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Dissociation of the P=C Ylidic Bond

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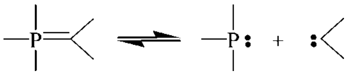
Dedicated to Professor Edgar Niecke

Keywords: Ylides / Carbenes / Phosphanes / Density functional calculations

The phosphorus ylides $RPh_2P{=}C(Mes)N{=}C(CF_3)_2$ [R = Ph, $Ph_2P(O)CH_2$] in solution undergo reversible dissociation of the P=C ylidic bond to give phosphanes RPh_2P and the carbene $MesC(\textbf{:})N{=}C(CF_3)_2$. The latter can be trapped as its mesomeric nitrile ylide by treatment with cyclohexene or phenyl isocyanate to give cyclic addition products.

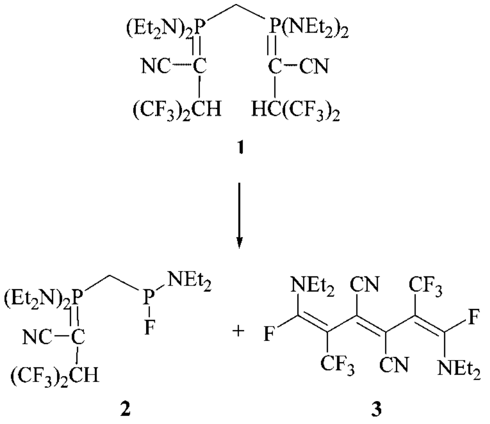
Introduction

The formation of phosphorus ylides by the reaction of trivalent phosphorus compounds with unstable carbenes generated in situ is well established (Scheme 1).[1]



Scheme 1.

The use of stable carbenes[2] in reactions with phosphanes, however, is almost unknown.[3] Although the chemistry of phosphorus ylides is rather well studied[4] and a large number of unstable ylides have been synthesised, the reverse process, namely decomposition of phosphorus ylides to give carbenes and phosphanes, has not been known up to now. We have reported previously that diylide **1**, which contains bulky diethylamino groups at phosphorus[5a] rather than dimethylamino groups,[5b] is not stable and undergoes an unusual decomposition reaction to give ylide **2** and triene **3** almost quantitatively. The most probable route for formation of the symmetric triene **3** is the dimerisation of the appropriate carbene, whose appearance in the reaction mixture can be explained in terms of cleavage of the ylidic bond to phosphorus (Scheme 2).



Scheme 2.

Whilst this paper was being prepared for publication a report was published on the cleavage of a phosphorus ylidic bond forming part of a strained four-membered ring to give a stable carbene.[6] We now have evidence to show that acyclic non strained ylides can also undergo such a decomposition.

Results and Discussion

We have found that ylides **4** and **7** are capable of reversible cleavage of the P=C bond in solution with the formation of carbene (nitrile ylide) **6** and phosphanes **5** and **8**, respectively. The equilibrium is shifted to the ylidic side. The amounts of phosphane and carbene in the reaction solution are too low for NMR spectroscopic observation,

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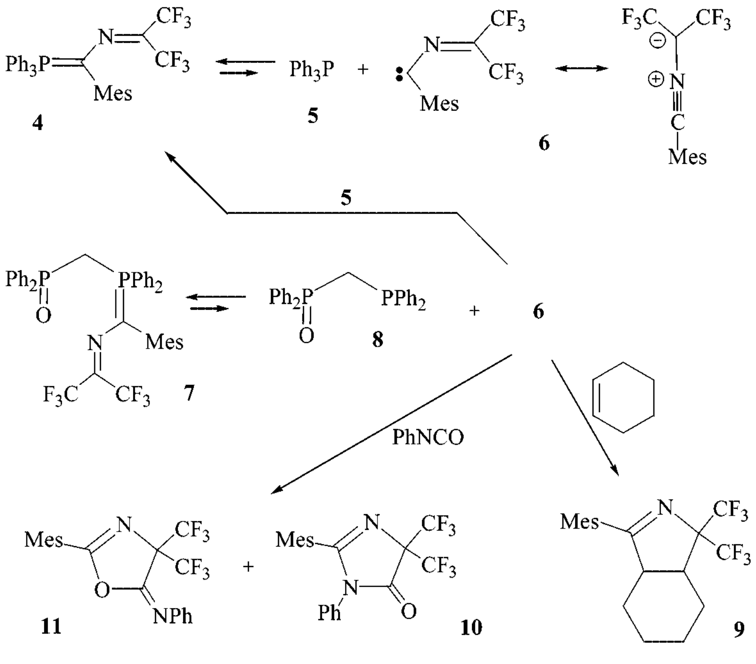
even upon heating to 50 °C. Although nitrile ylide **6** contains the bulky mesityl group it is not stable at 50–70 °C.[7] Because of the different thermodynamic stabilities of the starting ylides **4** and **7** their decomposition rates are also different. For example, ylide **7** decomposes completely in solution after 3–4 h at 70 °C whereas 80% of ylide **4** remains unchanged under the same conditions after 24 h. The ^{31}P NMR spectra of the reaction mixtures only display signals for the appropriate phosphanes **5** or **8** after completion of the decomposition.

The reversible character of the P=C ylidic bond cleavage as well as the presence of carbene **6** (or the mesomeric nitrile ylide) in the reaction mixture is in agreement with the fact that the rate of decomposition of the starting ylides becomes drastically shorter in the presence of trapping agents. For example, compound **6** reacts as a nitrile ylide with cyclohexene or phenyl isocyanate to give stable cyclic products **9** or **10** and **11** (Scheme 3). Other phosphanes that form more thermodynamically stable P=C bonds with **6** than the starting ylide can also be used as trapping agents. For example, heating of a solution of ylide **7** with triphenylphosphane (**5**) gave ylide **4** and compound **8** quickly and almost quantitatively.

The formation of carbene **6** and the appropriate phosphane is due to the dissociation of the $P^+–C^–$ ylidic bond and can be considered as a self-reduction reaction of the phosphorus ylides **4** and **7**. One could assume that the $P^+–C^–$ bond in these compounds should be longer than the normal ylidic bond. Indeed, our DFT calculations (RI-BP86/TZVP, see Experimental Section) show that the P–C1 bond length in compound **4** (Figure 1, a) is 1.81 Å, which is about 0.15 Å longer than the standard ylidic bond and comparable with the value of a phosphorus–carbon single bond.[8] This could be due to steric repulsion between the mesityl group at the carbon atom and the PPh_3 moiety. The decomposition of analogous ylides in which the mesityl group is replaced by the less bulky phenyl group proceeds in the same way but requires more time and a higher temperature. At first sight, this is in line with the suggestion made above. However, calculations carried out for the analogous compound with the Ph group (**4a**; Figure 1, b) indicate almost the same P=C bond length (1.80 Å). There is only one structural difference which can be related to the steric properties of the two aromatic moieties: the dihedral angle between the phenyl ring and the C1–N2–C3 plane in **4a** is about 66° whereas the Mes substituent in **4** is orthogonal (C^{ortho}–C4–C1–N2 angles are 99.2° and –86.5° and C^{ortho}–C4–C1–P5 angles are 86.8° and –87.5°). Additionally, similar C1–N2–C3 bond angles (ca. 137°) are found for both structures. This supports a significant contribution of the mesomeric structures **B** and **C**, where negative charge is formally localised on the terminal imino carbon and is additionally delocalised on the electron-withdrawing CF_3 substituents. This means that positive charge is localised simultaneously on phosphorus and at least partially on nitrogen due to the contribution of the form **C**. This latter formal positive charge on nitrogen is sufficiently counterbalanced by the polarisation of the C–N σ- and π-bonds towards nitrogen due to its higher electronegativity. Thus, the elongation of the P–C ylidic bond in **4** to 1.81 Å (compared with the classical polarised ylidic bond) is accounted for by the contribution of mesomeric structures **B** and **C**. The large Ar–C–N bond angle (approximately 131°) and the short C–N distances (1.31 and 1.32 Å for the central and terminal C–N bonds, respectively) are also in agreement with the contribution of form **C** (Scheme 4). This mesomeric form literally predetermines the P–C bond dissociation. The reaction product, nitrile ylide **6**, keeps



Scheme 3.

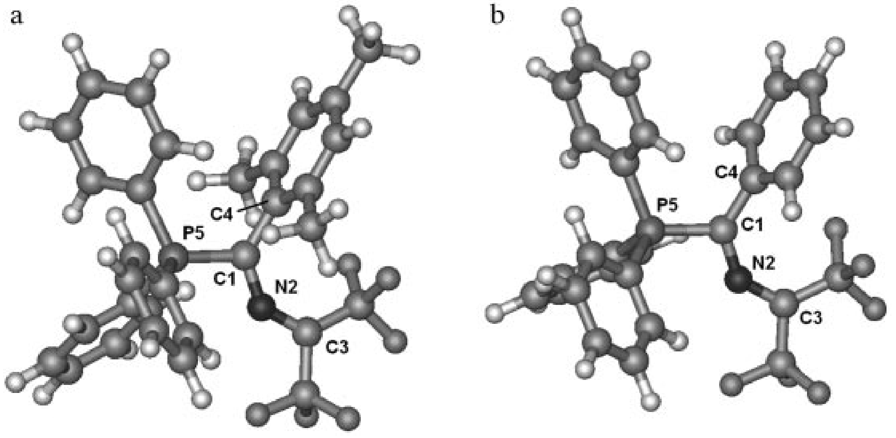
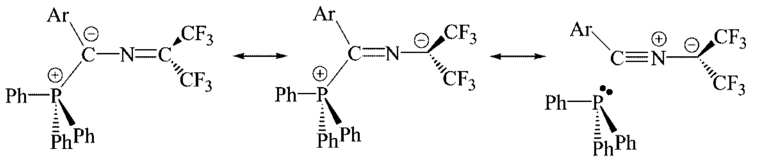


Figure 1. The equilibrium (RI-BP86/TZVP) structures of **4** (a) and **4a** (b). The most important bond lengths [Å] and bond angles [°] for **4** and **4a**, respectively, are: C1–N2 1.324, 1.327; N2–C3 1.312, 1.310; C1–C4 1.497, 1.493; C1–P5 1.808, 1.803; C1–N2–C3 137.0, 137.2; N2–C1–C4 131.2, 131.3; N2–C1–P5 107.6, 108.6; C4–C1–P5 120.4, 119.8.



Scheme 4.

many structural features inherent to this fragment as part of the starting ylide (Figure 2).

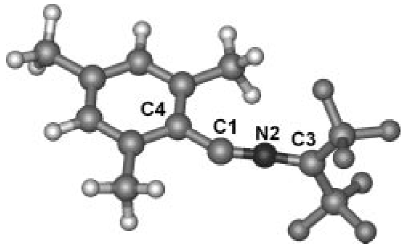


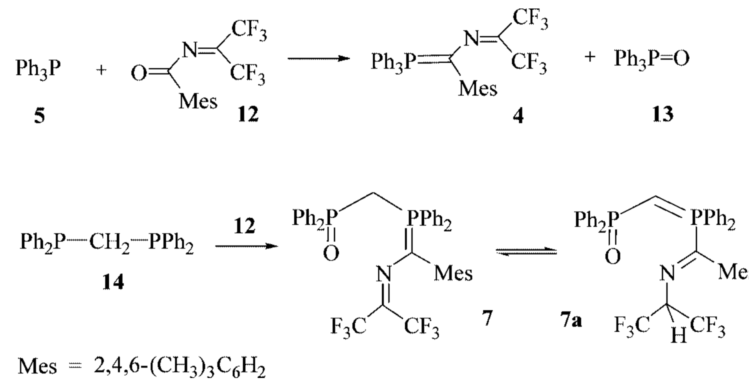
Figure 2. The equilibrium (RI-BP86/TZVP) structure of **6**. The most important bond lengths [Å] and bond angles [°] are: C1–N2 1.198, N2–C3 1.310, C1–C4 1.424; C1–N2–C3 173.7, N2–C1–C4 147.2.

Ylides **4** and **7** were synthesised by the reaction of triphenylphosphane (**5**) or bis(diphenylphosphanyl)methane (**14**) with the acylimine **12** of hexafluoroacetone. These reactions are quite interesting because they occur with complete cleavage of the C=O double bond. The formation of new bonds by the interaction of an electrophilic carbonyl group with trivalent phosphorus usually proceeds with the cleavage of only one bond of the carbonyl function. For this reason the formation of cyclic products is frequently observed. For example, the reaction of acylimines of hexafluoroacetone with phosphites has been shown to give Δ^4-1,4,2λ^5-oxazaphospholines.[9]

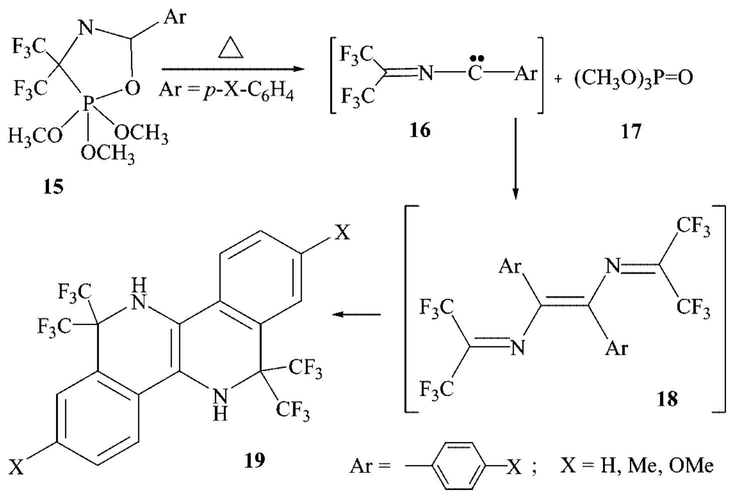
In solution, compound **7** exists in equilibrium with its structural isomer **7a** because of prototropic migration (Scheme 5). The isomers differ from each other in the positions of the ylidic bond and one of the protons. The distribution between the isomers depends on the polarity of the solvent used. In dichloromethane, for example, the equilibrium is shifted to isomer **7** whereas in hexane it is shifted to isomer **7a**. The isomers are readily distinguishable in the ^{19}F NMR spectrum by the signals of the non-equivalent CF_3 groups (compound **7**) and equivalent CF_3 groups (compound **7a**) bonded to sp^2 and sp^3 carbon atoms, respectively. The ylide **7a** contains a stabilizing diphenylphosphane oxide group at the ylidic bond and does not decompose on heating, isomerizing into the other isomer **7** as it disintegrates to form phosphane **8** and carbene **6**. No products that could result from the decomposition of isomer **7a** were found after the thermolysis either in the presence of trapping agents or without them.

Taking into account the reversible character of the formation of carbene **6** from ylides **4** and **7**, one can conclude that the formation of these ylides also includes the reaction of the same carbene with appropriate phosphanes. This conclusion is in agreement with our calculations. As the ArC–N bond angle of **6** was found to be 147.2°, this compound can display carbene-like properties. The intermediate formation of unstable carbenes has been indirectly confirmed in another deoxygenation reaction of a carbonyl group by phosphanes.[10]

In general, there are only a few examples known of the behaviour of nitrile ylides as imine-substituted carbenes, all of which are devoted to their dimerisation.[11] For example, the imine-stabilized carbene **16**, which results from the thermolysis or photolysis of 4,5-dihydro-1,2,3λ^5-dioxaphosphole (**15**), has been postulated as one of the intermediates in the formation of compound **19** (Scheme 6).[12]



Scheme 5.



Scheme 6.

In summary, our results show that nitrile ylides can display their carbene-like properties not only in dimerisation reactions but also in their reaction with phosphanes.

Experimental Section

General Remarks: All operations were performed under nitrogen in a dry box. The solvents were dried by the usual procedures. The NMR spectra were recorded with Varian Gemini 400 MHz and JEOL FX-90Q spectrometers. The mass spectrum of compound **9** was recorded with an Agilent 1100 LC/MSD spectrometer. The ^{1}H and ^{13}C chemical shifts are referenced to tetramethylsilane (TMS) and ^{19}F to CFCl$_3$. The ^{31}P chemical shifts were measured using 85% aqueous H$_3$PO$_4$ as an external standard.

Compound 4: Acylimine **12** (26 mg, 0.083 mmol) in thf (0.4 mL) was added to a solution of triphenylphosphane (**5**; 52 mg, 0.198 mmol) in thf (0.4 mL) at room temperature. After 24 h the NMR spectra of the light-yellow reaction mixture showed quantitative formation of ylide **4** and triphenylphosphane oxide (**13**). This mixture was used for the decomposition of **4** without further purification. ^{1}H NMR (CDCl$_3$): δ = 2.19 (s, 3 H, Me), 2.35 (s, 6 H, Me), 6.6–8.1 (m, 17 H, Ar) ppm. ^{19}F NMR (CDCl$_3$): δ = –56.83 (q, $^{4}J_{F,F}$ = 8.5 Hz, 3 F), 59.25 (qd, $^{4}J_{F,F}$ = 8.5, $J_{P,F}$ = 3.4 Hz, 3 F) ppm. ^{31}P NMR (CDCl$_3$): δ = 4.28 (s) ppm.

Compounds 7 and 7a: A solution of methylenebis(diphenylphosphane) (50 mg, 0.13 mmol) in CDCl$_3$ (0.4 mL) was added, whilst stirring, to a solution of acylimine **12** (50 mg, 0.16 mmol) in CDCl$_3$ (0.6 mL) over 2 min at 20 °C. After 10 min the NMR spectra showed almost quantitative formation of the isomers **7** and **7a**. This mixture was used for further reactions without purification.

7: ^{1}H NMR (CDCl$_3$): δ = 2.13 (s, 3 H, Me), 2.28 (s, 6 H, Me), 4.16 (dd, $^{2}J_{P,H}$ = 10.7, $^{2}J_{P,H}$ = 15.1 Hz, 2 H, P-CH_2-P), 6.57–8.05 (m, 22 H, Ar) ppm. ^{13}C NMR (CDCl$_3$): δ = 10.78 (dm, $J_{P,C}$ = 180.0 Hz, 1 C, P*C*CN), 26.22 (dd, $^{1}J_{P,C}$ = 25.4 Hz, $^{1}J_{P,C}$ = 85.8 Hz, P*C*P), 36.60 (d, $^{2}J_{P,C}$ = 2.9 Hz, 2 C, NMe$_2$), 36.76 (d, $^{2}J_{P,C}$ = 3.9 Hz, 2 C, NMe$_2$), 40.40 (d, $^{2}J_{P,C}$ = 15.6 Hz, 4 C, NMe$_2$), 45.62 [sept dd, $^{2}J_{P,C}$ = 16.6 Hz, $J_{P,C}$ = 5.9 Hz, $^{2}J_{F,C}$ = 29.3 Hz, 1 C, *C*H(CF$_3$)$_2$], 124.20 (q, $^{1}J_{F,C}$ = 282.9 Hz, 2 C, *C*F$_3$), 125.02 (d, $^{2}J_{P,C}$ = 10.8 Hz, *C*N) ppm. ^{19}F NMR (CDCl$_3$): δ = –56.6 (qd, $^{4}J_{F,F}$ = 8.5 Hz, $J_{P,F}$ = 2.5 Hz, 3 F), –58.5 (qd, $^{4}J_{F,F}$ = 8.5 Hz, $J_{P,F}$ = 3.4 Hz, 3 F) ppm. ^{31}P NMR (CDCl$_3$): δ = 6.3 (br. d, $^{2}J_{P,P}$ = 14.0 Hz), 23.7 (d, $^{2}J_{P,P}$ = 14.0 Hz) ppm.

7a: ^{1}H NMR (CDCl$_3$): δ = 1.33 (s, 1 H, P-C*H*-P), 1.82 (s, 3 H, Me), 1.97 (s, 6 H, Me), 4.27 (sept., $^{3}J_{F,H}$ = 5.9 Hz, 1 H, CF$_3$-C*H*-CF$_3$), 6.57–8.05 (m, 22 H, Ar) ppm. ^{19}F NMR (CDCl$_3$): δ = –68.48 (d, $^{3}J_{H,F}$ = 5.9 Hz, 6 F) ppm. ^{31}P NMR (CDCl$_3$): δ = 20.8 (d, $^{2}J_{P,P}$ = 20.3 Hz), 27.5 (d, $^{2}J_{P,P}$ = 20.3 Hz) ppm.

Compound 9: Ylide **7** (550 mg) was obtained in chloroform as described above. The solvent was removed in vacuo and the residue was dissolved in cyclohexene (1600 mg). The mixture was heated at 75 °C for 2 h. The excess of cyclohexene was removed and the residue was extracted twice with hexane (2 × 5 mL). Column chromatography on silica gel (hexane/toluene, 3:1) of the solid remaining after evaporation of hexane afforded 50 mg of a white product. M.p. 164–165 °C. ^{1}H NMR ($CDCl_3$): δ = 1.3–1.9 (m, 8 H), 2.20 (s, 6 H, Me), 2.28 (s, 3 H, Me), 2.90 (m, 1 H),, 3.38 (m, 1 H), 6.87 (br. s, 2 H, Ar) ppm. ^{13}C NMR ($CDCl_3$): δ = 20.03 (br. s), 20.35 (s), 20.51 (s), 20.67 (s), 21.47 (s), 39.90 (s), 52.93 (s), 85.25 (m), 123.63 (q, $^1J_{F,C}$ = 284 Hz, CF_3), 124.50 (q, $^1J_{F,C}$ = 284 Hz, CF_3), 128.76 (s), 128.85 (s), 130.79 (s), 134.34 (br. s), 135.80 (br. s), 138.71 (s), 190.64 (s) ppm. ^{19}F NMR ($CDCl_3$): δ = –67.56 (q, $^4J_{F,F}$ = 10.2 Hz, 3 F), –73.80 (q, $^4J_{F,F}$ = 10.2 Hz, 3 F) ppm. MS (APCI): *m/z* 378 $[M + H]^+$.

The same product was obtained when ylide **4**, obtained as described above (together with Ph_3PO), was heated in cyclohexene at 75 °C for 6 h.

Compounds 10 and 11: PhNCO (0.8 mL) was added to a reaction solution of ylide **4** obtained from acylimine **12** (50 mg) and triphenylphosphane (100 mg) in thf (0.8 mL) as described above and the mixture was heated at 60 °C for 10 h. The ^{19}F NMR spectrum showed almost quantitative formation of the isomers **10** and **11** (δ = –72.7 and –74.0 ppm, respectively; both 6 F), which were isolated chromatographically as described previously.[13]

When a solution of ylide **7** in $CDCl_3$ was heated at 55 °C in the presence of PhNCO the yield of compounds **10** and **11** was substantially lower (about 20%). The main process in this case is an addition reaction between PhNCO and ylide **4**. This product will be described in a subsequent paper.

Computational Details: All of the structures were fully optimised without symmetry constraints. The BP86 functional[14,15] with an approximate treatment of the electronic Coulomb interaction [resolution of identity (RI)[16] algorithm] and the triple-zeta valence (TZV) quality basis sets[17] implemented in the TURBOMOLE program set[18] was used for the geometry optimisation. One set of polarisation functions was added for all atoms (the standard TZVP basis sets included in the TURBOMOLE packet). An SCF convergence criterion SCFConv = 1.0×10^{-8} Hartree and the finest grid value (grid = 5) was used in the optimisation. All the structures were proved to be local minima in energy; the vibration analyses were performed by computing analytical first- and second-order derivatives.[19] A full account of the optimised geometries is given in the Supporting Information. The VMD program packet[20] was used for the graphical presentation of the calculated structures.

Acknowledgments

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[1] H. J. Bestmann, R. Zimmermann, in *Organic Phosphorus Compounds* (Eds.: G. M. Kosolapoff, L. Maier), Wiley-Interscience, New York, **1976**, vol. 3, chapter 5a.

[2] D. Bourissou, O. Guerret, F. P. Gabbai, G. Bertrand, *Chem. Rev.* **2000**, *100*, 39–91.

[3] N. Kuhn, J. Fahl, D. Blaser, R. Boese, *Z. Anorg. Allg. Chem.* **1999**, *625*, 729.

[4] O. I. Kolodiazhnyi, *Phosphorus Ylides*, Wiley-VCH, Weinheim, New York, Chichester, Brisbane, Singapore, Toronto, **1999**.

[5] a) I. Shevchenko, V. Andrushko, E. Lork, G.-V. Röschenthaler, *Eur. J. Inorg. Chem.* **2003**, 54–56; b) I. Shevchenko, V. Andrushko, E. Lork, G.-V. Röschenthaler, *Eur. J. Inorg. Chem.* **2002**, 2985–2990.

[6] Y. Canac, S. Conejero, M. Soleilhavoup, B. Donnadieu, G. Bertrand, *J. Am. Chem. Soc.* **2006**, *128*, 459–464.

[7] Only a nitrile ylide substituted with an adamantyl group is known to be stable in crystalline form at room temperature: E. P. Janulis, S. R. Willson, A. J. Arduengo III, *Tetrahedron Lett.* **1984**, *25*, 405.

[8] D. G. Gilheany, in *The Chemistry of Organophosphorus Compounds*, vol. 3 (Ed.: F. R. Hartley), John Wiley & Sons, Chichester, UK, **1994**, p. 1–44.

[9] J. Albanbauer, K. Burger, E. Burgis, D. Marquarding, L. Schabl, I. Ugi, *Justus Liebigs Ann. Chem.* **1976**, 36–53.

[10] D. V. Griffiths, J. C. Tebby, *J. Chem. Soc., Chem. Commun.* **1986**, 871–872.

[11] S. Fergus, S. J. Eustace, A. F. Hegarty, *J. Org. Chem.* **2004**, *69*, 4663–4669.

[12] K. Burger, K. Einhellig, G. Süss, A. Gieren, *Angew. Chem. Int. Ed. Engl.* **1973**, *12*, 156–157.

[13] K. Burger, H. Goth, W. Höhenberger, *Chem. Ztg.* **1977**, *101*, 453–454.

[14] A. D. Becke, *Phys. Rev. A* **1988**, *38*, 3098–3100.

[15] J. P. Perdew, *Phys. Rev. B* **1986**, *33*, 8822–8824.

[16] a) B. I. Dunlap, J. W. Conolly, J. R. Sabin, *J. Chem. Phys.* **1979**, *71*, 3396–3402; b) O. Vahtras, J. Almlöf, M. W. Feyereisen, *Chem. Phys. Lett.* **1993**, *213*, 514–518; K. Eichkorn, O. Treutler, H. Öhm, M. Häser, R. Ahlrichs, *Chem. Phys. Lett.* **1995**, *240*, 283–289.

[17] A. Schaefer, C. Huber, R. Ahlrichs, *J. Chem. Phys.* **1994**, *100*, 5829–5835.

[18] R. Ahlrichs, M. Bär, M. Häser, H. Horn, C. Kölmel, *Chem. Phys. Lett.* **1989**, *162*, 165–169; R. Ahlrichs, M. v. Arnim, in *Methods and Techniques in Computational Chemistry* MET ECC-95 (Eds.: E. Clementi, G. Corongiu), STEF, Cagliari, **1995**, p. 509 ff; see also http://www.cosmologic.de/QuantumChemistry/main_turbomole.html.

[19] P. Deglmann, F. Furche, R. Ahlrichs, *Chem. Phys. Lett.* **2002**, *362*, 511–518; P. Deglmann, F. Furche, *J. Chem. Phys.* **2002**, *117*, 9535–9538.

[20] VMD for WIN-32, Version 1.8.2 (December 4, 2003): W. Humphrey, A. Dalke, K. Schulten, *J. Mol. Graphics* **1996**, *14*, 33–38.

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