5. S. Chandrasekhar, *Liquid Crystals* (Cambridge Univ. Press, New York, ed. 2, 1992); P.-G. de Gennes and J. Prost, *The Physics of Liquid Crystals* (Oxford Univ. Press, New York, ed. 2, 1993).
6. Indirect amplification of surface-bound analytes can be achieved with the use of enzyme-linked IgGs that bind to antigenic regions on analytes (*3*). In contrast to our approach, these methods require the use of IgGs labeled with enzymes and incubation of the surface-bound analytes with IgGs for tens of minutes, during which time the enzyme-linked IgGs bind to the analytes. A second incubation step, typically taking several minutes, is then required to enzymatically transform substrates into colored products.
7. We prepared gold films on a stationary glass substrate with a fixed angle of incidence of gold during deposition. Analysis of atomic force microscopy images of these films reveals their roughness to be greatest in a direction parallel to the direction of deposition of the gold. Using ellipsometry, we have also measured anisotropy in the amplitude and phase of reflected light (J. J. Skaife, V. K. Gupta, N. L. Abbott, unpublished data). On these gold films, nematic LCs orient uniformly in a direction perpendicular to the direction of incidence of the gold and parallel to the plane of the surface [V. K. Gupta and N. L. Abbott, *Langmuir* **12**, 2587 (1996)]. A nematic LC has no preferred orientation in the plane of a gold film that is prepared by rotating the glass substrate during deposition of the gold.
8. J. Spinke *et al.*, *J. Chem. Phys.* **99**, 7012 (1993).
9. Mixed SAMs were also formed in a few minutes by using solutions that contained millimolar concentrations of the organothiols.
10. All thickness measurements were performed using a Rudolph Auto ellipsometer with light (633 nm) incident at an angle of 70°. A refractive index of 1.45 was used to estimate the thickness of bound layers of thiols and proteins. Standard deviations of the reported ellipsometric thicknesses (Δ) are ± 0.2 nm.
11. We used a form of Av modified to reduce nonspecific adsorption at surfaces (Neutravidin, Pierce). The molecular weight of Av is ~60 kD and its dissociation constant with biotin is $K_d = 10^{-15}$ M (*3, 8*) [P. C. Weber *et al.*, *Science* **243**, 85 (1989)].
12. Triton X-100 (Sigma) is a nonionic detergent that was added to the PBS to minimize nonspecific adsorption of proteins. Use of Triton X-100 reduced the nonspecific adsorption of Av on SAMs formed from C_8SH to $\Delta_{Av} = 0.2$ to 0.6 nm. Nonspecific adsorption of proteins on SAMs can also be minimized by using alkanethiols end-functionalized with oligoethylene glycol or hydroxyl groups [K. L. Prime and G. M. Whitesides, *J. Am. Chem. Soc.* **115**, 10714 (1993)].
13. When rotated between crossed polarizers, the light transmitted through the sample did not show a large modulation in intensity. This result indicates the absence of a preferred orientation of the LC within the cell. The general features of the optical textures were not influenced by variations in rates of cooling of the LC to the ambient temperature.
14. We have shown that specific binding of Av can cause reorientation of films of LCs as thick as 20 μm (~2×10^6 mesogens per protein). We did not investigate LC films thicker than 20 μm because the optical effects of birefringence within a 20-μm-thick film of LC are easily seen with the naked eye. The threshold surface mass of avidin that causes reorientation of the LC is a strong function of the manner of deposition of the gold, the composition of the mixed SAM, and the type of LC (J. J. Skaife and N. L. Abbott, unpublished data).
15. Values of K_d reported here correspond to values measured in bulk solution [see, for example, H. Bagci *et al.*, *FEBS Lett.* **322**, 47 (1993)].
16. Anti-Bi-IgG was purchased from Sigma BioScience and anti-FITC-IgG was purchased from Molecular Probes. All measurements were performed in PBS containing 0.5 μM IgG and 0.004% Triton X-100. After binding of the IgG in PBS, the samples were rinsed with deionized water and dried under a stream of nitrogen.
17. Uniform anchoring of nematic 5CB was measured on mixed SAMs formed on anisotropic gold films by coadsorption from an ethanolic solution of 9 mM $C_{11}SH$ and 1 mM $HS(CH_2)_{11}$-Ala-Ala-Pro-Phe-*p*-nitroanilide.
18. Fluorescein-labeled streptavidin (FITC-Av) was purchased from Pierce. All measurements were performed in PBS containing 0.5 μM FITC-Av and 0.004% Triton X-100. After binding of the FITC-Av in PBS, the samples were rinsed with deionized water.
19. Studies based on stress-induced chromatic transitions in polymer films have reported limits of detection for specific binding of pentavalent cholera toxin to ganglioside G_{M1} (molecular weight ~100 kD, $K_d \approx 10^{-10}$ M) to be 100 ppm (~1 μM) when using liposomes in solution and 20 ppm (~0.2 μM) when using supported films of the polymer (*4*). The use of this method to detect the binding of antibodies to antigens has not been reported.
20. The surfaces of a TNLC cell are designed such that the region of LC in contact with one surface is oriented at right angles to the region of LC in contact with the opposing surface (Fig. 2B). The LC sandwiched between the two surface regions of the cell undergoes a 90° twist-type deformation, and the polarization of linearly polarized light transmitted through such a cell is rotated by 90°. A twisted LC cell, when viewed between two parallel polarizers, appears dark. In contrast, a cell containing LC that is not twisted appears bright between parallel polars [B. Bahadur, Ed., *Liquid Crystals: Applications and Uses* (World Scientific, Singapore, 1990)].
21. A. Kumar *et al.*, *Acc. Chem. Res.* **28**, 219 (1995).
22. V. K. Gupta and N. L. Abbott, *Science* **276**, 1533 (1997).
23. The preferred orientation of nematic 5CB in the plane of the SAM is perpendicular to the direction of deposition of gold on SAMs formed from $C_{15}SH$ and parallel to the direction of deposition of gold on SAMs formed from C_8SH [V. K. Gupta and N. L. Abbott, *Phys. Rev. E* **54**, 4540 (1996)].
24. Supported in part by NSF grants CTS-9502263 and DMR-9400354 and by the Office of Naval Research Presidential Early Career Award for Scientists and Engineers (N.L.A.). We thank Boehringer Mannheim and W. Knoll for their gift of BiSH, and G. Lopez and K. Oppermann for helpful suggestions.

9 December 1997; accepted 9 February 1998

Isolation of a Benzene Valence Isomer with One-Electron Phosphorus-Phosphorus Bonds

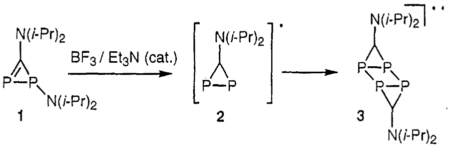
Yves Canac, Didier Bourissou, Antoine Baceiredo,
Heinz Gornitzka, Wolfgang W. Schoeller,* Guy Bertrand*

A tetraphosphabenzene analog of the postulated *anti*-tricyclohexylene, a singlet biradical valence isomer of benzene, has been isolated. The tricyclic derivative features one-electron phosphorus-phosphorus bonds, which result from the π*-π* interaction between two diphosphirenyl radicals. Such one-electron bonds may play a wider role in phosphorus chemistry.

Despite the long history associated with the chemistry of benzene (C_6H_6), new and fascinating benzene isomers are still being discovered (*1*). In contrast to the large number of possible C_6H_6 isomers [217 generated by a computer-aided procedure (*2*)], the number of possible valence isomers of benzene [$(CH)_6$] is quite small (Fig. 1). To date, only four such compounds have been observed experimentally (*3*): *cis*-Dewar benzene **A**, benzvalene **B**, prismane **C**, and bicycloprop-2-enyl **D**. Recent ab initio calculations have predicted that Mobius benzene **E** and *trans*-Dewar benzene **F** lie in very shallow minima on the potential energy profile, with energies 418 and 660 kJ/mol, respectively, higher than benzene (*4*); furthermore, benzmobiusstripane **G** has been proposed by Balaban (*5*). In addition to these valence isomers, which obey the octet rule, one can imagine a number of biradical structures. So far, none of these species have been isolated, although *anti*-tricyclohexylene **H** has been postulated to be the transition state in the Cope rearrangement of the bicycloprop-2-enyl derivatives **D′** into **D″** (*6*).

Heterobenzene chemistry, especially that involving the heavier main group elements, is comparatively poorly developed (*7*). For the phosphorus-containing series (P is isolobal to the CH fragment), several phospha- (*8*) and diphosphabenzene (*9*) valence isomer derivatives, a few 1,3,5-triphosphabenzene derivatives (*10*), and hexaphosphabenzene in the coordination sphere of transition metals (*11*) are known. No tetra- and pentaphosphabenzene species have been described.

We report here the synthesis of the transient diphosphirenyl radical **2** and the ensuing stable dimer **3** (Scheme 1). The latter



Scheme 1. Synthesis of diphosphirenyl radical **2** and of its stable dimer **3**. N(*i*-Pr)$_2$, diisopropylamino.

Y. Canac, D. Bourissou, A. Baceiredo, H. Gornitzka, G. Bertrand, Laboratoire de Chimie de Coordination du CNRS, 205, route de Narbonne, 31077 Toulouse Cedex, France.
W. W. Schoeller, Fakultät für Chemie der Universität, Postfach 10 01 31, D-33615 Bielefeld, Germany.

*To whom correspondence should be addressed. E-mail: gbertran@lcctoul.lcc-toulouse.fr

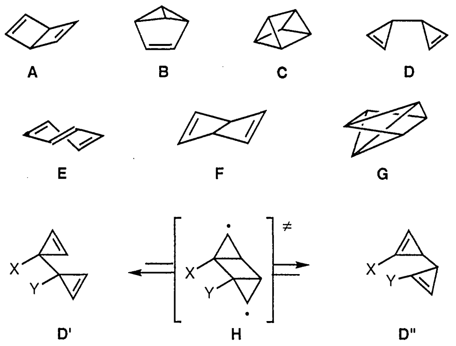


Fig. 1. Benzene valence isomers **A** through **G** and Cope rearrangement between derivatives **D′** and **D″**.

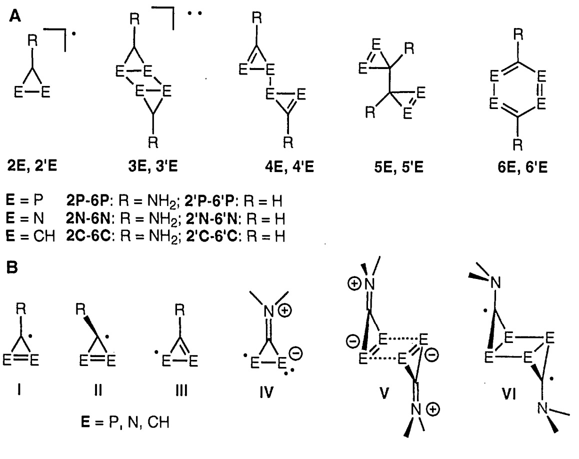


Fig. 3. (**A**) Schematic illustration of radicals **2** and dimers **3** through **6**. (**B**) Canonical structures of radicals **2** and dimers **3**. A priori, in the radical **2P** (E = P, R = NH$_2$), the single electron can reside at the C atom [$^2B_1$ state (C_{2v} symmetry), canonical structure **I**, or $^2A'$ state (C_s), canonical structure **II**], or alternatively at the P atoms [$^2A_2$ state (C_{2v}), canonical structures **III** and **IV**]. Because of the weakness of the P–P π-bond (142 kJ/mol), the calculations predicted that the energies of the $^2B_1$ and $^2A'$ states are higher by 195 and 148 kJ/mol, respectively, than that of the $^2A_2$ state (with zero-point energy corrections). An analysis of a multiconfiguration self-consistent field wave function emphasizes the closed-shell nature of **3P** [complete active space (12,12)/6-31g(d), c_1 = 0.9 of the leading ground-state configuration; the lowest energy triplet (^3B_u) is 280 kJ/mol higher in energy] and implies a strong electronic coupling of the two initially formed radicals **2P**. For the parent diphosphirenyl radical **2′P**, the energies of the $^2B_1$ and $^2A'$ states are 90 and 81 kJ/mol higher than that of the $^2A_2$ state. For the diazirinyl radical **2′N**, the energies of the $^2B_1$ and $^2A'$ states are 118 and 61 kJ/mol higher than that of the $^2A_2$ state.

compound is the first valence isomer derivative of a tetraphosphabenzene and can be related to *anti*-tricyclohexylene H (Fig. 1).

Treatment of 1*H*-diphosphirene 1 (*12*) with catalytic amounts of BF$_3$ (5%) and triethylamine (Et$_3$N) (5%) in tetrahydrofuran at 50°C for 2 hours led to the formation of a diamagnetic red solution (all manipulations were performed under Ar). After evaporation of the solvent and extraction with pentane, compound 3 was isolated in 45% yield as red crystals (melting point, 140°C) (Scheme 1).

The molecular weight, obtained by mass spectrometry (*13*), corresponded to a dimer of the diphosphirenyl radical 2, which formally results from the homolytic cleavage of the P–N bond of 1. The ^{31}P proton-coupled nuclear magnetic resonance (NMR) spectrum showed only a singlet at −164.5 ppm, suggesting the presence of a three-membered ring framework (*14*) and the absence of an amino group at the P. The high symmetry of the structure was confirmed by the ^{1}H and ^{13}C NMR spectra (*15*). Moreover, we carried out a single-crystal x-ray diffraction study of 3 (*16*). In the crystal structure (Fig. 2), the molecule is organized around an inversion center located at the center of a rectangular P$_4$ framework, which is almost perpendicular to two three-membered rings (P$_4$/P$_2$C: 97°); the NR$_2$ groups are slightly tilted out of the P–P–C planes (0.164 Å). The P–C and P–P bond lengths in the three-membered rings are within the range expected for single bonds; the C–N bond lengths are short, indicating a strong double-bond character, which is confirmed by the planarity of the N atoms. Interestingly, the P–P bonds between the two three-membered rings [2.634(3) Å] (parentheses indicate the error in the last digit) are by far the longest P–P bonds ever reported (*17*) but are clearly less than twice the P van der Waals radii (3.8 Å).

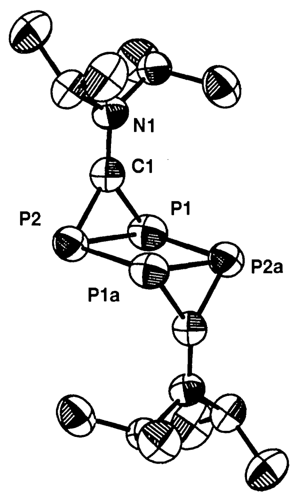


Fig. 2. Molecular view of **3** in the solid state (thermal ellipsoids with 50% probability). Selected bond lengths (in angstroms): P1–P2, 2.205(3); P1–P2a, 2.634(3); P1–C1, 1.743(6); P2–C1, 1.738(6); C1–N1, 1.336(7). Selected angles (in degrees): C1–P1–P2, 50.6(2); C1–P2–P1, 50.8(2); P1–C1–P2, 78.6(3); P1–C1–N1, 141.4(4); P2–C1–N1, 138.8(4); C1–P1–P2a, 94.9(2); P2–P1–P2a, 89.1(1); P1–P2–P1a, 90.9(1). Sum of the valence angles around N1, 359.9°.

To gain a better understanding of the nature of 3 and its formation from 2, we carried out ab initio calculations (*18*). For the radical 2P (E = P, R = NH$_2$) (Fig. 3A), the calculations predicted a $^2A_2$ ground state (canonical structures III and IV) (Fig. 3B). The spin density is equally distributed over the two P atoms, and the single occupied molecular orbital (SOMO) is the π* orbital of the P=P double bond. Because of the higher strength of the N–C π-bond (268 kJ/mol) compared with that of the P–C π-bond (180 kJ/mol) (*19*), derivative 2P is best described by the zwitterionic structure IV. The dimerization of the diphosphirenyl radical 2P is exothermic (−163 kJ/mol) and occurs by means of a π*-π* interaction (*20*) (Fig. 4), giving rise to the formation of 3P. A four-center bonding system with six π electrons (*21*) best describes the P$_4$ framework; each P–P bond between the two three-membered rings is formally a one-electron bond, which rationalizes the very long P–P bond distance. The most accurate, if any, Lewis-like representation of dimers 3 and 3P is the zwitterionic structure V (Fig. 3B). The biradical canonical structure VI best describes the triplet state in which the P–P distances between the three-membered rings lie in the range for classical P–P single bonds. The alternative P–P and C–C σ-dimers 4P and 5P are higher in energy than 3P, and even

Table 1. Calculated relative energies (in kilojoules per mole) for the radicals **2P**, dimers **3P** through **6P** (E = P; R = NH$_2$), **2′E**, and dimers **3′E** through **6′E** (E = P, N, CH; R = H).

Derivative	Energy	Derivative	Energy	Derivative	Energy	Derivative	Energy
2P	0	**2′P**	0	**2′N**	0	**2′C**	0
3P	−163	**3′P**	−209	**3′N**	−115	**3′C**	−325
4P	−106	**4′P**	−148	**4′N**	−115	**4′C**	−409
5P	−98	**5′P**	−245	**5′N**	−362	**5′C**	−409
6P	−178	**6′P**	−242	**6′N**	−520	**6′C**	−933

more striking, the energy of tetraphosphabenzene **6P** is only 15 kJ/mol lower (Fig. 3A and Table 1). The ground state of the parent diphosphirenyl radical **2′P** ($E = P$, $R = H$) is also $^2A_2$, and the π^*-π^*-dimer **3′P** is lower in energy than the P–P σ-dimer **4′P**.

It is of interest to compare these results with those reported for the analogous N- and C-containing series. On the basis of the formation of nitriles and N_2, Maeda and Ingold postulated that the bimolecular self-reaction of diazirinyl radicals proceeds by way of an N–N σ-dimer of type **4** (Fig. 3A) (*22*). Once again, calculations show that the diazirinyl radical **2′N** is in the $^2A_2$ ground state and that the energy of the π^*-π^*-dimer **3′N** is equal to that of the N–N σ-dimer **4′N**. Because this latter compound suffers from the antiaromaticity of the two 1*H*-diazirine moieties (*23*), dimers of types **3** and **4** are unlikely to be isolated in the N-containing series. Of course, the C–C σ-dimer **5′N** is much more stable, but its formation is also quite unlikely from the diazirinyl radical, because it would require the spin density to be located at the C atom of **2′N**, which is not the case.

In contrast to the diphosphirenyl **2′P** and diazirinyl **2′N** radicals, calculations predict a $^2A'$ ground state for the cyclopropenyl radicals **2′C** (canonical structure **II**, Fig. 3B), with one of the C atoms being strongly pyramidalized (*24*). It has been shown that cyclopropenyl radicals dimerize to form the corresponding bicycloprop-2-enyl derivatives **4′C** (*25*). Surprisingly, *anti*-tricyclohexylene **3′C**, which is best described as a singlet biradical, is calculated to have an energy only 83 kJ/mol above that of the previously isolated (*3*) C–C σ-dimer **4′C.**

Although benzene (**6′C**) is far more stable than its valence isomers **4′C** and of course **3′C**, in the corresponding N-containing series the difference in energy between the various isomers is much smaller, and the incorporation of P brings the stability of the π^*-π^*-dimer to the fore.

Up until the 1970s, the chemistry of the heavier main group elements was believed to be restricted to that involving single bonds as a result of the so-called "double-bond rule" (*26*). Now, after three decades devoted to the synthesis and study of four-electron and six-electron multiple bonds (*27*), the isolation of **3** suggests that one-electron bonds could also play an important role in phosphorus chemistry.

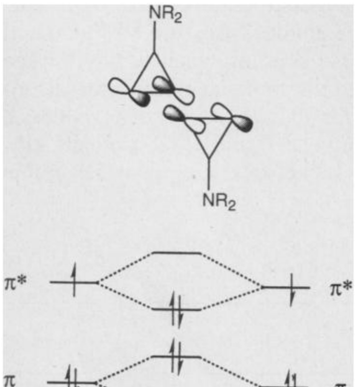


Fig. 4. Orbital diagram for the dimerization of the diphosphirenyl radical **2** into the π^*-π^*-dimer **3** (SOMO-SOMO interaction).

REFERENCES AND NOTES

1. I. Gutman and J. H. Potgieter, *J. Chem. Educ.* **71**, 222 (1994); W. C. Shakespeare and R. P. Johnson, *J. Am. Chem. Soc.* **112**, 8578 (1990); M. Christl, M. Braun, G. Müller, *Angew. Chem. Int. Ed. Engl.* **31**, 473 (1992).
2. H. Bock, *Angew. Chem. Int. Ed. Engl.* **28**, 1627 (1989).
3. E. E. van Tamelen and S. P. Pappas, *J. Am. Chem. Soc.* **85**, 3297 (1963); K. E. Wilzbach, J. S. Ritscher, L. Kaplan, *ibid.* **89**, 1031 (1967); T. J. Katz and N. Acton, *ibid.* **95**, 2738 (1973); W. E. Billups and M. M. Haley, *Angew. Chem. Int. Ed. Engl.* **28**, 1711 (1989).
4. R. P. Johnson and K. J. Daoust, *J. Am. Chem. Soc.* **118**, 7381 (1996).
5. A. T. Balaban, *Rev. Roum. Chim.* **11**, 1097 (1966); D. S. Warren and B. M. Gimarc, *J. Am. Chem. Soc.* **114**, 5378 (1992).
6. R. Weiss and H. Kölbl, *J. Am. Chem. Soc.* **97**, 3224 (1975).
7. A. R. Katritzky, C. W. Rees, E. F. V. Scriven, Eds., *Comprehensive Heterocyclic Chemistry* (Pergamon, Oxford, 1996); N. Tokitoh *et al.*, *J. Am. Chem. Soc.* **119**, 6951 (1997); W. Ando *et al.*, *ibid.*, p. 3629; A. J. Ashe III, S. Al-Ahmad, J. W. Kampf, *Angew. Chem. Int. Ed. Engl.* **34**, 1357 (1995); D. A. Hoic, W. M. Davis, G. C. Fu, *J. Am. Chem. Soc.* **117**, 8480 (1995); S. Qiao, D. A. Hoic, G. C. Fu, *ibid.* **118**, 6329 (1996).
8. G. Märkl, *Angew. Chem. Int. Ed. Engl.* **5**, 846 (1966); A. J. Ashe III, *J. Am. Chem. Soc.* **93**, 3293 (1971); N. Avarvari, P. Le Floch, F. Mathey, *ibid.* **118**, 11978 (1996); G. Märkl, in *Multiple Bonds and Low Coordination in Phosphorus Chemistry*, M. Regitz and O. J. Scherer, Eds. (Thieme, Stuttgart, 1990), pp. 220–257.
9. Y. Kobayashi, I. Kumadaki, A. Ohsawa, H. Hamana, *Tetrahedron Lett.* **41**, 3715 (1976); Y. Kobayashi *et al.*, *J. Am. Chem. Soc.* **102**, 252 (1980); D. Böhm *et al.*, *Angew. Chem. Int. Ed. Engl.* **34**, 198 (1995).
10. A. R. Barron and A. H. Cowley, *Angew. Chem. Int. Ed. Engl.* **26**, 907 (1987); P. Binger *et al.*, *ibid.* **34**, 2227 (1995).
11. O. J. Scherer, H. Sitzmann, G. Wolmershäuser, *ibid.* **24**, 351 (1985).
12. D. Bourissou *et al.*, *J. Chem. Soc. Chem. Commun.* **1997**, 2399 (1997).
13. The mass spectrum of **3** was recorded by chemical (NH_3) ionization: 366 ($M + NH_4^+$).
14. F. Mathey, *Chem. Rev.* **90**, 997 (1990).
15. The ^1H and ^{13}C NMR spectra of **3** showed only one type of CH group [^1H: chemical shift δ 3.34 (septuplet, $J_{H-H} = 6.6$ Hz) (J is the spin-spin coupling constant); $^{13}C\{^1H\}$: δ +54.0 (singlet)] and two types of CH_3 group [^1H: δ 0.88 and 0.94 (doublet, $J_{H-H} = 6.6$ Hz); $^{13}C\{^1H\}$: δ +21.0 and 21.5 (singlet)], in addition to a quaternary C [δ +162.2 (pseudo-triplet, $J_{P-C} = 83$ Hz)].
16. Crystal data of **3**: Cell constants and an orientation matrix for data collection correspond to the monoclinic space group $P2_1/n$, with $a = 7.615(2)$ Å, $b = 15.485(3)$ Å, $c = 8.209(2)$ Å, $\beta = 90.73(3)°$, and V (cell volume) = 965.9(4) Å^3. A half molecule, $C_7H_{14}NP_2$, per asymmetric unit (number of formula units per cell = 4), giving a formular weight of 174.13 and a calculated density (D_c) of 1.197 Mg m^{-3}. The data of the structure were collected on a STOE–Imaging Plate Diffraction System diffractometer at a temperature of 293 K with graphite-monochromated MoKα radiation (wavelength = 0.71073 Å) by using φ scans. We solved the structure by direct methods, using *SHELXS-96* [G. M. Sheldrick, *Acta Crystallogr. Sect. A* **46**, 467 (1990)]. The linear absorption coefficient, μ, for MoKα radiation is 0.385 mm^{-1}. The structure was refined with all data on F^2 with a weighting scheme of $w^{-1} = \sigma^2(F_o^2) + (g1 \cdot P)^2 + (g2 \cdot P)$ with $P = (F_o^2 + 2F_c^2)/3$ using *SHELXL-96* [G. M. Sheldrick, SHELXL-96, *Program for Crystal Structure Refinement* (Universität Göttingen, Göttingen, 1996)] [g is the weighting factor ($g1 = 0.0970$ and $g2 = 0.0000$) and F_o and F_c are the observed and calculated structure factors, respectively]. All non-H atoms were treated anisotropically. The H atoms were located by difference Fourier maps and refined with a riding model. The final cycle of full-matrix least square refinement was based on 5625 measured (1136 unique) reflections and 95 variable parameters and converged with the unweighted agreement factor equal to $R1\ [I > 2\sigma(I)] = 0.0542$ (I is the observed reflection intensity) and the weighted factor $wR2 = 0.1644$ for all data. Crystallographic details may be obtained from the corresponding author or from the Cambridge Crystallographic Data Centre, by quoting the full literature citation.
17. A. H. Cowley, *Chem. Rev.* **65**, 617 (1965); J. R. Durig, L. A. Carreira, J. D. Odom, *J. Am. Chem. Soc.* **96**, 2688 (1974); D. R. Lide, Ed., *CRC Handbook of Chemistry and Physics* (CRC Press, Boca Raton, FL, 1992), p. S. 9-1.
18. All quantum chemical calculations were performed at the MP2/6-31g(d) level with the Gaussian-94 set of programs: M. J. Frisch *et al.*, *Gaussian 94 (Revision A.1)* (Gaussian, Inc., Pittsburgh, 1995); P. C. Haribaran and J. A. Pople, *Chem. Phys. Lett.* **66**, 217 (1972); M. M. Francl *et al.*, *J. Chem. Phys.* **77**, 3654 (1982). For the doublet states, spin-projected energies were computed according to the procedure of Schlegel [H. B. Schlegel, *J. Chem. Phys.* **84**, 4530 (1986)].
19. W. W. Schoeller, C. Begemann, U. Tubbesing, J. Strutwolf, *J. Chem. Soc. Faraday Trans.* **93**, 2957 (1997).
20. Note that π^*-π^* interactions have been found in numerous inorganic molecules [T. Klapötke and J. Passmore, *Acc. Chem. Res.* **22**, 234 (1989); J. Beck, *Coord. Chem. Rev.* **163**, 55 (1997)], including in the solid-state structure of NO [W. J. Dulmage, E. A. Meyers, W. N. Lipscomb, *Acta Crystallogr.* **6**, 760 (1953); W. N. Lipscomb *et al.*, *ibid.* **14**, 1100 (1961). S. G. Kukolich, *J. Am. Chem. Soc.* **104**, 4715 (1982)], but so far no example directly involving P atoms has been reported. For example, $S_2I_4^{2+}$ is a π^*-π^* dimer [J. Passmore, G. Sutherland, T. Whidden, P. S. White, *J. Chem. Soc. Chem. Commun.* **1980**, 289 (1980)], but not the isoelectronic P_2I_4 [Y. C. Leung and J. Waser, *J. Phys. Chem.* **60**, 539 (1956)].
21. R. Gleiter, R. Bartetzko, P. Hofmann, *Z. Naturforsch. Teil B* **35**, 1166 (1980).
22. Y. Maeda and K. U. Ingold, *J. Am. Chem. Soc.* **101**, 837 (1979).
23. So far, only one example of these four-electron, three-membered heterocycles has been spectroscopically characterized [N. Dubau-Assibat, A. Baceiredo, G. Bertrand, *J. Am. Chem. Soc.* **118**, 5216 (1996)].
24. For calculations on cyclopropenyl and diazirinyl radicals, see also D. M. Chipman and K. E. Miller [*J. Am. Chem. Soc.* **106**, 6236 (1984)] and Y. G. Byun, S. Saebo, and C. U. Pittman Jr. [*ibid.* **113**, 3689 (1991)].
25. R. Breslow and P. Gal, *J. Am. Chem. Soc.* **81**, 4747 (1959); ______, H. W. Chang, L. J. Altman, *ibid.* **87**, 5139 (1965).
26. For a review of this topic, see N. C. Norman, *Polyhedron* **12**, 2431 (1993).
27. M. Regitz and O. J. Scherer, Eds. *Multiple Bonds and Low Coordination in Phosphorus Chemistry* (Thieme, Stuttgart, 1990).
28. Financial support of this work was provided by a grant from the Humboldt Foundation to H.G. and by the CNRS and Deutsche Forschungsgemeinschaft.

12 December 1997; accepted 5 February 1998