

Short Communication

X-Ray Crystal Structure of 1,2-Bis[bis(2-methylthiophenyl)phosphino]ethane

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Phosphines containing two or more phosphorus atoms linked together by hydrocarbon chains are of increasing interest as multifunctional ligands. The length and nature of the backbone connecting the phosphorus donors are major factors determining their chemistry. The property of phosphorus atoms to act easily as donor ligands in combination with different organic functional groups has extended their importance and synthetic scope. Multifunctional phosphines produce a rich coordination chemistry; an example is their use as co-catalysts and stabilising compounds.^{1–3}

Mainly three methods are used for the formation of the majority of phosphorus–carbon and phosphorus–hydrogen bonds: (1) via organometallic reagents (like *n*-BuLi or Grignard reagent) and halogenophosphines, (2) from metal phosphides or (3) by hydride reduction. In addition to these methods phosphines can also be prepared via other organophosphorus compounds.⁴

Al-Dulayammi *et al.*⁵ have prepared a range of diphosphine ligands containing additional donor groups. Their work contained the preparation of 1,2-bis[bis(2-methylthiophenyl)phosphino]ethane and its molybdenum and tungsten complexes.⁶ Mirabelli and coworkers^{7,8} have studied different bis(diphenylphosphino)alkanes, their gold(I) complexes and related compounds with medical application. These kinds of bisphosphines show anti-tumor activity in some murine tumor models.

As a part of our studies concerning multidentate ligands we have prepared and determined the X-ray crystal structure of 1,2-bis[bis(2-methylthiophenyl)phosphino]ethane.

Results and discussion

The synthesis of the ligand was performed by the reaction between lithiated *o*-bromothioanisole and

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1,2-dichlorophosphinoethane. This kind of reaction is often carried out using Grignard reagents.^{7,8} The crystal structure of 1,2-bis[bis(2-methylthiophenyl)phosphino]ethane is shown in Fig. 1. On the ethane C–C bond there is an inversion center. The structure of the ligand offers the interesting possibility for bi-, tri- or hexadentate coordination depending on the metal atoms used in the reactions.

Experimental

NMR spectra were recorded on a Bruker DPX400 spectrometer. Spectra were recorded in the solvent indicated, locked on solvent deuterium and referenced to residual solvent protons. Elemental analysis was recorded on a Perkin Elmer 2400 Series II CHNS/O analyzer. Single-

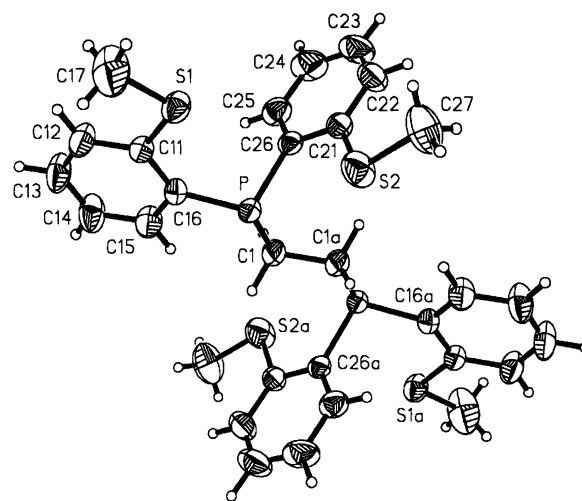


Fig. 1. X-Ray crystal structure of 1,2-bis[bis(2-methylthiophenyl)phosphino]ethane.

crystal X-ray determinations were recorded on a Siemens R3 m diffractometer. Commercially available reagents were used without further purification.

Synthesis and analysis. Liquid *o*-bromothioanisole (0.5 ml, 0.8 g, 3.8 mmol) in sodium-dried ether (10 ml) was treated dropwise with *n*-butyllithium (2.4 ml, 1.6 M in hexane, 3.8 mmol) at 0 °C under nitrogen with vigorous stirring. Stirring was continued for ca. 1 h, after which 1,2-bis(dichlorophosphino)ethane (0.17 ml, 0.11 g, 0.48 mmol) was slowly added. The resulting yellow precipitate was hydrolyzed with 0.2 M hydrochloric acid (20 ml). After 20 min stirring the white precipitate was filtered and washed with small portions of water and ether. The product (380 mg, 0.7 mmol, 69.6%) was dried *in vacuo* and recrystallized from dichloromethane. Found: C 61.37; H 5.40%. Calcd. for C₃₀H₃₂S₄P₂: C 61.83; H 5.53%. ¹H NMR (400 MHz; CDCl₃; standard TMS): δ 7.2 [H, m, Ar-H], 7.0 [H, m, Ar-H], 2.3 [3H, s, H -CH₃], 2.1 [2H, t, H -CH₂]. ³¹P-NMR (162 MHz; CDCl₃, standard H₃PO₄): δ -30.1 [1P, s].

Crystallography. The colourless crystals of C₃₀H₃₂P₂S₄ were obtained by recrystallisation from dichloromethane and mounted on a diffractometer. Diffraction data were collected at 293 K using graphite monochromated Mo K α radiation ($\lambda = 71.073$ pm). Crystal data and data collection parameters are compiled in Table 1. The total of 5226 reflections were recorded in the range $5.0 < 2\theta < 60.0^\circ$. Two standard reflections were measured every 98 reflections. The data were corrected empirically.

Table 1. Crystallographic data.

Chemical formula	C ₃₀ H ₃₂ P ₂ S ₄
Molecular weight/g mol ⁻¹	582.77
Crystal size/mm	0.30 × 0.35 × 0.35
Color	Colourless
Crystal system	Monoclinic
Space group	P2 ₁ /n
Unit cell dimensions/nm, °	<i>a</i> = 1.3586(3) <i>b</i> = 0.7729(2) <i>c</i> = 1.5570(5) β = 112.95(2)
Volume/nm ³	1.5054(7)
<i>Z</i>	2
Density _{calc.} /Mg m ⁻³	1.286
Absorption coefficient μ /mm ⁻¹	0.425
<i>F</i> (000)	612
2 θ limits/°	5.0–60.0
No. of measured reflections	5226
No. of independent reflections	4399
No. of observed reflections (<i>I</i> > 3 σ)	2954
No. of parameters refined	163
<i>F</i> _{obs} /No. of parameters ratio	18.1
Final <i>R</i> -indices [<i>I</i> > 3 σ (<i>I</i>)]	<i>R</i> ^a = 0.040, <i>R</i> _w ^b = 0.056
Goodness of fit	1.31
<i>T</i> /K	293
λ /pm	71.073 Mo K α

^a*R* = $(\sum \|F_o\| - |F_c|) / \sum \|F_o\|$. ^b*R*_w = $[\sum w(|F_o| - |F_c|)^2 / \sum w|F_o|^2]^{1/2}$, $w = w[1.0 - (\Delta F/6\sigma|F|)^2]$, where *w* was a Chebyshev polynomial for *F*_c.

The structure was solved by direct methods including full-matrix least-squares refinements using the Siemens SHELXTL PLUS system. Fractional coordinates and equivalent isotropic factors are listed in Table 2. Selected bond distances and angles are listed in Table 3.

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Table 2. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement coefficients (in pm²).

Atom	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>	<i>U</i> (eq) ^a
S(1)	3637(1)	1414(1)	4554(1)	4.6(1)
S(2)	2983(1)	179(1)	6925(1)	6.3(1)
P	1470(1)	1036(1)	4851(1)	3.3(1)
C(1)	63(2)	363(3)	4568(1)	4.2(1)
C(11)	2428(2)	1689(3)	3571(1)	3.5(1)
C(12)	2411(2)	2174(4)	2698(2)	5.3(1)
C(13)	1459(2)	2427(4)	1955(2)	6.4(1)
C(14)	500(2)	2185(4)	2049(2)	6.3(1)
C(15)	504(2)	1664(3)	2904(2)	5.0(1)
C(16)	1458(2)	1409(3)	3681(1)	3.4(1)
C(21)	2729(2)	-1510(3)	6091(2)	4.0(1)
C(22)	3113(2)	-3197(3)	6326(2)	5.7(1)
C(23)	2870(2)	-4461(3)	5651(2)	6.8(1)
C(24)	2273(3)	-4086(3)	4730(2)	6.6(1)
C(25)	1872(2)	-2418(3)	4481(2)	4.8(1)
C(26)	2087(2)	-1124(2)	5155(1)	3.4(1)
C(17)	4609(2)	2438(6)	4218(2)	9.8(2)
C(27)	3882(3)	-770(5)	7996(2)	8.6(1)

^a*U*(eq) is defined as one third of the trace of the orthogonalized *U*_{ij} tensor.

Table 3. Selected bond distances (in pm) and angles (in °).

Bond distances		Angles	
S(1)–C(11)	176.8(2)	C(11)–S(1)–C(17)	103.7(1)
S(1)–C(17)	178.4(4)	C(21)–S(2)–C(27)	104.3(1)
S(2)–C(21)	177.8(2)	C(1)–P–C(16)	101.4(1)
S(2)–C(27)	179.5(3)	C(1)–P–C(26)	97.5(1)
P–C(1)	186.1(2)	C(16)–P–C(26)	102.9(1)
P–C(16)	183.7(2)	P–C(1)–C(1A)	110.6(2)
P–C(26)	184.5(2)	S(1)–C(11)–C(12)	122.0(2)
C(1)–C(1A)	152.8(5)	S(1)–C(11)–C(16)	118.2(2)
C(11)–C(12)	140.0(3)	C(12)–C(11)–C(16)	119.7(2)
C(11)–C(16)	141.1(3)	C(11)–C(12)–C(13)	120.7(3)
C(12)–C(13)	137.2(3)	C(12)–C(13)–C(14)	120.6(3)
C(13)–C(14)	138.1(4)	C(13)–C(14)–C(15)	119.3(2)
C(14)–C(15)	138.8(4)	C(14)–C(15)–C(16)	121.8(2)
C(15)–C(16)	139.9(3)	P–C(16)–C(11)	119.8(1)
C(21)–C(22)	139.9(3)	P–C(16)–C(15)	121.8(2)
C(21)–C(26)	140.8(3)	C(11)–C(16)–C(15)	117.8(2)
C(22)–C(23)	137.6(4)	S(2)–C(21)–C(22)	123.2(2)
C(23)–C(24)	137.6(4)	S(2)–C(21)–C(26)	117.8(2)
C(24)–C(25)	139.4(3)	C(22)–C(21)–C(26)	119.0(2)
C(25)–C(26)	139.5(3)	C(21)–C(22)–C(23)	120.5(2)
		C(22)–C(23)–C(24)	121.0(2)
		C(23)–C(24)–C(25)	119.4(3)
		C(24)–C(25)–C(26)	120.7(2)
		P–C(26)–C(21)	119.5(2)
		P–C(26)–C(25)	121.0(1)
		C(21)–C(26)–C(25)	119.3(2)

References

1. Mayer, H. A. and Kaska, W. C. *Chem. Rev.* 94 (1994) 1239.
2. Stelzer, O. and Langhans, K. P. In: Hartley, F. R. Ed., *The Chemistry of Organo-phosphorus Compounds*, John Wiley & Sons, Chichester 1990, Vol. 1, Chap. 8.
3. Levason, W. In: Hartley, F. R. Ed., *The Chemistry of Organophosphorus Compounds*, John Wiley & Sons, Chichester 1990, Vol. 1, Chap. 15.
4. Gilheany, D. G. and Mitchell, C. M. In: Hartley, F. R. Ed., *The Chemistry of Organophosphorus Compounds*, John Wiley & Sons, Chichester 1990, Vol. 1, Chap. 7.
5. Al-Dulaymmi, M. F. M., Hitchcock, P. B. and Richards, R. L. *J. Organomet. Chem.* 338 (1988) C31.
6. Al-Dulaymmi, M. F. M., Hitchcock, P. B. and Richards, R. L. *Polyhedron* 10 13 (1991) 1549.
7. Mirabelli, C. K., Hill, D. T., Faucette, L. F., McCabe, F. L., Girard, G. R., Bryan, D. B., Sutton, B. M., Bartus, J. O., Crooke, S. T. and Johnson, R. K. *J. Med. Chem.* 30 (1987) 2181.
8. Hill, D. T., Johnson, R. K. and Mirabelli, C.K. *Eur. Pat. Appl.* 85300681.5 (1985).

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