Journal of Chemical Crystallography, Vol. 36, No. 12, December 2006 (© 2006)
DOI: 10.1007/s10870-006-9147-8

4-(*p*-Methylthio)phenyl-2,6-diphenyl phosphinine: The first X-ray crystal structure of a λ^3-triaryl-phosphabenzene

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Received May 15, 2006; accepted September 5, 2006

The new donor functionalized methylthio-phosphabenzene **3** was synthesized by reaction of the corresponding pyrylium salt with $P(SiMe_3)_3$. This compound was characterized crystallographically, showing eight independent molecules in the asymmetric unit. **3** crystallized in the orthorhombic space group $Pna2_1$ (no. 33) with cell parameters $a = 48.3565(8)$ Å, $b = 7.64784(7)$ Å, $c = 40.8432(4)$ Å, $V = 15104.7(3)$ Å^3. This result represents the first crystal structure analysis of a λ^3-triaryl-phosphabenzene.

KEY WORDS: Phosphinine; phosphabenzene; crystal structure; phosphorus-heterocycle.

Introduction

λ^3-Phosphabenzenes (phosphinines), the higher homologues of pyridines, are known for many decades, due to the pioneering work of Märkl and Ashe III in the late 1960s.[1,2] These heterocycles are planar, aromatic systems in which one –CH– group of the aryl moiety is substituted by a phosphorus atom. Up to now, a few λ^3-phosphabenzenes and their corresponding transition-metal complexes have been characterized crystallographically.[3] However, an X-ray crystal structure analysis of the original compound reported by Märkl, the 2,4,6-triphenyl-phosphabenzene, has still remained elusive, even though attempts have been made before.[4]

We recently reported on the preparation of hydroxy-substituted phosphinines, which were converted into chiral bidentate phosphabenzene-phosphites and applied as ligands in the rhodium-catalyzed hydrogenation of prochiral substrates.[5,6] During the course of our investigations on functionalized phosphabenzenes, a novel methylthio substituted phosphinine has been prepared. Single crystals of this compound were obtained, which were subject to an X-ray crystal structure analysis. We report here on the synthesis and the first X-ray crystallographic characterization of a λ^3-triaryl-phosphabenzene, which resembles the original compound reported by Märkl many decades ago.

Experimental

General considerations

All reactions concerning the synthesis of compound **3** were carried out under an argon

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atmosphere using standard Schlenk techniques. The solvents were dried and distilled prior to use. Elemental analyses were obtained from H. Kolbe, Mikroanalytisches Laboratorium, Mülheim (Germany). *p*-methylhiobenzaldehyde, acetophenone and $HBF_4 \cdot Et_2O$ (54 Gew.-% in Et_2O) were obtained from Aldrich and used without further purification. $P(SiMe_3)_3$ was prepared according to the literature.[7] ^1H, $^{13}C\{^1H\}$ and $^{31}P\{^1H\}$ NMR spectra were recorded on a Varian Gemini spectrometer at 200 and 400 MHz. Chemical shifts are reported relative to tetramethylsilane for ^1H and $^{13}C\{^1H\}$ as internal reference and to H_3PO_4 85% for $^{31}P\{^1H\}$.

Synthesis of p-methylthio-benzylidene-acetophenone (1)

The chalcone **1** was prepared according to a modified patent procedure:[8] A solution of acetophenone (22.1 mL, 22.8 g, 189.5 mmol) in ethanol (32 mL) was added slowly to an ice-cold solution of NaOH (9.62 g, 240.5 mmol) in ethanol (64 mL) and water (64 mL) under vigorous stirring. Subsequently, a solution of 4-methylthiobenzaldehyde (25 mL, 28.6 g, 187.9 mmol) in ethanol (32 mL) was added and the solution was stirred for two hours at 0°C and for overnight at room temperature. Water (150 mL) was added and stirring was continued for another 12 h, during which a yellow precipitate was formed. The solid was filtered off and dried in vacuo, resulting in a yellow, fine powder. Yield: 35.0 g (137.6 mmol, 73%). ^1H NMR ($CDCl_3$): δ (ppm) = 2.48 (s, 3H, $-SCH_3$), 7.22 (d, $J_{H-H} = 8.2$ Hz, 2H), 7.51 (m, 6H), 7.75 (d, $J_{H-H} = 13.6$ Hz, 1H), 8.00 (d, $J_{H-P} = 7.0$ Hz, 2H). ^{13}C NMR ($CDCl_3$): δ (ppm) = 15.06 ($-SCH_3$), 120.91, 125.89, 128.46, 128.62, 128.85, 131.29 (C_q), 132.75, 138.26 (C_q), 142.44 (C_q), 144.37, 190.50 (CO). Anal Calcd. for $C_{16}H_{14}OS$ (254.35): C, 75.56; H, 5.55. Found: C, 75.85; H, 5.80.

Synthesis of 4-(p-Methylthio)phenyl-2,6-Diphenyl pyrylium tetrafluoroborate (2)

A solution of **1** (20.0 g, 78.6 mmol) and acetophenone (4.72 g, 39.3 mmol, 4.6 mL) in dichloroethane (20 mL) was heated to T = 75°C and a solution of HBF_4 in diethylether (52%) (13.34 g, 78.6 mmol) was added drop wise. The solution turned dark red and stirring was continued for 2.5 h. After cooling the solution to room temperature, red crystals were forming. The solution was decanted off and the dark red solid was recrystallized from methanol. Yield: 10 g (22.6 mmol, 58%). ^1H NMR (DMSO-d_6): δ (ppm) = 2.62 (s, 3H, $-SCH_3$), 7.52 (d, $J_{H-H} = 7.4$ Hz, 2H), 7.77 (m, 6H), 8.52 (m, 6H), 9.00 (s, 2H, heteroarom.-H). ^{13}C NMR (DMSO-d_6): δ (ppm) = 14.34 ($-SCH_3$), 113.95, 126.09, 128.14, 129.01, 129.59, 130.26, 130.85, 135.26, 151.03, 163.94, 169.54. ^{19}F NMR (DMSO-d_6): δ (ppm) = –148.19, –148, 25 (3:1). Anal Calcd. for $C_{24}H_{19}BF_4OS$ (442.28): C, 65.18; H, 4.33. Found: C, 65.12; H, 4.33.

Synthesis of 4-(p-Methylthio)phenyl-2,6-Diphenyl phosphabenzene (3)

3.0 g (11.97 mmol, 2.04 equiv.) of $P(SiMe_3)_3$ was added drop wise at room temperature to a stirred solution of **2** (2.6 g, 5.9 mmol) in 20 mL of acetonitrile. The resulting dark reaction mixture was heated to $T = 85$°C and subsequently refluxed for 5 h. After cooling to room temperature, the volatiles were removed under vacuum. The residue was dissolved in CH_2Cl_2 and added to an appropriate amount of silica gel (ca. 3 g). Evaporation of the solvent was followed by flash chromatography with petroleum ether/ethyl acetate (19:1). Yield: 1.2 g (3.2 mmol, 55%) of a yellow solid. ^1H NMR (C_6D_6): δ (ppm) = 1.99 (s, 3H, $-SCH_3$), 7.15 (m, 8H, m-, p-phenyl-H), 7.21, 7.26 ($2 \times$ d, $J_{H-H} = 8.4$ Hz, 7.2 Hz, $2 \times 2H$, o-, m-methylthiophenyl-H), 7.66

(d, $J_{\mathrm{H-H}} = 8.0$ Hz, 4H, o-phenyl-H), 8.06 (d, $J_{\mathrm{H-P}} = 6.0$ Hz, 2H, heteroarom.-H). ^{13}C NMR ($CDCl_3$): δ (ppm) = 15.68 (-SCH_3), 127.20 (3C), 127.60, 128.00 (3C), 128.09, 128.13, 128.39, 128.50, 128.59, 128.71, 128.93, 143.38 (2 × d, $^2J_{\mathrm{C-P}} = 16.5$, 21.8 Hz, C_β), 138.78, 131.40 (d, $^3J_{\mathrm{C-P}} = 11.9$ Hz, C_γ), 172.30 (d, $^1J_{\mathrm{C-P}} = 51.8$ Hz, C_α). ^{31}P NMR (C_6D_6): δ(ppm) = 183.5. Anal Calcd. for $C_{24}H_{19}PS$ (370.45): C, 77.81; H, 5.17. Found: C, 77.73; H, 5.11.

*Crystal structure determination of (**3**)*

Crystals of **3** suitable for X-ray diffraction were obtained by slow recrystallization from acetonitrile under an argon atmosphere.

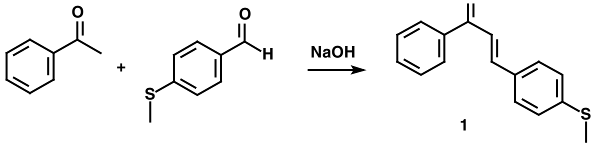
Reflections were measured on a Nonius KappaCCD diffractometer with rotating anode and graphite monochromator (λ = 0.71073 Å). The intensities were integrated with Eval14[9] using an accurate description of the crystal form and the diffraction geometry. Based on the internal R-value and the systematic extinctions, space group $Pna2_1$ (non-centrosymmetric) and Pnam (centrosymmetric) were considered. The structure was solved successfully with Direct Methods[11] in $Pna2_1$. Detailed inspection of the atomic coordinates with PLATON/ADDSYM[12] and the conformational differences between the eight crystallographically independent molecules rule out a transformation to an ordered structure in the centrosymmetric space group Pnam. Structure refinement was performed with SHELXL-97[13] on F^2 of all reflections (Table 1). Non-hydrogen atoms were refined freely with anisotropic displacement parameters. All hydrogen atoms were introduced in geometrically optimized positions and refined with a riding model. The non-centrosymmetric structure was refined as an inversion twin resulting in a twin fraction of 0.54(12). Positive residual density peaks in the difference Fourier map up to 2.14 e/Å^3 are an indication that the refinement model is only an incomplete approximation and that there must be significant disorder. Due to the disorder, not all intensity information is contained in the integrated Bragg peaks but also in additional diffuse scattering. Indeed, a close inspection of the raw CCD images shows, that all reflections *hkl* with $h = 2n + 1$ are diffuse residing on streaks in the *l* direction. This was visualized in the form of simulated "precission" images.[14] The stacking disorder for $h = 2n + 1$ is also reflected in an analysis of the normalized structure factors (E^2 values) using the SIR-97 software, which indicates a 30% pseudo-translational symmetry for $h = 2n$.[15] In order to obtain a stable least-squares refinement distance/angle (SHELXL-97/SAME) and displacement (SHELXL-97/ISOR) restraints were introduced.

Table 1. Crystal Data for **3**

Crystal data	Compound **3**
CCDC deposit no.	604687
Empirical formula	$C_{24}H_{19}PS$
Molecular weight	370.42
Crystal colour	yellow
Crystal size (mm^3)	0.66 × 0.12 × 0.09
Temperature (K)	150(2)
Crystal system	orthorhombic
Space group	$Pna2_1$ (no. 33)
a (Å)	48.3565(8)
b (Å)	7.64784(7)
c (Å)	40.8432(4)
V (Å^3)	15104.7(3)
Z	32
Calculated density (mg/m^3)	1.303
μ (mm^{-1})	0.261
Abs. correction method	multi-scan[10]
Abs. correction range	0.76–0.98
$(\sin\theta/\lambda)_{\max}$ (Å^{-1})	0.53
Reflections (measured/unique)	111884/18443
R_{int}	0.0789
Parameters/restraints	1882/3057
R_1/wR_2 [$I > 2\sigma(I)$]	0.1011/0.2338
R_1/wR_2 (all refl.)	0.1461/0.2731
S	1.061
$\rho_{\mathrm{min/max}}$ (e/Å^3)	−0.45/2.14

Geometry calculations, drawings and checking for higher symmetry were performed with the PLATON package.[12]

CCDC 604687 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The



Scheme 1. Synthesis of Chalcone **1**.

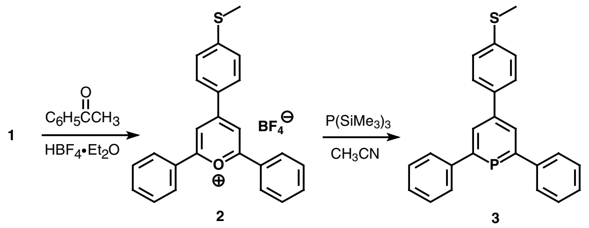
Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Results and discussion

The methylthio-functionalized chalcone (**1**) was prepared in high yields by condensation reaction of acetophenone and *p*-methylthio benzaldehyde, according to a modified patent literature (Scheme 1).[8]

Compound **1** was further converted into the corresponding dark-red pyrylium salt **2**[16] by reaction with acetophenone and $HBF_4 \cdot Et_2O$. Subsequently, treatment with $P(SiMe_3)_3$[7] gave the methylthio-functionalized phosphabenzene **3** (Scheme 2).

Phosphabenzene **3** was fully characterized by ^1H, ^{31}P and ^{13}C NMR spectroscopy as well as elemental analysis. The ^{31}P NMR spectrum of **3** shows a single resonance at $\delta = 183.5$ ppm. In the ^1H NMR spectrum a doublet at $\delta = 8.06$ ppm ($J_{H-P} = 6.0$ Hz) is characteristic for the two heteroaromatic protons, which couple to the phosphorus atom.



Scheme 2. Synthesis of 4-(*p*-methylthio)phenyl-2,6-diphenyl phosphinine **3**.

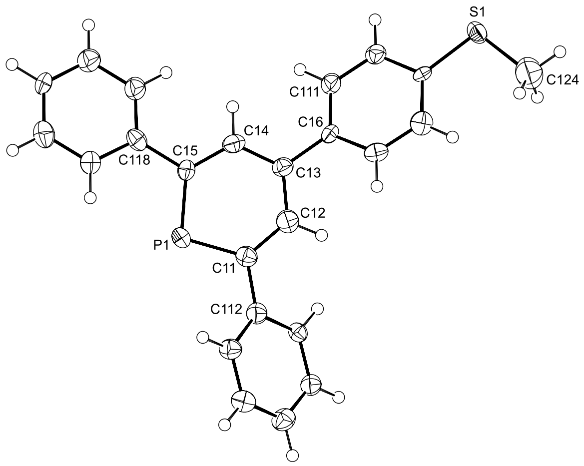


Fig. 1. Molecular Structure of **3** in the crystal (displacement ellipsoid plot[12] at 50% probability level). Only one of eight independent molecules is shown.

Yellow crystals of **3**, suitable for X-ray diffraction, were obtained by slow recrystallization from acetonitrile. **3** crystallized in space group $Pna2_1$ (orthorhombic) with eight independent molecules in the asymmetric unit. The molecular structure of one molecule is illustrated in Fig. 1.

The P-heterocycle is essentially planar due to the aromatic character of the phosphabenzene moiety. The maximal torsion angle within this ring is 7.3(13)°. The phenyl substituent in *para* position with respect to the phosphorous atom is slightly rotated out of this plane with magnitudes of the C14–13–C16–C111 torsion angles of 28.3(1)-40.2(10)°. The variation within these torsion angles is thus relatively small and the magnitudes closely resemble the expectation

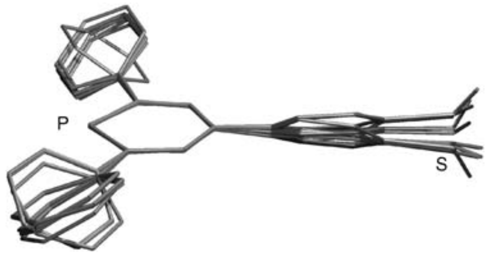


Fig. 2. Quaternion fit of the eight independent molecules of **3**. Hydrogen atoms are omitted for clarity.

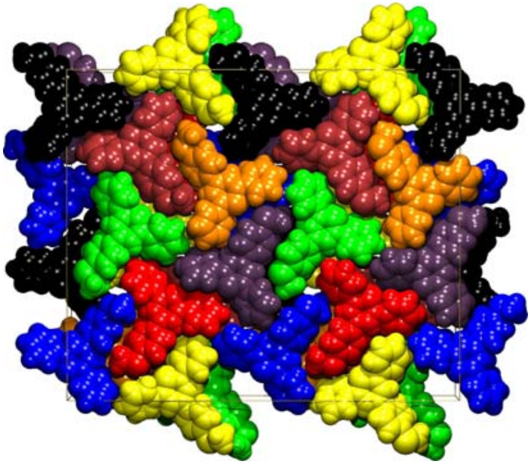


Fig. 3. Packing of the molecules of **3** in the unit cell as a space filling plot. View along the crystallographic-b axis. The eight independent molecules are shown in eight different colours (colour online).

values for biphenyl-type compounds.[17] A much bigger variation is found in the conformations in the ortho phenyl rings and S-Me group (Fig. 2).

Bond lengths and angles of the eight independent molecules were strongly restrained with respect to each other in the least-squares refinement. This resulted in P–C distances of 1.740(3)–1.747(3) Å with C–P–C angles of 101.64(13)-101.76(13)° and P–C–C intra-ring angles of 123.4(2)–123.6(2)°. The P–C bond length lies in-between a P–C single bond (triphenylphosphine: 1.83 Å[18]) and a P–C double bond (diphenylmethylenephosphaalkene: 1.66 Å[19]). As expected for an aromatic system there is no bond alternation between the C–C (1.390(4)-1.401(4) Å) and the P–C bond lengths of the P-heterocycle.

The molecules pack in layers perpendicular to the crystallographic b axis (Figs. 3 and 4) with pseudo-translational symmetry in the direction of the a axis. For clarity reasons the eight independent molecules in Fig. 3 have been visualized in eight different colours (colour online).

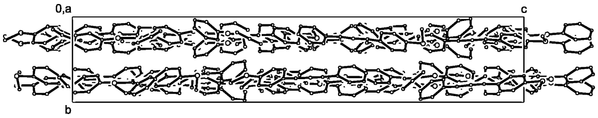


Fig. 4. Packing of the molecules of **3** in the unit cell. View along the crystallographic a-axis. Hydrogen atoms are omitted for clarity.

In summary, we have synthesized the new donor functionalized methylthio-phosphabenzene **3** by reaction of the corresponding pyrylium salt with $P(SiMe_3)_3$. This compound was characterized crystallographically, showing eight independent molecules in the asymmetric unit. This result represents the first X-ray structure analysis of a λ^3-triaryl-phosphabenzene.

Acknowledgment

This work was supported in part (ML, ALS) by the Council for the Chemical Sciences of the Netherlands Organization for Scientific Research (CW–NWO).

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