Are RR′C–PR″$(BH_3)_2$ ‘electron poor’ phosphorus ylides?—an *ab initio*–NMR study †

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Received (in Cambridge, UK) 26th June 2000, Accepted 7th September 2000

The parent RR′C–PR″$(BH_3)_2$, **3** (R, R′, R″ = H), has no minimum geometry with ylide structure. In contrast to ‘normal’ ylides, RR′C–PR″$_3$, which are destabilised when the substituents (R, R′) have π donor character, the investigated RR′C–PR″$(BH_3)_2$ require at least one amino group to form a stable ylidic structure (*e.g.* **4NH** with R = NH_2, R′ = H, and R″ = H). Without π donor substituents the molecules lack a tautomerisation barrier for the hydroborylation (RR′C=PH(BH_3)–BH_2H′→(RR′H′C–PH(BH_3)=BH_2). Compound **6**, cyclo-1-(C–PH$(BH_3)_2$)-2,5-$(NH)_2$-3,4-$(CH)_2$, is a model for the ylide recently obtained by Arduengo. Analysis of the electronic structure confirms his suggestion that a considerable delocalisation from the carbene moiety into the ‘electron poor’ PR″$(BH_3)_2$ group occurs. This electron delocalisation is reflected by the partial charge of the ylide group (−0.50 in **4HN**, −0.51 in **4NN**, and −0.85 in **6**) which is negative (positive in ‘normal’ ylides). The term ‘inverse ylides’ could express this special bonding situation.

Introduction

Before the 1980s the Wittig reaction[1–3] boosted application of phosphorus reagents in organic synthesis[4] and even nowadays new $\sigma^4\lambda^5$-P compounds[5–7] with outstanding properties are found. In the last two decades research in main group chemistry was guided by the fascination of E=C and even E=E double bonds (E being a higher than first-row element), which were concluded to be impossible.[8] Among the multiple bonds between carbon and a second row atom the $\sigma^2\lambda^3$-P=C bond has a distinguished position, due to its double-bond strength.[9–12] The $\sigma^4\lambda^5$-P=C bond is also considered to have double bond character and is referred to as an ‘ylene’ bond.[13–15] The geometric argument for a double bond is the experimentally determined short C–P distance,[13] which is confirmed by *ab initio* computations (for example at the B3LYP/6-311+G(d) level:[15] the C–P bond in H_2C=PH_3 (1.681 Å) is only slightly longer than the ‘classical’ P=C double bond in H_2C=PH (1.670 Å) and much shorter than the P–C distance of 1.872 Å in CH_3–PH_2). An argument against the double bond is based on the *ab initio* calculated ^{31}P NMR “chemical shifts [which] are close to their respective single bonding values”[15] but not to those with a double bond (^{31}P magnetic shieldings in ppm:[15] 32.5 for H_2C=PH, 421.7 for ‘H_2C–PH_3’, and 465.0 for H_3C–PH_2). In contrast to the ylene perception, the ylide description, H_3C^-–P^+H_2, emphasises the single bond character of C–P.[16–18] One argument for the ‘ylide’ description is a geometric parameter, the pyramidality of the tricoordinate carbon (described by the out-of-plane angle, which may be defined as the angle between the geometric centre of the two non-phosphorus atoms attached to carbon, the carbon and the phosphorus atom). Considering that “nonstabilised ylides prefer a non-planar carbon environment, due to the carbanionic character”[18] the out-of-plane angles between 18 and 25 degrees suggest a phosphonium–carbanion character for the alkyl-substituted R°_2C–PR°_3 with R° = H or CH_3. Another argument for C^α–P being a single bond in $R^\circ_2C^\alpha$–PR°_3 is the low C^α–P rotation barrier.[11,14,19,20] In agreement with computational results (C^α–P rotation barriers below 4 kJ mol^{-1} for the parent H_2C^α–PH_3)[11,14,19] the NMR investigations for $R^\circ HC^\alpha$–$P(C_6H_5)_3$ with R° being H, alkyl, or silyl show that the rotation cannot be frozen out at temperatures above −105 °C.[20] Only for R° being phenyl was coalescence obtained, which indicates a barrier of 35 kJ mol^{-1}.[20] The compromise of considering the ‘ylene’ and the ‘ylide’ as resonance structures, which mix to some extent, reduces the conflict without providing an ‘understandable’ picture (only the ‘ylide’ is depicted in Fig. 1; in the following ‘ylidic bond’ is used for all bonds between σ^4–P and σ^3–C irrespective of the actual polarisation and valence).

Analysis of the charge distribution obtained either from semi-empirical[3,16] or *ab initio* computations[3,14,17–19,21–35] provides quantities which characterise the C^α–P bond without being observables. Two basically different approaches to assigning charges to atoms and bonds occur: a) localisation to atomic basins (for example the ‘Atoms in molecules’ approach, AIM,[36] introduced by Bader), b) localisation to bonds (for example the Foster–Boys[37] localised molecular orbitals, FB-LMO, which are also used in IGLO[38] calculations of NMR shieldings). Early FB-LMO calculations show that the ylide bond is characterised by two bonds with charge centroids away from the line connecting C^α with phosphorus.[14,23] Recent AIM calculations give contradictory results: while the numerical data at the bond critical point[36] of the C^α–P bond of **1** are “typical for a covalent, yet significantly polar bond”,[15] the ρ(r) and the ε value are similar to that of H_2C=PH with a double bond (at the MP2/6-311+G(2d) level:[39] ρ is 0.194 and ε is 0.401 for H_2C=PH_3, ρ is 0.187 and ε is 0.345 for H_2C=PH). The concept of negative hyperconjugation[40] allows understanding of the stabilisation in the ylide bond as an interaction of a filled p-AO of anionic C^α with an empty, antibonding P–R″ valence orbital

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† The optimised geometries and computed NMR properties are available as supplementary data. For direct electronic access see http://www.rsc.org/suppdata/p2/b0/b005090n/

DOI: 10.1039/b005090n

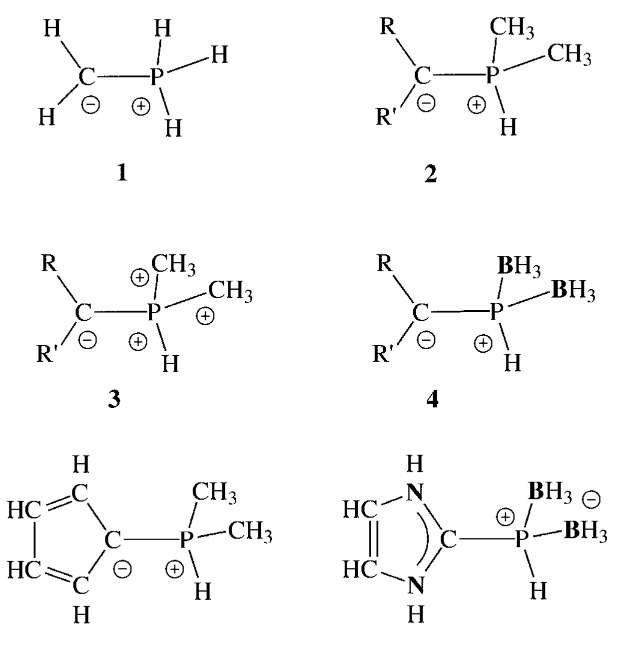


Fig. 1 Structures of classical ylides (**1**, **2**, and **5**), the dications **3**, and the ‘electron poor’ ylides **4** and **6**.

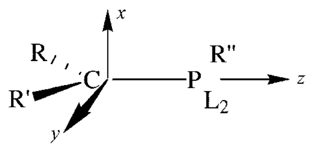


Fig. 2 Orientation of the ylides in a cartesian coordinate system.

(occupied p-AO in x and P–R″ in xz plane, H substituents on C$^\alpha$ in $+y$ and $-y$ direction, see Fig. 2). As a consequence of occupying the antibonding valence orbital the P–R″ bond length increases. The more drastic orbital concept uses fragment orbitals (depicted in Walsh diagrams) which are combined to form the MOs. From this frontier orbital approach the polarisation in $H_2C{=}PH_3$ towards the ‘fragment’ comprising the anionic carbon with the lower LUMO can be rationalised (orbital energies in eV:[35] of PH_3 are −10.4 HOMO, 4.9 LUMO and of singlet H_2C are −10.6 HOMO, 1.3 LUMO). When the ylide bond is ‘assembled’ in this way, negative hyperconjugation is reflected by the orbital interaction between the e symmetric fragment orbitals of PH_3 and the p_x-AO of CH_2. In this context two approximations should be mentioned. On the one hand, the d-AO at phosphorus, which is symmetry appropriate to mix with the e symmetric σ^* orbitals of the PH_3 fragment (p_x(P) combined antibonding with the set of s(H_{+y}), s(H_{-y}), s(H_x) AOs) is normally neglected.[21,24] Secondly, the phosphorus 3p AO is often[24] simplified to a 2p AO (fewer nodal planes) due to the lack of appropriate visualising tools. The MO figures in this study (generated with the MOLDEN[41] program) use correct AOs.[3] In general,[42] most studies agree that ylides **2** with alkyl substituents on carbon can be considered as ‘electron precise’ compounds.

This study investigates those ylides which formally lack two electrons and should therefore not be able to form the two-electron σ bonds depicted for **3** and **4** in Fig. 1 (the H_3C^+–P bond, H_3B–P respectively) assuming a carbanionic C$^\alpha$. Nevertheless, the experiment shows that compounds like **6** are stable.[5] What is the electronic structure of these unusual compounds of type **6**? The dication of **1** is found to be stable at the HF/6-31G(d) level of theory.[28] Can corresponding acyclic molecules of type **4** be stable? To answer the first question we have not only optimised the geometry of **6** and analysed its electronic structure, but additionally investigated the isoelectronic molecule **5**. To find out which substituents are required to make **4** type molecules stable the substituents R and R′ are varied (**4HN** indicates that R = H and R′ = NH_2 in the general formula of **4**). Furthermore, the question of why the C$^\alpha$–P bond is so much longer in **6** than in ‘normal’ ylides is addressed by comparing **6** with **1**, **2**, the dication of **2HH**, **3**, and the acyclic isomer of phosphorane cyclopropylide (**2CC**, where C indicates that R and R′ are CH_2 substituents; Fig. 1). For the previously unknown structures **4** the ^{31}P and ^{13}C NMR chemical shifts are predicted. The $\delta_{\text{calc.,P}}$ and $\delta_{\text{calc.,C}}$ values for the investigated structures are put in relation to geometric and electronic parameters of the minima to obtain further insight into the nature of these *new ylides*.

Computational methods

For geometry optimisation the B3LYP/631+G(d) method has been chosen, which provides only a slightly (0.005 Å) longer P–C bond for **1** than computations with the larger 6-311+G(d) (or 6-311++G(d,p), our calc.) basis set.[15] Corresponding MP2 calculations for **1** provide C–P distances which are shorter by 0.003 Å with 6-31+G(d), 0.008 Å with 6-311+G(d), 0.012 Å with 6-31G(d) and 6-311+G(2d), and 0.017 Å with 6-311++G(d,p) basis sets.[15,22,32,39] Molecular orbitals, MOs, are characterised either by their symmetry (within the C_s point group), by their energy (MO-1 is the lowest energy MO), or by their ‘frontier orbital character’ (HOMO is highest, HOMO-1 is one below highest occupied MO). In the population analysis the Mulliken method[43] was applied. The squared correlation coefficient is abbreviated as cc in the statistical considerations. On the optimised structures second derivative calculations were carried out (force constants, magnetic shieldings). Unless otherwise stated, the optimised structures are minima on the potential energy hypersurface (only positive harmonic frequencies at the B3LYP/6-31+G(d)//B3LYP/6-31+G(d) level). For selected minimum geometries the magnetic shielding of carbon and phosphorus was calculated at the GIAO/B3LYP/6-311+G(d)//B3LYP/6-31+G(d) level. The corresponding NMR chemical shifts can be derived with the theoretical references for PH_3 $\sigma(^{31}P) = 555.5$ ppm and for TMS $\sigma(^{13}C) = 183.3$ ppm calculated at the same level of theory. All calculations were done with the GAUSSIAN98[44] package of programs.

Results and discussion

A brief discussion of the MOs of the parent ylide, **1**, is followed by a report of the unstable ylides **3** and **4HH** (Fig. 1, where HH indicates that R and R′ are H in the general structure **4**). In the third section the RR′C fragment is varied from H_2C, to HC–NH_2, $C(NH_2)_2$, and the ‘Arduengo carbene’ model, imidazol-2-ylidene (Table 1) to see how it changes bonding towards and in $PH(CH_3)_2$ (**2HH**–**2CC**, **5**) and the $PH(BH_3)_2$ fragment (**4HH**–**4NN**, **6** and **7**). Finally, the NMR chemical shifts calculated for the ‘normal’ and the ‘electron poor’ compounds are presented (Table 2) to be related to molecular parameters (Fig. 9), and to be compared with available experimental data.

Electronic structure of $CH_2{=}PH_3$

In contrast to P–C conjugation in phosphaethenes, which can be described with two MOs, a σ(P–C) and a π(P–C) MO, the multiple bond character in the parent ylide, **1**, requires three canonical MOs. These three MOs are the 10 a', the 9 a', and the 8 a' MO (Fig. 3) and rationalise the remarkably short P–C bond in **1**, **2**, and related compounds with aryl substituents. The HOMO, MO 10 a', is basically a p_x-AO at carbon with additional π_x conjugation to P (axis system as specified in Fig. 2). MO 10 a' has two mirror planes: one orthogonal to x and another orthogonal to z going through the phosphorus

Table 1 Calculated properties of RR′C$^{\alpha}$–PHL$_2$ structures[a] for B3LYP/631+G(d) optimised geometries

No., pg	E_{tot}[a]	q(C)[b]	q(P)[b]	q(Y)[b]	R_{CP}[a]	Φ_{oop}[c]	$a_{\text{C}^{\alpha}\text{PH}}$[a]	R_{PH}[d]
1, C_s	−382.37761	−0.75	0.14	0.30	1.686	29.5	130.2	1.451
2HH, C_s	−461.03824	−0.78	0.21	0.35	1.684	27.8	125.9	1.451
2HN, C_1	−516.38061	−0.64	0.37	0.43	1.697	27.4	125.4	1.454
2NN, C_s	−571.73313	−0.52	0.39	0.48	1.712	29.4	125.0	1.458
2CC, C_s	−538.40635	0.84	0.13	0.28	1.787	15.2	110.9	1.406
3, C_s	−460.25643	−0.09	0.33	1.25	1.831	5.5	86.4	1.441
3′, C_s[e]	−460.25833	−0.07	0.20	1.22	1.833	0.0	104.8	1.404
4HH, C_s[e]	−434.43118	−0.84	0.45	0.34	1.663	18.1	130.4	1.432
4HH′, C_s[e]	−434.47064	−0.36	0.21	−0.18	1.676	0.0	103.4	1.413
4HN, C_1	−489.87798	−0.17	0.38	−0.50	1.802	11.7	97.2	1.415
4HN′, C_s	−489.87260	−0.15	0.28	−0.53	1.784	0.0	97.5	1.421
4NN, C_s	−545.27097	−0.04	0.52	−0.51	1.890	1.3	94.04	1.420
5, C_s	−614.67203	0.21	0.19	0.22	1.712	7.9	118.3	1.426
6, C_s	−621.48017	0.12	0.03	−0.85	1.849	4.4	96.1	1.420
7, C_s	−622.67387	0.32	−0.14	−0.94	1.851	2.4	94.4	1.421

[a] Geometries depicted in Figs. 1, 4, 5, and 8. Total energy in hartree. [b] Mulliken charges at B3LYP/6-311+G(d)//B3LYP/6-31+G(d) at carbon, C, phosphorus, P, and in the ‘phosphorus ylide’ group, Y, comprising PHL$_2$. [c] Out-of-plane angle, Φ_{oop}, as defined in Fig. 4. [d] Unless otherwise stated, geometries were optimised without symmetry constraint; the point group, pg, was obtained from symmetry analysis. [e] Not minimum structures.

Table 2 Magnetic shielding[a] calculated at GIAO/B3LYP/6-311+G(d) for optimised[b] geometries of RR′C$^{\alpha}$–PHL$_2$ molecules

No., symmetry	σ(P)[a]	σ(C)[a]	Σ_{P}EN(X)[c]
1, C_s	421.8	205.0	9.1
2HH, C_s	345.5	183.7	9.7
2HN, C_1	345.5	143.7	9.7
2NN, C_s	344.6	118.1	9.7
2CC, C_s	350.1	56.5	9.7
4HN, C_1	280.7	−37.2	8.7
4HN′, C_s	266.7	−44.7	8.7
4NN, C_s	304.1	−7.2	8.7
5, C_s	348.9	107.7	9.7
6, C_s	340.9	14.4	8.7
7, C_s	301.8	−21.2	8.7

[a] Theoretical references at GIAO/B3LYP/6-311+G(d)//B3LYP/6-31+G(d) for phosphorus, $\sigma(^{31}\text{P},\text{PH}_3) = 555.5$ ppm; $\delta_{\text{P}}(\text{PH}_3,\text{liq.}) = -240$ ppm. Phosphorus chemical shifts can be calculated with $\delta_{\text{P}}(\text{X}) - \delta_{\text{P}}(\text{PH}_3,\text{liq.}) = -(\sigma(\text{X, see this table}) - \sigma(\text{PH}_3))$. [b] Geometries depicted in Figs. 1, 4, 5, and 8. [c] Sum of the Allred Rochow electronegativities[49] of the atoms bound to phosphorus.

nucleus. The AO contribution of phosphorus to MO 10 *a*′ has ‘dp^2’ character. The d$_{xz}$ coefficient is small so that the character of a polarised p$_x$-AO dominates. While MO 10 *a*′ is dominated by its π_x bond character along the P–C bond, Fig. 3 shows that the MOs 9 *a*′ and 8 *a*′ have more σ C–P character.

The C–P bonding due to these three MOs is related to the out-of-plane angle of the R–C–R′ group. When R–C–R′ is bent towards P–R″ in the *xz* plane, as in the minimum structures, the π overlap in 10 *a*′ is slightly reduced while the π bond character of 8 *a*′ increases compared to the completely coplanar arrangement of R, C, R′, and P. Bending R–C–R′ away from P–R″ would decrease the π bonding of both MOs, 10 *a*′ and 8 *a*′. Since 9 *a*′ is dominated by its σ_{CP} bond character, bending in any direction reduces its overlap.

Other valence MOs are MO 6 *a*′ and MO 7 *a*′, which have σ and σ* character, and MO 2 *a*″ and MO 3 *a*″, which are the π and π* combinations of the H$_2$C and the PH$_3$ group orbitals. Since MO 2 *a*″ and MO 3 *a*″ have the H–P–C plane as nodal plane (mirror plane perpendicular to *y*, Fig. 2) their π overlap is independent of the bending of the R–C–R′ group but dependent on the C–P distance. Generally, the P–C bond in ylides elongates when the P–C bonding MOs corresponding to 10 *a*′ and 8 *a*′ are converted to group orbitals (either of the RCR′ or of the phosphine fragment) or when 9 *a*′ is strongly polarised.

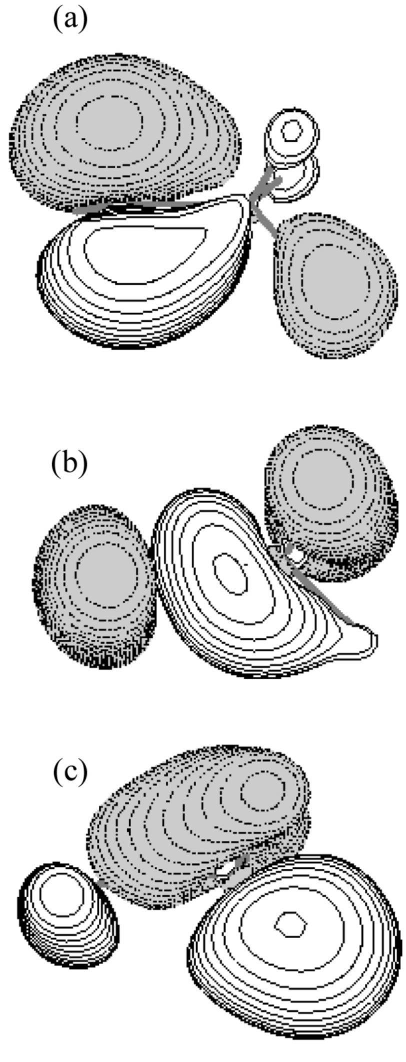
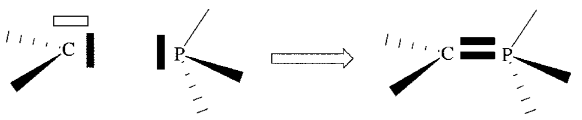


Fig. 3 Selected MOs with *a*′ symmetry (in C_s) of H$_2$C–PH$_2$, **1** (top to bottom): 10 *a*′ (is MO-13 = HOMO), 9 *a*′ (MO-11), and 8 *a*′ (MO-10).

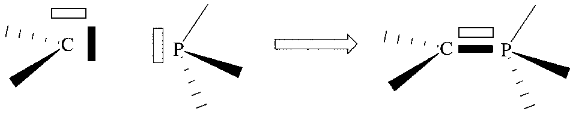
Unstable RR′C–PR″L$_2$ ylides

In the context of this study those ylides constructed by constraining the symmetry, which are not a minimum (**3** and **4HH**) but rearrange are considered ‘unstable’. In this sense the ‘electron poor’ diborophosphine, HP(BH$_3$)$_2$ is unstable ($E_{\text{rel}} = 136$ kJ mol^{-1}; in agreement with Sakai’s investigation[45] it rearranges to the adduct $H_2B–PH_2–BH_3$, $E_{rel} = 58$ kJ mol^{-1} and can further transform to the lowest energy isomer (E_{tot} at B3LYP/6-31+G(d) = −395.24850 hartree). In contrast, the isoelectronic $HP(CH_3)_2^{2+}$ dication is not unstable. The structure of the dication comprises a planar tricoordinate phosphorus and four C–H bonds (H–C–P angle 108°, H–C = 1.12 Å) which stabilise the phosphorus without a 'lone pair'. In the $HP(CH_3)_2^{2+}$ structure the P–C bonds are short (1.748 Å)—even shorter than in the TS of phosphorus inversion of the neutral molecule (1.839 Å). The $Me–CH–PH_3^{2+}$ isomer is 12 kJ mol^{-1} lower in energy than $HP(CH_3)_2^{2+}$, and separated from it by a considerable reaction barrier. This is in agreement with HF/631G(d) calculations for the parent ylide dication,[28] where the $H_3C–PH_2$ tautomer is 74 kJ mol^{-1} (2 kJ mol^{-1} at MP2/6-31G(d); 5 on the B3LYP level of this study) higher on the energy hypersurface.

In contrast to 'normal' phosphines (with an 'occupied' Lp, filled rectangle in eqn. (1)), the isoelectronic molecules $HP(CH_3^+)_2$ and $HP(BH_3)_2$ are characterised by an empty rectangle in eqn. (2).



(1)



(2)

Eqn. (1) is sometimes applied[29,46,47] to illustrate how the ylide bond can be constructed from a phosphine donor and a carbene acceptor. The single P–C bond in eqn. (2) indicates that the fragments are less strongly bound than in classical ylides (eqn. (1)). Nevertheless, the experiment[45] demonstrated that these unusual adducts can be stable. Furthermore, previous calculations[46] for $R_2C–AlCl_3$ with $R = NH_2$ and $AlCl_3$ being isoelectronic with PX_3^{2+} (for example $PR°(R^+)_2$ like the $PH(CH_3^+)_2$ dication) show that this kind of 'adduct' can be remarkably strong. Nevertheless, the simple adducts of this type considered here (H–C–H with $HP(CH_3^+)_2$ forming **3**; with $HP(BH_3)_2$ forming **4HH**, respectively) are both unstable. The C_s symmetric geometries **3** and **3′** differ only by 5 kJ mol^{-1} (Table 1) but both rearrange to $P(CH_3)_3^{2+}$, which is 111.2 kJ mol^{-1} lower in energy than **3′**. While in **3** there is an attempt to compensate for the lack of electrons to form two-centre bonds by forming a hydrogen bridge over the $H_2C–P$ bond, electrons are primarily 'missing' from the $H_2C–P$ π bond in **3′**. The **3′** geometry (Fig. 4, Table 1) resembles that of the TS of rotation around the ylide bond in neutral $Me_2HP{=}CH_2$ (C_s, $C^{\alpha}–P = 1.676$, two P–C with 1.856 Å), besides **3′** having a much longer $H_2C–P$ bond ($C^{\alpha}–P = 1.833$ Å). In both geometries, **3** and **3′**, the methyl groups have relatively short P–C bonds (1.818 and 1.845 Å), compared to those in neutral alkylphosphanes (1.87 Å). In $P(CH_3)_3^{2+}$, the effect of C–H bonds stabilising a cationic centre is extensively applied and the P–C bond length is only 1.768 Å. Due to the lack of any ylidic $H_2C–P$ π conjugation, the P–C bonds in **3** and **3′** are nearly as long as in $Me–PH_2$.

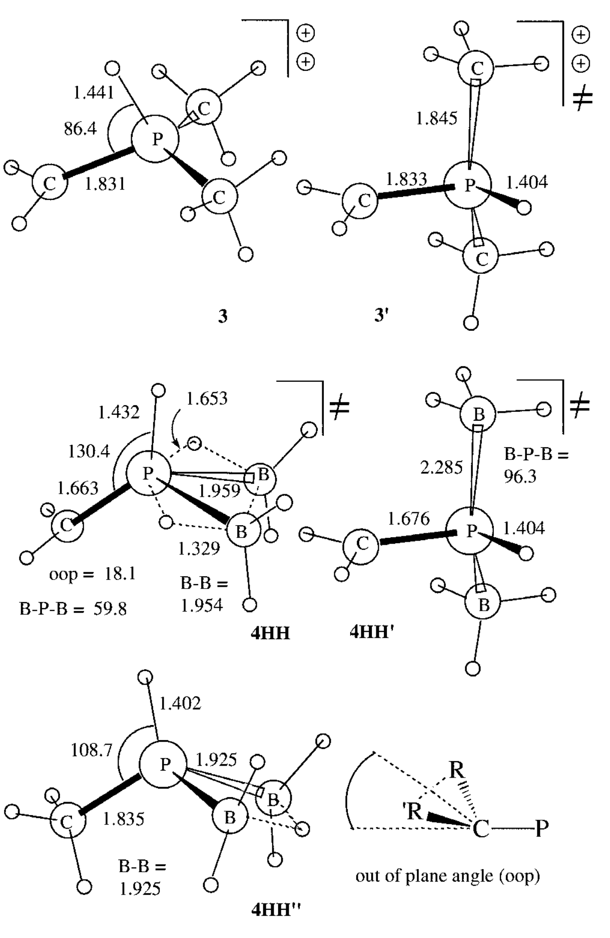
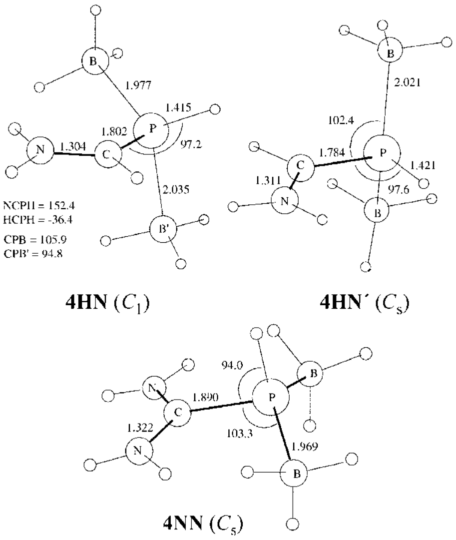


Fig. 4 B3LYP/6-31+G(d) geometries of C_s symmetric structures **3**, **3′**, **4HH**, **4HH′**, and **4HH″** (definitions of the 'out-of-plane' angle included).

4HH′ is the neutral heteroanalogue to **3′**. In contrast to **3′**, the $H_2C–P$ bond in **4HH′** is distinctly shorter than a single bond. Furthermore, the energetic difference between the two symmetry constrained 'rotamers' is much larger for $H_2C–P(BH_3)_2$ (104 kJ mol^{-1}) than for the isoelectronic $H_2C–P(CH_3)_2^{2+}$ (5 kJ mol^{-1}). The unusual structure **4HH** (shortest $H_2C–P$ bond within the molecules considered; Table 1) is disfavoured relative to **4HH′**. In **4HH′** the P–B bonds are nearly 0.3 Å longer than in $H_3P–BH_3$ (1.962 Å). The p-AO of the carbene fragment forms a π bond with the two σ*(P–B) group orbitals (negative hyperconjugation) in the phosphine fragment, so that the $C^{\alpha}–P$ bond is even shorter than in the parent ylide, **1**. Though the ylide bond is probably most pronounced in **4HH′**, this structure spontaneously rearranges to the methyl phosphinoborane **4HH″** which has one B–H–B bridge (Fig. 4) and is 273 kJ mol^{-1} lower in energy ($E_{tot} = −434.57473$ a.u.) than **4HH′**. The rearrangement from **4HH′**, or **4HH**, to **4HH″** is a tautomerisation, in which a B–H bond is transformed into a C–H bond. For the parent ylide, **1**, the tautomer $CH_3–PH_2$ is 222 kJ mol^{-1} lower in energy. We found the methyl and silyl derivatives of **4** (R, R′ = CH_3, SiH_3; see supplementary data) also to be unstable at B3LYP/6-31+G(d). Despite this preference for C–H over B–H bonding, the following section tries to answer the question of which substituents R and R′ make a RR′C–PR″L$_2$ ylide with L = BH_3 a stable structure (local minimum).

Stable RR′C–PR″L$_2$ ylides

In agreement with previous studies,[29] the amino group destabilises the ylide bond: the P–C bond length increases from **2HH**, **2HN**, to **2NN**. At first glance (Table 1) the same seems to apply for the 'electron poor' compounds **4HH** to **4NN** and **6**. Considering that stability increases from **4HH** and **4HH′** (not stable), as shown above, *via* the C_1 symmetric structure **4HN** to the minimum **4NN** (Fig. 5), this reveals that for these compounds the amino group is essential. Furthermore, it is remarkable that the amino groups are almost coplanar with the RR′CP plane (see Table 1: Φ_{oop} is 11.7° for **4HN**, 0.0° for **4NH′**, and 1.3° for **4NN**). This is in striking contrast to the destabilisation of the 'electron rich' ylides by enforced planar NH_2 groups reported earlier.[29]



4HN (C_1) **4HN′** (C_s)

4NN (C_s)

Fig. 5 B3LYP/6-31+G(d) geometries of the $(BH_3)_2HP–CH_{2-n}(NH_2)_n$ structures with $n = 1$ and 2; **4HN**, **4HN′**, and **4NN**.

To understand this change of the effect of the amino substituent the isostructural methylene (H_2C) and boryl (H_2B) are taken into consideration. While the full optimised mono-amino- and alkyl-substituted ylides resemble the bonding pattern of the parent (P–C is 1.658 $H_2C–PH_3$, 1.658 $(CH_3)HC–PH_3$, and 1.660 Å $(NH_2)HC–PH_3$ at HF/3-21+G*),[29] the methylene-substituted ylide **2CC** has a distinctly longer P–C bond than **1** or **2HH**. Geometry **2CC** is a stable structure which does not spontaneously rearrange to $CH_2{=}C(CH_3)–P(CH_3)_2$, cyclo-$(CH_2)_2(C–PH(CH_3)_2)$, or other isomers. The BH_2 group is also isostructural with the methylene substituent and provides an 'electron deficit' similar to that obtained when $(CH_3)_2$ is replaced by $(BH_3)_2$ (*e.g.* comparing **2NN** with **4NN**). For $BH_2–CH–PH_3$ ('planar') the largest methyl stabilisation energy was determined[29] in the 'first row sweep' of R in R–CH–PH_3. This seems to disagree with $BH_2–CH–PH_3$ having a relatively weak P–C bond (P–C is longer than for R = OH, or F). Considering the results from the previous section for the parent ylide this energetic effect can be understood as a strengthening of the B–C bond at the expense of the P–C bond: the B–C π bond uses the carbene fragment electrons, which would otherwise form the additional P–C bonding. Similarly in **2CC** the allyl conjugation of the $(CH_2)_2C$ group incorporates the carbene fragment electrons, which would otherwise strengthen the P–C bond. Structure **4CC**, $(CH_2)_2C–PH(BH_3)_2$, could be a minimum, which is isostructural with **2CC**, but is not stable (ylide geometry is only obtained from optimisation under constraint of symmetry). Due to replacement of CH_3 in **2CC** by BH_3 in **4CC** two electrons are either 'missing' in the two P–B bonds or in the $H_2C–C(PHL_2)–CH_2$ allyl system. As a consequence, spontaneous hydroborylation to $H_2C{=}C(CH_3)–PH(BH_3){=}BH_2$ occurs. Remarkably, the P–B bonds in this isomer differ by only 0.03 Å. In the parent compound of this unusual type of 'borane adduct', $H_2B{=}PH_2–BH_3$, the bond length difference is even less (P–BH_2 is 1.911, P–BH_3 is 2.017 Å at B3LYP/6-31+G(d); 1.906 and 1.999 Å at MP2/6-31G(d,p),[45] respectively). While no **4CC** geometry is stable, **4NN** has a minimum with an approximately coplanar N_2CP framework. Considering the ylide bond formed from the Lp(P) donating into the sp-AO of the carbene (eqn. (1)) results in occupation of the antibonding group orbitals of the N–C–N allyl π system (six π electrons from a: two Lp(N) and b: one fully occupied p-AO of the carbene fragment). The electrons from the amino group are delocalised into the 'electron poor' P–B bonds in **4NN**. This is reflected by the charge of the ylide group (q(Y) in Table 1), which changes from 0.43 in **2HN** to −0.50 in **4HN** and from 0.48 in **2NN** to −0.51 in **4NN**. The remaining positive atomic charge of phosphorus (q(P), Table 1) in all these structures shows that the BH_3 group is much more electron demanding than to be expected from the electronegativity of boron (which is approximately the same as for phosphorus). A further indicator for the 'use' of the electrons from the amino group in the 'electron demanding' $PH(BH_3)_2$ ylide group is the shortening of the P–B bonds: while in **4HH′** without amino groups on carbon P–B is 2.285 Å, it decreases to 2.021 (2.035 and 1.977, respectively) in the **4HN** structures, and to 1.969 in **4NN**. This donation from the π system of the amino groups to the ylide group is not accompanied by a shortening of the P–C bond as should result from hyperconjugation. Comparing the MOs of **4NN** (Fig. 7) with those of isoelectronic **2CC** (Fig. 6) shows similarity: the allylic π system is mainly found in the MO-20 (Fig. 7; corresponding π* is MO-22, not depicted) of **4NN** and the MO-27 of **2CC**. Nevertheless, the energetic position of these MOs is distinctly different: MO-27, π, and MO-28, π*, are the highest occupied orbitals of **2CC**; in contrast, MO-20 and MO-22 of **4NN** are far below the HOMO. Both sets of MOs have small coefficients at the atoms of the

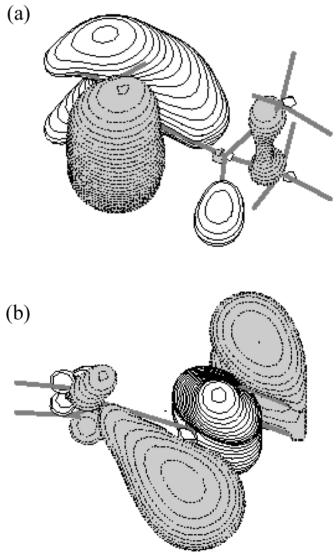


Fig. 6 Selected molecular orbitals with a' symmetry (in C_s) of $(CH_2)_2C–PHMe_2$, **2CC**: 17 a' (is MO-27 = HOMO-1, top), 15 a' (MO-23, bottom).

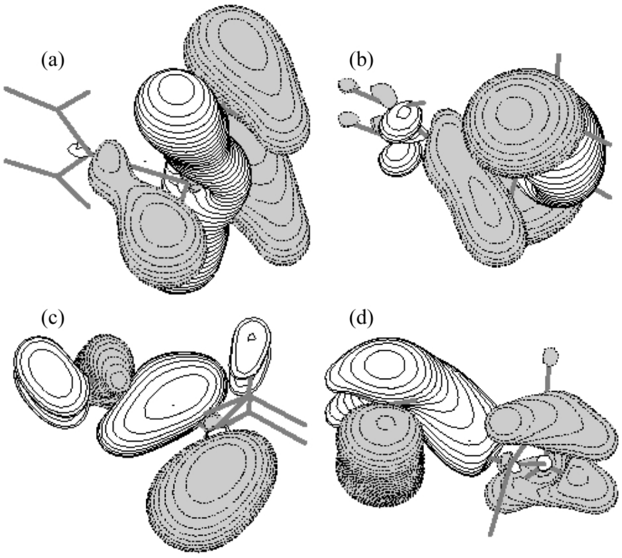
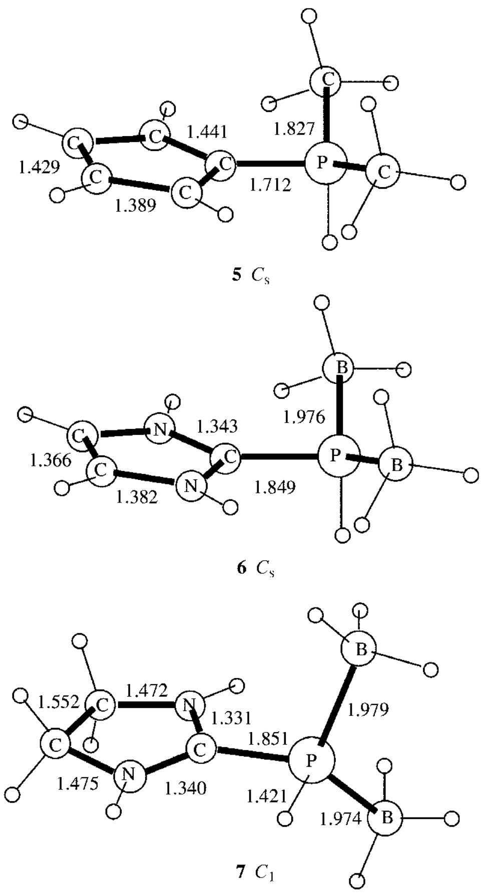


Fig. 7 Selected MOs with a' symmetry (in C_s) of $(NH_2)_2C–PH(BH_3)_2$ **4NN** (top left to bottom right): 17 a' (is MO-27 = HOMO-1), 15 a' (MO-23), 14 a' (MO-21), and 13 a' (MO-20).



5 C_s

6 C_s

7 C_1

Fig. 8 B3LYP/6-31+G(d) Geometries of **5**, **6**, and **7**.

ylide group (in contrast to the 10 *a*′ MO in **1**). The differences between **2CC** and **4NN** also lie in the MOs contributing to the P–C bonding: the MO corresponding to 9 *a*′ in **1** is MO-23 in **2CC**, while in **4NN** the MOs MO-27 and MO-23 resemble the AO combination of MO-11 of **1** with 9 *a*′ symmetry character. The two MOs, MO-27 and MO-23, in **4NN** are mainly group orbitals of the BH_3 moieties and have small contributions at the atoms of the carbene fragment. Therefore, these MOs do not contribute to additional P–C bonding as required for an ylide specific short P–C bond as in **1**. MO-21 of **4NN** (Fig. 7) corresponds to the 8 *a*′ MO in **1**. The orbital picture of **4HN** is more complex than for **4NN** partly due to the lower C_1 symmetry of the **4HN** minimum geometry. It shows the same characteristics as the MOs of **4NN** (therefore, they are neither depicted nor discussed here).

The effect of more electronegative substituents than N on the structure and the stability of **4** will only be discussed briefly here: in **4ON**, $(OH)(NH_2)C–PH(BH_3)_2$, one BH_3 is arranged as in the TS for hydroborylation and **4FN**, $F(NH_2)C–PH(BH_3)_2$, is unstable (rearranges to $CHF_2–PH(BH_3)=BH_2$). Due to the high electronegativity of R, donation into the P–B bonds is less effective in **4ON** (**4FN**, respectively) than in **4HN** or **4NN**. Can cyclic carbene fragments be more stable than their open-chain analogues?

RR′C–PR″(BH$_3$)$_2$ ylides with a cyclic carbene fragment

In the synthesized compounds of $RR'C–PH(BH_3)_2$ type the carbene fragment is a five-membered ring as in the molecules **5**, **6**, and **7** (Fig. 8). While cyclic delocalisation might have an effect on the ylide bonding, computations for **6** (potentially cyclic conjugate) and **7** (no π conjugation in the ring) show that this is negligible: not only is the difference of C^α–P only 0.002 Å but also the C^α–N distances differ by only 0.003 and 0.012 Å. The N–C^α–N angles in **6** (109.90°) and in **7** (109.20°) are almost equal. The only differences between **6** and **7** is the extent to which electron density (Table 1; *q*(C), *q*(P), and *q*(Y) shift of 0.2 to $PH(BH_3)_2$) is shifted towards the tetracoordinate phosphorus. Comparing **6** and **7** to **4NN** with an acyclic carbene fragment only the H–P–C^α angle remains more or less unchanged. As to be expected, the N–C^α–N angle in the acyclic **4NN** is much wider than in **6** and **7**. The shortening of C^α–P in **6** and **7** compared to **4NN** by 0.04 Å is moderate, but nearly half as large as the effect of the second amino substituent on C^α (**4HN** *vs.* **4NN**, Table 1). The corresponding C^α–P shortening in the classical ylides **5** compared to **2NN** is about twice as large. This demonstrates that a five-membered ring can have an additional effect on the ylidic bonding. Nevertheless, this effect is smaller in the new type than in the classical ylides.

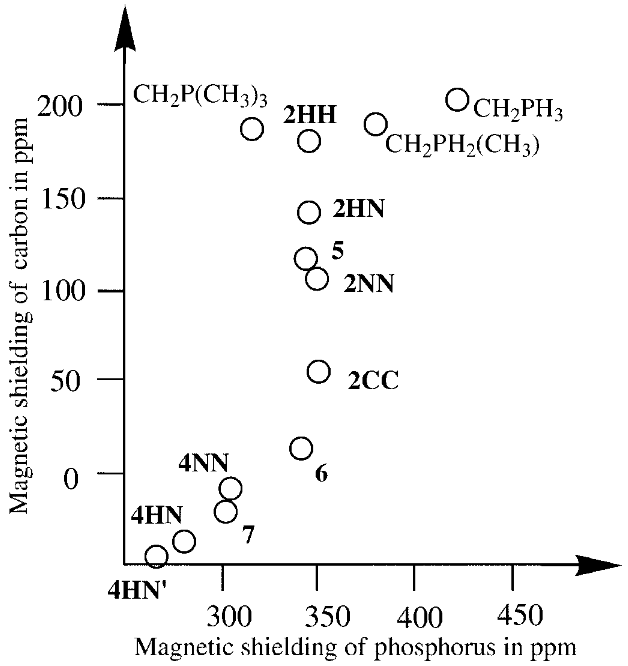


Fig. 9 Plot of σ^{13}C *vs.* σ^{13}P for the ylides **1**, **2**, **3**–**7**, and $H_2C=P(CH_3)_3$.

NMR properties

The magnetic shielding characterises the chemical environment of the carbon and the phosphorus of the ylides **1** to **7** (Table 2). In agreement with experimental findings, methyl groups as phosphorus substituents decrease the $\sigma(^{31}P)$ value (downfield shift of δ_P). The difference in $\sigma(^{31}P)$ between the members of the set of differently P alkyl-substituted molecules is approximately constant (36 ± 6 ppm per methyl replacing a hydrogen). In Fig. 9 the $\sigma(^{13}C^\alpha)$ are plotted against the $\sigma(^{31}P)$ values. For the $H_2C^\alpha–PH_n(CH_3)_{3-n}$ as well as for the amino-substituted $RR'C^\alpha–PH(BH_3)_2$ the $\sigma(^{13}C)$ are related to $\sigma(^{31}P)$ in such a way that both magnetic shieldings increase (slopes($\delta\sigma(^{13}C)/\delta\sigma(^{31}P)$): 4.3 and 1.2, see Fig. 9). In contrast, for **5**, **6**, the amino-substituted $RR'C^\alpha–PH(CH_3)_2$, and the molecule $(CH_2)_2C^\alpha–PH(CH_3)_2$, **2CC**, the change of the carbon shielding is not related to $\sigma(^{31}P)$: while shielding of ^{13}C decreases from 184 ppm in **2HH** *via* 118 (**2NN**) to 15 in **6**, the $\sigma(^{31}P)$ values of these molecules are all in the range between 345 and 350 ppm. Remarkably, the carbon chemical shift of **6** differs from that of the isoelectronic molecule **5**, by as much as 93 ppm. This reflects the different displacement of electrons from the N–C–N into the B–P–B in **6** compared to moderate donation from the C–C^α–C to the C–P–C moiety in **5**. While the ‘loss’ of most of the σ^3-C Lp electrons of C^α has a large effect, the ‘gain’ of electron density for the σ^4-P environment—without an Lp—has a negligible effect. Another remarkable difference occurs between the phosphorus shielding of **6** and **7**, which differ only in the ring closing group (‘spacer’ is –CH=CH– in **6** and $–CH_2–CH_2–$ in **7**). The γ substituent effect on $\sigma(^{31}P)$ is 39 ppm. In **7** with the stronger magnetic shielding of ^{31}P, the charge displacement into the $P(BH_3)_2$ moiety is slightly larger than in **6**. This increase of the negative charge of $P(BH_3)_2$ by a tenth of an electron is not reflected by a change of the C^α–P bond. Nevertheless, the $PH(BH_3)_2$ group is rotated by about 80 degrees in **7** with respect to the conformations in **6**. Despite different rotational $PH(BH_3)_2$ orientations a close relation between $\sigma(^{31}P)$ and $\sigma(^{13}C)$ with cc = 0.96 can be seen in Fig. 9 for the subset of the 'inverse ylides' ($RR'C–PH(BH_3)_2$ molecules). In general (in the molecules in Table 2), the magnetic shieldings neither correlate with geometric parameters (*e.g.* the P–C bond length) nor with the atomic charges (Table 1).

The chemical shift for $CH_2P(CH_3)_3$ ($\sigma(^{31}P) = 315.6$ ppm; Fig. 9) is 0 ppm, which is astonishingly close to the experimental value, −2.1 ppm.[48] The synthesized molecule[5] with $\delta_{exp.,P} = 121.5$ ppm has a phenyl group on phosphorus and mesityl groups on nitrogen, while the corresponding **6** has only H attached to P (due to computational limits). The effect of replacing the hydrogen by phenyl in **6** can be estimated from the difference between δ_P of $H_2P–H$(liq.) and $H_2P–C_6H_5$(liq.): +120 ppm. With this partial correction the computed $\delta_{est.,P}$ value 95 ppm (= −25 + 120) is obtained, which differs by about −28 ppm from $\delta_{exp.,P}$. Since this difference is well within the normal error of the applied computational method, the simulation is in agreement with the measurement. Furthermore, the crystallographic findings indicate that rotation around the C^α–P bond is facile, so that the NMR signal in solution is probably an average of rotational geometries. To estimate the effect of dangling the $\sigma(^{31}P)$ for the TS of C^α–P rotation is taken into consideration (not depicted, C^α–P = 1.838, C^α–N = 1.348, C^α–N′ = 1.345 Å, torsion angle H–P–C^α–N′ = 180°): 298 ppm. With the partial substituent correction, as applied above, a $\delta_{est.,P}$ of 137 (= 17 + 120) ppm is obtained for the TS ($E_{rel,6}$ = 25 kJ mol^{-1}), which differs by 16 ppm from $\delta_{exp.,P}$.

Conclusion

The structures of $RR'C–PR''(BH_3)_2$ models with R and/or R′ being amino groups agree with crystallographic data. Magnetic shieldings calculated at GIAO/B3LYP/6-311+G(d)//B3LYP/6-31+G(d) match the ^{31}P NMR chemical shifts of the synthesized derivative. In contrast to the kinetically stable parent ylide cation, its derivative $H_2C^\alpha–PR''(CH_3^+)_2$ and the neutral, isoelectronic $H_2C^\alpha–PR''(BH_3)_2$ molecule spontaneously rearrange. At least one amino substituent on C^α is required to obtain minimum structures with ylide character. The analysis of the molecular orbitals shows that the amino group(s) donate and thereby support the P–B bonding. This donation is less effective for more electronegative C^α substituents (*e.g.* OR, F). Nevertheless, the mono oxo heteroanalogue of **6**, cyclo-1-(C–PR″$(BH_3)_2$)-2-(O)-3,4-$(CH)_2$-5-(NH), is stable with R″ = H and can be expected to be synthetically accessible when R″ is an alkyl or aryl group. The corresponding structure with both amino groups in **6** replaced by oxygen is not stable. Cyclic conjugation of the carbene fragment is not required to obtain stable molecules of this new type of compound with a '$C^+–P^-$' polarised ylide bond.

Acknowledgements

The authors thank various Flemish science foundations (FWO-Flanderen, GOA-Program, and KULeuven Research Council) for continuous support. A. F. and T. V. are grateful for the support of the OTKA (grant T034768) and A. F. and A. D. appreciate support from the Belgian–Hungarian chemists exchange program.

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