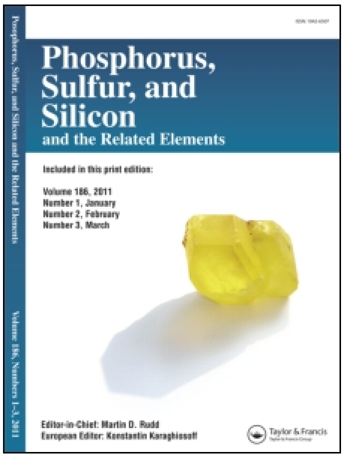

Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

SYNTHESIS AND MOLECULAR STRUCTURE OF Mes(H)P-P(H)Mes (Mes = 2,4,6-$Me_3C_6H_2$)

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To cite this Article Kurz, Stefan , Oesen, Hannes , Sieler, Joachim and Hey-hawkins, Evamarie(1996) 'SYNTHESIS AND MOLECULAR STRUCTURE OF Mes(H)P-P(H)Mes (Mes = 2,4,6-$Me_3C_6H_2$)', Phosphorus, Sulfur, and Silicon and the Related Elements, 117: 1, 189 — 196

To link to this Article: DOI: 10.1080/10426509608038785

URL: http://dx.doi.org/10.1080/10426509608038785

Phosphorus, Sulfur, and Silicon, 1996, Vol. 117, pp. 189–196
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SYNTHESIS AND MOLECULAR STRUCTURE OF Mes(H)P-P(H)Mes (Mes = 2,4,6-$Me_3C_6H_2$)

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(Received 29 June 1995; Revised 11 April 1996; In final 10 June 1996)

$Cp^\circ_2\overline{Zr(PMesPMes)}$ ($Cp^\circ = \eta^5$-C_5Me_4Et, Mes = 2,4,6-$Me_3C_6H_2$) reacts with phenylacetylene with cleavage of the Zr-P bonds and formation of Mes(H)P-P(H)Mes (**1**). **1** is also obtained from LiPHMes and 1,2-dibromoethane. The ^{31}P NMR spectrum of **1** shows the presence of both isomers (d,l and meso form). A crystal structure determination carried out on meso-Mes(H)P-P(H)Mes showed that in the solid state the bulky Mes groups have a *trans* arrangement.

Keywords: Dimesityldiphosphane; synthesis; molecular structure of meso-Mes(H)P-P(H)Mes

INTRODUCTION

In 1966 Issleib et al. reported that the reaction of zirconocene dibromide with $LiPR_2$ (R = Et, Bu) occurs with reduction to trivalent products and concomitant formation of P_2R_4.[1] Accordingly, when zirconocene dichloride is reacted with LiPHR (R = Bu^t, adamantyl) $P_2H_2R_2$ is formed as the oxidation product.[2] Although several diphosphanes of this type have been reported in the literature and studied by NMR spectroscopy,[3] there is only information on the solid-state structures of tetrasubstituted diphosphanes[4] P_2R_4 available to date.

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RESULTS AND DISCUSSION

During our investigation into the reactivity of the zirconocene diphosphene complex $Cp^{\circ}_2\overline{Zr(PMesPMes)}$ (Cp° = η^5-C_5Me_4Et, Mes = 2,4,6-$Me_3C_6H_2$) we observed that phenylacetylene cleaves the Zr-P bond with protonation of the $P_2Mes_2{}^{2-}$ ligand and formation of Mes(H)P-P(H)Mes (**1**) and $Cp^{\circ}_2Zr(C{\equiv}CPh)_2$.[5] Hydrolysis of $Cp''_2\overline{M(PRPR)}$ (Cp'' = η^5-$C_5H_3(SiMe_3)_2$, M = Zr, Hf, R = Ph; M = Zr, R = Bu^t) yields both isomers of the diphosphane R(H)P-P(H)R and $Cp''_2M(OH)_2$.[6] Similarly, cleavage of the Zr-P bond in $Cp^*_2\overline{(Zr(PMesPMes)}$ (Cp^* = η^5-C_5Me_5) by protic reagents was observed by D. W. Stephan et al.[7] The diphosphane **1** is also formed as a minor product in reactions of LiPHMes with zirconocene dichlorides.[8] However, no attempts were made to isolate **1** from these reactions. A high yield synthesis of **1** is the reaction of LiPHMes with 1,2-dibromoethane (Exp. Section). Similarly, Ph(H)P-P(H)Ph was obtained from KPHPh and 1,2-dibromoethane at −78°C.[3f]

Colourless crystals of **1** are obtained on cooling a toluene solution to −30°C. In the ^{31}P NMR spectrum, both diastereomers of **1** are observed (vide infra), i.e. no fractional crystallisation occured. Under the microscope the crystals all appear like (rhombohedral) and it can be seen that the rhombohedra are composed of fragments having the same shape, so that mechanical separation of the diastereomers was not possible.

Like the diastereomeric mixture of (2,4,6-$Bu^t_3C_6H_2$)(H)P-P(H)(2,4,6-$Bu^t_3C_6H_2$)[3a], (m.p. 144–147°C for a 5:1 mixture of d,l/meso), **1** exhibits a melting range. The majority of the substance melts in the range 77–85°C, and the remainder—crystals suspended in the initial melt—in the range 95–100°C.

In the i.r. spectrum, **1** exhibits the absorptions expected for the Mes ligands and the ν(PH) vibration at 2315 cm^{-1}. However, for Ph(H)P-P(H)Ph, two isomers of which are also present, two sharp signals were observed in the Raman spectrum at −140°C (2278 and 2283 cm^{-1}), while at 30°C only one broad absorption is observed at 2295 cm^{-1}.[3f] In the mass spectrum of **1**, the signal of highest intensity is the molecular ion peak at m/z 302.

In general, the three conformations shown in Figure 2 are possible for each of the two isomers. While for the less bulky Ph(H)P-P(H)Ph the *gauche* orientation of the lone pairs was assumed to be favoured (Figure 2, conformers A and D),[3f] comparable diphosphanes with sterically demanding ligands [$P_2H_2R_2$ with R = 2,4,6-$Bu^t_3C_6H_2$,[3a,3c] $C(SiMe_3)_3$[3e]] show the presence of conformers A and F with a mutually *trans* arrangement of the bulky substituents. However, while Bu^t(H)P-P(H)Bu^t [206.6 Hz (d,l) and 162.7 Hz (meso)][3g] and $(SiMe_3)_3C$(H)P-P(H)$C(SiMe_3)_3$ (139.7 and 351.5 ppm)[3e] exhibit a large difference in the $^1J_{PP}$ coupling constants, there is only a minor difference between those of the 2,4,6-

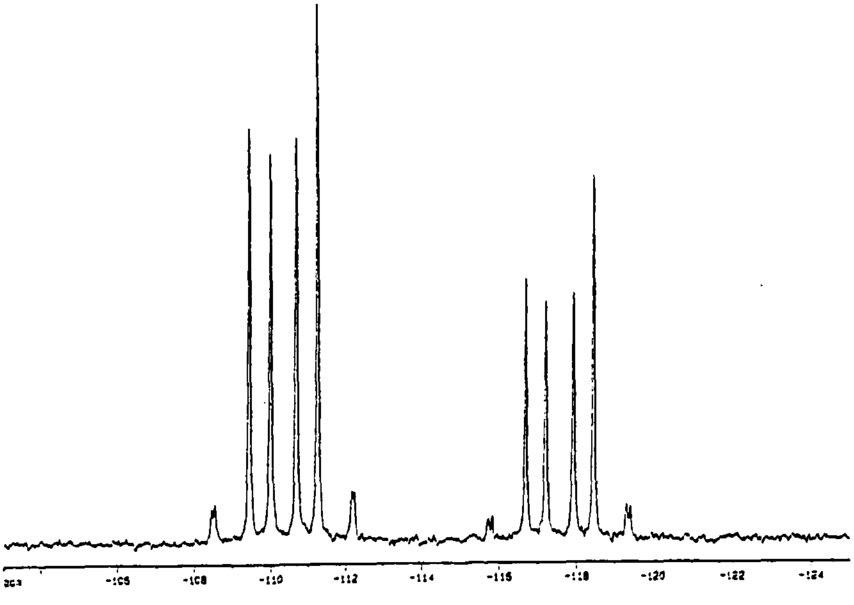

FIGURE 1 Proton coupled ^{31}P NMR spectrum of **1**.

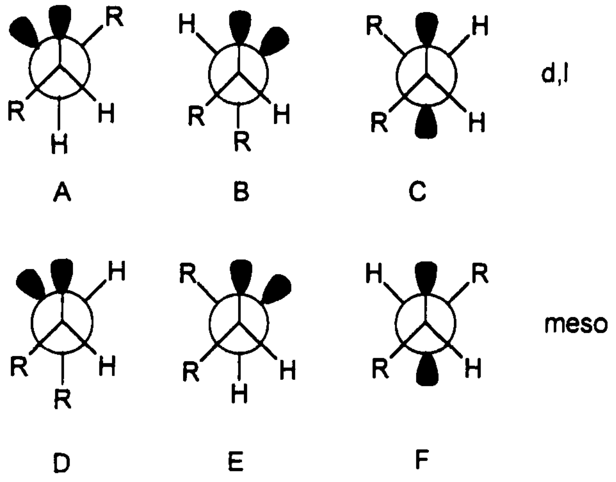

FIGURE 2 Possible conformations for the meso and d,l isomers of **1**.

$Bu^t{}_3C_6H_2$ derivative (191.8 and 190.6 ppm)[3a]. In comparison, for **1** the presence of conformers A and F appears probable for steric reasons, the difference in the chemical shifts of the two isomers being 7.2 ppm.

The ${}^{31}P\{{}^1H\}$ NMR spectrum of a solution of crystalline **1** shows singlets for both isomers of Mes(H)P-P(H)Mes, which split into multiplets on proton coupling [-109.9 ppm (d,l) and -117.1 ppm (meso); 60% d,l, 40% meso] (Figure 1). The ratio of meso and d,l isomers is not dependent on temperature. The ${}^1H$ NMR spectrum shows P-H resonances for the two isomers at 4.52 ppm, m (d,l) and 4.60 ppm, m (meso). The coupling pattern is that of an AA'XX' system. Observed and calculated coupling constants are given in Table I.[9,10] The assignment of meso and d,l isomers was made by comparison with the diphosphane $(2,4,6\text{-}Bu^t{}_3C_6H_2)(H)P\text{-}P(H)(2,4,6\text{-}Bu^t{}_3C_6H_2)$[3d], which shows comparable chemical shifts (d,l: -63.1 ppm, meso: -63.9 ppm) and coupling constants. If the dependence of vicinal ${}^3J_{HCCH}$ coupling constants on torsion angle (0° or 180°: large values, 90°: small values) is also applicable to the ${}^3J_{H(1)PPH(2)}$ coupling constants in R(H)P-P(H)R (R = $2,4,6\text{-}Bu^t{}_3C_6H_2$, $2,4,6\text{-}Me_3C_6H_2$), the signal which exhibits the larger ${}^3J_{H(1)PPH(2)}$ coupling constant corresponds to the meso isomer F (torsion angle 180°). Thus, the following assignments can be made for **1**: ${}^3J_{H(1)PPH(2)} = 7.8$ Hz (meso) and ${}^3J_{H(1)PPH(2)} = 4.8$ Hz (d,l), Table I.

A crystal structure determination was carried out on colourless crystals of **1**. **1** crystallises in the monoclinic space group $P2_1/c$. The centre of the P1-P1a bond coincides with a crystallographic inversion centre which generates the atoms designated (a) (Figure 3). The Mes ligands are *trans* to one another. The position of the P-H protons was determined from difference maps and, therefore, determination of the conformation (F, meso) in the solid state was possible.

However, as a ${}^{31}P$ NMR spectrum of crystalline **1** showed the presence of both conformers A and F in solution, crystals of both isomers are present in the solid, and it was clearly by chance that a crystal of this diastereomer was selected. Several attempts were made to pick a crystal of the d,l isomer, without success.

TABLE I Calculated coupling constants for **1** (standard deviation: ca ± 1 Hz) (observed coupling constants are given in parentheses)

d,l—MesP(H)-P(H)Mes	*meso—MesP(H)-P(H)Mes*
${}^1J_{PP} = 184.0$Hz(181)	${}^1J_{PP} = 175.0$Hz(175)
${}^1J_{PH} = 204.3$Hz(208)	${}^1J_{PH} = 202.0$Hz(205)
${}^2J_{P(1)H(2)} = 14.6$Hz (14)	${}^2J_{P(1)H(2)} = 10.5$Hz (11)
${}^3J_{H(1)H(2)} = 4.8$Hz	${}^3J_{H(1)H(2)} = 7.8$Hz

While for P_2R_4 (R = Bu^t,[4a] Cy[4b]) a *gauche* orientation of the lone pairs is observed, in P_2Mes_4[4c] the lone pairs adopt a *trans* arrangement due to the steric effect of the mesityl groups.

The P1-P1a [2.2284(11) Å] and P1-C1 [1.837(2) Å] bond lengths are in the range expected for P-P or P-C single bonds.[4] The C1-P1-P1a [98.33(6)°] and H1-P1-P1a [97.7(13)°] bond angles are smaller than expected for a tetrahedral environment and smaller than in P_2R_4 [R = Bu^t: 121.6(4),[4a] R = Cy: 108.0(3), 107.4(3),[4b] R = Mes: 111.4, 96.7°[4c]]. The P1-H1 bond length of **1** [1.31(3) Å] is in the range observed for metal-bound phosphanido ligands (e.g., L_nZr-PHR with R = 2,4,6-Pr$^i_3C_6H_2$: P-H 1.25(3) Å[11a]; R = 2,4,6-Bu$^t_3C_6H_2$: P-H 1.50(4) Å[11b]).

EXPERIMENTAL

General: All manipulations were carried out in an atmosphere of purified and dried argon. All solvents were rigorously purified and distilled under argon prior to use. NMR: Bruker ARX 250 and DRX 400 (250 or 400 MHz, ^{1}H, standard internal solvent; 101 or 162 MHz, ^{31}P, standard external 85% H_3PO_4). The i.r. spectrum was recorded as a KBr mull in the range 300–4000 cm^{-1}. MS: Varian

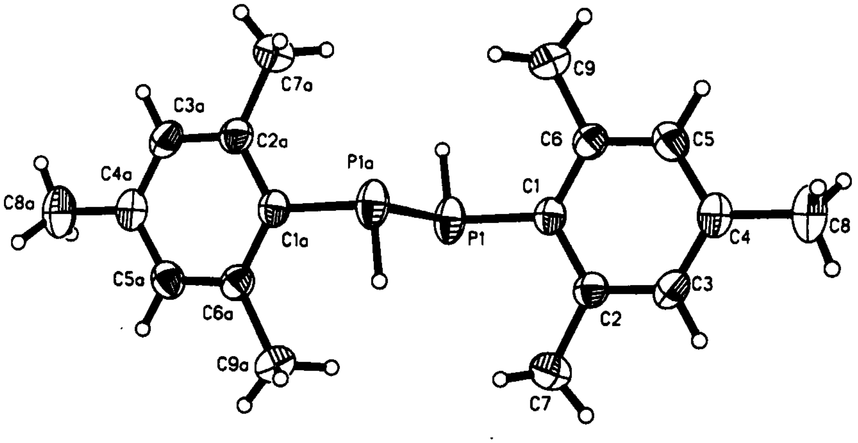

FIGURE 3 Molecular structure of meso-Mes(H)P-P(H)Mes showing the atom numbering scheme employed (SHELXTL Plus, 50% probability). Selected bond lengths and angles are as follows: P1-C1 1.837(2), P1-P1a 2.2284(11), P1-H1 1.31(3), C1-C2 1.409(3), C1-C6 1.414(3), C2-C3 1.389(3), C2-C7 1.513(3), C3-C4 1.383(3), C4-C5 1.387(3), C4-C8 1.509(3), C5-C6 1.383(3), C6-C9 1.507(3), C1-P1-P1a 98.33(6), H1-P1-P1a 97.7(13), C1-P1-H1 102.3(14), P1-C1-C2 118.7(2), P1-C1-C6 122.3(2), C2-C1-C6 119.0(2), C1-C2-C3 119.4(2), C1-C2-C7 121.6(2), C3-C2-C7 119.0(2), C2-C3-C4 122.1(2), C3-C4-C5 117.8(2), C3-C4-C8 121.7(2), C5-C4-C8 120.4(2), C4-C5-C6 122.5(2), C1-C6-C5 119.1(2), C1-C6-C9 121.9(2), C5-C6-C9 119.0(2).

MAT 711 (El, 70eV, 180°C). The melting point was determined with a Kofler-Boëtius apparatus and is uncorrected. $Cp^{\circ}_2\overline{Zr(PMesPMes)}$[5] and LiPHMes[5] were prepared according to literature procedures. Phenylacetylene (Fluka) and 1,2-dibromoethane are commercially available and were dried prior to use.

Dimesityldiphosphane

1) Reaction of $Cp^{\circ}_2\overline{Zr(PMesPMes)}$ with PhC≡CH

0.10 g (0.11 ml, 0.98 mmol) phenylacetylene is added to a green solution of 0.32 g (0.64 mmol) $Cp^{\circ}_2\overline{Zr(PMesPMes)}$ in 40 ml toluene. The resulting red solution is stirred at room temperature for 15 h. Then the volume is reduced to ca. 10 ml and the solution kept at −30°C. After 3 d colourless crystals of **1** are obtained (ca. 150 mg, ca. 78%).

2) Reaction of LiPHMes with 1,2-Dibromoethane

A slurry of 1.0 g (6.3 mmol) LiPHMes in 50 ml toluene is cooled to −30°C. Then a solution of 0.59 g (3.1 mmol) 1,2-dibromoethane in 10 ml of toluene is added with stirring. The mixture is allowed to warm to room temperature over night. LiBr is isolated by filtration and washed twice with 10 ml of toluene. The toluene solution is concentrated to 15 ml volume and kept at −30°C. After several days colourless crystals of **1** are obtained (0.9 g, 94%).

Properties and Spectroscopic Data of 1

M.p.: melting range 77–85 and 95–100°C (see above). A ratio of 3:2 for the d,l and meso isomers is observed in the NMR spectra. ^{31}P NMR (C_6D_6): −109.9 ppm, m (d,l), −117.1 ppm, m (meso). ^{1}H NMR (C_6D_6, ppm): 6.70 (s, 4H, 2,4,6-$Me_3C_6\mathit{H}_2$, d/l), 6.68 (s, 4H, 2,4,6-$Me_3C_6\mathit{H}_2$, meso), 4.52 (m, 2H, P-H, d,l), 4.60 (m, 2H, P-H, meso), 2.28 (s, 6H, o-Me in 2,4,6-$Me_3C_6H_2$, d/l), 2.31 (s, 6H, o-Me in 2,4,6-$Me_3C_6H_2$, meso), 2.04 (s, 3H, p-Me in 2,4,6-$Me_3C_6H_2$, meso), 2.06 (s, 3H, p-Me in 2,4,6-$Me_3C_6H_2$, d/l). MS (El, m/z): 302 (M^+, 100.00%), 287 (M^+ − CH_3, 2.20%), 269 (M^+ − $2CH_3$ − 2H, 35.56%), 182 ($P\text{-}PMes^+$, 9.92%), 151 ($P(H)Mes^+$, 94.56%), 119 (Mes^+, 43.42%), 105 ($Me_2C_6H_2{}^+$, 37.55%), and fragmentation products thereof. The observed isotope pattern of the molecular ion peak at m/z 302 is in good agreement with the calculated isotope distribution. I.r. spectrum (KBr, cm^{-1}): 2315 (s, νPH).

Crystal Data of Mes(H)P-P(H)Mes

$C_{18}H_{24}P_2$, M_r = 302.31, monoclinic, space group $P2_1/c$ (No. 14), a = 12.1416(14), b = 8.2960(10), c = 8.6314(10) Å, β = 99.996(2)°, U = 856.2(2) $Å^3$, Z = 2, D_C = 1.173 g cm^{-3}, μ = 2.43 cm^{-1}, 1223 independent reflections, F(000) = 324, final R indices: $R1$ = 0.0489, $wR2$ = 0.0941 (all data); $R1$ = 0.0400, $wR2$ = 0.0897 [$I > 2\sigma(I)$], [SMART CCD area detector system, Fa. Siemens, Mo-Kα radiation, λ = 0.71069, T = 203(2) K]. Further details of the X-ray structure analysis (thermal parameters, H atom coordinates, structure factors) have been deposited with the Fachinformationszentrum Energie, Physik, Mathematik, D-76344 Eggenstein-Leopoldshafen 2, Germany. This material may be requested, quoting the literature reference, the names of the authors, and the deposition number CSD 58852.

Acknowledgements

We gratefully acknowledge support of this work by the Deutsche Forschungsgemeinschaft and Fonds der Chemischen Industrie and thank the company Chemetall for a generous donation of lithium alkyls. We are indebted to Dipl. Chem. C. Frenzel, University of Leipzig, for the NMR spectra and Mr. D. Müller, University of Karlsruhe, for the mass spectrum.

Professor E. Hoyer on the occasion of his 65. birthday

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