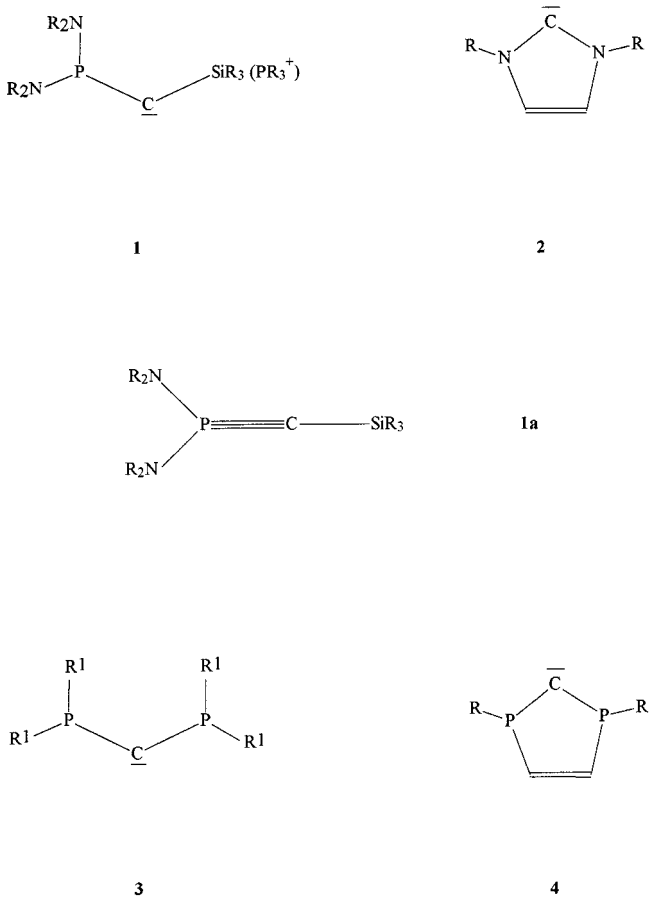
A phosphanyl group exerts much less π-conjugation properties than an amino group. On this basis, corresponding carbene structures exhibit much smaller singlet–triplet energy separations. Of the various structures investigated quantum-chemically the largest singlet–triplet energy separations are predicted for cyclic diphosphanylcarbenes, in which the two functional groups are incorporated into a ring system and the phosphorus atoms are substituted by phosphoraniminato groups. Then the singlet–triplet energy separations become essentially larger than for the Bertrand-type (push-pull) carbenes.

Introduction

Some time ago, Bertrand and co-workers reported in a series of pioneering investigations[1−9] the first syntheses of stable, isolable phosphanylcarbenes **1** (see Scheme 1). A prerequisite for the stability of the species is a substitution of the phosphanyl carbene with amino groups at phosphorus and an electron-withdrawing group (SiR_3, $PR_3^{(+)}$) at the carbon atom. The stabilizing effects of amino groups at the phosphorus and an electron-withdrawing group at the carbon atom have been rationalized by vinyl ylide structures, already suggested some time ago[1] for **1a** as a λ^5-phosphaalkyne structure. The assertion conforms with quantum-chemical calculations carried out later.[6] In other words, the positive charge at the phosphorus and the negative charge at the carbon atom are delocalized into the amino and the silyl (phosphonium) groups. It has been stated that the stabilities of the carbenes are often inversely proportional to the stability of the starting diazo compounds.[9]

Quantum-chemical calculations were first carried out on the singlet and triplet structural isomers of monophosphanylcarbene, H_2PCH.[10] An almost planar singlet state is predicted, with an inversion barrier of only 4 kcal mol^{-1}. It results in the electronic ground state, but only 3 kcal mol^{-1} lower in energy than the triplet state. The results are in agreement with more sophisticated calculations using the multiconfiguration-based unitary coupled electron pair approximation on parent phosphanyl carbenes.[11]

However, this study anticipates a somewhat larger energy difference (10 kcal mol^{-1}) between singlet and triplet states lowest in energy. While these two quantum chemical studies consider only a monophosphanyl-substituted carbene, a third study[12] examined the role of silicon substitution at the carbon (SiH_3) and of amino groups at the phosphorus atom. In essence, here the singlet−triplet energy separation is increased (13.9 kcal mol^{-1} in advantage to the singlet state, at PMP4 level) and the calculations indicate that this effect parallels an opening of the P−C−Si angle (135.7° predicted at MP2 level).



Scheme 1

Another representative of a stable carbene is the imidazol-2-ylidene **2** reported by Arduengo et al.[13][14] In this type of structure, the electron-deficient divalent carbon center is π-conjugated with two amino groups.[14][15] The carbenic nature and the question of their stabilities is presently under intensive debate, in particular the role of the heteroatom substituents.[16−22] To this end, a "mixed" car-

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bene which contains a phosphanyl and an amino group has been observed in transient formation recently.[23]

One of the major questions is an analysis of the electronic properties of carbene structures which combine both features: that of the types **1** and **2**. This will be discussed in the present quantum-chemical study. We evaluate the following aspects in detail: (1) Symmetrical, phosphanyl-substituted carbenes **3** and unsymmetrical, Bertrand-type carbenes **1** with various donors (acceptors) at the phosphorus (carbon) atom; and finally (2) the effect of incorporation of phosphanyl groups into ring systems, such as in **4** and related ring systems. We will show that a phosphoraniminato ligand ($-NPH_3$) is more effective than an amino group, to enhance the singlet−triplet energy separation in a phosphanylcarbene.

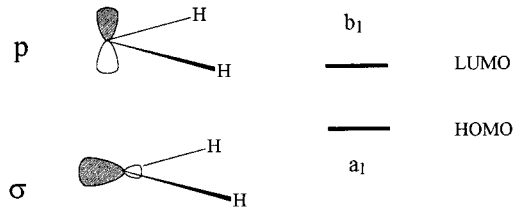
Theoretical Section

All calculations were performed with the Gaussian set of programs.[24] For the optimization of structures, double-ζ basis sets [6-31g(d,p)][25−28] were used. These basis sets include a single set of polarization functions at all atoms. In order to account for a proper electron correlation treatment, the optimization of structures was at times performed at a density functional level, utilizing the hybrid density function of Becke, Lee and Parr.[29] All structures were characterized by corresponding vibrational analysis, to identify these as energy minima on the corresponding electronic hypersurfaces. For some cases, the optimized geometries were energetically refined by single-point calculations at 6-311+g(d,p) basis set level[30][31] within the coupled cluster approximation, including single and double excitations from the ground state wavefunction, and triple excitation by corrections [CCSD(t)].[32][33] For the studied cases, the more elaborate CCSD(t) calculations parallel the results of the density functional (DFT) calculations at B3LYP level. As a consequence, general trends on singlet stabilities of carbenes can be explored on a large series of structures at the DFT level. The analysis of electron densities were performed within the Weinhold-Reed partitioning scheme.[34][35] Further investigations were also undertaken with Bader's method of "atoms in molecules" (AIM),[36] in order to analyze in more detail the nature of bonding in the corresponding structures.

Results and Discussion

a. Symmetrically Substituted Diphosphanylcarbenes

The frontier orbitals of a carbene, e.g. of the simplest representative methylene, are given as in Scheme 2. In the lowest energy singlet state, two electrons reside in the σ-orbital ($^1\sigma^2\rangle$, $^1A_1$ configuration) while in the lowest energy triplet state, one electron is in the σ and the other electron in the p orbital ($^3\sigma^1p^1\rangle$, $^3B_1$ configuration). It is the well-known picture of carbenes.[37−39] As a consequence, triplet carbenes possess widened R−C−R angles as relative to their singlet counterparts. One expects that in a carbene CR_2, the valence angle R−C−R increases with decreasing electronegativity of R.[40][41] For the methylene, the density functional calculations yield an energy difference of 12.2 kcal mol^{-1} between both electronic configurations [at B3LYP/6-31g(d,p) level], in favour of the triplet ($^1A_1$, CH = 1.119 Å, H−C−H = 100.0°; $^3B_1$, CH = 1.082 Å, H−C−H = 133.5°). This value may be compared to 9.0 kcal mol^{-1} obtained from the detailed experimental investigations.[42]



Scheme 2

In order to gain insight into the bonding of the phosphanylcarbenes, a variety of substituted carbenes were studied. A summary of symmetrically substituted species, CR_2 (R = phosphanyl unit) were calculated and the most important facets (singlet−triplet energy separations, relevant bonding parameters) are collected in Table 1.

Table 1. Relevant bonding parameters (bond lengths in Å, bond angles in °) and energy separations between singlet and triplet states of symmetrically substituted R_2C carbenes

Substituent	State	PC	∢PCP	Δ*E* (kcal mol^{-1})
PH_2	$^1A_1$	1.682	137.7	0.0 (0.0)
	^3B	1.765	137.7	8.4 (7.3)[a]
NH_2	$^1A_1$[b]	1.343	112.2	0.0
	^3B	1.392	122.5	51.1 (52.1), [58.5,[c] 50.7][d]
F	$^1A_1$[b]	1.313	104.1	0.0
	$^3B_1$[b]	1.325	120.1	52.1 (54.1) [56.6][e]
PF_2	^1A	1.651	154.2	0.0
	^3B	1.776	140.5	3.8
$P(NH_2)_2$	^1A	1.675	136.5	0.0
	^3B	1.761	139.9	0.6
$P(CH_3)_2$	^1A	1.672	141.7	0.0
	^3B	1.750	138.6	11.8
$P(SiH_3)_2$	^1A	1.696	138.6	0.0
	^3B	1.759	140.0	9.4
$PH(NPH_3)$	^1A	1.680	141.2	0.0
	^3B	1.740	135.6	16.0
$P(NPH_3)_2$	^1A (C_1)	1.622, 1.775	135.9	0.0
	^3B (C_2)	1.756	127.7	15.1

[a] In parentheses values with CCSD(t)/6-311+g(d,p)//B3LYP/6-31g(d,p) + zero-point vibrational energy correction. − [b] C_{2v} symmetry. − [c] Ref.[45] − [d] Ref.[44] − [e] S. Koda, *Chem. Phys.* **1982**, *66*, 383−390.

In most cases the species adopt a C_2 symmetry in their equilibrium structures (singlets and triplets). The matter may be illustrated for the parent diphosphanylcarbene, in

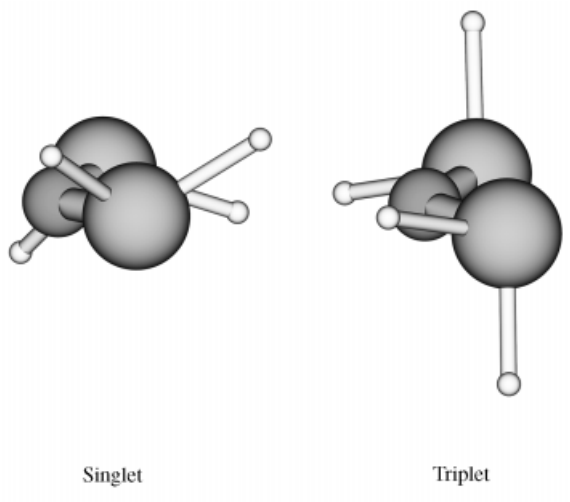


Figure 1. Molden plots of singlet and triplet diphosphanylcarbene

the Molden plots shown in Figure 1[43] of the singlet (left) and triplet (right) structures.

In the lowest energy singlet state (C_2 symmetry, P−C = 1.682 Å, P−C−P = 137.7°), the lone pairs at the phosphanyl groups tend to overlap with the empty p-orbital at the central carbon atom, so as to adopt π-conjugation, while in the lowest energy triplet state, the P−C bonds are elongated (1.765 Å, P−C−P = 137.7°) but the lone pairs at the phosphanyl substituents are almost perpendicularly oriented with respect to the central p-orbital. In both states the P−C−P angles are identical. Similar features were already predicted by previous quantum-chemical studies.[10]

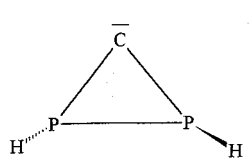
For comparison, we also included in our considerations the diaminocarbene. It adopts a planar (C_{2v} symmetry) structure in the singlet state, while the triplet state is confined to a twisted geometry (C_2 symmetry), in agreement with previous considerations.[44][45] For the diphosphanylcarbenes, the P−C distances are shorter in the singlet than in the triplet states. It indicates a stronger overlap in the former than in the latter. There is, however, an essential difference in the phosphanyl versus amino substitution. For R = NH_2 (diaminocarbene) in the singlet state the N−C−N valence angle is more acute than in the triplet state (112.2 vs. 122.5°). The trend is less unique for the various substituted diphosphanylcarbenes. The P−C−P angle is similar in both states [R = PH_2, $P(SiH_3)_2$, $P(CH_3)_2$, $P(NH_2)_2$], or even larger in the singlet relative to the triplet (R = PF_2) states.

Most of the singlet−triplet splitting is due to the height of the inversion barrier at the nitrogen or phosphorus atom. The large value for ΔE in the *N*-substituted carbenes is due to the low barrier at N (ca. 6 kcal mol^{-1} in NH_3)[46] which strongly stabilizes the singlet by allowing some back-donation into the vacant orbital. The much higher value for P (ca. 35 kcal mol^{-1} for PH_3)[46] leads to an inability of the P lone pair to stabilize the singlet and hence ΔE is much smaller. In addition, the more bent the phosphorus is compared to nitrogen (H−P−H in PH_3 is ca. 95° and H−N−H in NH_3 is ca. 109°), the more the triplet state will be stabilized as the lone pair at P is less repulsive than the lone pair on N when interacting with the single electron in the out-of-plane orbital on the carbene center. Since the C−N distance is much shorter than the C−P distance, the effects at the nitrogen are stronger than at the phosphorus atom. In accordance with Bent's rule,[47−49] within pyramidalization, the s-character of the lone pairs increases and the phosphorus atom utilizes more p-character in the formation of the σ-P−C bonds. It becomes a more electropositive substituent towards the central carbon atom. On this basis, it prefers a bonding situation in which the central carbon atom is expected to become more linear. At least this argument explains the essential difference in bonding between the singlet states of CR_2, R = PH_2 versus PF_2.

On the basis of these arguments, phosphanyl substituents with electronegative atoms [R = PF_2, $P(NH_2)_2$] possess small energy differences between singlet and triplet states lowest in energy. On the other hand, substituents which in general are known to decrease the inversion barrier in a phosphane [R = $P(CH_3)_2$, $P(SiH_3)_2$] increase the energy splitting. We have also studied the use of a phosphoraniminato group[50][51] [R = $P(PH(NPH_3)$] as a ligand at the phosphorus atom. The largest energy differences between singlet and triplet is obtained in this case. One may consider these substituents as extremely strong nucleophiles which increase the donor capability of a phosphanyl group. We have also probed the case of two phosphoraniminato ligands at the same phosphorus atom (see Table 1). It does not further increase the singlet−triplet energy gap. In the singlet state only one PR_2 (R = NPH_3) group is capable of interacting with the central carbon atom such as to maximize π-conjugation. The other PR_2 group is more strongly pyramidalized and avoids π-overlap with the central carbon atom. Overall, it causes reduction of the singlet equilibrium structure to C_1 symmetry. According to the population analysis in the investigated singlet structures (NBO and Laplacian of the electron densities), the carbon atom carries an excess negative charge (ca. −1.5 el), the phosphorus atoms are positively charged and the multiple bonding between the phosphorus and the carbon atom is weak (ca. 1.3 Wiberg bond indices).

Next we will discuss the bonding situation in diphosphanylcarbenes which are incorporated in a ring system. In these structures, a sharpened P−C−P angle is enforced which should be of more advantage to a singlet than to a triplet state. Various cases were studied and are collected in Table 2.

The singlet−triplet energy gap increases with increasing size of the ring system (Scheme 3). It is smallest for the 1.2-diphosphacyclopropenylidene (**5**, ΔE = 2.9 kcal mol^{-1}). The incorporation of a double bond in the five-membered ring system **4** (R = H) versus **7** slightly shortens the P−C bonds and concomitantly increases the singlet−triplet splitting. Compound **4** is the phosphorus analogue of the Arduengo carbene **2**.[15] We predict for the latter a sizeable energy splitting of 80.0 kcal mol^{-1} between lowest energy singlet and triplet states. Our findings are in agreement with previous calculations on this structure (ΔE = 79.3,[52]



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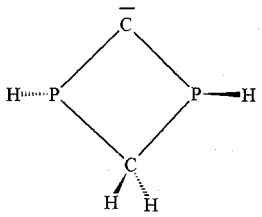

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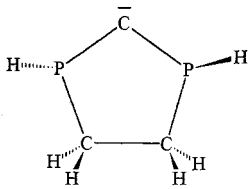

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Scheme 3

Table 2. Cyclic diphosphanylcarbenes (C_2 symmetry)

Compound	State	PC	∢PCP	ΔE(kcal mol^{-1})
5	^{1}A	1.775	72.1	0.0
	^{3}B	1.876	82.8	2.9 (3.6)
6	^{1}A	1.793	90.2	0.0
	^{3}B	1.817	101.2	8.0
7	^{1}A	1.759	106.6	0.0
	^{3}B	1.793	123.4	13.3
4 (R = H)	^{1}A	1.679	114.2	0.0
	^{3}B	1.808	120.0	17.3
4 (R =CH_3)	^{1}A	1.714	101.9	0.0
	^{3}B	1.784	121.8	20.1
4 (R = F)	^{1}A	1.697	98.6	0.0
	^{3}B	1.785	123.4	12.1
4 (R =Cl)	^{1}A	1.710	99.1	0.0
	^{3}B	1.783	122.8	9.1
4 (R = NH_2)	^{1}A	1.714	100.9	0.0
	^{3}B	1.793	122.7	15.9
4 (R = NPH_3)	^{1}A	1.712	101.6	0.0
	^{3}B	1.792	121.7	24.9
4 (R = PPH_3)	^{1}A	1.725	102.0	0.0
	^{3}B	1.775	121.7	19.2

84.5[45] kcal mol^{-1}). Similar aspects have been found for the singlet−triplet energy separation in the Arduengo carbene **2** versus its hydrogenated analogue[53] and have been attributed to the effect of additional divalent state stabilization energy (DSSE).[54] In other words, in the singlet and to a lesser extent in the triplet states, additional cyclic π-delocalization is gained. The incorporation of the phosphanyl units into the five-membered ring system considerably stabilizes the singlet state of the carbene.[45] According to our calculations the singlet can be further stabilized by introduction of a phosphoraniminato ligand at the phosphorus atom (**4**, R = NPH_3). Thus one expects that the phosphorus analogue of the Arduengo carbene is a rather stable species. The population analysis indicates similar electron distributions to the alicyclic congeners for the ring structures. However, the P−C bonds are strengthened, as witnessed by their shortening. We have also tested the phosphorus analogue of the phosphoraniminato ligand (R = PPH_3). It appears to be less effective in the singlet stabilization than the former ligand (R = NPH_3).

b. Asymmetrical Phosphanylcarbenes

Next we will discuss the cases in which only one phosphanyl group is attached to the electron-deficient carbene center. The most prominent example is the push−pull substituted carbene **1**, already well investigated by quantum chemical investigations.[6][12] These calculations indicate that electron-withdrawing substituents at the carbon atom possess a particular role in the stabilization of a singlet carbene.[12] However, a detailed investigation of related substituents has hitherto not been given. In this section we want to demonstrate the influence of various substituted phosphanyl groups on the singlet stability of the various substituted species. We record here in more detail the results of the unsymmetrically substituted carbenes $R^1R^2PCR^3$, with R^1 and R^2 being different substituents and with R^3 as various electron-withdrawing groups. The results of the quantum-chemical investigations are collected in Table 3.

Table 3. Singlet−triplet energy separations and relevant bonding parameters of asymmetrically substituted carbenes, $R^1R^2PCR^3$

R^1	R^2	R^3	State	PC	∢PCR^3	ΔE (kcal mol^{-1})
H	H	H	^{1}A	1.641	113.9	0.0
			^{3}A	1.764	131.9	6.5 (7.6)
H	H	CH_3	^{1}A	1.642	127.0	0.0
			^{3}A	1.770	135.5	3.0 (3.8)
H	H	CF_3	^{1}A	1.624	122.5	0.0
			^{3}A	1.767	132.3	5.7
H	H	SiH_3	^{1}A	1.607	133.5	0.0
			^{3}A	1.755	155.6	4.4 (6.2)
NH_2	NH_2	SiH_3	^{1}A	1.559	151.1	0.0
			^{3}A	1.749	156.5	11.1
NH_2	NH_2	$PH_3^{(+)}$	^{1}A	1.545	176.4	0.0
			^{3}A	1.745	136.3	26.1
NH_2	NH_2	CF_3	^{1}A	1.584	126.4	0.0
			^{3}A	1.760	133.3	11.8
H_3PN	H	H	^{1}A	1.616	120.7	0.0
			^{3}A	1.765	130.7	17.1
H_3PN	H	SiH_3	^{1}A	1.588	140.7	0.0
			^{3}A	1.746	180.0	21.8
H_3PN	H	$PH_3^{(+)}$	^{1}A	1.589	141.7	0.0
			^{3}A	1.760	135.1	31.8

In agreement with the previous considerations,[10][12] the singlet−triplet separation for the monophosphanylcarbene is fairly small. Given a diaminophosphanyl ligand, R^3 is most effective in the order $SiH_3 \approx CF_3 < PH_3^{(+)}$. Most

noticeable is again the fact that the phosphoraniminato ligand reveals a particular role in the stabilization of the carbene. The most stable carbene is predicted to be the case with one phosphoraniminato ligand and one phosphonium group at the carbon centre. Alternatively, stable carbenes require diamino substitution at the phosphorus atom. The Wiberg bond indices indicate a bond with almost double-bond character between the phosphorus and the carbon atom for these structures, superimposed by a strong charge separation between them. It is in conformity with previous considerations.[12] We note that recently a quantum-chemical study on parent phosphanylcarbene H_2PCH and related structures has been reported.[55] Regarding these findings, the reported structural details of H_2PCH are similar, while for the push−pull carbene $(H_2N)_2PCSiH_3$ the reported singlet−triplet energy separation is essentially larger (26.9 kcal mol^{-1}) than our value (11.1 kcal mol^{-1}, see Table 3).[56]

It is of interest also to examine the effect of push−pull substitution in the case of aminocarbene, H_2NCH. We calculate for it a singlet−triplet energy separation of 29.8 kcal mol^{-1} [B3LYP/6-31g(d,p) with ZPE correction]. The energy gap decreases to 20.6 kcal mol^{-1} when the hydrogen atom is replaced by a silyl group. In other words, a push−pull mechanism which is operative in the phosphanylcarbenes, does not hold true for the aminocarbene, the singlet−triplet energy gap is even considerably decreased. It is known that silyl groups tend to bring the triplet character of a carbene to the fore.[57][58] Finally, these values are related to the experimental results of the aminophosphanylcarbene.[23] We predict an energy gap in ΔE = 27.8 kcal mol^{-1}, almost similar in magnitude to the monoaminocarbene. The diaminocarbene resulted to ΔE = 51.1 kcal mol^{-1}, in agreement with previous quantum-chemical investigations (see Table 1).

Conclusions

The effect of various types of substituents on the singlet−triplet energy separations have been studied by density functional theory. The results of our investigations can be summarized as follows:

(1) The singlet−triplet energy separation in the diphosphanylcarbenes can be increased by suitable substitution at the phosphorus atom. In the parent compound, the energy gap is fairly small, but it increases by alkyl substitution or most effectively by substitution with a phosphoraniminato ligand.

(2) A considerable stabilization of the singlet species is observed by incorporation of the diphosphanyl ligand into a five-membered ring system, resulting in the phosphorus analogue of the Arduengo carbene. Again the singlet−triplet energy separation is increased by introduction of the phosphoraniminato ligand.

(3) Asymmetric phosphanylcarbenes are most stable in the case of the phosphorus atom being substituted by amino groups or alternatively by the phosphoraniminato ligand and the carbon atom in addition being attached to an electron-withdrawing substituent, such as a silyl or a phosphonium group.

Our theoretical analysis predicts new types of substitutent patterns which are effective in stabilizing singlet ground states of phosphanylcarbenes. Its verification may be a challenge to the experimental chemist. Further investigations will be dedicated to an investigation of the nucleophilic versus electrophilic character[37] of phosphanylcarbenes, towards cycloaddition reactions as well as to their transition metal complexation properties.

Acknowledgments

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