Table I. ^{1}H NMR Chemical Shifts of Pyrene (1), Perylene (2), and Tetraanions **3** and **4**[7]

	pyrene (1)	pyrene[a] dianion	pyrene tetraanion (3)	perylene (2)	perylene tetraanion (4)	isopyrene[a]	isopyrene dianion[a]
center of gravity of ^{1}H NMR bands	8.15	0.97	5.3	7.89	5.35	8.05	6.72
$\Delta\langle\delta\rangle$ from the neutral compd		7.18	2.85		2.54		1.33[b]

[a] Data taken from ref 3. [b] The isopyrene has a LUMO with a nodal plane which does not bisect the central carbon atoms: so this orbital is not a pure peripheral one, a fact which explains the reduced paratropicity revealed in isopyrene dianion.[3]

two systems have already been subjected in the past to reduction by metals. A doubly charged paratropic species was detected as a dilithium salt[3] of **1** to yield $\mathbf{1}^{2-}$ and a disodium salt salt was reported to be formed by metal reduction of **2**.[4] Comparison of the reported ^{1}H NMR spectra of these two charged systems shows a striking difference between them. Upon reduction of **1** to $\mathbf{1}^{2-}$ the proton chemical shift's center of gravity $\Delta\langle\delta\rangle$ shifts upfield by 7.18 ppm, while the total change in reduction of **2** is only 2.54 ppm. This difference cannot be ascribed to the nonsimilarity of the π periphery of these hydrocarbons as they accomodate 14- and 18π electrons and **1** and **2**, respectively.[5] Simple HMO of **1** and **2** show that each one of them has a LUMO orbital exhibiting a nodal plane through the central carbon atoms.[6] This leads to an important conclusion: in $\mathbf{1}^{2-}$ and $\mathbf{2}^{2-}$ the molecular orbitals which are occupied by the two additional electrons represent those of a pure peripheral annulene.

This discrepancy tempted us to study the metal reduction of **1** and **2**. Reduction of **1** with sodium metal at room temperature (THF-d_8, sealed degassed tube) was monitored by ^{1}H NMR spectroscopy.[7] After 4 days the deep purple solution exhibited a well-resolved AB_2M spectrum; the AB_2 part is centered at 5.68 ppm, the M part at 4.40 ppm, and the center of gravity of the entire spectrum at 5.30 ppm (Table I). This spectrum remains unchanged for weeks. During the first 4 days no proton bands were detected, presumably due to the formation of radical species and fast bimolecular electron-transfer processes. This ^{1}H NMR spectrum is entirely different from the spectrum of the paratropic species $\mathbf{1}^{2-}$ reported previously which was obtained with lithium metal at −80 °C.[8] An experiment conducted in dimethoxyethane showed the same spectrum. Oxidation of the anion solutions with O_2 afforded **1** as a sole product. These experiments indicate that the ^{1}H NMR bands could not originate from a reaction product of the anion itself or the anion and solvent. Quenching with D_2O afforded tetradeuteriotetrahydropyrene (*m*/*e* 210, P + 1 = 211) as shown by electron capture and chemical ionization mass spectrometry,[9] accompanied by a mixture of partially dehydrogenated products (*m*/*e* 202–209). We followed the formation of the various species in the reaction of pyrene and sodium by repeated sampling experiments. Samples were taken from the reaction mixture, quenched with water, and titrated potentiometrically to follow the formation of base. The amount of sodium was followed by atomic absorption. The amount of base and sodium increased with time, and after 4 days 3.3–4.0 equiv of base and 3.2–4.0 atoms of sodium were detected per molecule of **1**. No further increase of base and sodium could be detected even after 14 days. These results clearly indicate the formation of a quadruply charged anion **3**, i.e., $\mathbf{1}^{4-}$.[10]

Similar experiments were conducted with the perylene system (**2**). The ^{1}H NMR spectrum[7] of the purple solution formed by contact between **2** and sodium after 1 week afforded an identical ^{1}H NMR spectrum to that reported by Lawler et al.[4] (Table I) and assigned to the formation of a dianion. Quenching with D_2O as mentioned before[9] showed clearly the formation of a tetradeuteriotetrahydroperylene species (*m*/*e* 260) which oxidizes in air to give tetradeuterioperylene along with other dehydrogenated products. We believe that these spectroscopic and chemical results demonstrate that the reaction of perylene (**2**) with sodium does in fact form a tetraanion.

The ^{1}H NMR bands summarized in Table I emphasize the highly aromatic diatropic character of the neutral systems; even more so, our findings point out the aromatic character of the two quadruply charged species as manifested by their diatropicity.[11,12]

Additional studies including ^{13}C and ^{23}Na NMR spectroscopies of these systems are under way for the purpose of gaining a deeper insight into these multiply charged species.

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(3) Müllen, K. *Helv. Chim. Acta* **1978**, *61*, 2307–2317.

(4) Lawler, R. G.; Ristagno, C. V. *J. Am. Chem. Soc.* **1969**, *91*, 1534–1535.

(5) The dianion of tetracene (18π electrons) shows ^{1}H NMR bands at high field.[4]

(6) "Dictionary of Hückel Molecular Orbitals (HMO) Heilbronner and Straub"; Springer Verlag: Berlin, 1966; Section 8, 16, 20.

(7) In *THF-d_8*, recorded with the aid of Bruker WH-300 pulsed FT spectrometer operating at 300.133 MHz, deuterium lock, Aspect 2000 computer, 32K memory.

(8) The reduction of **1** to $\mathbf{1}^{2-}$ was conducted by Müllen with lithium at −80 °C.[3]

(9) Du Pont 21-490 B single focusing instrument equipped with a commercial dual CI/EI source. Reagent gas was isobutane, source temperature 160 °C. The spectra were run by Dr. Shmuel Zitrin, Mass Spectrometry Unit, Criminal Identification Division, Police Headquarters, Jerusalem.

(10) The respective triply charged species being a radical anion could not be detected by ^{1}H NMR spectroscopy.

(11) The well-accepted correlation of Schaeffer and Schneider[12] predicts that the centers of gravity of the ^{1}H NMR absorptions for **3** and **4** should appear at ca. 4.2 ppm. The data shown (Table I) emphasize the enhanced diatropicity of these tetraanions.

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Synthesis and Structure of Bis(2,4,6-tri-*tert*-butylphenyl)diphosphene: Isolation of a True "Phosphobenzene"

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In 1877 Köhler and Michaelis[1] reported the isolation of a compound which was thought to be the phosphorus analogue of azobenzene, "$C_6H_5P{=}PC_6H_5$". The phosphobenzene structure for the compound, however, was proved to be incorrect. In the early 1960's the compound was shown to have an oligomeric structure by means of molecular weight determination[2] and subsequently by X-ray crystallographic analysis.[3]

A number of reports on cyclopolyphosphine $(RP)_n$ (n = 3–6) have appeared in the literature since the structure of the phenyl derivative was elucidated.[4] Up to date the smallest cyclophosphine is $(C_2F_5P)_3$.[5] The presence of the monomeric and dimeric species

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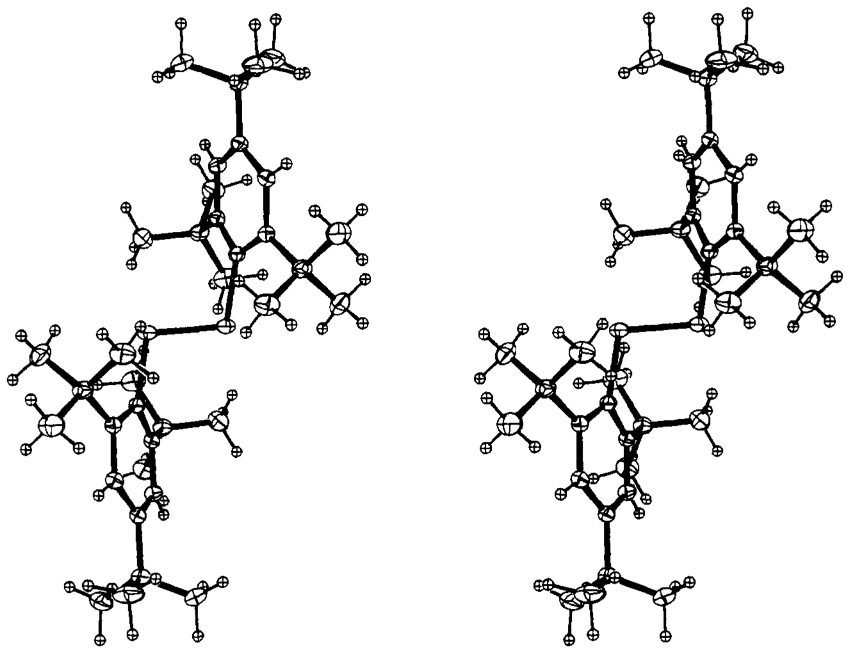
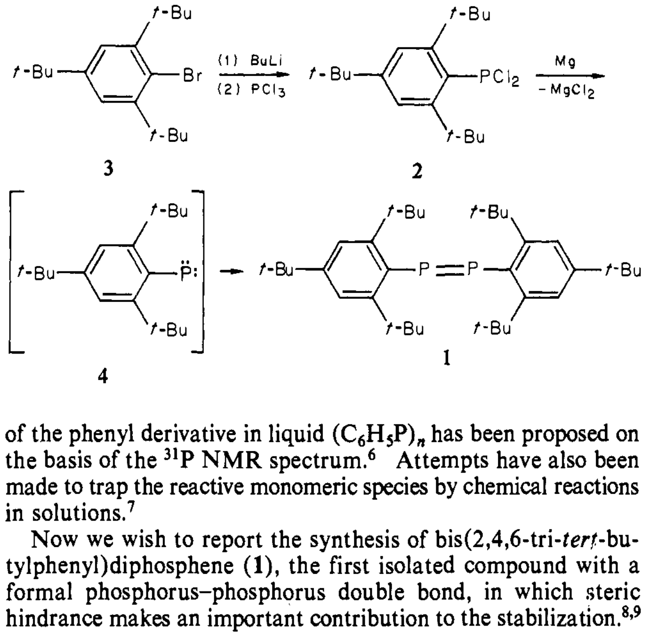


Figure 1. Stereoscopic view of bis(2,4,6-tri-*tert*-butylphenyl)diphosphene (**1**) along the twofold axis as determined by X-ray analysis.

Scheme I



of the phenyl derivative in liquid $(C_6H_5P)_n$ has been proposed on the basis of the ^{31}P NMR spectrum.[6] Attempts have also been made to trap the reactive monomeric species by chemical reactions in solutions.[7]

Now we wish to report the synthesis of bis(2,4,6-tri-*tert*-butylphenyl)diphosphene (**1**), the first isolated compound with a formal phosphorus-phosphorus double bond, in which steric hindrance makes an important contribution to the stabilization.[8,9]

The synthesis of **1** was performed according to the reaction sequence shown in Scheme I.

(2,4,6-Tri-*tert*-butylphenyl)lithium[10] was prepared in tetrahydrofuran (THF) at -78 °C. Phosphorus trichloride was added to the solution at that temperature and then refluxed for 1 h. (2,4,6-Tri-*tert*-butylphenyl)phosphonous dichloride (**2**) was obtained almost quantitatively. The Friedel-Crafts-type reaction of 1,3,5-tri-*tert*-butylbenzene with phosphorus trichloride failed to give **2**.[11] The reaction of **2** with magnesium metal in THF under argon at room temperature immediately gave an orange solution, and the solvent was removed by rotary evaporation to give an orange red solid, bis(2,4,6-tri-*tert*-butylphenyl)diphosphene (**1**), which corresponds to a dimerized product of phosphinidene intermediate **4**. Recrystallization from pentane gave an analytically pure sample (mp 175-176 °C dec), in 54% yield based on 2,4,6-tri-*tert*-butylbromobenzene (**3**). Compound **1** is thermally stable and can be handled in air. It is soluble in most organic solvents without decomposition; mass spectrum, calcd for $C_{36}H_{58}P_2$, *m/e* 552.4012; found, *m/e* 552.4012; molecular weight determination (vapor phase osmometric method: M_r 552.1 (in benzene). UV (CH_2Cl_2) λ_{max} 284 (ϵ 15660), 340 (7690), and 460 (1360) nm. ^{31}P NMR (C_6D_6) δ -59.00 (from external 85% H_3PO_4);[12] ^{1}H NMR (CCl_4) δ 7.30 (s, 4 H, aromatic), 1.45 (s, 36 H, *o-t*-Bu), and 1.35 (s, 18 H, *p-t*-Bu). Anal. Calcd for $C_{36}H_{58}P_2$: C, 78.28; H, 10.58. Found: C, 78.20; H, 10.67. The UV spectrum of **1** and the color are very similar to those of bis(2,4,6-tri-*tert*-butylphenyl)diazene,[13] supporting the structure of **1**.

Figure 1 shows a stereoscopic view of **1**[14] and indicates that two phosphorus atoms are sterically protected by the *o-tert*-butyl groups. The molecular structure has a crystallographic twofold axis.[15] Certain important bond distances and bond and dihedral angles are as follows: P-P = 2.034 (2), P-C = 1.862 (2) Å; P-P-C = 102.8 (1), C-P-P-C = 172.2 (1)°. The phosphorus-

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(7) (a) Schmidt, U. *Angew. Chem., Int. Ed. Engl.* **1975**, *14*, 523 and references cited therein. As for phosphinidene oxides and sulfides, see: (b) Yoshifuji, M.; Nakayama, S.; Okazaki, R.; Inamoto, N. *J. Chem. Soc., Perkin Trans. 1* **1973**, 2065, 2069. (c) *Bull. Chem. Soc. Jpn.* **1975**, *48*, 546, 3733. (d) *Ibid.* **1976**, *49*, 1173.

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(15) Crystallographic data of **1** (recrystallized from pentane): monoclinic, $a = 16.980$ (6), $b = 9.840$ (3), $c = 20.612$ (7) Å; $\beta = 98.75$ (5)°, $\rho_{obsd} \simeq 1.07$ g/cm^3; $Z = 4$ in space group $C2/c$. Diffractometer data (3014) were measured by $\omega/2\theta$ scan with Mo Kα radiation up to $2\theta = 50°$ of which 615 were regarded as unobserved [$I < 3\sigma(I)$]. The structure was solved by using a multisolutioin weighted tangent formula approach [Germain, G.; Main, P.; Woolfson, M. M. *Acta Crystallogr., Sect. B* **1970**, *24*, 274]. Full-matrix least-squares refinement with anisotropic temperature factors for nonhydrogen atoms and isotropic hydrogens converged to a standard crystallographic residual of 0.039 [Busing, W. R.; Martin, K. O.; Levy, H. S. "A Fortran Crystallographic Least Square Program", USAEC Report ORNL-TM-305, Oak Ridge National Laboratory, Oak Ridge, TN, 1965]. The details of the crystallographic data will be published elsewhere and the theoretical studies are in progress (Hirotsu, K.; Higuchi, T.; Matsushita, T.; Nishimoto, K.; Yoshifuji, M.; Shima, I.; Inamoto, N.).

phosphorus bond distance in **1** is much shorter than the reported average values in $(C_6H_5P)_5$ [2.217 (6) Å][16] and $(C_6H_5P)_6$ [2.237 (3) Å][17] in spite of the strong steric hindrance in **1**, indicating that the bond in the diphosphene has considerably double bond character. All intermolecular approaches correspond to the van der Waals interactions.

Reaction of **1** in carbon tetrachloride with chlorine gas at room temperature gave (2,4,6-tri-*tert*-butylphenyl)phosphonic dichloride almost quantitatively after treatment with water. The same result was obtained in the presence of methanol.

The compound **1** is the first isolated phosphobenzene with a localized P=P bond in contrast to [(trifluoromethyl)phosphinidene]tributylphosphorane[18] with a delocalized P=P bond. Compound **1** may serve as a good model for theoretical studies as well as studies in organic and inorganic chemistry. Further investigation of the chemical properties and reactions of **1** is now in progress.

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Supplementary Material Available: Table of atomic positional and thermal parameters for **1** (2 pages). Ordering information is given on any current masthead page.

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^{183}W NMR Spectroscopy: $^2J_{W-W}$ Coupling. Structural Application to 1–12 Heteropolytungstates

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Iso- and heteropolytungstates are well-known compounds,[1] but only a few X-ray structures have been published. Very recently, Acerete et al.[2,3] and Gansow et al.[4] have used tungsten NMR spectroscopy (^{183}W: spin $^1/_2$, 14.27% natural abundance, sensitivity 5.8×10^{-2} compared to ^{13}C) to delineate some trends in the electronic structure of chosen heteropolytungstates via chemical shift studies. In fact, tungsten-183 is characterized by a huge chemical range (±3000 ppm/Na_2WO_4), and any subtle change in tungsten chemical environment will be reflected on its chemical shift. Moreover, a tungsten NMR experiment is performed on solution, which allows the chemist to study time-dependent systems, as it will be shown in this communication, and the structural indications obtained through such an experiment can nicely complement an X-ray structure.[2,4,5]

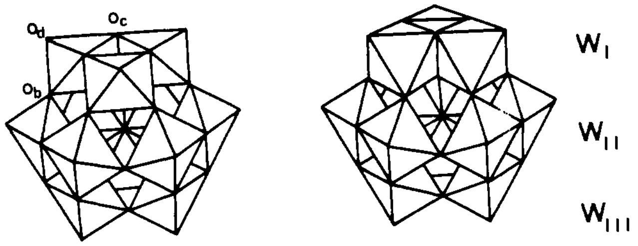

Figure 1. α and β isomerism in Keggin structure (oxygen O_a which are bound to three W are not indicated in the figure).

Heteropolytungstates belonging to 1–12 series are represented by the general formula $X^nW_{12}O_{40}^{(8-n)-}$ (X = H_2, P, B, Si, etc.). The more symmetrical structure (α type, ideal symmetry T_d) is shown in Figure 1.[6,7] In this arrangement, four W_3O_{13} moieties are clearly seen, which result in the 12 octahedrons sharing corners and linking via edges. The four O_a-type[8] oxygens define a tetrahedral cavity where the X heteroelement is found. By rotating one W_3O_{13} group by 60°, a less symmetrical β-type structure[7] (Figure 1) is derived from the α one (ideal symmetry C_{3v}). These two kinds of structures are easily discriminated in tungsten NMR spectroscopy: α structure, one singlet (12 equivalent tungsten atoms); β structure, 3 peaks in the ratio 1:2:1.

$H_2W_{12}FO_{39}^{5-}$[9] (I) belongs to the α-type series,[10] but the fluorine atom introduces a C_{3v} symmetry. Its tungsten NMR spectrum shows three types of tungsten resonances in a 1:2:1 ratio: a doublet (δ −94.3 ± 0.1, J_{W-F} = 32 ± 1 Hz) and two singlets (δ −104.1 ± 0.1, −108.6 ± 0.1). This result confirms nicely the proposed structure[11] in which the fluorine atom, bound to three tungsten atoms, replaces an O_a-type oxygen (Figure 1).

The magnetic nonequivalence of the three tungsten groups allows, for the first time, homonuclear $^2J_{W-W}$ coupling to be resolved (Figure 2). These coupling constants fall into two well-defined classes: coupling between two tungsten atoms within the same W_3O_{13} moiety (W–O_c–W bond), 5 ± 1 Hz and coupling between one tungsten atom in a W_3O_{13} group and one tungsten atom in a $W_3O_{12}F$ group (W–O_b–W bond), 22 ± 1 Hz. To these two very different coupling constant values do correspond two different kinds of bonding scheme with characteristic bond angles and W–W distances (Table I).

The β-$SiW_{12}O_{40}H_4$[15,16] molecule possesses the same symmetry as I. Its ^{183}W NMR spectrum shows[17], again, three types of tungsten atoms (δ −109.7 ± 0.1, −114.7 ± −129.8 ± 0.1; ratio 1:2:1) corresponding to the W_I, W_{II}, W_{III} peaks in Figure 1, the more intense resonance (δ −114.7) being attributed to the six central tungsten atoms (W_{II}). $^1J_{W-W}$ homonuclear couplings are

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(9) All the ^{183}W spectra have been recorded on a Bruker WM 250 spectrometer. Tungsten frequency 10.42 MHz. Recording conditions: 15-mm tubes, ca. 0.3 M heteropolyacid or heteropolyanion (sodium salt of the "tungstate X") without buffer or supporting electrolyte) in D_2O, 1-s waiting time, 60° pulse, 5000 to 20 000 scans; reference Na_2WO_4, 2 M in D_2O, temperature 294 K.

(10) Chauveau, F.; Doppelt, P.; Lefebvre, J. *J. Chem. Res. Synop.* **1981**, 155. *J. Chem. Res., Miniprint* **181**, 1937–1944. $[H_2W_{12}FO_{39}]H_5$ obtained by the procedure given in this paper is thermodynamically stable and exhibits electrochemical and spectroscopic (polarogram and UV spectrum) properties of the α series.

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