



Application of a base-induced [1,2]-rearrangement to synthesize thiophosphonate bidentate S(sp²)-N monoanionic ligand: Characterization of its silver and palladium complexes

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ABSTRACT

The *O,O*-diethyl thiophosphonate functional group has been introduced on position 2 of a pyrrole heterocycle following a two steps sequence that makes use of a [1,2] base-induced rearrangement applied for the first time to a *O,O*-diethyl thiophosphoramidate intermediate. This rearrangement has been studied by low temperature NMR and the intermediates have been fully characterized. The coordination of this monoanionic bidentate (N,Ssp²) ligand to silver or palladium is studied. The bidentate ligand **2** (*O,O*-diethyl pyrrol-2-ylthiophosphonate), associated with a palladium precursor, produces in the presence of triethylamine the complex trans-[Pd(η²-**2'**)₂] **3** (**2'** is deprotonated ligand **2**). Ligand **2** also reacts with silver oxide in dichloromethane to give an unstable complex **2'**-Ag that can be stabilized by addition of triphenylphosphine to produce the coordination complex **4** [Ag(η²-**2'**)(PPh₃)₂].

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1. Introduction

The synthesis of original ligands possessing a good stability in the presence of air and moisture constitute a valuable interest for applications in the field of catalysis [1] after being associated with a metal or as building blocks to define coordination polymers [2]. With the aim to synthesize coordination complexes obtained from air and moisture stable ligands, the use of the phosphorus(V) functional group to design new ligands has drawn our attention. Phosphorus(V) functional groups which are usually air and moisture stable have been used in many coordination complexes. It must be noted that the coordination site in this phosphorus(V) functional group can be an oxygen, a sulfur or a nitrogen atom, respectively, present in the following double bonds: P=O (e.g. phosphonate [3]), P=S (e.g., phosphine thiooxide [4]) or P=N (e.g., iminophosphorane [5]). The nature of the metallic partner that can be coordinated to these atoms is greatly dependent of the hardness/softness of the binding site of these P(V) ligands.

Concerning the functional groups possessing a P=S double bond, the majority of the coordination studies report the use of phosphine thiooxide, probably due to the simplicity of their synthesis by a simple thiooxidation of phosphine. Nevertheless some coordination complexes involving thiophosphoramidate [6], or thiophosphonate [7] have been reported. The limitation of their use in coordination chemistry could arise from synthetic difficulties since their preparation usually requires the use of very air sensitive phosphorus(III) intermediates. We have recently reported the synthesis of *O,O*-diethylthiophosphonate achieved, from phenol derivatives and *via* stable phosphorus V intermediates [8], by a base-induced [1,3] phospho-Fries [9] rearrangement. On the basis of our recent results, we report herein the synthesis of *O,O*-diethylthiophosphonate-pyrrole *NH,S* ligand *via* a [1,2] phospho-Fries rearrangement. It must be noted that this kind of rearrangement has been previously used to produce phosphinethiooxides [10]. In the present work an important effort has been done to characterize, by low temperature NMR spectroscopy, the intermediate species involved in the course of this [1,2] phospho-Fries rearrangement. Furthermore, the temperature at which the [1,2]-rearrangement occurs has been determined. Finally The coordination behavior of this new pyrrolic *N,S*-ligand is illustrated by the characterization of palladium and silver complexes.

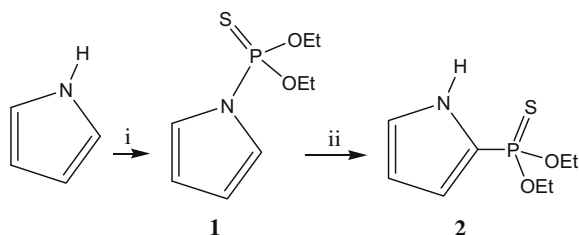
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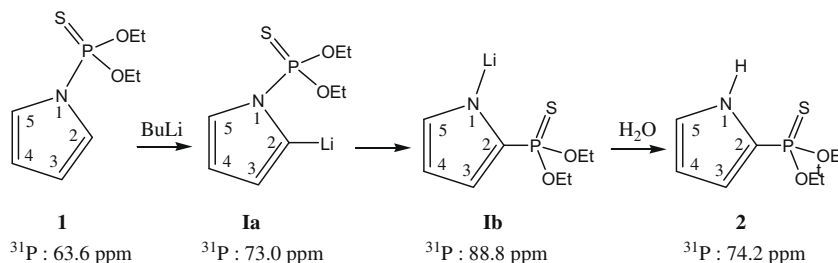
2. Results and discussion

2.1. Synthesis of the thiophosphonate and low temperature NMR study of [1,2] phospho-Fries rearrangement

O,O-diethylpyrrol-2-ylthiophosphonate **2** has been synthesized following a two step process which comprises the generation of the *N*-lithium salt of pyrrole by deprotonation with *n*-butyllithium followed by addition of *O,O*-diethylchlorothiophosphate (a deprotonation by sodium hydride is also successful). According to this procedure the thiophosphoramidate **1**, which results from a *N*-thiophosphonylation, is isolated in 91% yield (Scheme 1, Step i). The synthesis of thiophosphonate **2** from **1** is then achieved by orthometallation of **1** with *n*-butyllithium at $-80\text{ }^{\circ}\text{C}$. After warming to room temperature and hydrolysis **2** is obtained by a [1,2]-rearrangement leading to the formation of a C–P bond (Scheme 1, step ii). Compound **2** is characterized by a ^{31}P NMR signal at 74.2 ppm and the observation, by ^{13}C NMR, of the signal of a tertiary carbon as a doublet at 122.27 ppm ($^1J_{\text{CP}} = 187.1\text{ Hz}$) which is consistent with the presence of a C–P bond. In spite of the poorly *ortho*-directing effect of the sulfur atom, the yield of this rearrangement is high (95%). It is worth noting that this [1,2]-rearrangement occurs more easily than the analogous [1,3]-rearrangement in the phenolic series [8]. Indeed in the latter case, when the metallation is achieved by abstraction of a hydrogen atom with BuLi, a low yield of transposed complex is obtained (15%) [8]. The efficiency of this [1,2]-rearrangement probably results from a selective lithiation in the α -position of the nitrogen atom (**1a**, Scheme 2) as a result of the proximity of both nitrogen and oxygen atoms of the thiophosphoramidate group. The driving force of this reaction could be the formation of a lithium amidure (after the [1,2]-rearrangement) (**1b**, Scheme 2) which would be more stable (less basic) than the carbanion initially formed (**1a**, Scheme 2). Base-assisted [1,2]- or [1,3]-rearrangements, which are well documented, have been previously used to synthesize 2-hydroxyphenylphosphonate [11], 2-mercaptoarylphosphonate [12] or phosphonodiamidate [13] compounds. In the pyrrolic series, a [1,2]-rearrangement has been reported to produce a phosphine oxide or a phosphine thiooxide [10]. However, to the best of our knowledge, this report represents the first example of a [1,2]-rearrangement producing an



Scheme 1. (i) *n*-BuLi, $-80\text{ }^{\circ}\text{C}$, THF, then *O,O*-diethylchlorothiophosphate, $-80\text{ }^{\circ}\text{C}$ to RT. (ii) *n*-BuLi, THF, $-80\text{ }^{\circ}\text{C}$ to RT then hydrolysis.



Scheme 2. Intermediates observed in the course of the base-induced [1,2]-rearrangement of **1** into **2**.

O,O-dialkylthiophosphonate. This rearrangement is very selective: the nucleophilic addition of *n*-butyllithium on the phosphorus atom was never observed. This selectivity can be explained by the poor polarization of the P=S bond that produces a phosphorus atom with a weak electrophilic character. This result is to compare with that obtained by Buono and coworkers [14], who observed that a base-induced [1,3]-rearrangement involving a phosphoramidate (P=O bond) was not efficient when *n*-BuLi was used as a base due to the addition of *n*-BuLi on the electrophilic phosphorus. This comparison illustrates the weaker reactivity of the thiophosphoramidate *versus* phosphoramidate towards nucleophilic reagents. In order to get further information about the intermediates involved in this [1,2] base-induced rearrangement, a ^{31}P NMR monitoring of the reaction was performed at low temperature. Below $-40\text{ }^{\circ}\text{C}$, only the signal of the starting compound **1** ($\delta^{31}\text{P}$: 63.6 ppm) was observed. Between -35 and $-40\text{ }^{\circ}\text{C}$ the metallation of the pyrrole in α -position from the nitrogen atom gives rise to intermediate **1a** ($\delta^{31}\text{P}$: 73.0 ppm). At nearly the same temperature this intermediate is converted into a second product **1b** (Scheme 2 and Fig. 1).

Fig. 1 illustrates the evolution of the reaction performed at $-38\text{ }^{\circ}\text{C}$. In order to characterize intermediates **1a** and **1b**, the reaction, after 10 h at $-38\text{ }^{\circ}\text{C}$ was cooled down to $-80\text{ }^{\circ}\text{C}$. The resulting reaction mixture was then found to be composed of **1** (28%), **1a** (48%) and **1b** (24%). From this mixture at $-80\text{ }^{\circ}\text{C}$, compounds **1a** and **1b** were unambiguously characterized by several NMR experiments (^1H , ^{31}P , ^{13}C , COSY ^1H - ^1H , HMBC ^1H - ^{13}C , HMBC ^1H - ^{31}P , HMBC ^1H - ^{15}N and HMQC ^1H - ^{13}C). Moreover, in an independent reaction, compound **1b** was obtained quantitatively by reaction of **2** with *n*-BuLi. The NMR data of compounds **1**, **1a**, **1b** and **2** are summarized in Table 1. The lithiation of **1** produced intermediate **1a** characterized by a deshielded ^{31}P NMR resonance and by the observation of three aromatic signals in ^1H NMR. ^{13}C NMR displacements of this intermediate were indirectly determined by HMQC ^1H - ^{13}C sequences. ^{15}N NMR chemical shifts, (determined by ^1H - ^{15}N HMBC sequences), strongly depend on the electron density around the nitrogen atom. Noticeably, for the lithiated species **1a** (-196.6 ppm) and even more for **1b** (-133.5 ppm), the ^{15}N NMR values are shifted toward the lower fields. Even if in earlier reports intermediates of type **1a** and **1b** were suggested to be formed in base-induced rearrangements (formation of arylphosphonate [12] or phosphonodiamidate [14]), to the best of our knowledge this report represents the first full characterization of these intermediates by multinuclear NMR experiments.

2.2. Coordination

The coordination properties of the bidentate ligand **2** were studied as reported in Schemes 3 and 4. A palladium complex has been readily obtained by reaction, at room temperature, of two equivalents of **2** with $[\text{PdCl}_2(\text{MeCN})_2]$ and triethylamine. The obtained palladium complex **3** is air stable and has been purified by silica gel chromatography. Its ^{31}P NMR spectrum displays only one signal

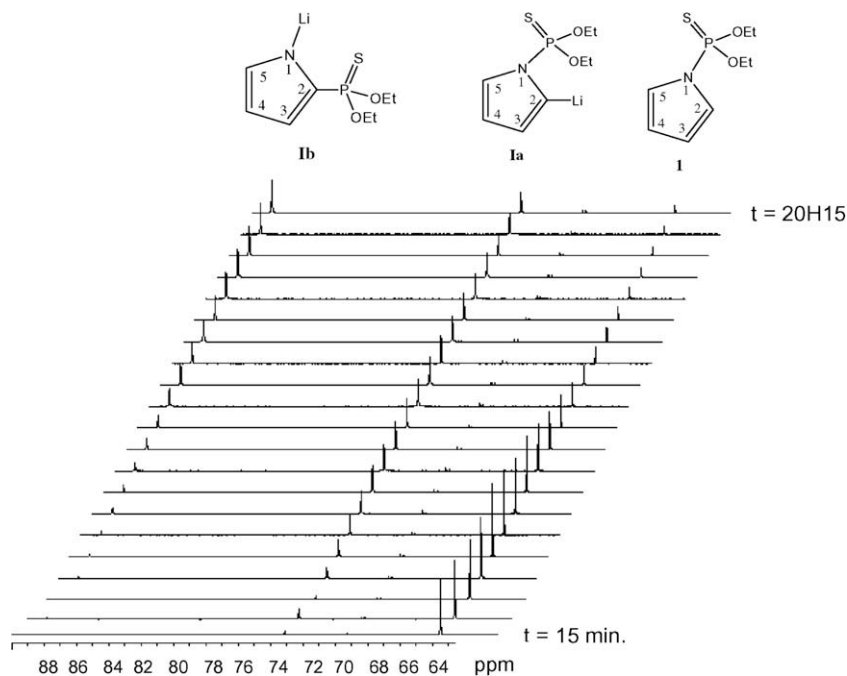
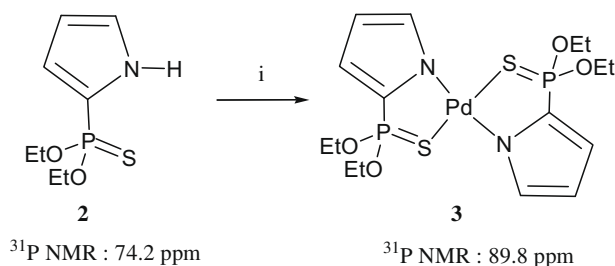


Fig. 1. ^{31}P NMR spectrum (from 60 to 90 ppm; THF + ^8D -THF -38°C) showing the chemical species observed after the addition of *n*-BuLi on a THF solution of **1** at -80°C . The first spectrum was recorded after 15 min at -38°C . The different spectra were drawn every hour.

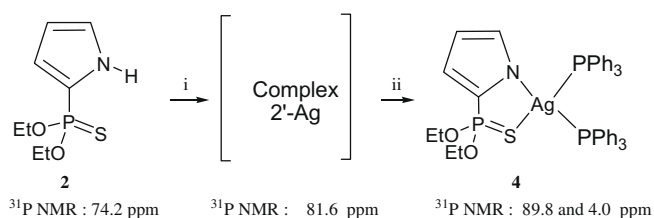
Table 1
NMR data of the aromatic part of compounds **1**, **2**, **1b** and of intermediate **1a**.

	1 (CDCl_3)	1a (^8D -THF)	1b (^8D -THF)	2 (CDCl_3)
^{31}P	63.6	73.0	88.8	74.2
^{15}N	-210.0	-196.6	-133.5	-226.2
^1H (Ar)	6.17 (H3; H4) 7.04 (H2; H5)	5.89 (H3) 5.92 (H4) 7.20 (H5)	6.02 (H4) 6.48 6.80	6.30 (H4) 6.72 (H3) 6.98 (H5)
^{13}C (Ar)	112.65 (C3, C4, $J_{\text{CP}} = 10.1$ Hz) 123.5 (C2, C5, $J_{\text{CP}} = 6.7$ Hz)	110.8 123.3 124.0 (C5) C2 ^a	109.9 (C4, $J_{\text{CP}} = 12$ Hz) 114.8 ($J_{\text{CP}} = 29$ Hz) 127.3 (C2, $J_{\text{CP}} = 124$ Hz) 133.9 ($J_{\text{CP}} = 26$ Hz)	110.5 (C4, $J_{\text{CP}} = 13.4$ Hz) 116.5 (C3, $J_{\text{CP}} = 15.9$ Hz) 122.3 (C2, $J_{\text{CP}} = 187.1$ Hz) 123.4 (C5, $J_{\text{CP}} = 11.6$ Hz)

^a Not determined.



Scheme 3. Synthesis of complex **3**. (i) $\text{PdCl}_2(\text{MeCN})_2$, NEt_3 , THF, 20° .



Scheme 4. Synthesis of complex **4**. (i) Ag_2O , CH_2Cl_2 (ii) PPh_3 .

at 89.8 ppm which corresponds to a deshielding of 15.6 ppm compared to the resonance of the free ligand **2** (74.2 ppm). This deshielding suggests a possible coordination of the P=S group to palladium *via* its sulfur atom. Indeed, similar deshielding effects ($\Delta\delta$ from 9.2 to 13.9 ppm) are observed when phosphine thiooxide groups are coordinated to a palladium atom [4h,4d]. The structure of **3**, which adopts a *trans*-square planar configuration has been established by X-ray diffraction study (Fig. 2). The angles S1-Pd1-N1 and S1'-Pd1-N1 (respectively $90.92(4)^\circ$ and $89.08(4)^\circ$) are in agreement with a square planar complex. The P=S bond in **3** (1.9972(6) Å) is lengthened when compared to the values of P=S bond length of free thiophosphonate or phosphine thiooxide (from 1.921(2) to 1.966(2) Å) [15,16]. In **3** the Pd-S bond (2.3382(5) Å) is longer than those reported for triarylphosphine thiooxide Pd complexes (2.317(2) to 2.321(2) Å) [4i,17]. Probably due to the presence of two *trans* N pyrrolic atoms, the Pd-N bonds (2.0264(13) Å) are slightly shorter than those observed in a bis(oxazoliny)pyrrole palladium complex (Pd-N = 2.039(8)–2.052(8) Å) [18]. Several attempts to prepare a silver complex by reaction of ligand **2** with silver oxide in dichloromethane at room temperature suggest the formation of a new compound whose spectroscopic data (see Section 4) are indicative of the complexation of ligand **2** to the metal *via* the S atom of the thiophosphonate group (deshielding of ~ 7.5 ppm of the phosphorus NMR signal of

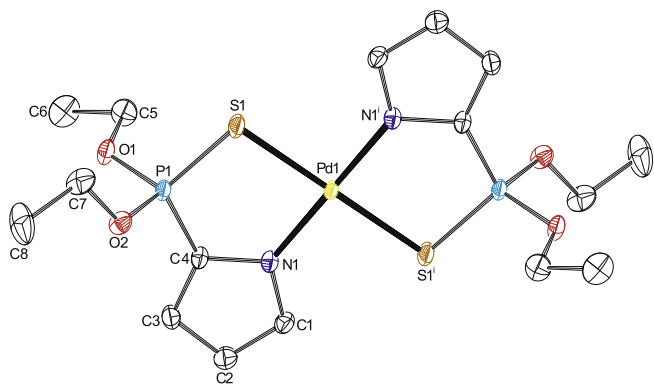


Fig. 2. Displacement ellipsoid plot (50% probability level) of **3** in the solid state. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg.): Pd1–S1 2.3382(5), Pd1–N1 2.0264(13), P1–S1 1.9972(6), P1–C4 1.7388(17), P1–O1 1.5800(12), P1–O2 1.5644(12); S1–Pd1–N1 90.92(4), S1'–Pd1–N1 89.08(4), S1–P1–C4 108.96(6), P1–C4–N1 118.27(13), P1–S1–Pd1 98.78(2). Symmetry operation: $1-x, 1-y, 1-z$.

this function at 81.6 ppm) and via the pyrrolic nitrogen (disappearance of the N–H resonance at 9.0 ppm). This complex was found to be unstable and we were unable to isolate it. However, addition of two equivalents of triphenylphosphine allowed us to obtain a new complex (**4**) which was stable even in the presence of air and light (Scheme 4). The structure of this complex **4** (see below) suggests that its unstable precursor involves a complexation of the N and S atoms of ligand **2** on a single metal: this entity “**2'-Ag**” could be weakly stabilized by molecules of solvent or by water (ligand **2'** corresponds to the ligand **2** deprotonated on the nitrogen atom of the pyrrole heterocycle). The ^1H NMR spectrum of **4** confirms the presence of two PPh_3 ligands together with **L2'**; its ^{31}P NMR spectrum displays at room temperature two signals at 90.0 and 5.7 ppm that are attributed to the thiophosphonate group and to the triphenylphosphine ligands, respectively. Compared to the starting ligand **2**, the complexation of the sulfur atom of the thiophosphonate group on the silver atom induces a deshielding of the phosphorus resonance (15.6 ppm). The absence of $J_{\text{P}-\text{Ag}}$ coupling constants between the phosphorus atoms of PPh_3 and the metal suggests that the two phosphines undergo rapid exchanges on the NMR time scale at room temperature. The reality of this dynamic system has been established by a low temperature ^{31}P NMR study (Fig. 3). The thin signal observed for the phosphines at 5.7 ppm at 25 °C broadens as the temperature decreases and coalesces at –62 °C to evolve at lower temperature into a doublet centered at 4.3 ppm ($J_{\text{P}-\text{Ag}}^{107} = 346.26$ Hz; $J_{\text{P}-\text{Ag}}^{109} = 399.08$ Hz). These coupling constants are typical of a (phosphine) $_2\text{Ag}$ system [19]. The equivalence of the two phosphines at low temperature suggests a tetrahedral coordination around the metal. In the observed range of temperature the thiophosphonate signal remains unchanged (singlet at 90.0 ppm). The lability of the phosphines is again shown by reaction of **4** with an excess of triphenylphosphine. When one equivalent of PPh_3 is added to **4**, the ^{31}P NMR spectrum of the solution performed at room temperature displays a single signal in the phosphine resonance area (at 1 ppm) showing a rapid exchange on an NMR scale between the two phosphines linked to the metal and the free phosphine in solution. By cooling down this solution, the signal becomes broad and coalesces at –50 °C. It then evolves at lower temperature and gives rise to the doublet previously observed and to the signal of the free PPh_3 at –6.85 ppm. Even in the presence of an excess of PPh_3 (Fig. 3b) there is no sign of hemilability of ligand **2** with an eventual insertion of PPh_3 into the Ag–S bond; the signal of the thiophosphonate group remains unchanged. It is noteworthy that the

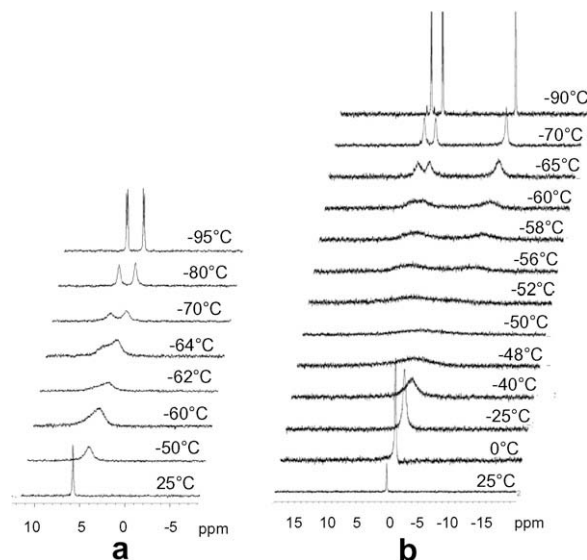


Fig. 3. Low temperature ^{31}P NMR spectra of complex **4**. (3a) Thermal evolution from 25 to –95 °C of the ^{31}P NMR signals of the PPh_3 ligands of **4**. (3b) Evolution of the same signal in the presence of an excess of PPh_3 .

stoichiometry of the reaction of formation of **4** is not affected by reducing the amount of the added phosphine to one equivalent. Crystals of **4** suitable for an X-ray diffraction study were obtained from a hexane– CH_2Cl_2 (90/10) mixture at –40 °C. Fig. 4 displays the ORTEP drawing of the molecule and some selected bonds and angles. The molecular structure study of **4** shows that the silver atom of this complex is linked to ligand **2'** and to two PPh_3 . The coordination angles around Ag1 are in agreement with a pseudo tetrahedral coordination around the metal center. This is illustrated by the angles S1–Ag1–N1 (84.25(7)), N1–Ag1–P2 (104.76(8)) and P2–Ag1–P3 (119.88(3)). Furthermore the distances of P2 and P3 atoms from the plane defined by the atoms Ag1, N1 and S1 are respectively 2.140(1) and 2.216(1) Å, respectively. In complex **4**, the ligand **2'** is *N,S*-chelated to the metal giving rise to a five-membered metallacycle with a reduce bite angle (N1–Ag1–S1 = 84.25(7)°). This angle is smaller than that observed for complex **3** displaying the same ligand on a square planar palladium (90.92(4)°). It is, however larger than S–Ag–S angles observed for dithiocarbamate or dithiophosphinate ligands forming four-membered metallacycles on tetrahedral Ag metal centers (68.00(2)° and 74.71(3)°, respectively) [20]. The P=S bond of **4** is shorter than its homologue of the same ligand on **3** (1.9603(12) Å vs 1.9972(6) Å). It is also shorter than the P=S distances observed for thiophosphine [19d] or dithiophosphinate [20b] Ag complexes (from 1.990(3) Å to 2.004(1) Å). However, similar short P=S bonds have been observed for a thiophosphinate Ag complex [21] (from 1.957(2) Å to 1.971(2) Å). These distances are longer than those observed for the P=S bonds of free thiophosphonate or phosphine thiooxide ligands (from 1.921(2) Å to 1.966(2) Å [15,16]. Compared to similar bond lengths (average of 2.35 Å) described in the literature [19c,22], the Ag–N distance observed for **4** is rather short (2.273(3) Å). On the other hand, the Ag–P distances are rather long: 2.4492(9) and 2.4761(9) Å compared to similar Ag– PPh_3 bonds previously described (from 2.3465(6) to 2.4736(10) Å) [19c,20a,22a–c,23]. The value of the angle P2–Ag1–P3 measured between the two PPh_3 ligands (119.88(3)°) is small when compared to their homologues on several Ag complexes (from 122.02(4)° to 135.158(9)°) [19c,22a,c,d]. The structure of **4** then confirms that for a given phosphane, the Ag–P bond length is expected to increase as the Ag–P–Ag angle decreases. A correlation has already

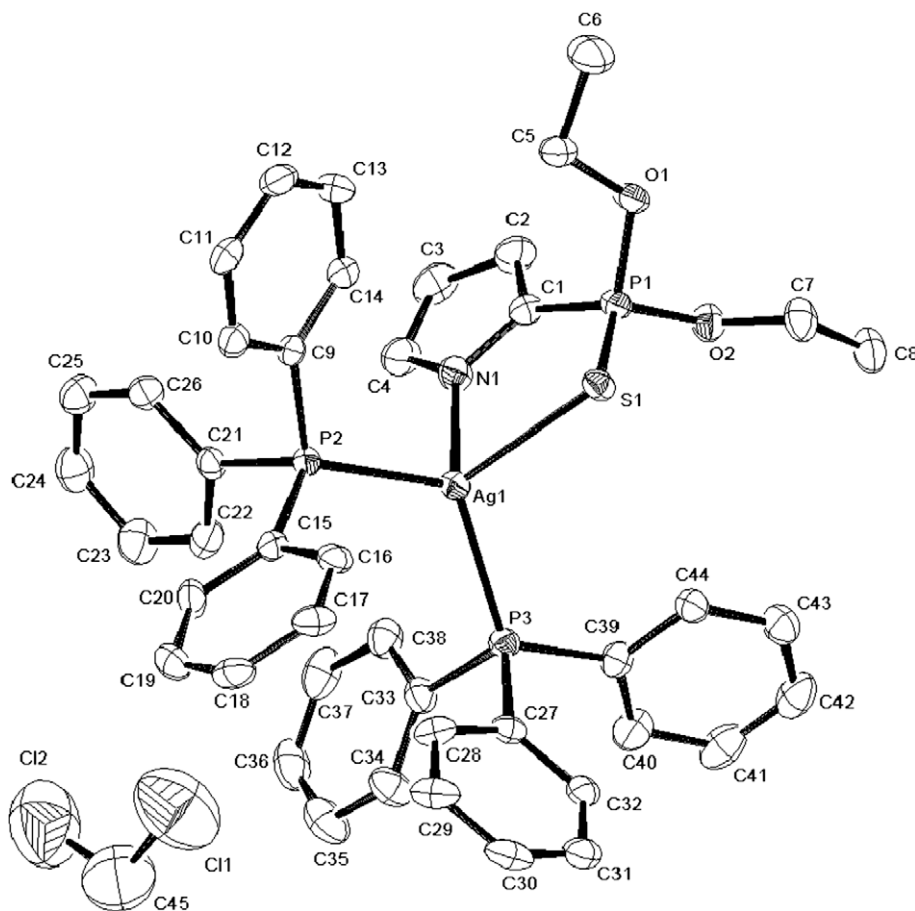


Fig. 4. Displacement ellipsoid plot (50% probability level) of **4** in the solid state. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg.): Ag1–S1 2.7169(9), Ag1–N1 2.273(3), Ag1–P2 2.4761(9), Ag1–P3 2.4492(9), P1–S1 1.9603(12), S1–Ag1–N1 84.25(7), N1–Ag1–P2 104.76(8), S1–Ag1–P3 111.61(3), S1–Ag1–P2 112.96(3), P2–Ag1–P3 119.88(3), N1–Ag1–P3 117.93(8), P1–S1–Ag1 95.67(4). Dihedral angles: N1–S1–Ag1–P3 117.80(1), S1–N1–Ag1–P2 112.27(1).

been observed between P–Ag–P angles and $^1J_{\text{Ag-P}}$ measured in solution for some Ag complexes [22d,24], for example, an average value of $^1J_{\text{Ag-P}} = 387$ Hz has been observed for a P–Ag–P angle of 122.51° ; 411 Hz for 127.75° and 455 Hz for 135.15° . The value found for **4** (372.34 Hz for 119.88°) is in good accordance with these previous results.

3. Conclusion

A new (S,NH)-bidentate ligand displaying a pyrrole core and one thiophosphonate functional group in position 2 of pyrrole heterocycle have been prepared. This ligand is air and moisture stable. Its synthesis has been performed by a base-induced [1,2]-rearrangement which has been applied, for the first time, to the synthesis of thiophosphonates. Its synthesis uses the nitrogen atom of the pyrrole ring to introduce the functional group on the α -position possessing a sp^2 -hybridized sulfur atom as a binding site. This reaction proceeds in two steps: firstly, an *ortho*-lithiation and secondly a [1,2]-migration of the thiophosphono group from the nitrogen to the α -carbon atom. The lithiated intermediate has been fully characterized by low temperature, multinuclear NMR experiments (^1H , ^{13}C , ^{31}P , ^{15}N). The lithiation step occurs between -35 and -40°C and the rearrangement proceeds almost at the same temperature. After deprotonation of **2** performed by an additional amine or by the metallic precursor itself (Ag_2O), the monoanionic N,S-bidentate ligand **2'** has been coordinated to palladium and silver. In the first case an air stable $\text{Pd}[\mathbf{2}']_2$ complex is isolated. In the second case, the formation of an unstable silver complex has been

observed but addition of triphenylphosphine produces an air and light stable silver complex $\text{L}'\text{Ag}(\text{PPh}_3)_2$. It can be concluded that N,S-pyrrole-thiophosphonate ligand is readily obtained in high yield following a base-induced [1,2]-rearrangement. This ligand can be coordinated to palladium or silver under mild conditions producing air and light stable complexes.

4. Experimental

4.1. General

All manipulations involving air and moisture sensitive organometallic compounds were performed using standard Schlenk techniques under nitrogen. Pentane and toluene were dried over Na sand, THF and diethyl ether over Na/benzophenone, and CH_2Cl_2 was dried over CaH_2 . All solvents were freshly distilled under nitrogen prior to use. NMR spectra (^1H (300.1 MHz), ^{13}C (75.5 MHz), and ^{31}P (121.4 MHz)) experiments were recorded on a Varian Inova 300 MHz spectrometer. Low temperature NMR experiments were recorded on a Bruker DRX500 equipped with an indirect 5 mm probhead TBI $^1\text{H}/\{\text{BB}\}/^{13}\text{C}$. Chemical shift values are reported in ppm (δ) and referenced internally to residual solvent signals (^1H , ^{13}C) or externally (^{31}P , H_3PO_4 85%; ^{15}N , neat CH_3NO_2). All reagents were purchased from Acros Chemicals and used as received. Elemental analyses were performed by Kolbe, Mikroanalytisches Laboratorium, Mülheim an der Ruhr, Germany and by the "Centre de Mesures Physiques de l'Ouest" Rennes, France.

4.2. $C_4H_4N-P(S)(OEt)_2$, *O,O*-diethyl-*N*-pyrrolylthiophosphoramidate (**1**)

Butyllithium (1.6 M in hexane; 40 mL, 65 mmol) is added dropwise to a solution of Pyrrole (4.0 g; 59.7 mmol) in THF (60 mL) at -80°C . After 30 min at -80°C , a solution of *O,O*-diethylchlorothiophosphate (11.26 g; 59.7 mmol) in THF (10 mL) is added at -80°C . The temperature of the solution is raised to 20°C in 5 h time. Then the mixture is stirred at 20°C overnight. The resulting solution is poured into water (150 mL) and the solution is extracted twice with diethylether (2×80 mL). The organic phase is washed with brine (60 mL) and dried over MgSO_4 . Filtration and evaporation of the solvents produce a pale yellow oil which is purified by Kugelrohr distillation (4×10^{-2} Torr; 80°C). Compound **1** is obtained as a colorless oil (11.94 g) in 91% yield. ^1H NMR (CDCl_3): δ 1.28 (m, 6H, $\text{CH}_3\text{-CH}_2\text{-O}$), 4.05 and 4.18 (2m, 4H, $\text{CH}_3\text{-CH}_2\text{-O}$), 6.30 (m, 2H, $\text{C}^3\text{-H}$ et $\text{C}^4\text{-H}$); 7.12 (m, 2H, $\text{C}^2\text{-H}$ et $\text{C}^5\text{-H}$). ^{31}P (CDCl_3): δ 63.6. ^{13}C (CDCl_3): δ 15.92 (d, $^3J_{\text{CP}} = 7.9$ Hz, CH_3), 62.68 (d, $^2J_{\text{CP}} = 4.6$ Hz, $\text{CH}_3\text{-CH}_2\text{O}$), 112.65 (d, $^3J_{\text{CP}} = 10.1$ Hz, C_3 and C_4), 123.06 (d, $^2J_{\text{CP}} = 6.7$ Hz, C_2 and C_5).

4.3. $(2-(\text{NHC}_4\text{H}_3)\text{-P(S)(OEt)}_2)$, *O,O*-diethyl pyrrol-2ylthiophosphonate (**2**)

Butyllithium (1.6 M in hexane; 31.7 mL, 50.7 mmol) is added dropwise to a solution of *O,O*-diethyl-*N*-pyrrolylthiophosphoramidate **1** (10.10 g; 46.0 mmol) in THF (50 mL) at -80°C . The solution is slowly left to reach 20°C (5 h) and then stirred at 20°C overnight. The obtained mixture is poured into a saturated aqueous ammonium chloride solution (100 mL) and extracted twice with diethylether (2×90 mL). The organic phase is treated as above to produce after distillation ($4.10\text{-}2$ Torr; 115°C) compound **2** as a colorless oil (9.64 g) in 95.4% yield. ^1H NMR (CDCl_3): δ 1.28 and 1.29 (2t, $^3J_{\text{HH}} = 7.0$ Hz, 6 H, $\text{CH}_3\text{-CH}_2\text{-O}$), 4.06 (m, 4H, $\text{CH}_3\text{-CH}_2\text{-O}$), 6.30 (m, 1H, $\text{C}_3\text{-H}$), 6.72 (m, 1H, $\text{C}_2\text{-H}$), 6.98 (m, 1H, $\text{C}_4\text{-H}$), 9.00 (s broad, 1H, N-H). ^{31}P (CDCl_3): δ 74.2. ^{13}C (CDCl_3): δ 15.93 (d, $^3J_{\text{CP}} = 7.9$ Hz, CH_3), 62.68 (d, $^2J_{\text{CP}} = 5.2$ Hz, $\text{CH}_3\text{-CH}_2\text{O}$), 110.47 (d, $^3J_{\text{CP}} = 13.4$ Hz, $\text{C}_3\text{-H}$), 116.51 (d, $^2J_{\text{CP}} = 15.9$ Hz, $\text{C}_2\text{-H}$), 122.27 (d, $^1J_{\text{CP}} = 187.1$ Hz, C_1), 123.38 (d, $^4J_{\text{CP}} = 11.6$ Hz, $\text{C}_4\text{-H}$). IR (ATR, cm^{-1}): 740, 773, 949, 1013, 1081, 1161, 1217, 1388, 2981, 3381.

4.4. Monitoring of the base-induced rearrangement

Three hundred milligrams (1.37×10^{-3} mole) of **2** in a small schlenk tube are dissolved in 5 mL of THF. The solution is cooled to -80°C and 0.92 mL of cold BuLi in solution 1.5 N in hexanes is then added. The mixture is stirred for 5 min then quickly transferred into an NMR tube itself transferred into the probe of the NMR machine at -80°C . The obtained spectra are mentioned in Table 1 and Fig. 1. See supporting informations for the different NMR sequences.

4.5. *Trans* bis(diethyl pyrrol-2-ylthiophosphonate)palladium (II), *trans*-[Pd($\kappa^2\text{-}(N, S) 2\text{-}(\text{NC}_4\text{H}_3)\text{-P(S)(OEt)}_2)$]₂ (**3**)

To a suspension of palladium dichloride bis(acetonitrile) (174 mg), in THF (10 mL) is added a solution of *O,O*-diethyl pyrrol-2-ylthiophosphonate **2** (300 mg; 1.37 mmol) and triethylamine (0.20 g; 1.98 mmol) in THF (3 mL). The reactional mixture is stirred at 20°C for 48 h. The solution is then concentrated *in vacuo* and the residue is purified by flash chromatography on silicagel (pentane/ethyl acetate: v/v: 100/10) to produce pure complex **3** as orange-red solid in 55% yield (200 mg). Recrystallisation in a diethylether/hexane mixture produces crystals suitable for single X-ray diffraction analysis. m.p.: 158°C . ^1H NMR (CDCl_3): δ 1.37 (t,

$^3J_{\text{HH}} = 7.0$ Hz, 12 H, $\text{CH}_3\text{-CH}_2\text{-O}$), 4.12 and 4.28 (2m, 8H, $\text{CH}_3\text{-CH}_2\text{-O}$), 6.26 (m, 2H, C-H), 6.62 (m, 2H, C-H), 7.08 (m, 2H, C-H). ^{31}P (CDCl_3): δ 89.8. ^{13}C (CDCl_3): δ 16.14 (d, $^3J_{\text{CP}} = 8.2$ Hz, CH_3), 64.98 (d, $^2J_{\text{CP}} = 4.3$ Hz, $\text{CH}_3\text{-CH}_2\text{O}$), 111.01 (d, $J = 12.8$ Hz, CH), 117.91 (d, $J = 24.4$ Hz, CH), 125.59 (d, $^1J_{\text{CP}} = 199.3$ Hz, C-P), 137.71 (d, $J = 21.1$ Hz, CH). IR (ATR, cm^{-1}): 729, 776, 794, 958, 973, 1007, 1098, 1190, 1248, 1389. Anal. Calc. for $\text{C}_{16}\text{H}_{26}\text{N}_2\text{O}_4\text{P}_2\text{S}_2\text{Pd}$: C, 35.40; H, 4.83; N, 5.16; S, 11.81. Found: C, 35.51; H, 4.73; N, 5.12; S, 11.88%.

4.6. Complexation of $2\text{-}(\text{NC}_4\text{H}_3)\text{-P(S)(OEt)}_2$ by $(\text{Ag})_2\text{O}$

A solution of silver oxide (143 mg; 0.62 mmol) and *O,O*-diethyl pyrrol-2-ylthiophosphonate **2** (270 mg; 1.23 mmol) in dichloromethane (10 mL) is stirred in the dark for 16 h. The dark suspension is then filtered on celite and the pad is rinsed with dichloromethane (20 mL). The colorless filtrate is concentrated *in vacuo* to produce a viscous colorless oil (380 mg; 95% yield). This intermediate complex is unstable and a chloroform solution of this complex turns black after few hours. Before degradation its NMR spectroscopic characterization was as follow: ^1H NMR (CDCl_3): δ 1.30 and 1.31 (2t, $^3J_{\text{HH}} = 7.0$ Hz, 6 H, $\text{CH}_3\text{-CH}_2\text{-O}$), 4.10 (m, 4H, $\text{CH}_3\text{-CH}_2\text{-O}$), 6.35 (m, 1H, C-H), 6.85 (m, 1H, C-H), 6.94 (m, 1H, C-H). ^{31}P (CDCl_3): δ 81.6 (s).

4.7. $[\text{Ag}\{\{\kappa^2\text{-}(N, S) 2\text{-}(\text{NC}_4\text{H}_3)\text{-P(S)(OEt)}_2)\}\{\kappa^1\text{-}(P) \text{P}(\text{C}_6\text{H}_5)_3\}]_2$ (**4**)

To the dark suspension obtained above, two equivalents of PPh_3 (2.46 mmol, 645 mg) in solution in dichloromethane were added at room temperature and the resulting mixture stirred for 3 h. After filtration on celite and evaporation of the solvent, a colorless oil is obtained. When washed with hexane at -20°C this oil crystallizes to give a white powder (785 mg, 75% yield). Crystallisation of this powder in a hexane/ CH_2Cl_2 mixture (90/10) affords crystals suitable for a X-ray diffraction study. ^1H NMR (CD_2Cl_2): δ 1.18 (t, $^3J_{\text{HH}} = 6.75$ Hz, 6H, $\text{CH}_3\text{-CH}_2\text{-O}$), 3.78 and 3.85 (2m, 4H, $\text{CH}_3\text{-CH}_2\text{-O}$), 6.32 (d, $^3J_{\text{HH}} = 1.5$ Hz, 1H, C-H), 6.75 (d, $^3J_{\text{HH}} = 2.0$ Hz, 1H, C-H), 6.96 (d, $^3J_{\text{HH}} = 3.5$ Hz, 1H, C-H) 7.39–7.26 m, 30H, $\text{P}(\text{Ph})_3$). ^{31}P (CD_2Cl_2): δ 89.8 (P=S), 4.0 $\text{P}(\text{Ph})_3$. ^{13}C (CD_2Cl_2): δ 16.05 (d, $^3J_{\text{CP}} = 8.3$ Hz, CH_3), 62.46 (s, $\text{CH}_3\text{-CH}_2\text{O}$), 111.06 (s, CH), 115.0 (d, $J_{\text{CP}} = 26.0$ Hz, CH), 125.50 (d, $^1J_{\text{CP}} = 199.1$ Hz, C-P), 135.05 (d, $J_{\text{CP}} = 27.0$ Hz, CH), 128.80 (d, $J_{\text{CP}} = 8.5$ Hz, aromatic CH), 129.80 (s, aromatic CH), 134.00 (d, $J_{\text{CP}} = 17.0$ Hz, aromatic CH), 134.25 (d, $J_{\text{CP}} = 15.0$ Hz, aromatic CP) Anal. Calc. for $\text{C}_{44}\text{H}_{43}\text{NO}_2\text{P}_3\text{SAg}$: C, 62.12; H, 5.10; N, 1.65; S, 3.77. Found: C, 61.91; H, 5.18; N, 1.66; S, 3.51%.

4.8. Crystal structure determinations

X-ray intensities were measured, for **3**, at a temperature of 150 K on a Nonius KappaCCD diffractometer with rotating anode (graphite monochromator, $\lambda = 0.71073 \text{ \AA}$) up to a resolution of $(\sin\theta/\lambda)_{\text{max}} = 0.65 \text{ \AA}^{-1}$ and, for **4**, at 100 K on an Oxford Diffraction X-Calibur 2 CCD diffractometer with ordinary sealed X-ray tube (graphite monochromator, $\lambda = 0.71073 \text{ \AA}$) up to $(\sin\theta/\lambda)_{\text{max}} = 0.62 \text{ \AA}^{-1}$. The structures were solved with automated Patterson methods (DIRDIF-99 [25]) for **3** or direct methods (SHELXS-97 [26]) for **4** and refined with SHELXL-97 [26] against F^2 of all reflections. Non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms were located in a difference Fourier map. Hydrogen atoms of the pyrrole rings in **3** were refined freely with isotropic displacement parameters; all other hydrogen atoms in **3** and **4** were refined with a riding model. The structure of **3** was refined as a pseudo-orthorhombic twin with a twofold rotation about the c^* axis as twin operation. The twin fraction refined to

Table 2

Summary of crystal data, intensity measurement and structure refinement for compounds **3** at 150 K and **4** at 100 K.

	3	4
Formula	C ₁₆ H ₂₆ N ₂ O ₄ P ₂ PdS ₂	C ₄₅ H ₄₅ AgCl ₂ NO ₂ P ₃ S
Fw	542.85	935.56
Crystal color	Orange	Colourless
Crystal size [mm]	0.51 × 0.36 × 0.30	0.22 × 0.15 × 0.06
Crystal system	Monoclinic	Triclinic
Space group	P ₂ ₁ /n (No. 14)	P $\bar{1}$ (No. 2)
a [Å]	8.4244(12)	13.0140(7)
b [Å]	12.3934(8)	13.4931(6)
c [Å]	10.4326(10)	13.6775(7)
α [°]	–	68.726(4)
β [°]	90.171(8)	77.947(4)
γ [°]	–	85.914(4)
V [Å ³]	1089.2(2)	2188.73(19)
Z	2	2
D _x [g/cm ³]	1.655	1.420
μ [mm ⁻¹]	1.214	0.777
Absorption correction method	Multi-scan	Multi-scan
Absorption correction range	0.62–0.70	0.951–0.955
Reflection (measured/unique)	32604/2498	18450/8919
Parameter/restraints	139/0	498/4
R ₁ /wR ₂ [<i>I</i> > 2 σ (<i>I</i>)]	0.0149/0.0378	0.0403/0.1175
R ₁ /wR ₂ [all reflection]	0.0156/0.0382	0.0555/0.1270
S	1.098	1.077
$\rho_{\text{min/max}}$ [e/Å ³]	–0.67/0.24	–1.44/1.20

0.4890(7). Geometry calculations and checking for higher symmetry was performed with the PLATON program [27].

Further details of the crystal structure determinations for **3** and **4** are given in Table 2.

5. Supplementary material

CCDC 736696, 734792 contain the supplementary crystallographic data for complexes **3** and **4**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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