Bis-2-thienyldiethylaminophosphane as a Ligand in Late Transition Metal Complexes and its Transformation to Bis-2-thienylphosphane

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Dedicated to Professor Hubert Schmidbaur on the occasion of his 80th birthday

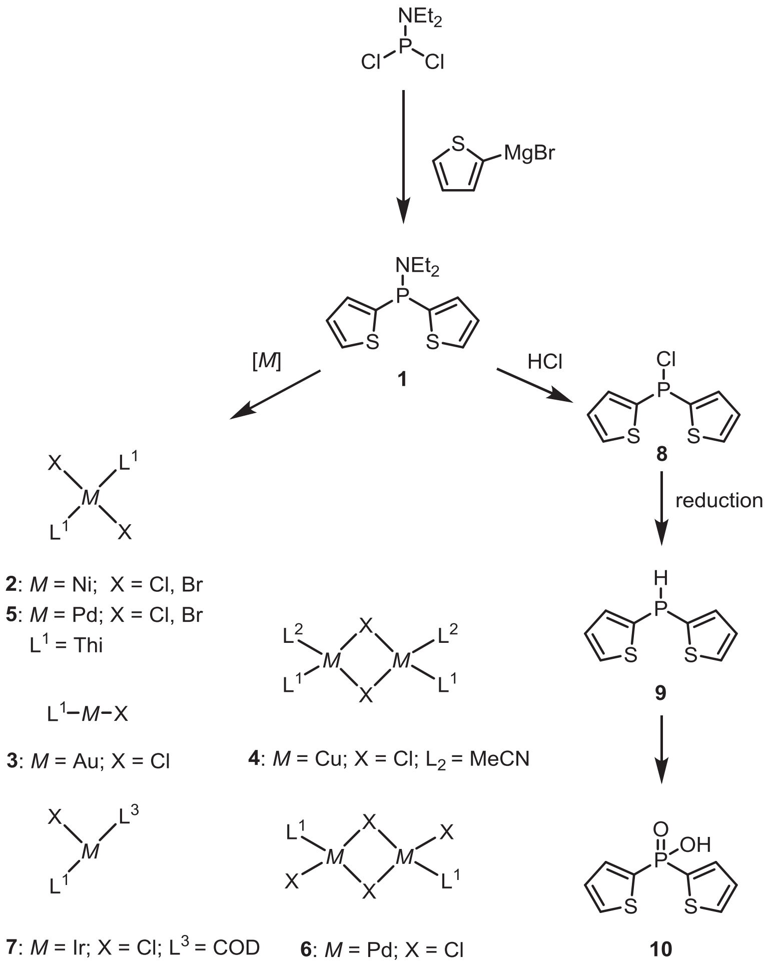
Bis-2-thienyldiethylaminophosphane $(C_4H_3S)_2PNEt_2$ (**1**) is introduced as a ligand for late transition metal complexes ($[(H_3C_4S)_2PNEt_2]_nMX_mL_p$), with M = Ni(II), Au(I), Cu(I), Pd(II), Ir(I), X = Cl, Br and L = NCMe, COD, (**2**–**7**). Reactions of **1** with the late transition metal salts $NiCl_2$·dme, $(Me_2S)AuCl$, CuCl, $PdCl_2(PhCN)_2$, and $[Ir(COD)Cl]_2$ yield the complexes $[\{(H_3C_4S)_2PNEt_2\}_2\cdot NiCl_2]$ (**2**), $[(H_3C_4S)_2PNEt_2\cdot AuCl]$ (**3**) $[(H_3C_4S)_2PNEt_2\cdot CuCl(CH_3CN)]_2$ (**4**), $[\{(H_3C_4S)_2PNEt_2\}_2\cdot PdCl_2]$ (**5**), $[\{(H_3C_4S)_2PNEt_2\}_2\cdot PdCl_2]_2$ (**6**), and $[(H_3C_4S)_2PNEt_2\cdot IrCl(COD)]$ (**7**). In addition, the transformation of **1** to the valuable chlorine-substituted starting material $(H_3C_4S)_2PCl$ (**8**) and the related conversion of **8** to the secondary phosphane $(H_3C_4S)_2PH$ (**9**) is reported. The complexes **2**–**7** are stable under inert gas conditions and were characterized by single-crystal X-ray studies, NMR spectroscopy, and elemental analysis.

Key words: Phosphorus, Sulfur, Transition Metals, Phosphane, Ligand Design

Introduction

Phosphane ligands are key auxiliary ingredients to numerous transition metal complexes used in catalytic processes [1]. Hence ligand design has been in the focus over the last decades and gains more and more importance in a large variety of synthetic applications. A phosphane ligand is introduced to fine-tune the electronic and steric properties of the complexes in order to increase their catalytic efficiency. Among phosphane ligands, triphenylphosphane is convenient and widely used but several other systems are also applied. We started to employ the ligand periphery in metal coordination by introducing chelating heteroaromatic substituents next to the donating center [2, 3]. This chelating ligand system was altered by replacing the bridging CH unit isoelectronically by N [4, 5], P [6, 7] or As [8, 9]. Ligating is particularly important with transition metals to invoke a certain reactivity in *e. g.* organic syntheses and organometallic reactions [10 – 12]. Among the late transition metals palladium is most prominent [13], but raising interest in nickel [14], copper [15], iridium [16 – 18], and gold [19, 20] shows that those metals are almost on par. In this paper we embarked on the ligand $(H_3C_4S)_2PNEt_2$ (**1**) due to the fact that it contains an amino group for the coordination of hard metals. The central phosphorus atom as well as the heteroaromatic sulfur atoms of the thienyl groups (Thi; SC_4H_3) were expected to coordinate softer metals, in particular late transition metals, according to Pearson's concept [21, 22].

There are many examples of Mn [23], Re [24], Rh [25], and Os [26] complexes reported in the literature investigating the coordination of *P*-thienyl motifs to get a deeper insight into the industrially most important mechanism of the hydrodesulfurization (HDS) of crude petroleum [27]. The interaction of thiophene and its side chain-substituted derivatives with (late) transition metals have been in the focus of interest since several years, showing to be a versatile ligand with different coordination modes, *e. g.* S-; η^2-; η^5-; η^4-; S-μ_2-; η^4,S-μ_3-bound [28]. Recently, Yang, Zhu and Roesky *et al.* reported the introduction of a $PThi_2$ moiety to stabilize germylenes as promising precursors for



Scheme 1. Reaction of **1** with the metal salts $NiCl_2 \cdot dme$, $(Me_2S)AuCl$, CuCl, $PdCl_2(PhCN)_2$, and $[Ir(COD)Cl]_2$, and reduction to **9** including side products formed.

further metal coordination [29]. In the course of our studies on the coordination of **1** to different late transition metals, we also became interested in the transformation of **1** *via* the chlorine intermediate to bis(2-thienyl)phopshane (Thi_2PH) (**9**) to have an even more versatile *P*,*S*-ligand at hand. We envisaged Thi_2PH to act as a *S*,*S*-; *P*,*S*- or μ-*P*,*S*-donor. Herein we report on our current status of this investigation.

Results and Discussion

The precursor Cl_2PNEt_2 can be turned into the *P*,*N*,*S*-ligand $(H_3C_4S)_2PNEt_2$ (**1**) *via* a Grignard reaction with 2-bromothiophene [30]. In the course of the Grignard reaction the complete removal of the formed magnesium halide salts is crucial to obtain the pure compound [31]. The addition of a late transition metal salt gives *mono*- and *bi*-nuclear metal complexes (**2**–**7**, Scheme 1, left) or reduction to bis(2-thienyl)phosphane (**9**) *via* bis(2-thienyl)chlorophosphane (**8**) takes place (Scheme 1, right). The metal complexes were obtained by a reaction of **1** with the late transition metal salts $NiCl_2 \cdot dme$, $(Me_2S)AuCl$, CuCl , $PdCl_2(PhCN)_2$, and $[Ir(COD)Cl]_2$, respectively. For the synthesis of the complexes **2**–**7** (Scheme 1) the appropriate metal salt was dissolved in toluene, and **1** was added. The reaction mixture was stirred until the salt was completely dissolved, stored at −20°C, and single crystals could be obtained after several days.

The soft late transition metals nickel(II), copper(I), palladium(II), iridium(I), and gold(I) were chosen to be attractive acceptors for the soft donor atoms phosphorus and sulfur and to study their coordination behavior towards **1**. The phosphane metal complexes **2**–**7** are colorless to red crystalline compounds which are stable under an inert atmosphere and soluble in common organic solvents. **2**–**7** were characterized by single-crystal X-ray diffraction and multinuclear NMR spectroscopy.

Single-crystal X-ray diffraction

The molecular structures of compounds **2**–**7** were established by single-crystal X-ray crystallography and are shown in Fig. 1 – 6. Crystallographic data for **2**–**7** are summarized in Table 1. The molecular structure of the nickel complex **2** is shown in Fig. 1. Complex **2** crystallizes in the triclinic space group $P\bar{1}$ with $Z = 2$. The nickel atom exhibits a distorted tetrahedral geometry and is coordinated by the phosphorus atoms of two phosphane ligands and two halogen atoms. In all complexes presented in this article the halogen position is occupied by Cl and/or Br, in changing ratios. The bromine stems either from the Grignard reaction side product impurity or from the metal halide salt employed to obtain **2**–**7**. Therefore, metal-halogen bond lengths are not particularly reliable but were found to be within the expected range. The thienyl rings of **1** are, similar to those in 2-thienyllithium structures [32], rotationally disordered along the P–C bond. The site occupation factors (SOF) of the positional disorder of the thienyl moieties are given in the Crystallographic Section. A preference of the orientation of the thienyl rings towards the metal ion is not indicated in any of the solid-state structures [33]. Nickel complexes are powerful tools for C–C bond formation. Prominently the name of Negishi is associated with Ni catalysis, and his studies brought the application of nickel into cross-coupling reactions [14]. Phosphanes are frequently used as ligands in the active complexes to stabilize the metal ion in the zero oxidation state. The cross-coupling reactions between Grignard reagents and C(sp^2)-halides reported by Kumada is only one example for this behavior [34].

Since the last decade gold came into the focus of chemistry as a versatile and powerful noble metal catalyst in organic synthesis. The active catalyst is often coordinated by a phosphane ligand [35] and is for example used in the oxidative oxyarylation of alkenes [36]. Furthermore, thienylphosphane-gold interactions support the electronic properties in conducting polymers [37]. The gold atom in **3** is coordinated by a chloride atom and the phosphorus atom of **1** in a linear fashion (P–Au–Cl 176.9(1)°), common for phosphane-gold-halogen complexes (Fig. 2). The P–Au distance is 2.233(1) Å and within the range of R_3P–Au bond lengths (P–Au av. 2.261 Å). The thienyl moieties show positional disorder (both site occupation factors refine each to 0.92) due to a rotation about the P–C bond. Therefore, the sulfur atoms do not show any preferred orientation, and no Au–S interaction can be observed (shortest distance 3.574 Å). The gold atoms of neighboring complexes show no aurophilic interactions [38, 39] as found in numerous other gold(I) compounds [33]. The distance between two adjacent gold atoms is longer than 5 Å and therefore too large for possible Au···Au interactions. Neither do the thienyl sulfur atoms of adjacent molecules donate to the gold atom.

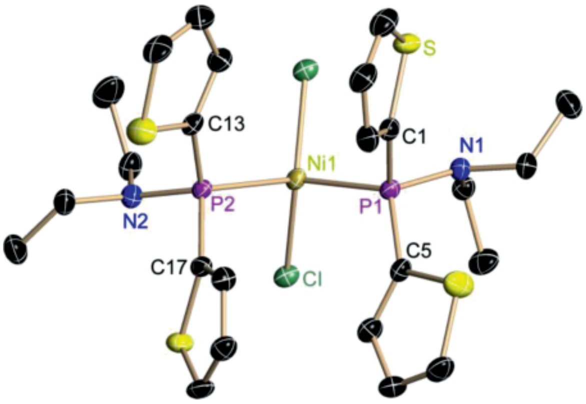


Fig. 1 (color online). Molecular structure of **2**. Anisotropic displacement parameters are depicted at the 50 % probability level. The toluene solvent molecule, the disorder of the thienyl moieties and of the halogen atoms, and H atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): P(1)–Ni(1) 2.310(1), P(2)–Ni(1) 2.311(1), P(1)–C(1) 1.796(3), P(1)–C(5) 1.800(3), P(1)–N(1) 1.666(2), P(2)–C(13) 1.794(3), P(2)–C(17) 1.799(5), P(2)–N(2) 1.665(2); P(1)–Ni(1)–P(2) 105.6(1), C(1)–P(1)–C(5) 103.0(1), C(13)–P(2)–C(17) 103.1(1).

Phosphane-coordinated copper complexes are widely applied in many fields of inorganic and organic synthesis, *e. g.* the 1,4-reduction of enones [40]. The soft copper(I) ion can be coordinated by a phosphorus atom [41] or, for example, by the soft sulfur atom

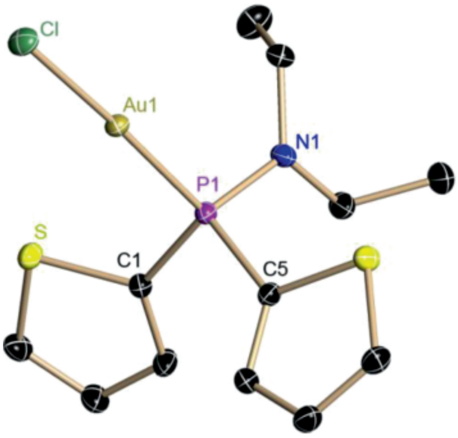


Fig. 2 (color online). Molecular structure of **3**. Anisotropic displacement parameters are depicted at the 50 % probability level. The disorder of the thienyl moieties and of the halogen atoms, and H atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): P(1)–Au(1) 2.233(1), P(1)–C(1) 1.801(1), P(1)–C(5) 1.798(1), P(1)–N(1) 1.655(1); P(1)–Au(1)–Cl(1) 176.9(1), C(1)–P(1)–C(5) 102.2(1).

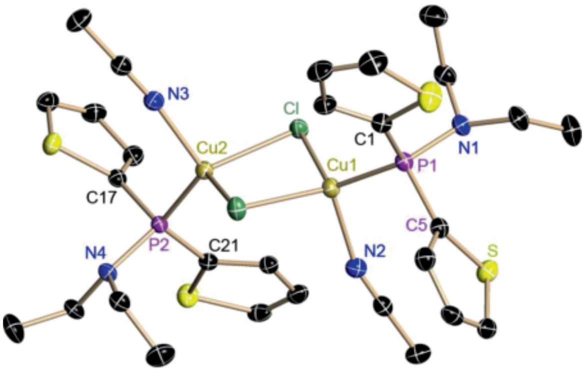


Fig. 3 (color online). Molecular structure of **4**. Anisotropic displacement parameters are depicted at the 50 % probability level. The disorder of the thienyl moieties and of the halogen atoms, and H atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): P(1)–Cu(1) 2.204(1), P(2)–Cu(2) 2.202(1), Cu(1)–N(2) 2.062(2), Cu(2)–N(3) 2.013(2), P–C 1.810(1); P(1)–Cu(1)–N(2)106.1(1), P(2)–Cu(2)–N(3) 111.6(1), C(1)–P(1)–C(5) 102.1(1), C(17)–P(2)–C(21) 100.1(1).

of thiophene [42, 43]. Therefore **1** is a potential ligand to coordinate copper(I) ions either *via* the phosphorus atom or the thienyl sulfur atom. Copper(I) chloride was dissolved in acetonitrile, and **1** was added. The reaction mixture was stirred until the salt was dissolved, and the solution was stored at −20 °C. The copper(I) complex **4** crystallizes in the triclinic space group $P\bar{1}$ with $Z = 2$. The two copper and two μ-bridging halogen atoms form a Cu_2X_2 (X = Cl, Br) four-membered ring [44]. Both copper atoms are tetrahedrally coordinated by the phosphorus atom of **1**, a nitrogen atom of an acetonitrile molecule and the μ-bridging chlorine atoms, respectively. The copper atoms in **4** show no interactions (shortest Cu···S 4.853(3) Å) with the sulfur atoms of the thienyl side arms.

The P–Cu bond lengths (av. 2.203(1) Å) are similar to those found in $[(Ph_3P)CuCl(NC_5H_5)]_2$ (2.395(1) Å) [45] and agree well with the mean values for all published Cu–P bond lengths (2.257 Å) in the Cambridge Structural Database (CSD) [33]. A comparison of the P–C bond length in **3** (av. 1.797(3) Å) with those in **4** (av. 1.809(2) Å) showed no differences, whereas the P–N distance is slightly elongated by ∼0.02 Å. The acetonitrile nitrogen atoms are at a distance of 2.062(2) and 2.013(2) Å from Cu(1) and Cu(2), respectively. The angles around the phosphorus atoms show a tetrahedral geometry similar to that of **3** (av. C–P–C 101.1(1)° and C–P–N 105.9(1)°). Selected bond lengths and angles of the copper(I) complex **4** are summarized in the caption of Fig. 3.

As mentioned in the introduction, palladium atom is salient among transition metals in organometallic catalysis. Thienyl-substituted phosphanes, *e. g.* Thi_3P, in which the central phosphorus atom coordinates to the palladium are applied in palladium complexes. By replacing triphenyl-phosphane by thienyl-substituted phosphanes, the outcome of a reaction can be improved [46]. Phosphorus-free thiophene ligand-stabilized palladium complexes are also catalytically active [47], *e. g.* by promoting the isomerization of 1-hexene to internal hexenes [48]. Besides catalysis thiophenes, polythiophenes and thienyl-containing phosphane palladium complexes are applied in conducting polymers [49], [50]] as well as in palladium-based molecular magnets [51]. In such molecules a coordination of the thienyl sulfur atom to palladium center has frequently been reported.

Crystals of products from the reaction of **1** with $PdCl_2(PhCN)_2$ were obtained by the reported procedure. Two palladium complexes, *i. e.* **5** and **6**, were obtained from reactions with different stoichiometries of 1 : 2 and 1 : 1 (metal : ligand) for **6** and **5**, respectively. Complex **5** is mononuclear (Fig. 4), whereas **6** consists

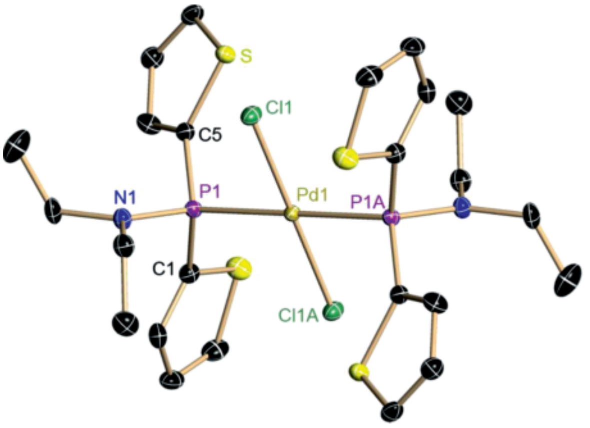


Fig. 4 (color online). Molecular structure of **5**. Anisotropic displacement parameters are depicted at the 50 % probability level. The disorder of the thienyl moieties and of the halogen atoms, and H atoms are omitted for clarity. Average bond lengths (Å) and angles (deg): P(1)–Pd(1) 2.336(1), P(1)–C(1) 1.808(2); C(1)–P(1)–C(5) 99.7(1), N(1)–P(1)–Pd(1) 110.4(1). Symmetry-generated atoms are labelled with A (symmetry code: $-x+1$, $-y+1$, $-z$).

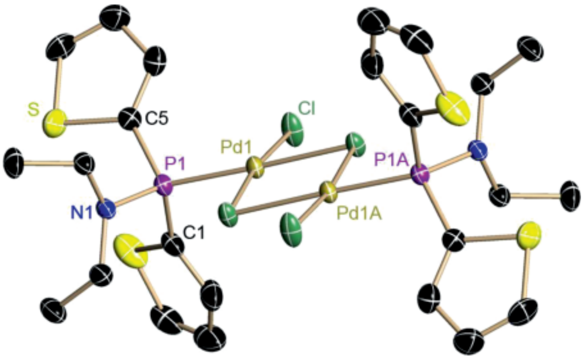


Fig. 5 (color online). Molecular structure of **6**. Anisotropic displacement parameters are depicted at the 50 % probability level. The toluene solvent molecule, the disorder of the thienyl moieties and halogen atoms, and H atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): P(1)–Pd(1) 2.208(1), P(1)–C(1) 1.780(3), P(1)–C(5) 1.784(3), P(1)–N(1) 1.660(2); C(1)–P(1)–C(5) 108.0(1). Symmetry-generated atoms are labelled with A (symmetry code: $-x+1$, $-y+1$, $-z+1$).

of a binuclear palladium species (Fig. 5). The formation of mononuclear or binuclear species can be tuned either by stoichiometry [52] or by the choice of the solvent [53]. By varying the polarity of the solvent it is possible to obtain either mononuclear or dinuclear palladium complexes with phosphane and halogen ligands. In both cases the palladium ions show a square-planar coordination sphere by the halide atoms and the phosphorus atom of **1**. The mononuclear complex **5** crystallizes as a non-merohedral twin (BASF: 0.20) in the triclinic space group $P\overline{1}$ with four independent complex halves in the asymmetric unit.

The palladium atom in **5** shows a square-planar coordination made up from the phosphorus atoms of two molecules of **1** and two halide atoms, each ligand pair in a mutual *trans* orientation. Similar to the situation in **3** and **4** the halide positions are occupied by chlorine and bromine atoms, respectively. A strict separation and positional refinement of these atoms was not possible. For the same reason the M–X (X = Cl, Br) distances are not discussed. The average Pd–P bond length (2.336(1) Å) of the four independent complexes fits well into the typical range of complexes of this kind, *e. g.* [((ThiPh$_2$)$_2$P)$_2$PCl$_2$] [54]. The average Pd–P bond length from the CSD [33] for P–Pd–P fragments is 2.304 Å which is in agreement with the distances found in **5**.

From the stoichiometric reaction of **1** with the palladium precursor crystals of **6** were obtained after storage at −20 °C for several days. The binuclear palladium complex **6** crystallizes in the monoclinic space group $P2_1/n$ with half a molecule in the asymmetric unit. A perspective view of **6** is shown in Fig. 5. The difference in the structural motif of **6** compared to **5** is the formation of a Pd$_2$X$_2$ four-membered ring. The palladium atoms are μ-bridged by two halide atoms, and the square-planar geometry around each Pd atom is completed by a halide atom and the phosphorus atom of **1**. The Pd–P bond length of 2.208(1) Å is comparable to the P–Pd distance found in [{(C$_4$H$_8$ON)Ph$_2$P}$_2$Pd$_2$Cl$_2$(μ-Cl$_2$)], 2.215(1) Å) [55], in which the central phosphorus atom is also coordinated by two aryl carbon atoms and an amine nitrogen atom. The Pd–P bond length in **6** is significantly shorter (∼ 0.13 Å) compared to that in **5**. This can be explained by electron depletion due to the three electron-withdrawing halide atoms. This bond shortage can also been detected in the P–C bond lengths P(1)–C(1) 1.780(3) Å and P(1)–C(5) 1.784(3) Å which are slightly shorter compared to those in **1** (∼0.02 Å).

The most prominent field of iridium complexes is the wide application as catalysts in hydrogenation reactions. Among these catalysts [56], a variety of phosphorus-based ligands can be found in

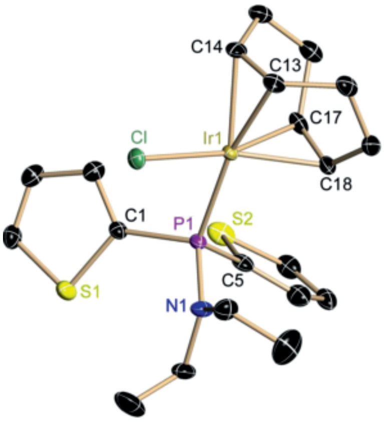


Fig. 6 (color online). Molecular structure of **7**. Anisotropic displacement parameters are depicted at the 50 % probability level. The toluene solvent molecule, the disorder of the thienyl moieties and H atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): P(1)–Ir(1) 2.289(1), P(1)–C(1) 1.816(2), P(1)–C(5) 1.803(10), P(1)–N(1) 1.659(2), Ir(1)–C(13) 2.222(2), Ir(1)–C(14) 2.206(2), Ir(1)–C(17) 2.128(2), Ir(1)–C(18) 2.110(2); C(1)–P(1)–C(5) 101.6(5).

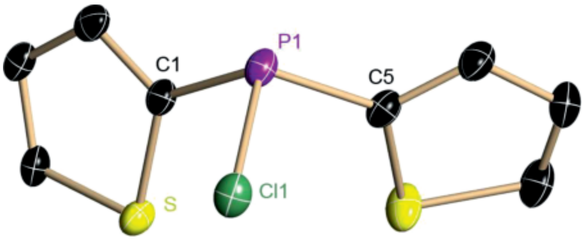


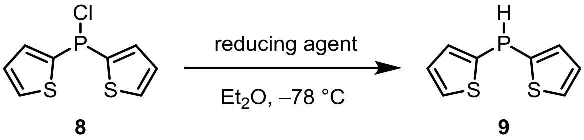
Fig. 7 (color online). Molecular structure of **8**. Anisotropic displacement parameters are depicted at the 50 % probability level. The disorder of the thienyl moieties and H atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): P–C av. 1.803(4), P–Cl av. 2.105(1); C–P–C av. 105.0(2), C–P–Cl av. 99.4(1).

heterobimetallic clusters [57]. Recently *P*,*N*,*P*-pincer complexes of iridium entered the flourishing field of nitrogen formation and nitrogen fixation [18]. Single crystals of the iridium complex **7** were obtained by the same procedure as described for **2**–**6** using $[IrCl(COD)]_2$ as an iridium precursor. Complex **7** crystallizes in the triclinic space group $P\bar{1}$ with the whole complex in the asymmetric unit (Fig. 6). In the mononuclear complex the iridium(I) atom is coordinated by the phosphorus atom of **1**, a halide and a cyclooctadiene ligand. Both double bonds of the cyclooctadiene moiety coordinate to the iridium atom. The Ir–C distances to the corresponding carbon atoms are Ir(1)–C(13) 2.222(3) Å, Ir(1)–C(14) 2.206(2) Å, Ir(1)–C(17) 2.128(2) Å, Ir(1)–C(18) 2.110(2) Å, *i. e.* two longer and two shorter bonds are present. Similar to the other complexes a positional disorder of the halide ion occurs (SOF: 76:24 / Cl:Br). The mass spectrometry analysis of **7** confirms the presence of both halides ($m/z = 605.0$ for chloride and 649.0 for bromide), but unfortunately, the ratio of Cl to Br could not be determined from the mass spectrum. Similar to the previously mentioned complexes **2**–**6**, the two thienyl rings show no preferred orientation towards the Ir(I) atom. Remarkably, only one of the rings showed a typical rotational disorder (SOF = 55 : 45), whereas the other sulfur atom (S1) points away from the iridium ion.

Bis(2-thienyl)chlorophosphane complex **8** was prepared starting from **1** according to the published method [30]. After filtration of the crude product through Celite and removal of *n*-pentane, **8** was obtained in high yields. The crystals were suitable for single-crystal X-ray diffraction. **8** crystallizes in the orthorhombic space group *Fdd*2 with two independent molecules in the asymmetric unit (Fig. 7). The thienyl groups are rotationally disordered. The P–Cl distance in **8** is 2.10(4) Å and in good accordance with the bond lengths reported in the literature (2.04 Å from gas-phase electron diffraction [58]; and 2.055 – 2.071 Å in the solid state [33]).

To transform **8** into the versatile, potentially *P*,*S*-donating secondary phosphane Thi_2PH (**9**), different hydride transfer agents (DIBAL, $LiAlH_4$ [29], K-selectride and $LiBH_4$) were tested in order to find the best reaction conditions (Scheme 2).

When **8** is added to an ethereal solution of DIBAL or $LiAlH_4$ the reaction is almost quantitative, and side-products are mostly suppressed. In reactions where the reduction agent is added to **8** the diphosphane Thi_4P_2 [29] is formed in ratios larger than 1 : 3, confirmed by NMR experiments.



Scheme 2. Reduction of **8** with reducing agents (DIBAL, $LiAlH_4$, K-selectrid and $LiBH_4$) to **9**.

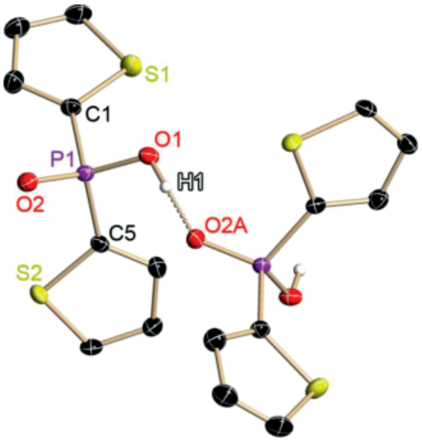


Fig. 8 (color online). Molecular structure of $Thi_2PO(OH)$ (**10**). Anisotropic displacement parameters are depicted at the 50 % probability level. The minor-occupied position of the disordered thienyl moieties and H atoms, except for O–*H*, are omitted for clarity. Selected bond lengths (Å) and angles (deg): P–C av. 1.771(2), P–O2 1.497(1), P–OH 1.551(1), O–H···O2A 1.61(3); C–P–C 111.4(1), O–P–O 117.8(1). Symmetry code: $-x+3/2, y-1/2, -z+1/2$.

During the work-up of the reactions another side product could be isolated and characterized. Crystals of dithienylphosphinic acid (**10**) are formed when **9** is exposed to air or to improperly degassed water. Compound **10** crystallizes in the monoclinic space group $P2_1/n$ with one molecule in the asymmetric unit. The molecules of **10** form coordination chains *via* hydrogen bonding between the hydroxyl protons and the oxygen atoms (O(2A)) of adjacent molecules (Fig. 8).

Conclusion

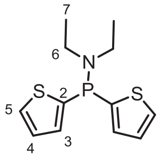
This work reports the synthesis and structural comparison of bis(2-thienyl)-diethylamino-phosphane (**1**) coordinated transition metal complexes **2**–**7**. All compounds show metal-phosphorus interactions. Although literature examples have shown that the coordination of the thienyl-S atom to late transition metals, *e. g.* nickel(II), gold(I), copper(I), palladium(II), and iridium(I), is feasible the thienyl sulfur atoms of the here reported structures show no interaction to any of the late transition metals. The main reason for the non-coordination, besides the stronger donor capacity of phosphorus, could be the missing pre-coordination of the sulfur atoms. The insertion of a linker, *e. g.* a CH_2 group, between the phosphorus atom and the thienyl moiety would lead to a widened bite-angle rendering a *P,S*-coordination more likely [59, 60], converting them to promising *P,N,S*-Janus-Head ligands [61]. The resulting five-membered metallacycles are less strained than the four-membered rings in the complexes reported here without a linker. Reduction and the hydrogen exchange reaction of the *sec.* phosphane are auspicious and under investigation. The transformation of **1** to Thi_2PH was shown to be challenging ($Thi_2PO(OH)$, Thi_4P_2 as side products) but is possible by a careful work-up of the crude reaction mixture.

Experimental Section

All reactions and manipulations were performed under an inert gas atmosphere using standard Schlenk techniques or in a glove box. Used solvents were dried over Na, K or Na/K alloy, respectively, and distilled under nitrogen prior to use. The precursors Cl_2PNEt_2 and Thi_2PNEt_2 (**1**) were prepared by slightly changed literature methods [30]. ^1H, $^{13}C\{^1H\}$, $^{31}P\{^1H\}$ NMR spectra were recorded using Bruker Avance DPX 200, 300 MHz spectrometers. Chemical shifts δ are measured in ppm and the coupling constant J in Hz. For the ^1H and $^{13}C\{^1H\}$ NMR spectra tetramethylsilane was used as external standard. Used abbreviations for multiplets are as followed: br = broad signal, s = singlet, d = doublet, dd = doublet of doublets, ddd = doublet of doublets of doublets, m = multiplet, q = quartet. A few crystals were transferred to NMR tubes and dissolved in $[D_6]$benzene. All spectra were recorded at room temperature. The labelling scheme of the atoms is given in Scheme 3. Mass spectra were recorded on a MAT 95 EI-MS spectrometer at 70 eV. Elemental analyses were carried out for all compounds, but due to halide disorder and air sensitivity reliable values could not be obtained.

Synthesis of $(H_3C_4S)_2PNEt_2$ *(**1**)* [30]

To a mechanically stirred (KPG) solution of PCl_3 (68.7 g, 0.5 mol, 43.7 mL, 1 eq.) in diethyl ether (650 mL) $HNEt_2$ (73.1 g, 1 mol, 104 mL, 2 eq.) was added dropwise at −78 °C, and the reaction mixture was allowed to warm up overnight. The precipitate was filtered off with a frit (P2) of large diameter and washed with Et_2O (6 × 60 mL). The solvents were removed under reduced pressure and the crude



Scheme 3.

product distilled (oil bath at 60 – 70 °C). Cl_2PNEt_2 was obtained as a colorless liquid (72.2 g, 0.42 mol, 60.4 mL, 83 %; Lit: 88 % [62]). The purity of the product was confirmed by NMR spectroscopy (^{31}P: $\delta = 162.4$ ppm). To a suspension of magnesium turnings (16.7 g, 0.69 mol, 2.5 eq.) in thf (80 mL) a few drops of 2-bromothiophene were added until the reaction started, and the rest (99.7 g, 0.61 mol, 57.3 mL, 2.22 eq.) were added dropwise to maintain the reaction. After the reaction was finished and cooled to room temperature, the unreacted magnesium was filtered off. The filtrated was cooled to 0 °C, and Cl_2PNEt_2 (47.8 g, 0.28 mol, 40 mL, 1 eq.) was added dropwise within 1 h, and the mixture was stirred for another hour. Pentane (200 mL) was added, the precipitate was filtered off (P2 frit) and washed with pentane (5 × 50 mL). The volume of the collected solution was reduced, filtered (P4 frit with Celite) and washed with pentane (3 × 15 mL) again. After removal of the solvent, **1** could be obtained as a brownish liquid (41.3 g, 0.15 mol, 49.1 mL, 56 %). $C_{12}H_{16}NPS_2$ ($M = 269.37$). – MS (EI, 70 eV): $m/z = 269$ $[M]^+$, 197 $[M\text{–}NEt_2]^+$. – ^{1}H NMR (300.13 MHz, C_6D_6): $\delta = 0.90$ (t, $^3J = 7.1$ Hz, 6 H, CH_3), 3.08 (dq, $^3J = 10.8$, 7.1 Hz, 4 H, CH_2), 6.81 (ddd, $^3J = 4.8$, 3.5, 1.3 Hz, 2 H, 4-H), 7.17 ppm (m, 4 H, 3-H, 5-H). – ^{13}C NMR (75.47 MHz, C_6D_6): $\delta = 14.59$ (d, $^3J = 3.8$ Hz, CH_3), 44.33 (d, $^2J = 15.8$ Hz, CH_2), 127.96 (d, $^3J = 5.9$ Hz, 4-*C*), 130.60 (d, $^3J = 2.2$ Hz, 5-*C*), 133.62 (d, $^2J = 23.8$ Hz, 3-*C*), 143.29 ppm (d, $^1J = 30.3$ Hz, 2-*C*). – ^{31}P NMR (121.49 MHz, C_6D_6): $\delta = 38.69$ ppm.

*General procedure for the synthesis of compounds **2**–**7***

The corresponding metal salt was dissolved in a dry solvent, and **1** was added (details see below). After stirring for 24 h at room temperature the precipitate was filtered off, and the remaining solution was placed in a freezer for crystallization. Within a few days single crystals suitable for X-ray experiments were obtained.

Synthesis of $[\{(C_4H_3S)_2PNEt_2\}_2\cdot NiCl/Br_2]$ (**2**)

To $[NiCl_2(diglyme)]_2$ (0.60 g, 1.4 mmol, 1.0 eq.) dissolved in toluene (15 mL) one equivalent of **1** was added. After several days at −20 °C light-green crystals could be isolated. – MS (EI, 70 eV): $m/z = 442$ $[M_{Br/Cl}\text{–}L]^+$, 362 $[M_{Cl}\text{–}L\text{–}Cl]^+$, 329 $[M_{Cl}\text{–}L\text{–}Cl_2]^+$, 269 $[Thi_2PNEt_2]^+$, 197 $[Thi_2P]^+$, 115 $[PThi]^+$.

Synthesis of $[(C_4H_3S)_2PNEt_2\cdot AuCl/Br]$ (**3**)

$(Me_2S)AuCl$ (0.05 g, 0.17 mmol, 1.0 eq.) was dissolved in toluene (30 mL), and **1** (0.05 g, 0.21 mmol, 1.2 eq.) was added. After several days at −20 °C only a few yellow crystals could be isolated.

Synthesis of $[(C_4H_3S)_2PNEt_2\cdot CuCl/Br\,(CH_3CN)]_2$ (**4**)

To copper(I)chloride (0.1 g, 10 mmol, 1.0 eq.) dissolved in abs. acetonitrile (10 mL) **1** (0.27 g, 11.6 mmol, 1.16 eq.) was added at room temperature, and the mixture was stirred for 24 h. The reaction mixture was filtered through a glass filter, and the filtrate was stored at −35 °C for 7 days. Yellow crystals of **4** could be isolated (0.089 g, 20 %). – ^{1}H NMR (300.13 MHz, C_6D_6): $\delta = 0.96$ (t, $^3J = 7.0$ Hz, 6 H, CH_3), 3.34 (dq, $^3J = 14.0$, 7.0 Hz, 4 H, CH_2), 6.74 (ddd, $^3J = 4.9$, 3.6, 1.5 Hz, 2 H, 4-H), 7.07 (m, 2 H, 3-H), 7.82 ppm (ddd, $^3J = 7.8$, 3.5, 1.1, 2 H, 5-H). – ^{31}P NMR (121.49, C_6D_6) : $\delta = 30.5$ ppm.

Synthesis of $[\{(C_4H_3S)_2PNEt_2\}_2\cdot PdCl/Br_2]$ (**5**)

To bis(benzonitrile)palladium(II) chloride (0.79 g. 2.06 mmol, 1 eq.) dissolved in toluene (25 mL) one equivalent of **1** was added. Only a few crystals of the product could be isolated.

Synthesis of $[\{(C_4H_3S)_2PNEt_2\}\cdot PdCl/Br_2]_2$ (**6**)

A few crystals of **6** could be isolated, which were used for analysis. – ^{1}H NMR (300.13 MHz, C_6D_6): $\delta = 1.03$ (t, $^3J = 7.1$ Hz, 6 H, CH_3), 3.47 (m, 4 H, CH_2), 6.75 (ddd, $^3J = 4.6$, 1.7, 0.9 Hz, 2 H, 4-H), 7.06 (m, 2 H, 3-H,), 7.93 ppm (ddd, $^3J = 6.8$, 3.3, 1.1, 2 H, 5-H). – ^{31}P NMR (121.49 MHz, C_6D_6): $\delta = 49.70$ ppm.

Synthesis of $[(C_4H_3S)_2PNEt_2\cdot IrCl/Br(C_8H_{12})]$ (**7**)

To bis(1,5-cyclooctadiene)diiridium(I) dichloride (10 mg, 1.5×10^{-2} mmol, 0.5 eq.) dissolved in toluene (5 mL) was added one equivalent of **1** (8 mg, 0.03 mmol). A few crystals of **7** could be isolated, which were used for analysis. – MS (EI, 70 eV): $m/z = 649.0$ $[M_{Br}]^+$, 605.0 $[M_{Cl}]^+$, 577.0 $[M_{Br}\text{–}NEt_2]^+$, 566.0 $[M_{Br}\text{–}Thi]^+$, 534.0 $[M_{Cl}\text{–}NEt_2]^+$, 496.0 $[M_{Cl}\text{–}COD]^+$, 458.9 $[M_{Br}\text{–}COD\text{–}Thi]^+$, 269.0 $[Thi_2PNEt_2]^+$, 197.0 $[Thi_2P]^+$, 115.0 $[PThi]^+$, 91.0 $[Tol\text{–}H]^+$. – ^{31}P NMR (121.49 MHz, C_6D_6): $\delta = 49.19$ ppm.

Synthesis of $(C_4H_3S)_2PCl$ (**8**) [30]

Through a solution of **1** (21.3 g, 79 mmol, 25.3 mL) in pentane (500 mL) gaseous HCl was passed at 0 °C for 30 – 45 min. The precipitated $Et_2NH\cdot HCl$ was filtered off and washed with pentane (3 × 20 mL). The solvents were removed under reduced pressure, and the product was obtained as slightly yellow crystals (18.0 g, 77.5 mmol, 98 %). – ^{1}H NMR (300.13 MHz, C_6D_6): $\delta = 6.58$ (ddd, $^3J = 5.0$, 3.6 Hz, $^4J = 1.6$ Hz, 2 H, 4-H), 7.04 (dd, $^3J = 4.9$, $^4J = 1.1$ Hz, 2 H, 5-H), 7.25 ppm (ddd, $^3J = 6.7$, 3.5, $^4J = 1.1$ Hz, 2 H, 3-H). – ^{31}P NMR (121.49 MHz, C_6D_6): $\delta = 53.36$ ppm.

Table 1. Crystallographic data for **2**–**8** and **10**.

	2	**3**	**4**	**5**	**6**	**7**	**8**	**10**
Empirical formula	$C_{31}H_{40}Cl_{1.48}Br_{0.52}N_2S_4P_2Ni$	$C_{12}H_{16}Cl_{0.95}Br_{0.05}NS_2PAu$	$C_{28}H_{38}Cl_{1.9}Br_{0.1}N_4S_4P_2Cu_2$	$C_{24}H_{32}Cl_{1.78}Br_{0.22}N_2S_4P_2Pd$	$C_{38}H_{48}Cl_{3.75}Br_{0.25}N_2S_4P_2Pd_2$	$C_{23.5}H_{32}Cl_{0.76}Br_{0.24}NS_2PIr$	$C_8H_6ClS_2P$	$C_8H_7O_2S_2P$
CCDC no.	1011475	1011472	1011473	1011477	1011476	1011474	1011478	1011479
M_r	783.62	503.78	823.02	725.79	1088.85	662.01	232.67	230.23
Crystal size, mm^3	$0.12 \times 0.1 \times 0.08$	$0.10 \times 0.05 \times 0.05$	$0.12 \times 0.08 \times 0.03$	$0.2 \times 0.12 \times 0.12$	$0.08 \times 0.07 \times 0.04$	$0.11 \times 0.10 \times 0.10$	$0.17 \times 0.10 \times 0.02$	$0.2 \times 0.05 \times 0.05$
Crystal system	triclinic	monoclinic	triclinic	triclinic	monoclinic	triclinic	orthorhombic	monoclinic
Space group	$P\bar{1}$	$P2_1/n$	$P\bar{1}$	$P\bar{1}$	$P2_1/n$	$P\bar{1}$	$Fdd2$	$P2_1/n$
a, Å	11.175(2)	7.896(2)	9.040(2)	11.796(2)	9.901(2)	8.179(2)	23.319(3)	12.307(2)
b, Å	11.357(2)	10.748(2)	13.599(2)	15.737(3)	15.915(3)	9.873(2)	58.509(6)	6.290(2)
c, Å	14.426(3)	18.415(3)	15.166(3)	17.501(2)	14.479(2)	16.129(3)	5.666(2)	13.650(3)
α, deg	86.64(2)	90	101.22(2)	63.96(2)	90	78.81(2)	90	90
β, deg	80.43(2)	99.32(2)	96.09(2)	85.82(2)	102.35(2)	88.14(3)	90	113.90(2)
γ, deg	89.89(3)	90	101.64(3)	87.83(3)	90	73.07(2)	90	90
V, Å^3	1802.2(6)	1542.2(5)	1770.6(6)	2911.2(8)	2228.7(7)	1221.9(4)	7731(3)	966.1(4)
$D_{\text{calcd.}}$, g cm^{-3}	1.44	2.17	1.54	1.66	1.62	1.80	1.60	1.58
Z	2	4	2	4	2	2	32	4
Abs. coeff., mm^{-1}	1.6	10.2	1.8	1.5	1.5	6.2	0.9	0.7
θ range, deg	1.434 – 26.755	2.201 – 37.089	1.385 – 26.768	1.298 – 27.572	1.926 – 27.121	1.287 – 27.484	1.392 – 26.825	1.883 – 26.752
Data/restraints/Parameters	7607/454/461	7865/400/243	7548/442/467	13 426/2340/921	4932/425/320	5604/337/362	4140/631/291	2044/340/196
R_{int}	0.0452	0.0240	0.0551	0.070	0.0463	0.0318	0.0648	0.0249
$R1/wR2$ $[I > 2\,\sigma(I)]^{a,b}$	0.0357/0.0685	0.0156/0.0286	0.0316/0.0641	0.0274/0.0543	0.0293/0.0569	0.0145/0.0337	0.0304/0.0611	0.0236/0.0610
$R1/wR2$ (all data)	0.0513/0.0741	0.0239/0.0304	0.0446/0.0695	0.0372/0.0580	0.0419/0.0622	0.0153/0.0340	0.0352/0.0625	0.0278/0.0636
Flack (x)	–	–	–	–	–	–	0.00(4)	–
$\Delta\rho$ (max/min), e Å^{-3}	0.44/−0.47	0.91/−1.07	0.40/−0.42	0.50/−0.37	0.65/−0.44	0.72/−0.55	0.26/−0.26	0.36/−0.26

[a] $R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; [b] $wR2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{0.5}$.

*Synthesis of ($C_4H_3S)_2PH$ (**9**)*

8 (7.05 g, 30.4 mmol, 1 eq.) dissolved in Et_2O (25 mL) was added slowly at −78 °C to a solution of diisobutylaluminum hydride (4.75 g, 33.4 mmol, 1.1 eq.) dissolved in Et_2O (30 mL). The mixture was allowed to warm up overnight. The formed salts were filtered (P4 frit, Celite), washed with Et_2O (3 × 5 mL), and all volatile compounds were removed *in vacuo*. The reaction yielded **9** and the byproduct **10**. Distillation led to the decomposition of **9**. – ^1H NMR (300.13 MHz, C_6D_6): $\delta = 6.95$ (dd, $^3J_{HH} = 3.6$ Hz, $^4J_{HH} = 1.2$ Hz, 2 H, 3-H), 6.73 (dd, $^3J_{HH} = 5.1$ Hz, $^4J_{HH} = 1.2$ Hz, 2 H, 5-H), 6.64 (dd, $^3J_{HH} = 5.1$ Hz, $^3J_{HH} = 3.6$ Hz, 2 H, 4-H), 5.46 ppm (d, $^1J_{PH} = 222.0$ Hz, 1 H, P*H*). – $^{13}C\{^1H\}$ NMR (75.48 MHz, MHz, C_6D_6): $\delta = 135.54$ (d, $^1J_{PC} = 120.8$ Hz, 2-C), 130.93 (s, 5-C), 127.72 (m, 3-C), 127.55 ppm (m, 4-C). – ^{31}P NMR (78.48 MHz, C_6D_6): $\delta = -90.63$ ppm (dt, $^1J_{PH} = 227.7$ Hz, $^3J_{PH} = 5.9$ Hz).

*X-Ray structure determinations of **2**–**8** and **10***

Single crystals were selected from a Schlenk flask under argon atmosphere and covered with perfluorated polyether oil on a microscope slide, which was cooled with a nitrogen gas flow using the X-Temp2 equipment [63–65]. An appropriate crystal was selected using a polarizing microscope, mounted on the tip of a MiTeGen© MicroMount or on a glass fiber, fixed to a goniometer head, and shock-cooled by the crystal cooling device.

The data for **2**–**8** and **10** were collected from shock-cooled crystals at 100(2) K [64]. The data of **2**–**8** and **10** were obtained on an Incoatec Microsource [66] instrument using mirror-monochromatized MoK_α radiation ($\lambda = 71.073$ pm) and an APEX II detector with a D8 goniometer. The data of **2**–**8** and **10** were integrated with SAINT [67], and an empirical absorption correction and scaling were applied (SADABS [68]). The structures were solved by Direct Methods (SHELXS-97 [69]) and refined by full-matrix least-squares methods against F^2 for all data (SHELXL [70, 71]) within the SHELXLE GUI software [72].

All non-hydrogen atoms were refined with anisotropic displacement parameters. The hydrogen atoms were refined isotropically at calculated positions using a riding model with their U_{iso} values constrained to 1.5 times the U_{eq} of their pivot atoms for terminal sp^3 carbon atoms and 1.2 times for all other carbon atoms. Disordered moieties were refined using distance restraints and restraints on the anisotropic displacement parameters. The CCDC numbers, crystal data and experimental details for the X-ray measurements are listed in Table 1.

CCDC 1011472–1011479 (see Table 1) contain the supplementary crystallographic data for this paper. 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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