Heteroatom Chemistry
Volume 2, Number 1, 1991

Bis(diisopropylamino)phosphanyldiazomethane: A Building Block for the Synthesis of Stable Carbene and Nitrilimines

Guy Bertrand

Laboratoire de Chimie de Coordination du CNRS, 205, route de Narbonne, 31077 Toulouse Cédex, France

Received 26 June 1990.

ABSTRACT

Thermolysis of [bis(diisopropylamino)phosphanyl](trimethylsilyl)diazomethane **1** *affords the corresponding carbene* **2**, *which is stable enough to be spectroscopically characterized. This species possesses a phosphorus–carbon multiple-bond character as shown by the 2 + 3 and 2 + 2 cycloaddition reactions observed with trimethylsilyl azide or N_2O and ethyl cyanoformate, respectively. On the other hand,* **2** *undergoes all the classical reactions of a carbene: cyclopropanation reaction with electron-poor alkenes, carbon–hydrogen bond insertion, and carbene–carbene coupling with isonitriles. Compound* **2** *reacts with trimethylsilyl triflate affording a stable methylenephosphonium salt* **15**. *Treatment of the lithium salt of the [bis(diisopropylamino)thiophosphoranyl]diazomethane* **18** *with the bis(diisopropylamino)phosphanyl chloride leads to a stable nitrilimine* **3**. *Thermolysis of* **3** *affords the isomeric diazo derivative* **20**, *while photolysis gives rise to thiophosphoranylnitrile* **21** *and cyclodiphosphazene* **23**. *Regioselective 2 + 3 cycloadditions are observed with electron-poor dipolarophiles. Addition of trimethylsilyl triflate to* **3** *leads to a stable electrophilic nitrilimine* **29**.

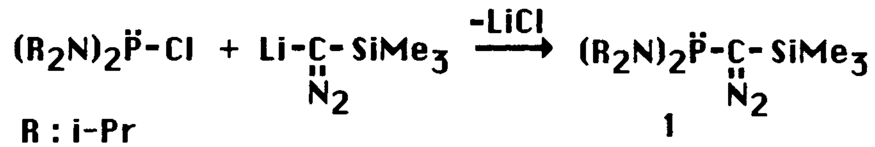
RESULTS AND DISCUSSION

The ability of transition metals to stabilize electron-deficient species such as carbenes, nitrenes, phosphinidenes [1], or other types of highly reactive organic or inorganic species is now well established. Less often, it has been shown that a similar role could be played by heavier main group elements. For example, sulfenylnitrenes [2] or phosphanylnitrenes [3] can be relatively stable. Here, we report that the [bis(diisopropylamino)-phosphanyl](trimethylsilyl)carbene **2** is an isolable compound possessing the characteristics of a normal carbene and of a polarized λ^5-phosphaacetylene. We also show that the precursor of this compound, namely the [bis(diisopropylamino)phosphanyl](trimethylsilyl)diazomethane **1**, is an excellent building block for the synthesis of the first stable nitrilimine **3**.

Synthesis of [Bis(diisopropylamino)phosphanyl]-(trimethylsilyl)diazomethane 1

Diazo compounds are classical precursors of carbenes. Although diazo-λ^5-phosphorus derivatives are well documented [4], as far as we know, no examples of molecules possessing a diazo group bonded to a λ^3-phosphorus atom have been reported before our work [5, 6]. This class of compounds, like phosphane azides, could have been very unstable due to possible intermolecular reactions of the diazo moiety with the phosphorus lone pair [7]. Taking into account the observed stability of the bis(diisopropylamino)phosphane azide [3, 8] we chose to prepare the (trimethylsilyl)[bis(diisopropylamino)phosphanyl]diazomethane **1**. Treatment of the lithium salt of (trimethylsilyl)diazomethane [9] with a stoichiometric amount of bis(diisopropylamino)chlorophosphane [10] led to the desired product **1** in 85% isolated yield (Scheme 1).

1042-7163/91/$3.50 + .25



SCHEME 1

The red oily diazo derivative **1** was stable enough to be purified by distillation at 85–90°C (10^{-2} mm Hg) without noticeable decomposition.

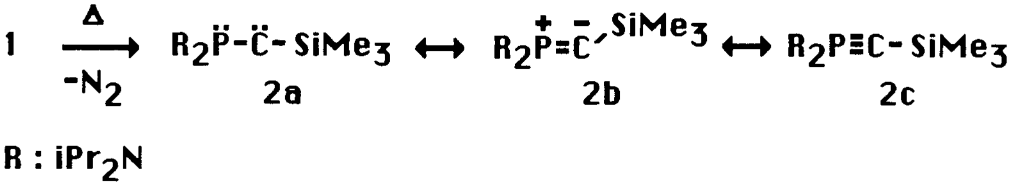
[Bis(diisopropylamino)phosphanyl]-(trimethylsilyl)carbene **2**

Having in hand the precursor, we first attempted to generate the carbene by photolysis. According to ^{31}P NMR spectroscopy, a major product (δ ^{31}P: -40) was formed when the irradiation of **1** was performed in the absence of trapping agents. However, all attempts to isolate the derivative corresponding to this signal failed. Interestingly, flash thermolysis of **1**, at 250°C, under vacuum, produced the same species in 80% yield as a red oily material identified as the desired phosphanylcarbene **2**: bp 75–80°C (10^{-2} mm Hg); UV λ_{max} = 300.4 nm (Scheme 2).

This compound is stable for several weeks at room temperature, in benzene solution. The high field chemical shift in ^{31}P NMR and the large ^{1}J(PC) and ^{2}J(PSi) coupling constants observed for **2**, compared with those of **1** or trimethylsilyl λ^3-phosphaalkyne [11] (Table 1), suggest an increase of the number of valence bonds of the phosphorus atom. The low field signal in ^{13}C NMR is in the range expected for a multiply-bonded carbon. In marked contrast with ^{1}H and ^{13}C NMR data available for other bis(diisopropylamino)phosphanes, the four isopropyl groups are equivalent in the case of **2**, arguing for an increase of the N–P–N angle (allowing free rotation of the substituents) and perhaps for a symmetrical molecule. Theoretical calculations performed on H_2PCH predicted [12] that there are three minima on the total potential energy surface: in **2a** the phosphorus atom would be pyramidal, **2b** would be a planar molecule but bent at the carbon, while **2c** would be planar and linear. Thus, on the basis of NMR spectroscopy, it is clear that **2** possesses a multiple-bond character and is most probably a λ^5-phosphaacetylene **2c**.

Although **2** is thermally stable, it is quite reactive. Both multiple-bond and carbene reactivity have been observed.

The multiple bond character of **2** was demonstrated by its reaction with trimethylsilyl azide. The final product, diazo derivative **5**, was isolated in 92% yield. The initially formed 2 + 3 cycloadduct **4** was characterized by NMR spectroscopy, at 4°C. This reaction is strictly analogous to that often re-



SCHEME 2

TABLE 1 NMR Data for **1**, **2** and P≡CSiMe$_3$. (Chemical shifts are expressed in ppm; coupling constants with phosphorus, reported in hertz, are in brackets.)

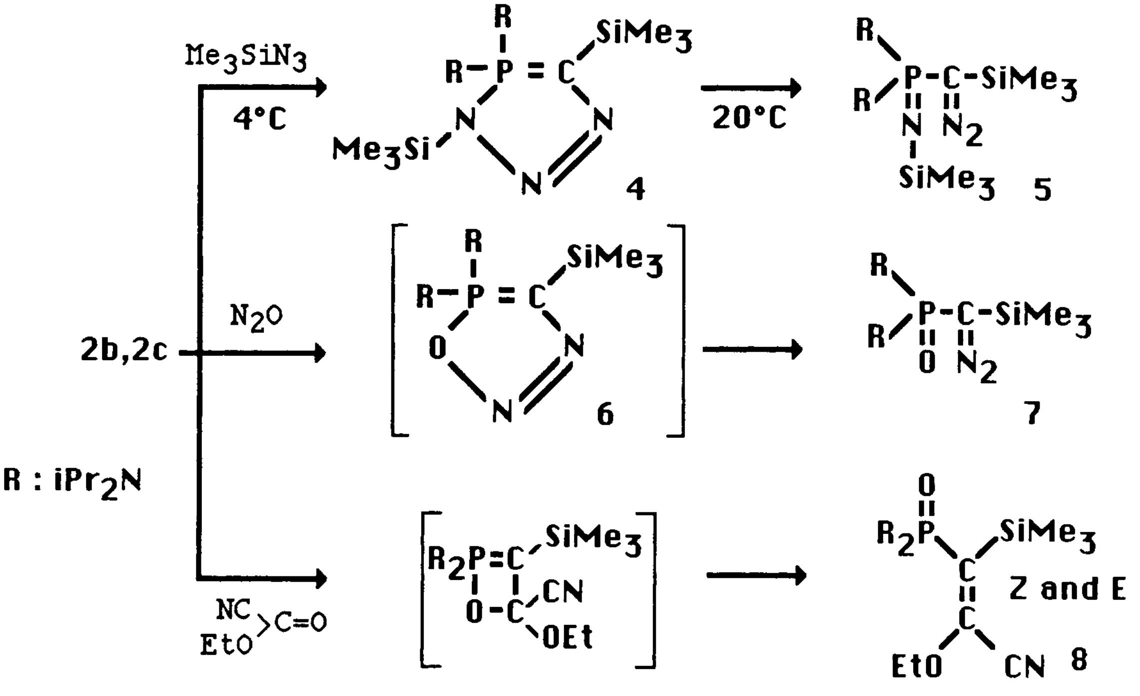
	1	*2*	*P≡CSiMe$_3$*
^{31}P	+56	−40	+96
^{13}C SiCH$_3$	−0.8 (5.3)	3.9 (10.6)	
CH$\underline{C}$H$_3$	23.8, 23.9, 25.0, 25.1	22.6	
$\underline{C}$HCH$_3$	48.0 (12.0)	48.6 (2.3)	
$\underline{C}$	28.3 (90.9)	142.7 (159.3)	201.4 (13.9)
^{29}Si	+1.7 (43.1)	−19.7 (59.3)	
^{1}H SiCH$_3$	−0.23	+0.46 (1.1)	
CHC$\underline{H}_3$	1.17, 1.20	1.22	
C$\underline{H}$CH$_3$	3.32 (12.2)	3.38 (18.3)	

ported between azides and alkynes [13]. A similar 2 + 3 cycloaddition pathway was observed for the reaction of **2** with N_2O. In this case, the initially formed 5-membered ring **6** could not be spectroscopically observed, but the resulting diazo compound **7** was isolated in 86% yield. Lastly, when a very electron-poor carbonyl group, such as in ethyl cyanoformate, is used, a mixture of Z and E phosphorylalkene **8** is obtained, suggesting a 2 + 2 cycloaddition process, followed by ring opening (Scheme 3).

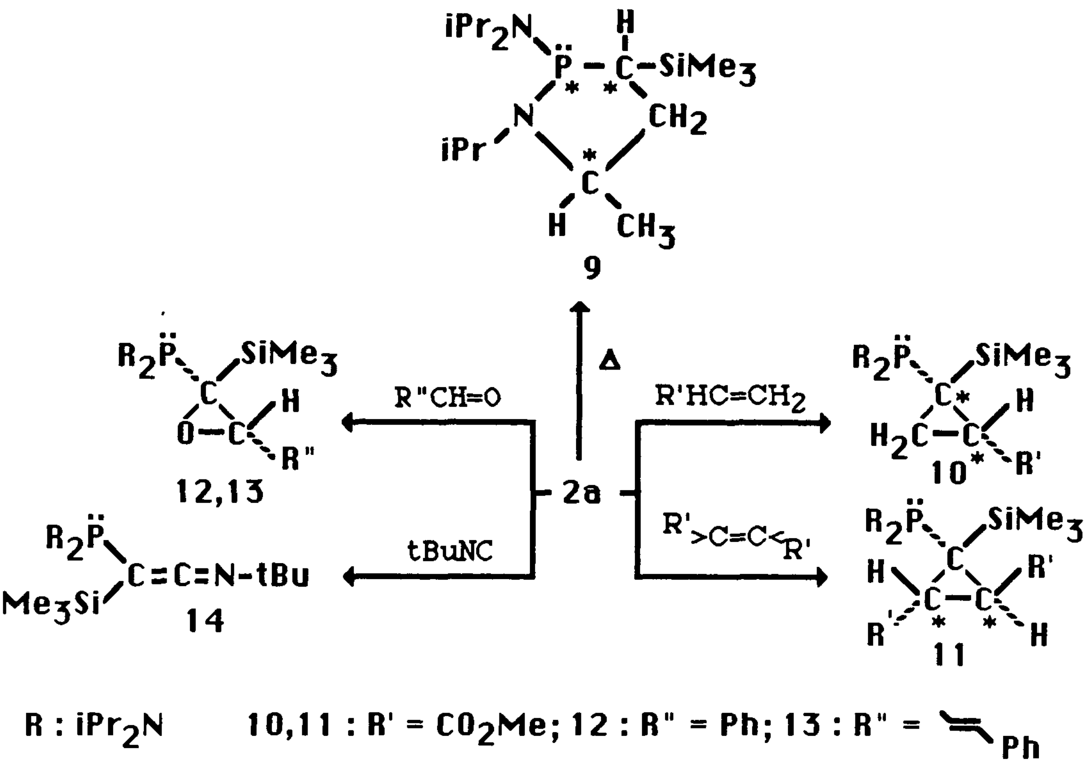
The pyrolysis of **2**, at 300°C under vacuum, afforded the four 5-membered ring diastereoisomers **9** in 90% total yield; the two major isomers were isolated in pure form after treatment with elemental sulfur. This results can be explained in terms of insertion of singlet carbene **2a** into a methyl C—H bond of an isopropyl substituent, although the total regioselectivity of this ring closure—no trace of 4-membered ring—is surprising. Taking into account the drastic experimental conditions used, one could argue that the formation of heterocycles **9** involves an excited state of **2**. More convincing evidence for the carbene character of **2**, in the ground state, arises from the results observed with alkenes, aldehydes, and isonitriles. Compound **2** does not react with alkyl substituted alkenes or conjugated dienes [14], but readily adds to electron-poor olefins such as methyl acrylate and dimethyl fumarate, affording the corresponding cyclopropanes **10** and **11**. Surprisingly, only one isomer is obtained; their structures suggest a syn specificity of the carbene attack [15], and that the stereochemistry about the double bond is maintained. Compound **2** does not react with dimethyl ketone but readily adds to benzaldehyde and *trans*-cinnamaldehyde, affording oxiranes **12** and **13**, respectively, as only one diastereoisomer. Lastly, carbene **2** reacts with *tert*-butyl isocyanide affording the corresponding keteneimine **14** in 90% yield. This can be considered as a carbene–carbene coupling reaction (Scheme 4).

These results, as a whole, clearly establish that **2** is a nucleophilic carbene. Due to the phosphorus lone pair conjugation, the p_πLUMO is expected to lie significantly higher in energy, preventing any electrophilic character. According to simple extended Hückel calculations, **2** should be located between dimethoxycarbene and methoxy(dimethylamino)carbene on the Moss carbene selectivity spectrum [16]: In the model H_2PCH the p_πLUMO is calculated at −9.2 eV while it lies at −9.6 and −8.9 eV in $(MeO)_2C$ and $MeOCNMe_2$, respectively. On the other hand, the $n_\sigma > p_\pi$ separation is calculated at 2.7 eV for H_2PCH, 2.5 eV for $(MeO)_2C$, and 3.1 eV for $MeOCNMe_2$. The stereospecificity of the cyclopropane formation as well as the coupling reaction with the isonitrile suggest that **2** has a singlet ground state, although ab initio calculation [12] found a singlet-triplet energy separation of only 3 Kcal/mole in favor of the singlet state.

Taking into account its stability and reactivity, phosphanyl carbene **2** is certainly a very powerful building block in organic and in inorganic chemistry. For example, **2** can be used as a starting material for the synthesis of a new type of low coordinated phosphorus compound, namely a



SCHEME 3



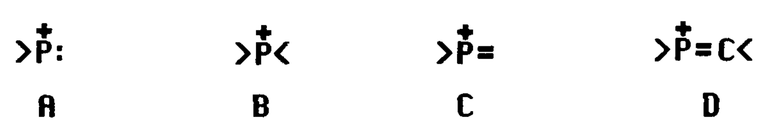
SCHEME 4

methylenephosphonium salt **15**. Two types of phosphorus cations (**A** [17], **B**) have previously been structurally characterized. In contrast, no X-ray data are available concerning tricoordinated phosphorus cation **C** [18]. Methylenephosphonium ions (**D**) have only been postulated as transient intermediates [19] but never isolated [20] (Scheme 5). This new class of phosphorus cation is of special interest since they are valence isoelectronic to olefins and have been computed to be planar with a short phosphorus-carbon bond length [21].

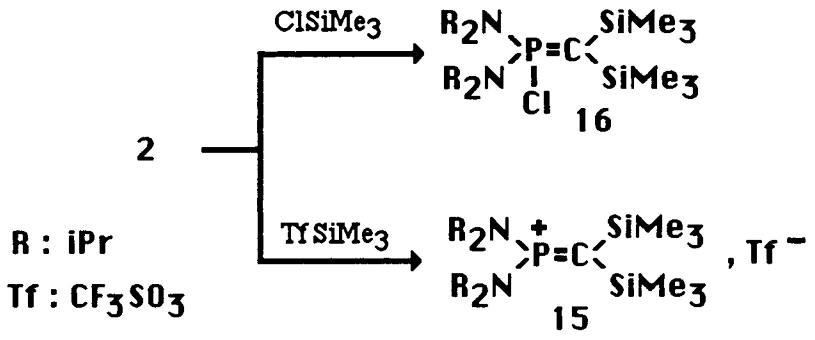
Addition of trimethylchlorosilane to **2** led to phosphorus ylide **16** suggesting that the use of a silyl derivative containing a nonnucleophilic anion would afford the desired cation **15**. Indeed, reaction of [bis(diisopropylamino)phosphanyl](trimethylsilyl)carbene **2** with trimethylsilyl triflate at room temperature gave clean conversion to methylenephosphonium ion **15** (yellow crystals, extremely air sensitive, mp 80°C dec., 70% yield) (Scheme 6).

In contrast to P-halogenated ylide **16**, derivative **15** is poorly soluble in non-polar solvents. The ^{31}P chemical shift (+130.8) and the ^{13}C chemical shift of the tricoordinated carbon (+76.51, J_{PC} = 87.6 Hz) are significantly deshielded compared with those of related phosphorus ylides, as expected for a cationic species. The ionic structure of **15** was unambiguously determined by an X-ray crystal structure analysis [5d].

Several aspects of the structure merit discussion. The positive charge at phosphorus is delocalized onto the adjacent nitrogen atoms, as shown by their planar geometry [22] and the short P–N bond lengths (1.61 vs. 1.68 Å in H_2PNH_2) [23]. The structural parameters for the framework atoms (P1 and C1) are as expected for a valence isoelectronic olefin: 1) the P–C distance of 1.62 Å is short, even compared to that in phosphaalkenes (1.64–1.69 Å) [24], and in good agreement with that from a theoretical study on the parent compound (1.624 Å) [21]; 2) the geometry at both P1 and C1 is strictly planar (±0.01 Å). However, the dihedral angle between these two planes (Figure 1) corresponds to a twist of the double bond by 60°. This value is sign-



SCHEME 5



SCHEME 6

ficantly larger than that reported by Sakurai (50.2°) for the most crowded olefin [25].

In order to rationalize the simultaneous existence of the short P—C bond and the large twist angle, a model developed by Trinquier [26] to describe the bonding in phosphorus ylides can be employed. This involves the interaction of a phosphenium ion with a p_π^2 closed-shell singlet excited carbene. The energy required for reaching the p_π^2 configuruation from a n_σ^2 configuration is largely compensated by the building of the ylidic bond, which is basically a dative bond (phosphenium lone pair → carbene empty n_σ) plus a partial back-donation (carbene occupied p_π → phosphenium empty d_π).

In summary, we have shown that the bis(diisopropylamino)phosphanyl group is able to stabilize a carbene in the α-position. The resulting species undergoes all the classical reactions of usual carbenes: cyclopropanation, CH insertion, and carbene–carbene coupling reactions. However, this compound also presents a phosphorus–carbon multiple-bonded character as shown by their 2 + 2 and 2 + 3 cycloaddition reactions.

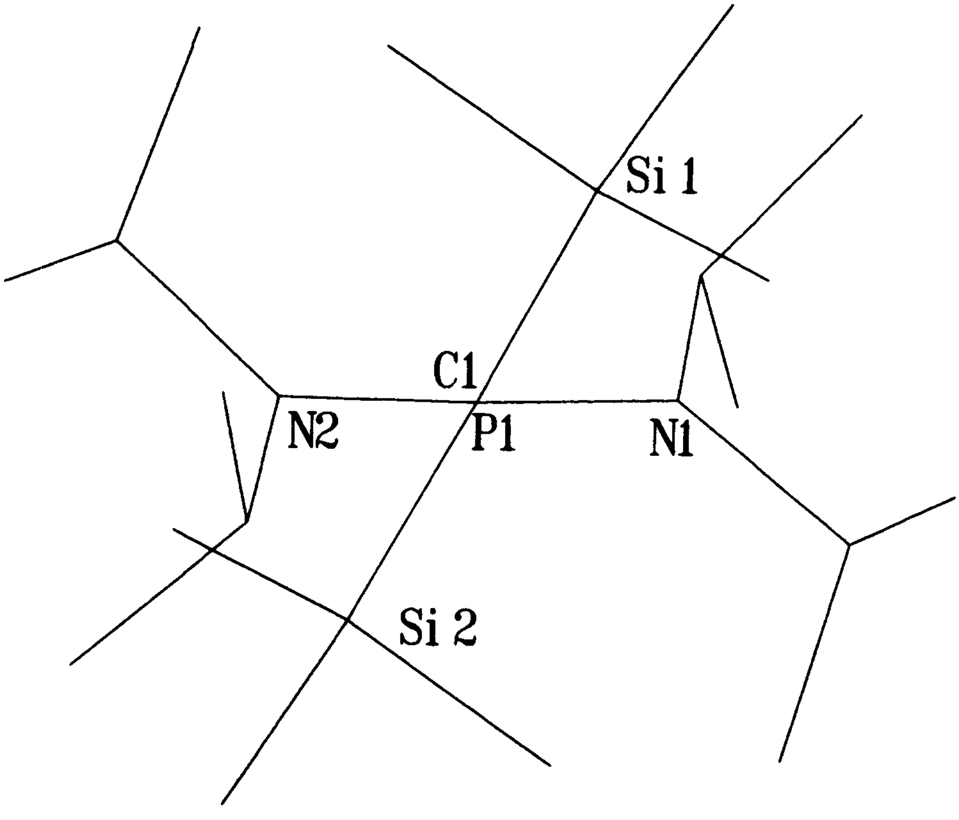
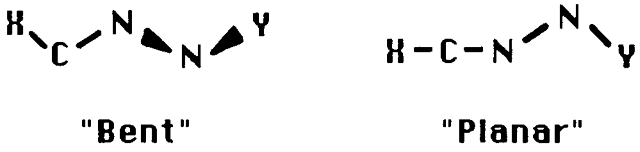


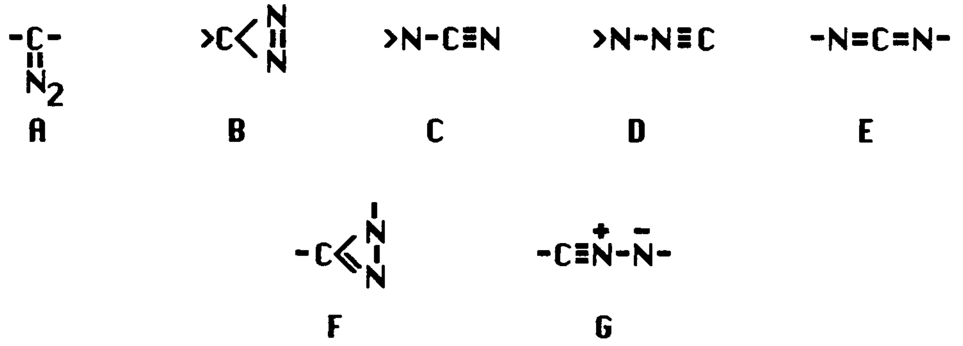
FIGURE 1 View of methylenephosphonium salt **15** looking through the phosphorus-carbon bond.

C-[bis(diisopropylamino)thiophosphoranyl] Nitrilimine **3**

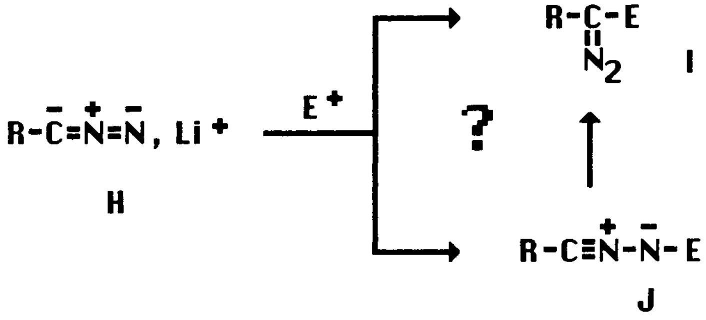
Among the classical isomers of diazo derivatives **A**, diazirines **B**, cyanamides **C**, isocynamides **D**, and carbodiimides **E** have been reported. In contrast, no example of isodiazirine **F** is known. Concerning the last isomer, namely nitrilimine (**G**), transient derivatives were first prepared by Huisgen et al. in 1959 [27] (Scheme 7). They have been widely used in organic synthesis, in regioselective 1,3 dipolar cycloadditions [28]. Up to now, they have only been observed by IR and UV spectroscopy in 85K matrix [29a–c], by mass [29c] or real time photoelectron spectroscopy [30] in the gas phase. Nitrilimines are commonly prepared, as transient species, by dehydrohalogenation of hydrazonoyl halides, dehydrogenation of aldehyde hydrazones, and thermolysis or photolysis of tetrazoles or related heterocycles such as oxadiazolinones, oxathiadiazolinones, and sydnones [28]. Our approach is totally different and relies on the attack of an electrophile at the terminal nitrogen atom of diazo lithium salts **H**. Indeed, although it is generally admitted that electrophiles react with salts of type **H** giving the corresponding substituted diazo derivative **I**, one can imagine that the first step of this reaction is in fact the formation of nitrilimine **J**, which subsequently rearranges into **I**. The nitrilimine **J**–diazo **I** rearrangement has already been postulated [31] to explain the nature of the products obtained in the thermolysis of potential nitrilimine precursors (Scheme 8).

Starting from diazo derivative **1**, we have prepared two phosphorus-substituted diazolithium salts **17** and **18** as indicated in Scheme 9. We have studied the reactivity of lithium salts **17** and **18** with various phosphorus electrophiles. Although the phosphino diazo lithium salt **17** reacts with the bis(diisopropylamino)chlorophosphane to give the bis(phosphanyl)diazomethane **19** (orange crystals, 85% yield, characterized by a single X-ray diffraction study [32]), the thiophosphino analog **18**, under the same experimental conditions, gives rise to the stable nitrilimine **3** (mp 100°C), as white crystals, in 85% isolated yield [33]. The isomeric (thiophosphoranyl)(phosphanyl)diazomethane structure **20** was readily ruled out by comparing spectral data of **3** with those of an authentic sample of **20** (Table 2), prepared by the action of a stoichiometric amount of elemental sulfur on **19** (Scheme 10). Theoretical calculations [34] predicted that two geometries are possible for nitrilimines: a bent allenyl type and a planar propargyl anion type.

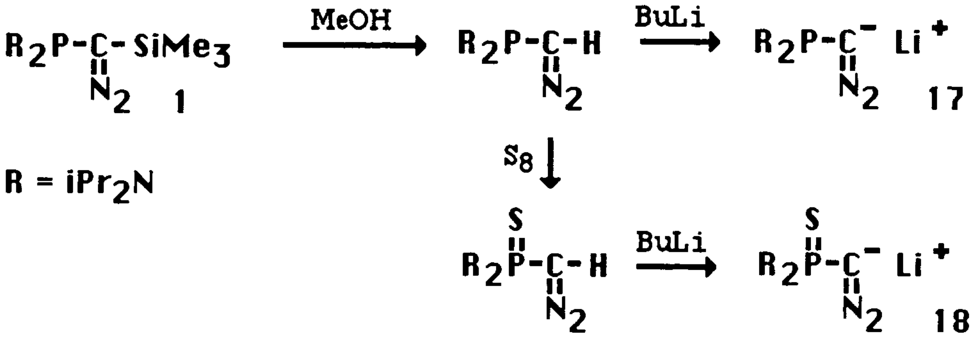




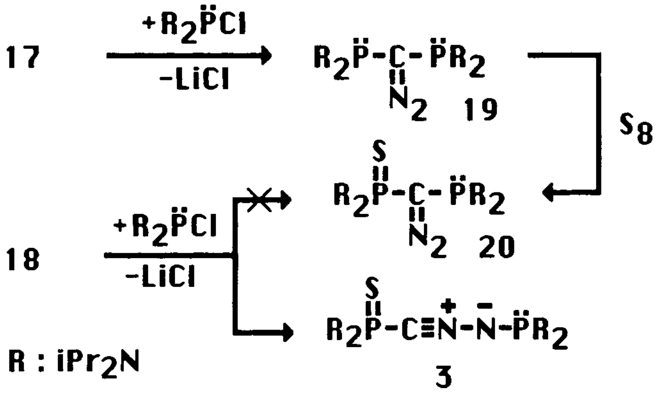
SCHEME 7



SCHEME 8



SCHEME 9



SCHEME 10

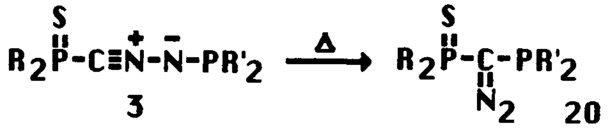
In the solid state, nitrilimine **3** has a structure halfway between the planar and the bent. Of special interest, the CNN skeleton is almost linear (173.6°) with rather short C–N (1.18 Å) and N–N (1.24 Å) bond lengths. In other words, the most important resonance form seems to be $-\overset{-}{C}=\overset{+}{N}=N-$. The planar structure would imply a negative charge on the terminal nitrogen atom ($-C\equiv\overset{+}{N}-\overset{-}{N}-$), which is strongly unfavored in the case of **3** because of the presence of the phosphorus lone pair. The comparison between P(2)N(20) bond length (1.777 Å) and the other phosphorus-nitrogen bond lengths of the molecule (1.646–1.683 Å) strongly suggest that even in this geometry, there is a repulsion between the phosphorus and nitrogen lone pairs of **3**.

Although **3** is thermally stable in the solid state, it rearranged into the isomeric diazo derivative **20** by heating, in chloroform solution, at 55°C during 6 hours. This result, as well as some new findings [35] from our laboratory strongly suggest that nitrilimines are the kinetic products of electrophilic attack at a diazolithium salt, while the diazo isomers are the thermodynamic products (Scheme 11).

It has been shown by matrix spectroscopy that under irradiation, nitrilimines rearrange into carbodiimides or undergo cleavage of the nitrogen–nitrogen bond [29]. In the case of nitrilimine **3**, we

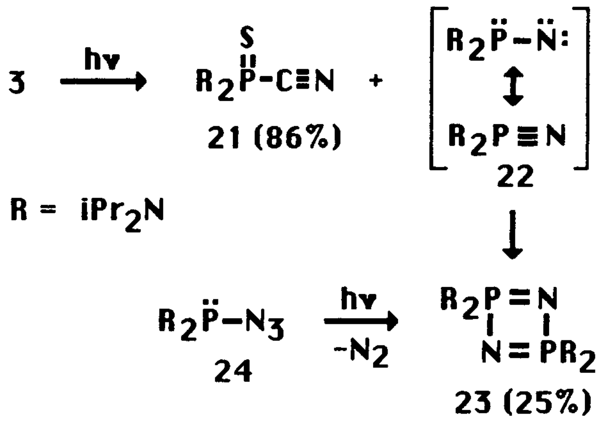
TABLE 2 Selected Spectral Data for **3** and **20**. (Coupling constants with phosphorus, reported in hertz, are in parentheses.)

		3	*20*
^{31}P NMR		+35.4 +99.9 (5.25)	+74.5 +72.8 (140.10)
	CH_3	22.53, 22.55, 23.01, 23.03 24.03, 24.11, 24.46, 24.58	23.97, 24.05, 24.80, 24.82 25.82, 25.85
^{13}C NMR			
	CH	46.00(12.10), 46.46(5.58)	47.34(5.28), 48.52(14.82)
	C	61.04(99.00)	42.61(36.71 and 74.03)
IR		2040 cm^{-1}	2028 cm^{-1}



SCHEME 11

only observed the cleavage of the N—N bond leading to thiophosphoranyl nitrile **21** and to [bis(diisopropylamino)]phosphanyl nitrene **22**, which dimerized into the cyclodiphosphazene **23**. We have already shown [3] that **22**, generated by photolysis of the corresponding azide **24**, behaved as a phosphonitrile, a compound possessing a formal phosphorus–nitrogen triple-bond, and led to **23** (Scheme 12).

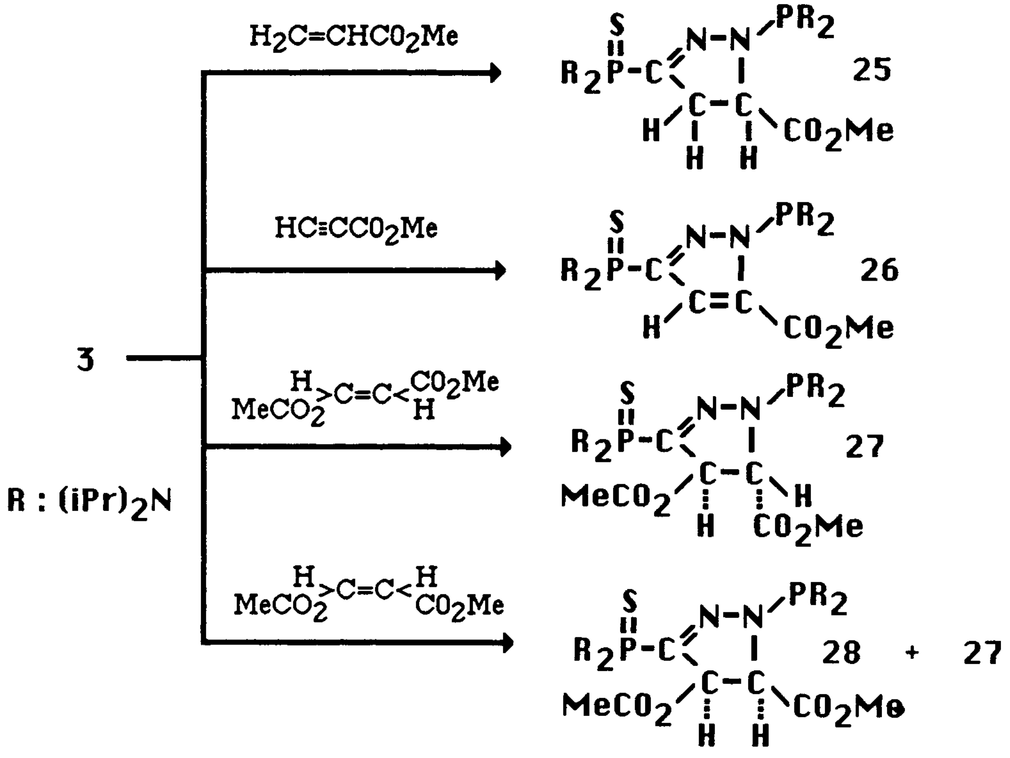


SCHEME 12

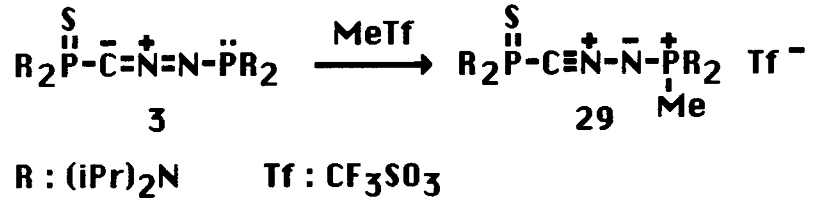
Nitrilimine **3** only reacts with electron-poor dipolarophiles. Concerning the orientation of the addition of unsymmetrically bonded olefins (methyl acrylate) or alkynes (methyl acetylenecarboxylate), a good regioselectivity, yielding the 5-substituted pyrazolines **25** or pyrazoles **26** was observed. An adequate rationalization for the observed regioselectivity was given by Houk [34] using FMO theory. Nitrilimine **3** reacted with dimethyl fumarate, at room temperature, affording the trans adduct **27**, while with dimethyl maleate the reaction occurred only at 55°C giving a mixture of cis (**28**) and trans adducts (**27**) (Scheme 13).

Surprisingly, it is also possible to use the tricoordinated trivalent phosphorus as a second center of functionality of **3**. Indeed, when **3** was treated with a stoichiometric amount of methyl triflate, a clean reaction occurred leading to a new nitrilimine **29**, which was obtained as white crystals (mp 100–102°C) after recrystallization from a THF/ether solution [36] (Scheme 14).

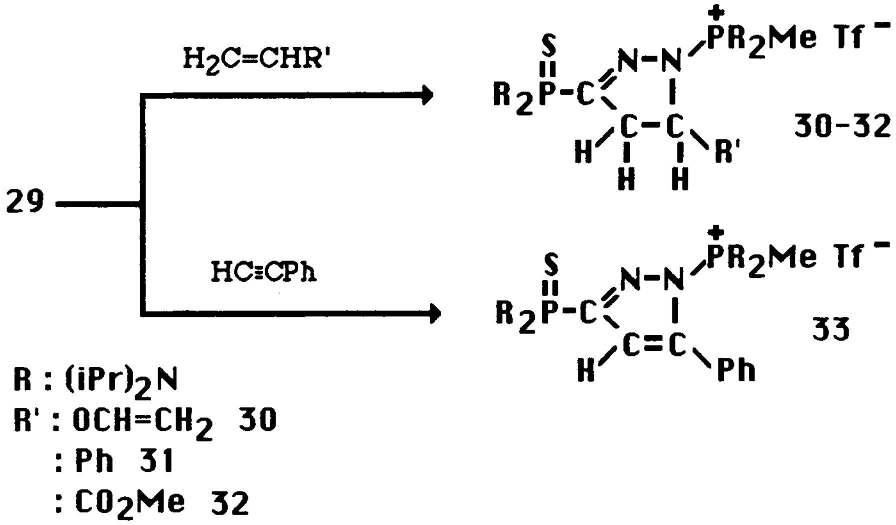
The structure of **29** was confirmed by an X-ray diffraction study. Concerning the angles, the most dramatic change compared to **3** is observed for PCN, which tends toward linearity (164°). In **29**, the CNNP skeleton is almost planar (178°), and the carbon–nitrogen and nitrogen–nitrogen bond lengths are shorter and longer, respectively, than in **3**. All these results are in perfect agreement with the theoretical



SCHEME 13



SCHEME 14



SCHEME 15

calculations that predicted an increasing stability of the planar geometry, relative to the bent, when the negative charge is shifted to the nitrogen terminus. Note that the nitrogen-phosphorus bond length is considerably shorter (1.62 Å) than in **3** (1.78 Å), confirming the stabilization of the negative charge on nitrogen by the phosphorus cation. In terms of valence bond terminology, a $-C\equiv\overset{+}{N}-\overset{-}{N}-$ propargylic structure represents the electronic structure of **29** fairly well, while as mentioned before, a $-\overset{+}{C}=\overset{-}{N}=N-$ cumulenic structure best illustrates **3**.

In contrast to **3**, nitrilimine **29** is strongly electrophilic. It reacts with an electron-rich olefin such as ethyl vinyl ether at room temperature, while styrene requires 14 h at 60°C, and 20 h at 80°C are necessary for the electron-poor olefin, methyl acrylate. Reaction with phenylacetylene is finished after 10 h at 55°C (Scheme 15). The dipolarophilic activity series of **29** was confirmed by competition experiments. All these reactions occurred with complete regiospecificity (according to NMR spectroscopy), yielding the 5-substituted pyrazolines **30–32** or pyrazole **33** in good yield.

The electrophilic substitution of diazolithium salts is a new and effective synthetic method for nitrilimines. Thirty years after the discovery by Huisgen of transient derivatives of this type, we have shown that they can be isolated at room temperature. Depending on the nature of the substituents, regioselective 2 + 3 cycloaddition is observed with electron-poor or electron-rich olefins or alkynes.

CONCLUSION

The bis(diisopropylamino)phosphanyl group allowed the stabilization of a carbene in the α-position and of nitrilimines. These compounds are both prepared from the easily available [bis(diisopropylamino)phosphanyl](trimethylsilyl)diazomethane. Recent studies in our group demonstrate that the replacement of only one diisopropylamino group by a dimethylamino substituent has a dramatic change on the stability of the resulting products.

REFERENCES

[1] P. B. Hitchcock, M. F. Lappert, W-P. Leung, *J. Chem. Soc. Chem. Commun.*, 1987, 1282.
[2] (a) O. Glemser, R. Mews, *Angew. Chem. Int. Ed. Engl.*, *19*, 1980, 883 and references cited therein. (b) R. S. Atkinson, B. D. Judkins, *J. Chem. Soc., Perkin Trans.*, *1*, 1981, 2615.
[3] (a) G. Sicard, A. Baceiredo, G. Bertrand, J. P. Majoral, *Angew. Chem. Int. Ed. Engl.*, *23*, 1984, 459. (b) A. Baceiredo, G. Bertrand, J. P. Majoral, G. Sicard, J. Jaud, J. Galy, *J. Am. Chem. Soc.*, *106*, 1984, 6088. (c) A. Baceiredo, G. Bertrand, J. P. Majoral, F. El

Anba, G. Manuel, *J. Am. Chem. Soc., 107,* 1985, 3948. (d) G. Bertrand, J. P. Majoral, A. Baceiredo, *Acc. Chem. Res., 19,* 1986, 17.

[4] (a) M. Regitz: *Diazoalkanes,* Georg Thieme Verlag, Stuttgart, 1977. (b) M. Regitz, G. Maas, *Top. Curr. Chem., 97,* 1981, 71. (c) M. Regitz, G. Maas: *Diazo Compounds, Properties and Synthesis,* Academic Press, Orlando, 1986.

[5] (a) A. Baceiredo, G. Bertrand, G. Sicard, *J. Am. Chem. Soc., 107,* 1985, 4781. (b) A. Igau, H. Grützmacher, A. Baceiredo, G. Bertrand, *J. Am. Chem. Soc., 110,* 1988, 6463. (c) A. Igau, A. Baceiredo, G. Trinquier, G. Bertrand, *Angew. Chem. Int. Ed. Engl., 28,* 1989, 621. (d) A. Igau, A. Baceiredo, H. Grützmacher, H. Pritzkow, G. Bertrand, *J. Am. Chem. Soc., 111,* 1989, 6853. (e) A. Baceiredo, A. Igau, G. Bertrand, M. J. Menu, Y. Dartiguenave, J. J. Bonnet, *J. Am. Chem. Soc., 108,* 1986, 7868. (f) J. M. Sotiropoulos, A. Baceiredo, G. Bertrand, *J. Am. Chem. Soc., 109,* 1987, 4711.

[6] Some other α-diazophosphanes have recently been reported: (a) H. Keller, M. Regitz, *Tetrahedron Lett., 29,* 1988, 925. (b) H. Keller, G. Maas, M. Regitz, *Tetrahedron Lett., 27,* 1986, 1903. (c) H. Keller, Dissertation, Universität Kaiserslautern, 1988.

[7] (a) H. Staudinger, J. Meyer, *Helv. Chim. Acta, 2,* 1919, 619. (b) G. Singh, H. Zimmer, *Organometal. Chem. Rev.,* 1967, 279.

[8] (a) K. C. Paciorek, R. Kratzer, *Inorg. Chem., 3,* 1964, 594. (b) G. Tesi, C. P. Haber, C. M. Douglas, *Proc. Chem. Soc.,* 1960, 219. (c) R. H. Neilson, *Inorg. Chem., 20,* 1981, 1679.

[9] T. Aoyama, S. Inove, T. Shioiri, *Tetrahedron Lett., 25,* 1984, 433.

[10] O. J. Scherer, W. Glabel, *Chem-Ztg., 99,* 1975, 246.

[11] R. Appel, A. Westerhaus, *Tetrahedron Lett., 22,* 1981, 2159.

[12] M. T. Nguyen, M. A. McGinn, A. F. Hegarty, *Inorg. Chem., 25,* 1986, 2185.

[13] (a) G. Himbert, M. Regitz, *Synthesis,* 1972, 571. (b) G. Himbert, D. Frank, M. Regitz, *Chem. Ber., 109,* 1976, 370. (c) P. Grunanger, P. V. Finzi, C. Scotti, *Chem. Ber., 98,* 1965, 623.

[14] Dimethoxycarbene, the archetypical nucleophilic carbene, does not react with alkyl-substituted olefins. (a) R. A. Moss, M. Wlostowski, S. Shen, K. Krogh-Jespersen, A. Matro, *J. Am. Chem. Soc., 110,* 1988, 4443. (b) R. W. Hoffmann, W. Lillienblum, B. Dittrich, *Chem. Ber., 107,* 1974, 3395. (c) R. W. Hoffmann, M. Reiffen, *Chem. Ber., 109,* 1976, 2565.

[15] M. Brookhart, W. B. Studabaker, *Chem. Rev., 87,* 1987, 411.

[16] For a detailed study on the relative degree of electrophilicity or nucleophilicity of carbenes see: R. A. Moss, *Acc. Chem. Res., 13,* 1980, 58.

[17] A. H. Cowley, R. A. Kemp, *Chem. Rev., 85,* 1985, 367.

[18] (a) J. Rahil, P. Haake, *J. Org. Chem., 46,* 1981, 3048. (b) J. Michalski, C. Radziejewski, Z. Skrypczynski, W. Dabrowski, *J. Am. Chem. Soc., 102,* 1980, 1974. (c) L. Maier, *Z. Anorg. Allg. Chem., 345,* 1966, 29. (d) M. R. Marre, M. Sanchez, R. Wolf, *Phosphorus Sulfur, 13,* 1982, 327. (e) M. Sanchez, M. R. Marre, J. F. Brazier, J. Bellan, R. Wolf, *Phosphorus Sulfur, 14,* 1983, 331. (f) M. Mulliez, J. P. Majoral, G. Bertrand, *J. Chem. Soc. Chem. Commun.,* 1984, 284.

[19] Th. A. Van der Knaap, F. Bickelhaupt, *Tetrahedron Lett., 23,* 1982, 2037.

[20] Abstraction of chloride by AlCl$_3$ from a P-chloromethylenephosphorane was claimed by Appel et al to give a methylenephosphonium ion as characterized by ^{31}P NMR and elemental analysis. However, the relatively high field ^{31}P chemical shift of the product makes this assignment unlikely: R. Appel, R. Schmitz, *Chem. Ber., 116,* 1983, 3521.

[21] L. L. Lohr, H. B. Schlegel, K. Morokuma, *J. Phys. Chem., 88,* 1984, 1981.

[22] The geometry of the (R$_2$N)$_2$P fragment is quite similar to that reported for the corresponding phosphenium ion: A. H. Cowley, M. C. Cushner, J. S. Szobota, *J. Am. Chem. Soc., 100,* 1978, 7784.

[23] A. H. Cowley, D. J. Mitchell, M. H. Whangbo, S. Wolfe, *J. Am. Chem. Soc., 101,* 1979, 5224.

[24] (a) L. N. Markovski, V. D. Romanenko, A. V. Rouban: *Acyclic Dicoordinated Phosphorus Derivatives,* Kiev-Science, 1988. (b) S. Lochschmidt, A. Schmidpeter, *Phosphorus Sulfur 29,* 1986, 73. (c) R. Appel, F. Knoll, I. Ruppert, *Angew. Chem. Int. Ed. Engl., 20,* 1981, 731.

[25] H. Sakurai, K. Ebata, C. Kabuto, Y. Nakadaira, *Chem. Lett.,* 1987, 301.

[26] G. Trinquier, J. P. Malrieu, *J. Am. Chem. Soc., 109,* 1987, 5303.

[27] R. Huisgen, M. Seidel, J. Sauer, J. W. McFarland, G. Wallbillich, *J. Org. Chem., 24,* 1959, 892.

[28] (a) R. Huisgen, *Angew. Chem., Int. Ed. Engl., 2,* 1963, 565 and 633. (b) P. Caramella, P. Grünanger: *1,3 dipolar Cycloaddition Chemistry,* Wiley, New York, 1984. (c) R. Huisgen, M. Seidel, G. Wallbillich, H. Knupfer, *Tetrahedron, 17,* 1962, 3. (d) A. Eckel, R. Huisgen, G. Wallbillich, D. Grashey, E. Spindler, *Chem. Ber., 100,* 1967, 2192.

[29] (a) H. Toubro, A. Holm, *J. Am. Chem. Soc., 102,* 1980, 2093. (b) H. Meier, W. Heinzelmann, H. Heimgartner, *Chimia, 34,* 1980, 504 and 506. (c) C. Wentrup, S. Fisher, A. Maquestiau, R. Flammang, *Angew. Chem., Int. Ed. Engl., 24,* 1985, 56.

[30] H. Bock, R. Dammel, S. Fisher, C. Wentrup, *Tetrahedron Lett., 28,* 1987, 617.

[31] (a) C. Wentrup, *Helv. Chim. Acta, 61,* 1978, 1755. (b) R. Gleiter, W. Rettig, C. Wentrup, *Helv. Chim. Acta, 57,* 1974, 2111. (c) A. Padwa, T. Caruso, S. Nahm, A. Rodriguez, *J. Am. Chem. Soc., 104,* 1982, 2865. (d) W. Reichen, *Helv. Chim. Acta, 59,* 1976, 1636. (e) A. Padwa, T. Caruso, D. Plache, *J. Chem. Soc. Chem. Commun.,* 1980, 1229. (f) A. Padwa, T. Caruso, S. Nahm, *J. Org. Chem., 45,* 1980, 4065. (g) C. Wentrup, *Chimia, 31,* 1977, 258.

[32] M. J. Menu, M. Dartiguenave, Y. Dartiguenave, J. J. Bonnet, G. Bertrand, A. Baceiredo, *J. Organomet. Chem., 372,* 1989, 201.

[33] (a) G. Sicard, A. Baceiredo, G. Bertrand, *J. Am. Chem. Soc., 110,* 1988, 2663. (b) M. Granier, A. Baceiredo, G. Bertrand, *Angew. Chem. Int. Ed. Engl., 27,* 1988, 1350. (c) M. Granier, A. Baceiredo, Y. Dariguenave, M. Dartiguenave, M. J. Menu, G. Bertrand, *J. Am. Chem. Soc., 112,* 1990, 6277.

[34] (a) P. Caramella, K. N. Houk, *J. Am. Chem. Soc., 98,* 1976, 6397. (b) P. Caramella, R. W. Gandour, J. A. Hall, C. G. Deville, K. N. Houk, *J. Am. Chem. Soc., 99,* 1977, 385 and references therein.

[35] F. Castan, A. Baceiredo, G. Bertrand, *Angew. Chem. Int. Ed. Engl., 28,* 1989, 1250.

[36] M. Granier, A. Baceiredo, V. Huch, M. Veith, G. Bertrand, *Inorg. Chem.,* in press.