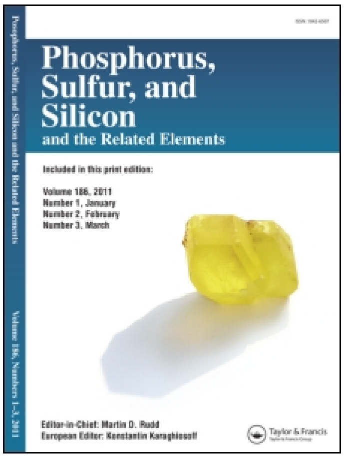

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(HYDROXYALKENYL)-DIPHENYLPHOSPHINE OXIDES, THEIR LITHIUM SALTS AND ZINC COMPLEX

Jordanka Petrova[a]; Erhard T. K. Haupt[b]; Snezhana Momchilova[a]; John C. Tebby[c]
[a] Faculty of Chemistry, Sofia University, Sofia, Bulgaria [b] Institute of Inorganic and Applied Chemistry, University of Hamburg, Hamburg 13, FRG [c] Staffordshire University, Division of Chemistry, School of Sciences, Stoke-on-Trent, UK

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(HYDROXYALKENYL)-DIPHENYLPHOSPHINE OXIDES, THEIR LITHIUM SALTS AND ZINC COMPLEX

JORDANKA PETROVA,*† ERHARD T. K. HAUPT,‡
SNEZHANA MOMCHILOVA† and JOHN C. TEBBY§

†Faculty of Chemistry, Sofia University, 1 J. Bourchier Avenue,
1126 Sofia, Bulgaria; ‡Institute of Inorganic and Applied Chemistry,
University of Hamburg, Martin-Luther-King Pl. 6, D-20146 Hamburg 13, FRG;
§Staffordshire University, Division of Chemistry, School of Sciences,
College Road, Stoke-on-Trent ST4 2DE, UK

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The synthesis and structural characteristics of the lithium salt and zinc complex of $Ph_2P(O)CPh{=}CHOH$ **1** are described. While the lithium salt **2** is a stable mixture of (E)- and (Z)-enolate forms **2b** and **2c**, the zinc complex **3** seems to coordinate as a chelate of phosphonate and acetate groups with some dynamic behaviour in solution. Additionally, the oxide $Ph_2P(O)CH{=}CHC[P(O)Ph_2]{=}CHOH$ **5** and its lithium salt **6** are obtained and their structures and conformations elucidated by NMR spectroscopy (^1H, ^{31}P, ^{13}C).

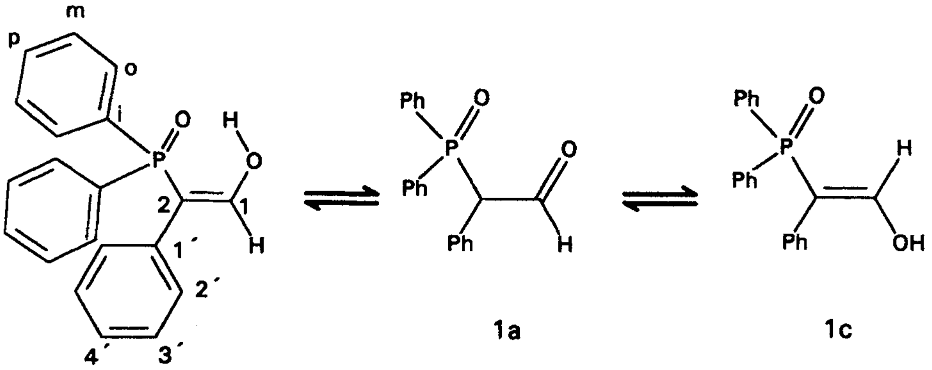
Key words: 2,4-Bis(diphenylphosphinyl)-1,3-butadienol, hydroxyalkenyldiphenylphosphine oxides, lithium salt, NMR (^1H, ^{31}P, ^{13}C).

INTRODUCTION

β-Ketophosphine oxides coordinate to metals in a variety of reactions and structures. The properties of the complexes with transition metals[1–4] and lanthanides[5,6] have been studied extensively. Investigations about the coordination chemistry of the enol forms of the corresponding aldehydes, as well as their keto-enol tautomerism, however, are not wide-spread.[7–10] Our recent study on the stereochemistry of alkali salts and transition metal complexes of enol forms of phosphonoacetaldehydes[11–13] showed some specificity in comparison to β-dicarbonyl-compounds. In the present work we report the synthesis and structure of the lithium salt and zinc complex of 2-(diphenylphosphinyl)-2-phenyl-ethenol **1** (**2** and **3** respectively) as well as data concerning the stereochemistry of the starting ligands **1** and 2,4-bis(diphenylphosphinyl)-1,3-butadienol **5** and the lithium derivatives **6** of the latter.

RESULTS AND DISCUSSION

The phosphine oxide **1** (m.p. 222–224°C) was prepared using the method described by Regitz.[7,14] On the basis of IR-spectral data (1140 cm^{-1} = $\nu_{P=O}$, 1637 cm^{-1} = $\nu_{C=C}$ and 2630 cm^{-1} = ν_{OH}) and referring to a report about keto-enol tautomerism



1b **1a** **1c**

SCHEME 1

of phosphonoacetaldehyde[15] the authors[7,14] consider this product to be the (Z)-enol. Later, IR and NMR studies of other authors[12,16,17] have shown that the bands at about 1630 and 2600–2700 cm^{-1} in phosphonoaldehydes are characteristic of (E)-enols. According to IR (in nujol) and NMR data (in DMSO-d_6), the product we obtained is almost pure (E)-enol **1c**. Only a small quantity of the aldehyde **1a** (Scheme 1) is observed in solution, but not in the solid state. In the literature,[8,9] only the ^1H-NMR of the aldehyde **1a** (m.p. 189–190°C, δ_H 9.95) in $CDCl_3$ is described. The NMR spectrum (in DMSO||) of the major product **1** (Table I) obtained by us showed a doublet at δ_H 6.73, J(HP) 11.1 Hz (H1) which is consistent with *cis*-oriented phosphorus and hydrogen atoms in **1c**, the ratio (E)-enol **1c**/aldehyde **1a** being 8:1. The ^{31}P-NMR spectrum showed the presence of one major signal at δ_P 27.33 and a small one at δ_P 23.29. In accordance with the ^1H-NMR data, we attribute the signal at δ_P 23.29 to the aldehyde **1a** and that at δ_P 27.33 to the (E)-enol **1c**. In order to measure the *cis* P—C═C—H coupling constants in similar phosphine oxides we synthesized the ethers $Ph_2P(O)CPh{=}CHOMe$ **7** and $Ph_2P(O)CH{=}CHOEt$.[7] It was shown by means of ^1H-NMR, that the values of ^3J(HP) are 10.3 (11[7]) and 10.9 Hz respectively and the *trans* H—C═C—H coupling constant for the latter was 13.7 Hz, which confirm the (E)-configuration of both compounds. Additionally, the value of ^2J(PC) 26.1 Hz in the ^{13}C NMR¶ of **1c** is in agreement with literature data for keto- and aldo-phosphonates[12,18] and confirms also its (E)-configuration. The high value of the melting point and the very low solubility of the compound is an indication of possible dimeric or oligomeric structures (Figure 1). Recently, our crystallographic study on the structure of substituted β-hydroxy-ethylphosphonates showed similar centrosymmetric dimers of hydrogen-bonded molecules.[19] The lithium derivative **2** was obtained using *n*-butyl-lithium in tetrahydrofuran at low temperature in an argon atmosphere. The salt is very

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||The product **1** is poorly soluble in most organic solvents.

¶^{13}C NMR assignments of the phosphine oxide **1** (see Experimental) are based on the results of the APT spectrum, coupling constants and relative intensities of the signals.

TABLE I

^{1}H and ^{31}P NMR data of phosphine oxides **1–3**, **5** and **6**

Compound (solvent)	δ_H(ppm), J(Hz)					δ_P(ppm)
	H1	H2	H3	H4	Others	
1a	9.73	5.66	–	–	7.07-7.69	23.29
(DMSO-d_6)	HP=2.3	HP=11.8			$H_{arom.}$	
1c	6.73	–	–	–	7.07-7.69	27.33
(DMSO-d_6)	HP=11.1				$H_{arom.}$	
2b	8.54	–	–	–	–	28.73
(DMSO-d_6)	HP=26.9					
2c	7.88	–	–	–	see exp.	32.57
(DMSO-d_6)	HP=6.7					
3	7.86	–	–	–	6.8-7.6	42.03
($CDCl_3$)	HP=28.9				$H_{arom.}$	
					1.72 CH_3 acetate	
5	6.83	–	7.35	6.40	7.4-7.75	23.62(P4)
(DMSO-d_6)	H1P2=9.3		H3H4=17.4	H3H4=17.4	$H_{arom.}$	27.84(P2)
	H1P4=1.9		H3P2=21.3	H4P4=24.4		
			H3P4=21.3			
6-E	8.15	–	7.24	5.80	–	25.34(P4)
(DMSO-d_6)	H1P2=3.1		H3H4=17.0	H3H4=17.0		29.61(P2)
	H1P4=3.1		H3P2=22.4	H4P4=26.5		
			H3P4=22.4			
6-Z	8.83	–	7.03	4.89	–	24.12(P4)
(DMSO-d_6)	H1P2=25.1		H3H4=17.4	H3H4=17.4		30.33(P2)
			H3P2=17.5	H4P4=25.5		
			H3P4=21.2			

hygroscopic and poorly soluble in most organic solvents. The elemental analysis indicates the coordination of half a molecule of water, which is also detected in the IR- and ^{1}H-NMR spectra. The ^{31}P-NMR (in DMSO) of **2** showed signals at δ_P 32.57 and 28.73 respectively with an intensity ratio of 100:1. In the ^{1}H-NMR-spectrum the major olefinic proton has ^{3}J(HP) 6.7 Hz, while the minor signal has ^{3}J(HP) 26.9 Hz. Thus, we attribute the peak at δ_P 32.57 to the (E)-enolate **2c** and that at 28.73 to the (Z)-enolate **2b** (Figure 2). The relative proportion of the isomers **2b** and **2c** formed in the metallation may be predetermined by the position of the equilibrium **1b** ↔ **1c** or on the interconversion **2b** ↔ **2c** in the chosen solvent.

The zinc complex of **3** was obtained by metal exchange using the sodium salt of **1** and zinc acetate dihydrate in methanol. Elemental analysis indicated its formula to be $L_4Zn_3(O_2CCH_3)_2$ where $L{=}Ph_2P(O)CPh{=}CH{-}O^-$. The compound decomposes in DMSO. Thus, NMR spectra are only available in $CDCl_3$ or CD_2Cl_2. The ^{31}P-NMR shows a single signal with a downfield ^{31}P chemical shift (42.03 ppm) which testifies the presence of a strong PO ··· Zn interaction (Figure 3). In a

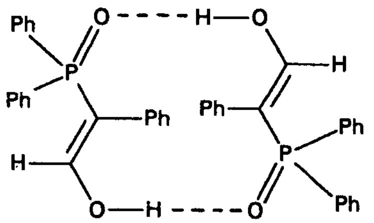
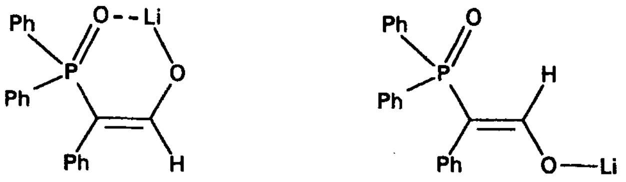


FIGURE 1 Possible dimeric structure of **1c**.



2b **2c**

FIGURE 2 Structure of the lithium salts **2b** and **2c**.

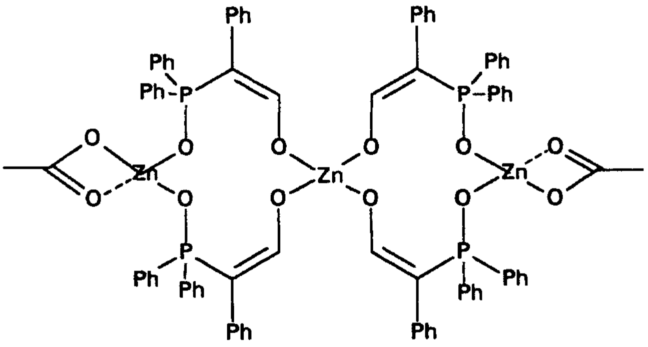
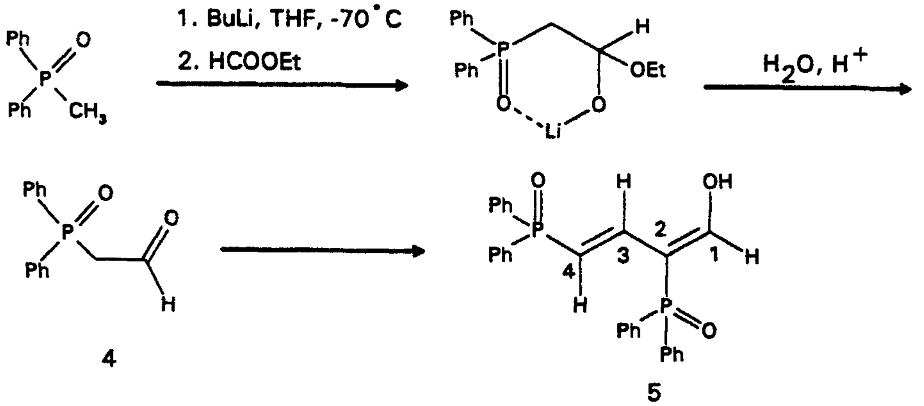


FIGURE 3 Possible structure of the Zn-complex **3** [$L_4Zn_3(O_2CCH_3)_2$, $L{=}Ph_2P(O)CPh{=}CH{-}O^-$].

proton-coupled spectrum, this signal splits into a doublet of triplets due to couplings with the olefinic and aromatic protons. The J(HP) vicinal coupling constant of 28.9 Hz (from ^{1}H-NMR) is assigned to a *trans*-orientation of the phosphorus and hydrogen atoms in the (Z)-enolate. The ^{13}C-NMR spectrum is also in accordance with this chelate structure **3** (see Experimental), although some of the signals are slightly broadened. Signals from the two phenyl groups bonded to phosphorus were readily assigned and correspond generally to the literature data for diphenylphosphine oxide[20] with the exception of ^3J(CP) for the *meta* carbon (found 4.5 Hz, Lit.[20] 12 Hz). Some problems arise with the ^{1}H-NMR spectra. Expected signals for **3** are present, but depending on solvent, temperature and field-strength the spectra change strongly in the aromatic as well as in the methyl part. Especially for the methyl-signals, the observed situation is obscure. It seems, that a second and/or further species exist in solution which have different exchange characteristics than the major compounds and which complicate a better identification of **3** via integration. In favourable situations, the second compound with sharpened signals in the aromatic part is visible. Strong overlapping in the ^{1}H-NMR spectra as well as concentration problems for the ^{13}C-NMR spectra prevent a detailed analysis till now. Thus, structure **3** remains tentatively deduced from the analytical data with the additional information, that the main compound in solution has an all-(Z) configuration at the olefinic bond in contrast to the (E)-configuration of the starting oxide **1c**, which can be explained by a ready interconversion of the tautomers **1**-Na or isomerisation (E)-enolate ↔ (Z)-enolate of **3** in a polar solvent (MeOH) due to favourable intramolecular H-bonding. The driving force could be steric reasons in **3** which also prevent the existence of other stereoisomers, e.g. with the phosphorus directed to the central zinc atom. The crystal structure determination was not available till now because of problems with the crystallization.

Diphenyl-2-oxo-ethylphosphine oxide $Ph_2P(O)CH_2CHO$ **4** can be obtained by rearrangement of substituted oxiranes,[8] as well as from the corresponding imides[10] or nitrophosphine oxides.[9] However, an attempt to prepare the oxide **4** using the simpler and more common method involving reaction of lithiated diphenylmethylphosphine oxide with ethylformate gave the diphenylphosphine oxide **5** (Scheme 2). The spectral characteristics of the product obtained this way differed significantly



SCHEME 2

from those of the aldehyde and enol forms of phosphine oxide **4** described in the literature.[8–10] The ^1H, ^{31}P and ^{13}C NMR data in DMSO, as well as the elemental analysis, showed it to be the dioxide **5**. The ^{13}C NMR spectrum exhibits two groups consistent of four aromatic carbons in the area δ_C 134–138, which were assigned to C_{ipso}, C_{para}, C_{ortho} and C_{meta} (see Experimental), in agreement with the multiplicity selection of an APT experiment.[25] The chemical shifts of C1, C2, C3 and C4 correspond well to the literature data for phosphonobutadienols.[11] The assignments of P4 (δ_P 23.6) and P2 (δ_P 27.8) are easily achieved by single-frequency-proton-decoupling, e.g. P4 is correlated to the proton-signal at δ_H 6.4 (H4). The analysis of the ^1H NMR spectrum is straightforward despite the fact, that the signal of H3 is strongly overlapped by the aromatic protons. A simple DID-spectrum[21] revealed the splitting pattern (Figure 4). Thus, from the unequivocally determined coupling constants *J*(H3P4) 21.3 Hz and *J*(H3H4) 17.4 Hz the (E)-configuration at the double bond C3C4 is proven [*J*(H3P4) *trans* = approx. 40 Hz]. For the second half of the molecule the analysis is somewhat complicated by the lack of a proton at C2 as an indicator. The strong reduction of the coupling *J*(H1P2) to 9.3 Hz is characteristic of enol phosphonates and supported the (E)-configuration as well. Further evidence for the overall configuration is indicated by the 1.9 Hz long range coupling ^5J(H1P4), which is a result of a regular zig-zag-configuration (W-coupling). Assuming Karplus-type relationships for ^3J(C4P2)[22] and ^3J(H3P4),[23] the values of 5.6 and 21.3 Hz lead to an approximated angle of either 40° or 120°, respectively. These values correspond with s-*cis*-vs. s-*trans*-type conformation at the single bond C2C3. The preference was established using a 2D-Heteronuclear-Overhauser-Experiment (HOESY)[24] as is shown in Figure 5. This spectrum yielded correlations from P4 to H4 and H3, respectively, as expected for the *trans*-bond C3-C4. The more interesting signals correlated P2 and H1 [*J*(P2H1) = 9.3 Hz] as

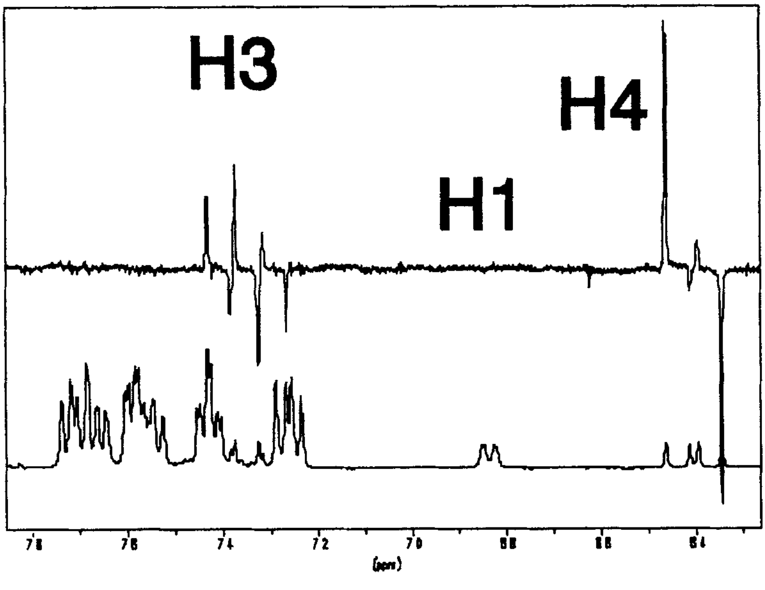


FIGURE 4 ^1H-DID-spectrum of the phosphine oxide **5** in DMSO-d_6.

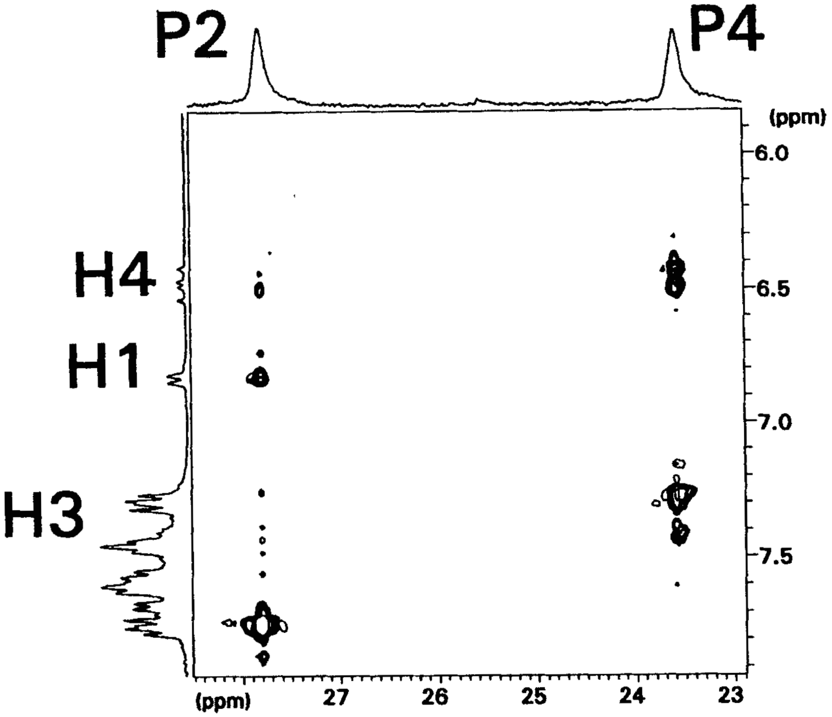


FIGURE 5 2D-Heteronuclear-Overhauser experiment (H,P-HOESY) of the phosphine oxide **5**.

well as, somewhat reduced, P2 and H4[††] (the remaining signals are due to Overhauser effects to the aromatic substituents). Thus, the complete set of NMR data is well consistent with the all *trans* conformation shown on Scheme 2 with a slight distortion around the central single bond and gives the explanation for the lack of J(PP).

The lithium derivative of oxide **5**, 2,4-bis(diphenylphosphinyl)-1,3-butadienolatolithium **6** was obtained analogously to the salt **2**, using *n*-butyllithium at −70°C in tetrahydrofuran. It was isolated in a pure state as pale yellow crystalline salt, which is hygroscopic and soluble in highly polar solvents. The IR spectra of the salt **6** in nujol contained an absorption at 1540 cm^{-1} due to $C{=}C$ valence vibrations, thus a low frequency shift of 80 cm^{-1} being observed in respect to the starting oxide **5**. The ^{31}P NMR in DMSO showed the presence of a major compound with δ_P 29.61 (P2) and 25.34 (P4) as well as a minor compound with δ_P 30.33 and 24.12 respectively, the ratio of the compounds being 10:1,5. The ^{1}H, ^{31}P and ^{13}C NMR data indicate that the major compound has the configuration of the starting phosphine oxide **5**. In this case, the overlap of H3 with the aromatic part is much stronger, but in the H,H-COSY spectrum (Figure 6) the doubled triplet structure is resolved easily in the cross-peak pattern. On the other hand the downfield signal (H1) has no proton-proton coupling. In comparison to the phosphine oxide **5** the mainly all-

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[††] A homonuclear NOESY-experiment yields no signals for correlations among the olefinic protons.

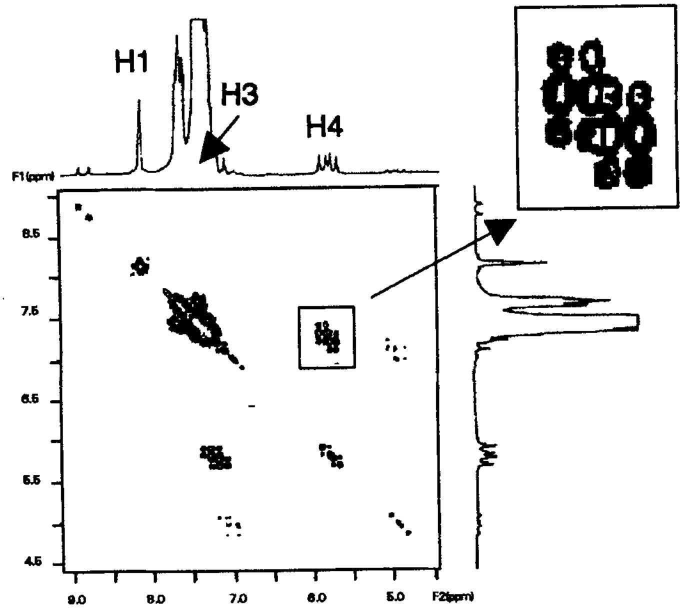
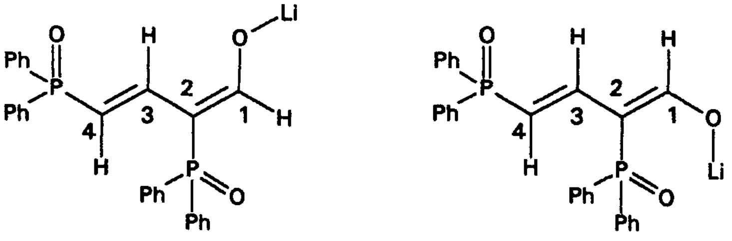


FIGURE 6 H,H-COSY spectrum of the lithium derivatives **6**.

trans conformation of the molecule is maintained. This is deduced from the lack of *J*(H1H3) and the presence of a small five bond *J*(H1P4) coupling constants. The ^{13}C chemical shifts differ significantly, which is due to the increased electron availability at the oxygen and this effect extends through the whole conjugated system. The increased polarisation also influences the ^{1}H NMR, the main changes occurring for H1 and H4, while H3 is more or less unaffected (the order of the chemical shifts changes from H4, H1, H3 to H4, H3, H1 from upfield to downfield). The changed electron availability at O1 has a pronounced effect on several coupling constants. Thus, *J*(C4P4) and *J*(C2P2) are increased remarkably and *J*(C4P2) increases from 5.6 Hz to nearly 8 Hz. If the Karplus relationship also holds for this latter coupling, then the angle between C4 and P2 is reduced to approx. 30 degrees. This would explain the shift difference of H4 (from 6.4 to 5.8) because it comes closer to the influence of the neighboring substituents at P2 (and again has an influence on the conjugated system vice versa). In the ^{1}H NMR, the main influence is the reduction of *J*(H1P2) from 9.3 to 3.1 Hz which again reflects the changed electronic situation at the oxygen. Thus, the structure is best described when the organic part is identical to the phosphine oxide **5** and only Li is substituted at the oxygen (Figure 7). For the minor compound, the ^{1}H NMR spectrum exhibits similar patterns (see Table I).

The relatively small change in *J*(H3H4) and the very marked increase in *J*(H1P2) (from 3.1 to 25.1 Hz) indicates that the minor compound is the (Z)-isomer (Z)-**6**. The continued absence of the coupling *J*(PP) indicates that the minor isomer has s-*trans* conformation and the even greater shielding of H4 (4.89 ppm) compared to the major (E)-isomer indicates that the lithium is coordinated to the P2 phosphoryl oxygen which would orientate the phenyl groups towards H4 (Figure 7).



(E)-6

(Z)-6

FIGURE 7 Structures of the lithium derivatives **6**.

EXPERIMENTAL

The solvents tetrahydrofuran (thf), diethylether and hexane were dried by distillation from sodium-benzophenone. The reactions with BuLi and tert-BuOK were carried out under argon. The NMR spectra were recorded at 20°C on a JEOL FX 90Q/270 spectrometer, the $^{31}P\{H\}$ spectra being recorded at 36.23 MHz in 10 mm tubes, as well as on a BRUKER AM-360 or a VARIAN Gemini-200 BB spectrometer in either 10 or 5 mm tubes at room temperature. ^{1}H-NMR spectra are referenced to internal TMS, ^{13}C NMR spectra to the solvent signal (DMSO-d_6 = 39.5 ppm, $CDCl_3$ = 77.0 ppm) and ^{31}P NMR spectra to external 85% aq H_3PO_4. The ^{13}C multiplicities are determined via APT spectra[25]. Data from the AM-360 are processed on a PC using 1D- and 2D-WINNMR software.

2-(Diphenylphosphinyl)-2-phenyl-ethenol **1**. Phosphine oxide **1** was obtained using the literature method.[7,14] M.p. 222–224°C. (Lit.[7] 222–224°C) ν max/cm^{-1} 1140 (P=O), 1430 (P—Ph), 1600 and 1635 (C=C) and 2600 (OH) (Nujol); δ_H δ_P (see Table I), δ_C (DMSO-d_6) 107.41 [1C,s, *J*(CP) 112.7 Hz, C2], 126.26 (1C,d, C4′), 127.71 (2C,d, C3′), 128.47 [4C,d, *J*(CP) 11.8 Hz, C-*m*], 129.90 [2C,d, *J*(CP) 4.3 Hz C2′], 131.42 [2C,d, *J*(CP) 2.8 Hz, C-*p*], 131.58 [4C,d, *J*(CP) 9.2 Hz, C-*o*], 133.18 [2C,s, *J*(CP) 103.4 Hz, C-*i*], 133.84 [1C,s, *J*(CP) 6.4 Hz C1′], 154.92 [1C,d, *J*(CP) 26.1 Hz, C1].

2-(Diphenylphosphinyl)-2-phenyl-ethenolato-lithium **2**. To a solution of *n*-butyl lithium (1 mmol, 1.6 M in hexane) in 2 cm^3 of thf at −80°C under argon a suspension of phosphine oxide **1** (m.p. 222–224°C, 0.330 g, 1 mmol) in 12 cm^3 of thf was added dropwise. The reaction mixture was stirred for 3 h at −70°C and left overnight at −30°C. The precipitate (0.100 g) of the starting phosphine oxide (m.p., tlc) was filtered off, the filtrate concentrated in vacuum up to 2–3 cm^3 and 5 cm^3 of diethyl ether added to the solution. After stirring for 1 h at room temperature the crystalline product was filtered off, washed with ether and dried in vacuum to give 2-(diphenylphosphinyl)-2-phenyl-ethenolato-lithium **2** (0.200 g, 59.5%). The product does not melt up to 340°C and is slightly soluble in chloroform and DMSO. (Found: C, 71.6; H, 5.3; Li, 2.2. $C_{20}H_{16}O_2PLi$. 1/2H_2O requires C, 71.6; H, 5.1; Li, 2.1%); ν max/cm^{-1} 1125–1170 (P=O), 1450 (P—Ph), 1550 and 1580 (C=C) and 2600–2800 (OH) (Nujol); δ_H, δ_P (see Table I) and δ_H 7.85 (2H, d, 7.9 Hz, H2′), 6.91 (2H, t, 7.9 Hz, 7.2 Hz, H3′), 6.66 (1H, t, 7.2 Hz, H4′), 7.3–7.4 (6H, mult), 7.6–7.7 (4H, mult), δ_C (major, **2c**, DMSO) 91.33 [1C,s, *J*(CP) 127.9 Hz, C2], 120.45 (1C,d, C4′), 126.44 (2C,d, C3′), 126.97 [2C,d, *J*(CP) 8.4 Hz, C-*p*], 127.64 [4C,d, *J*(CP) 11.5 Hz, C-*m*], 129.58 [2C,d, *J*(CP) 1.9 Hz, C2′], 131.93 [4C,d, *J*(CP) 9.1 Hz, C-*o*], 138.19 [2C,s, *J*(CP) 100.6 Hz, C-*i*], 141.20 [1C,s, *J*(CP) 10.5 Hz, C1′], 175.02 [1C,d, *J*(CP) 25.8 Hz, C1].

Bis-(Z)-2-(diphenylphosphinyl)-2-phenyl-ethenolato-zinc. Zinc acetate **3**. To a suspension of oxide **1** (0.330 g, 1 mmol) in 7 cm^3 of anhydrous methanol, sodium hydroxide (0.04 g, 1 mmol) was added. After dissolving (2–3 min stirring) zinc acetate dihydrate (0.220 g, 1.0 mmol) was added. The reaction mixture is left for four days at room temperature. The crystals of the complex **3** (0.33 g, 83%) were filtered off, washed with methanol-ether 1:3 and recrystallized from methanol. M.p. 135–138°C. The complex was soluble in chloroform and dichloromethane. (Found: C, 63.4; H, 4.7; Zn, 12.5. $C_{84}H_{68}O_{12}P_4Zn_3$ requires C, 63.4; H, 4.4; Zn, 12.3%); ν max/cm^{-1} 1130 (P=O), 1450 (P—Ph), 1540 and 1590 (C=C and CO_2^-) (Nujol). δ_H, δ_P (see Table I), δ_C ($CDCl_3$) 96.11 [1C,s, *J*(CP) 116.95 Hz C2], 125.25 [1C,d, C4′], 130.74 [4C,d, *J*(CP) 4.50 Hz, C-*m*], 131.43 [2C,d, *J*(CP) 2.92 Hz, C-*p*], 131.91 [2C,s, *J*(CP) 106.6

Hz, C-*i*], 132.01 (2C,d, C3′), 132.27 [4C,d, *J*(CP) 11.7 Hz, C-*o*], 132.53 (2C,d, C2′), 137.4 (1C,s, *J*(CP) 11.7 Hz, C1′], 173.11 (1C,d, C1), 179.15 (CO-acetate), 23.61 (CH_3-acetate).

2,4-Bis(diphenylphosphinyl)-1,3-butadienol **5**. To a cooled to −60°C solution of *n*-BuLi (27.5 mmol, 1.6 M in hexane) in thf (30 cm^3) a suspension of diphenylmethylphosphine oxide (5.40 g, 25 mmol) in 60 cm^3 of thf is added. The reaction mixture is kept 1 h at −55 to −60°C. Ethylformate (2.04 g, 27.5 mmol) in 6 cm^3 of thf is added to the obtained yellow solution and the reaction mixture is stirred for 1/2 h, after that the temperature is raised gradually to 20°C (for 1/2 h), cooled to 0°C and water (25 cm^3) is added dropwise. After stirring at this temperature for 1/2 h the aqueous layer is washed with ether (2 × 6 cm^3), cooled again to 0°C and acidified with 4M HCl to pH = 1. The aqueous layer is extracted twice with dichloromethane, the combined organic solution is washed with water and dried with $MgSO_4$. The raw product (4.13 g, thick oil) is recrystallized from dichloromethane-hexane 1:2 to give the oxide **5** (2.65 g, 45%) with m.p. 195–198°C. (Found: C, 70,6; H, 5.1. $C_{28}H_{24}P_2O_3$ $1/2H_2O$ requires C, 70.1; H, 5.3%, ν max/cm^{-1} 1120, 1160 and 1170 ($P{=}O$), 1450 (P—Ph), 1600 and 1620 ($C{=}C$), 2500 and 3200 (OH). (Nujol); δ_H, δ_P (see Table I), δ_C (DMSO-d_6) 104.5 [1C,s, *J*(C2P2) 114.9 Hz, *J*(C2P4) 18.3 Hz, C2], 118.6 [1C,d, *J*(C4P4) 104.8 Hz, *J*(C4P2) 5.6 Hz, C4], 137.9 [1C,d, *J*(C3P4) = *J*(C3P2) = 5.5 Hz, C3], 160.8 [1C,d, *J*(C1P2) 24.4 Hz, C1], 128.79/128.59 [8C,d, *J*(CP) 11.6/11.2 Hz C-*m*], 131.39/130.31 [8C,d, *J*(CP) 9.7/9.7 Hz, C-*o*], 131.99/131.68 [4C,d, *J*(CP) 2.1/2.3 Hz, C-*p*], 133.21/131.72 [4C,s, *J*(CP) 104.0/104.5 Hz, C-*i*].

2,4-Bis(diphenylphosphinyl)-1,3-butadienolato-lithium **6**. To a cooled to −70°C suspension of **5** (0.470 g, 1 mmol) in 30 cm^3 of thf a solution of *n*-BuLi (1 mmol, 1.6 M in hexane) in 10 cm^3 of thf is added dropwise. The reaction mixture is stirred for 1.5 h at −70°C and 1/2 h at −60°C. The temperature is allowed to reach room temperature and the precipitate is filtered and washed with 6 cm^3 of ether-thf (2:1) and after that with 5 cm^3 of ether. The raw product suspension in 10 cm^3 of ether is stirred for 1/2 h and after filtration and washing with ether the lithium salt **6** was isolated (0.40 g, 84%). It is soluble in CH_3OH, DMSO and dimethylformamide. (Found: C, 69.4; H, 6.0; Li, 1.4. $C_{28}H_{23}P_2O_3Li.C_2H_5OC_2H_5$ requires C, 69.8; H, 6.0; Li, 1.3%); ν max/cm^{-1} 1120, 1160 and 1180 ($P{=}O$), 1450 (P—Ph), 1540 and 1600 ($C{=}C$) (Nujol). δ_H, δ_P (see Table I), δ_C (DMSO-d_6) 94.47 [1C,s, *J*(C2P2) 125.5 Hz, *J*(C2P4) 15.7 Hz, C2], 99.37 [1C,d, *J*(C4P4) 116.3 Hz *J*(C4P2) 7.8 Hz, C4], 144.86 [1C,d, *J*(C3P4) 5.4 Hz, *J*(C3P2) 10.6 Hz, C3], 178.70 [1C,d, *J*(C1P2) 24.2 Hz, C1], 128.07/127.98 [8C,d, *J*(CP) 11.3/11.0 Hz, C-*m*], 130.49/130.20 [4C,d, *J*(CP) 2.9/2.9 Hz, C-*p*], 131.70/130.60 [8C,d, *J*(CP) 9.0/9.5 Hz, C-*o*], 136.66/136.40 [4C,s, *J*(CP) 101.1/99.9 Hz, *C-i*].

1-Methoxy-2-phenylethenyldiphenylphosphine oxide **7**. A solution of diazomethane in ether was added in portions to a cooled to 0–5°C suspension of phosphine oxide **1** (0.500 g, 1.5 mmol) in 10 cm^3 of anhydrous methanol until a stable yellow colour of the reaction mixture persisted. After stirring for 1/2 h at 0–5°C, 1 h at 10°C and 1 h at room temperature the solvents were removed in vacuum and the residue was recrystallized twice from benzene-hexane 1:1 to yield 1-methoxy-2-phenylethenyldiphenylphosphine oxide **7** (0.330 g, 57%), m.p, 144–145°C. (Found: C, 75.7; H, 5.7. $C_{21}H_{19}PO_2$ requires C, 75.4; H. 5.7%); δ_H ($CDCl_3$) 3.73 (3H,s, OMe), 6.92 [1H,d, *J*(HP) 10.3 Hz], 7.12–7.24 (5H,s, broad), 7.35–7.50 (6H, multiplet), 7.60–7.70 (4H, multiplet).

1-Ethoxy-2-ethenyldiphenylphosphine oxide was prepared according to the literature.[7] M.p. 140–141°C, Lit. 140–141°C; δ_H ($CDCl_3$) 1.30 [3H, t, *J*(HH) 8 Hz, CH_3], 3.94 [2H, q, *J*(HH) 8 Hz, OCH_2], 5.26 [1H, t, ^3J(HH) = ^2J(HP) 13.7 Hz, H2], 7.03 [1H, dd, ^3J(HH) 13.7, ^3J(HP) 10.9 Hz, H1], 7.30–7.55 (6H, multiplet), 7.66–7.75 (4H, multiplet).

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