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Sulfurization of Phosphanylphosphinidene Ligand: Access to Phosphinothioyltrithiophosphonato Platinum(II) Complexes

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ABSTRACT

The reactivity of phosphanylphosphinidene Pt(0) complexes [DppePt(η^2-P-P*t*Bu$_2$)] (**1**) and [(*p*-Tol$_3$P)$_2$Pt(η^2-P-P*t*Bu$_2$)] (**2**) toward sulfur was studied. Reactions of **1** and **2** with an excess of sulfur led to the formation of the first transition metal complexes **3** and **4** with phosphinothioyltrithiophosphonato ligands with the formula [*t*Bu$_2$P(=S)-P(=S)S$_2$]$^{2-}$. In contrast to previous reports on the phosphanylphosphinidene moiety sulfurization, the P-P bond was not cleaved during these reactions. The structures of sulfurization products **3** and **4** were elucidated using NMR spectroscopy, X-ray diffraction, and DFT calculations.

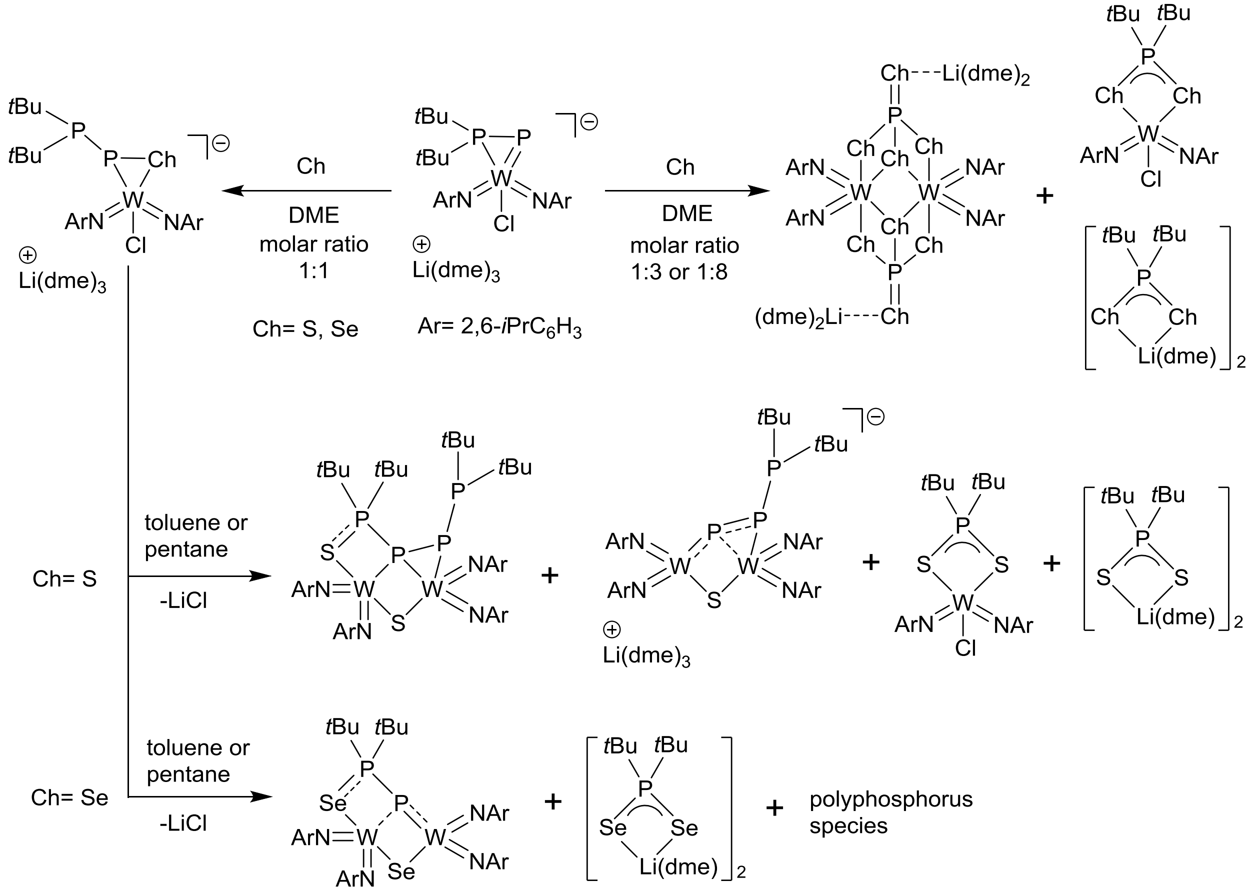
INTRODUCTION

It is well known that phosphinidenes have long been established as short-lived intermediates, which are stable under cryogenic matrix conditions[1]. These species can be captured with trapping reagents, mainly unsaturated hydrocarbons[2] and Lewis bases such as stable carbenes[3] or phosphines[4]. The stabilization can also be accomplished via coordination to the metal centers[5][6][7]. Phosphinidene complexes are important transferring vehicles of an R-P moiety to organic or inorganic molecules. Schrock *et al*. have shown the Phospha-Wittig reactivity of phosphinidene Ta(V) complex[8]. Stephan *et al*. proved that the reactive [Cp$_2$Zr(PR)(PMe$_3$) is a powerful donor of the PR moiety[9]. Recently, we have shown that [Cp$_2$Zr-η^1-P-P*t*Bu$_2$)(PPhMe$_2$)] or [(DippN)$_2$W(Cl)(η^2-P-P*t*Bu$_2$)]$^-$ transfer P-P*t*Bu$_2$ moiety to [(*p*-Tol$_3$P)$_2$PtCl$_2$][10]. In 2016, Bertrand *et al.* synthesized the first isolable singlet phosphanylphosphinidene R$_2$PP. It was both kinetically and electronically stabilized, where R$_2$ is a very bulky, nitrogen-based chelate substituent[11].

Phosphinidene chalcogenides are also very reactive transient species, and up to now, no free phosphinidene chalcogenides were isolated. Similarly, as phosphinidenes, they can be stabilized as adducts with carbenes or as ligands in transition metal coordination spheres. Trapping experiments have revealed that R–P=Ch (R = 2,6-dimethoxyphenyl, Ch = S, Se) displays singlet-carbene-like reactivity[12]. Mathey found that the electronic structure of Me-P=S differs from the structure of a typical phospha-alkene and it can also react as a carbene. He applied a mild protocol to generate Ph-P=S and demonstrated that it reacts with 2,3-dimethylbutadiene yielding an [2+4] adduct[13]. Ragogna *et al.* generated phosphinidene chalcogenides R–P=Ch from four-membered heterocycles (R-P(μ_2-Ch)$_2$P-R, R = 2,6-Mes$_2$C$_6$H$_3$, Ch = S, Se). The monomeric R–P=Ch, which is probably the reactive intermediate in the solution, can be trapped as an adduct with a stable carbene and in the Diels-Alder reaction with 2,3-dimethylbutadiene displaying typical olefin reactivity and yielding an [2+4] adduct[14]. The promising access to complexes with phosphinidene chalcogenides as ligands is to oxidize phosphinidene or primary phosphido complexes using free chalcogens or chalcogen sources. The reports on the oxidation of such complexes are scarce and until recently are rather limited to dinuclear phosphinidene complexes. The oxidation in air of anionic phosphido (PHMes*) bridged complexes (H-DBU)[M$_2$Cp$_2$(μ_2-PHMes*)(CO)$_4$] (M = Mo, W) yields anionic (H-DBU)[MCp(CO)$_2${P(O)Mes*)][15][16]. Oxidation of the latter anion with [Cp$_2$Fe]BF$_4$ yields [Mo$_2$Cp$_2$(CO)$_4${P(O)Mes*}$_2$] containing two terminally bound P(O)Mes* units[17]. Anionic oxophosphinidene complex (H-DBU)[MoCp(CO)$_2${P(O)Mes*)] can be oxidized with dimethyloxirane or S$_8$ forming (H-DBU)[MoCp(CO)$_2${*O,P*-OP(O)Mes*)] or (H-DBU) [MoCp(CO)$_2${*S,P*-SP(O)Mes*)], respectively[18]. The dinuclear molybdenum complexes possessing bridging phosphinidene ligands (RP, where R= H, Mes*, C$_5$H$_4$) exhibit high reactivity towards chalcogens (Ch = O, S, Se, Te) giving the rich family of molybdenum complexes with bridging chalcogenophosphinidene ligands (RPCh, R= H, Mes*, C_5H_4) or very rare dithiophosphorane ligands (RPS_2, R= Mes*, C_5H_4) [19]. Electrophilic complexes [$Mn_2(CO)_8$(*μ*-PR)] (R = TMP, *i*Pr_2N) react with sulfur yielding products in which the P=S moiety of the thiophosphinidene bridging ligand is side-on bound to the metal center[20]. Moreover, [Fe_2Cp_2(μ-PCy)(*μ*-CO)$(CO)_2$] reacts rapidly with O_2 or S_8, yielding [Fe_2Cp_2{*μ*-P(E)R}(μ-CO)$(CO)_2$] where E = O, S, and R = Cy, Ph[21][22]. Dinuclear scandium phosphinidene (P-Ar, Ar = 2,6-$Me_2C_6H_3$) bridged complex reacts with Se, Te, or Ph_3P=Ch (Ch = S, Se) with formation of Sc-Ch-Sc motif and transforming P-Ar ligands into $[ArP–PAr]^{2-}$[23]. Dimeric Pt(0) phosphinidene bridged complex $[(Dppe)Pt(\mu\text{-}PMes)]_2$ can be oxidized in air to form $[(Dppe)Pt\{\mu\text{-}P(O)Mes\}]_2$. Interestingly, sulfur cleaves the Pt–P bonds, yielding a monomeric trithiophosphonato complex [(Dppe)Pt(S_3PMes)][24]. Several other complexes of nickel group metals with the trithiophosphonato ligand $(RP(=S)S_2\text{-}\kappa S{:}\kappa S')^{2-}$ are known, but they were not synthesized *via* sulfurization of related phosphinidene complexes. It was reported on synthesis of [$L_2Pt(S_3PPh)$] via a sulfurization of [{$PhP(NPh)_2S$-*κS*:*κN*}PtL_2] (L = Ph_3P, ½Dppp) [25]. Due to high chloro-philicity of Ti^{IV} centre, [$Cp^{Me}{}_2Ti(S_3PR)$] reacts with [$DppeNiCl_2$] yielding [DppeNi(S_3PR)] (R = *p*-$MeOC_6H_4$)[26]. Other examples are [$(PhEt_2)_2Ni(S_3PPh)$] and [$(PhEt_2)_2Ni(S_2PPh)$] ($(PhPS_2)^{2-}$ = $(PhPS_2\text{-}\kappa S{:}\kappa S')^{2-}$) that were formed in the reaction of $PPhEt_2$ with $PhP(S)(SiMe_3)_2$ and $NiCl_2$ and further studied with XRD[27]. Woollins *et al.* have studied the reactions of Lawessons reagent with [$(R_3P)_2PtCl_2$] and [$(Ph_3P)_2Pt(C_2H_4)$], providing series of complexes with $[S_3PR]^{2-}$ ligands[28][29].

Very recently, we have studied the reactivity of monomeric anionic phosphanylphosphinidene complex $[(2,6\text{-}DippN)_2W(Cl)(\eta^2\text{-}tBu_2P\text{-}P)]^-$ toward sulfur and selenium. In molar ratio 1:1, in donor solvents, the first step was a formation of [(2,6-

DippN)$_2$W(Cl)(1,2-η-Ch=P–P*t*Bu$_2$)]$^-$ [30]. In nonpolar solvents, these complexes are not stable and undergo reactions leading to different dinuclear tungsten complexes[30] (Scheme 1).



Scheme 1. Reactivity of phosphanylphosphinidene tungsten complex towards chalcogens.

The investigation presented in this paper was carried out to study the reactivity of Pt(0) complexes **1**[31] and **2**[32] with the formula [L$_2$Pt(η^2-P=P*t*Bu$_2$)] (L = ½Dppe, *p*-Tol$_3$P) toward sulfur. According to the properties of spectator ligands, which are strong σ-donors, complexes **1** and **2**, as well as [(DippN)$_2$W(Cl)(η^2-P-P*t*Bu$_2$)]$^-$ are nucleophilic ones[33][34][35]. Recently, we have reported a DFT study on the bonding properties of phosphanylphosphinidene ligands in transition metal complexes[10]. If it is sterically possible, one will observe side-on coordination of the R$_2$P-P ligands to the metal center. However, the bonding type and the P-P bond character within the phosphanylphosphinidene ligand substantially depend on the present metal (early *vs.* late TMs). Thus, the Pt(0) complexes **1** and **2**, which are herein studied, differ significantly from tungsten(VI) complexes. Firstly, platinum phosphanylphosphinidene complexes are more nucleophilic than tungsten counterparts, which is manifested by reactions with metal carbonyls, where [$L_2Pt(\eta^2\text{-}P{=}P\mathit{t}Bu_2)$] reacts easily with [$(OC)_5M{\cdot}THF$] yielding stable [$L_2Pt(1,2\text{-}\eta\text{-}\mathit{t}Bu_2P{=}P\text{-}M(CO)_5$] (M = Cr, W)[36] but [$(DippN)_2W(Cl)(\eta^2\text{-}P\text{-}P\mathit{t}Bu_2)$]$^-$ formed [$(DippN)_2W(Cl)(1,2\text{-}\eta\text{-}\mathit{t}Bu_2P\text{-}P\text{-}M(CO)_5$]$^-$ in reversible reactions and these products are not stable and dissociated with the regeneration of starting W(VI) complex[37]. Secondly, the geometry of $\mathit{t}Bu_2P{=}P$ moiety in platinum complexes resembles the one observed for free, “bottleable” Bertrand’s singlet phosphanylphosphinidene, where the most striking structural feature of this ligand is a very short (double) P-P bond[10][31][32]. The singlet phosphanylphosphinidene is stabilized via coordination to Pt(0) metal center in an ethene-like manner. Otherwise, in the case of the W(VI) complex, the P-P bond displays a rather single bond character. Moreover, a significant π-interaction is present between the phosphinidene P-atom and the metal center resulting in P-W multiple bonding. The W(VI) complex can be seen as a result of the interaction of the triplet phosphanylphosphinidene moiety with the triplet metal fragment[10][38][39]. In this paper, we present our results concerning the reactivity of Pt(0) phosphanylphosphinidene complexes toward elemental sulfur.

EXPERIMENTAL

General information

All experiments were carried out under an argon atmosphere using Schlenk techniques. All manipulations were performed using a standard vacuum, Schlenk, and glove box techniques. All solvents were purified and dried using common methods. Solvents for NMR spectroscopy (C_6D_6 and THF-d_8) were purified using metallic sodium. Sulfur was kept under reduced pressure to remove traces of water. The phosphanylphosphinidene platinum complexes **1** and **2** were synthesized according to the literature [40][32]. NMR spectra were recorded on a Bruker Avance III HD 400 MHz spectrometer at ambient temperature (external standard TMS for ^{1}H and ^{13}C; 85% H_3PO_4 for ^{31}P). The chemical identity of ^{13}C nuclei was determined by ^{13}C/^{1}H correlation spectra. UV-Vis spectra were measured on Thermo Scientific Evolution 220 UV-Visible spectrophotometer.

Diffraction reflections intensity data were collected on an IPDS 2T dual-beam diffractometer (STOE & Cie GmbH, Darmstadt, Germany) at 120.0(2) K with CuK$_a$ or MoK$_a$ radiation of a microfocus X-ray source (GeniX 3D Mo High Flux, Xenocs, Sassenage, 50 kV, 1.0 mA, l = 1.54186 Å). The investigated crystal was thermostated in a nitrogen stream at 120 K using CryoStream-800 device (Oxford CryoSystem, UK) during the entire experiment. Data collection and data reduction were controlled by X-Area 1.75 program (STOE). The multi-scan absorption correction was performed on the integrated reflections by a combination of frame scaling, reflection scaling, and a spherical absorption correction ($\mu = 10.16$ mm^{-1}). The structures were solved by intrinsic phasing methods (ShelXT) and refined anisotropically using the program's package OLEX238 and SHELX-2015[41][42][43]. Positions of the CH hydrogen atoms were calculated geometrically and taken into account with isotropic temperature factors and refined in the usual, default riding model.

Elemental analysis was performed at the University of Gdańsk using a Vario El Cube CHNS apparatus.

[DppePt{S$_2$P(S)–P(S)*t*Bu$_2$}] (3)

A solution of [DppePt(η^2-*t*Bu$_2$P=P)] (0.216 g, 0.28 mmol) in 4 mL THF was added dropwise to solid sulfur (0.036 g, 1.12 mmol) at -30°C. The reacting mixture was warmed up to room temperature and stirred for 24 h. Then the resulting solution was concentrated to half of its volume and ^{31}P{^{1}H} NMR spectrum was measured. Yellow crystals of **3** were obtained from the THF solution layered with pentane (0.111 g,0.119 mmol, yield 42 %) at -30°C.

NMR data:

^{1}H NMR (THF-d$_8$, 400 MHz, δ): 1.55 ppm (d, $^3J_{PH}$ = 14.9 Hz, 18H, C(C**H$_3$**)$_3$), 2.31 ppm (br, 2H, PC**H$_2$**), 2.50 ppm (br, 2H, PC**H$_2$**), 7.40-7.53 (12H, *m,p*-C**H**), 7.65-7.68 (br, 4H, *o*-C**H**), 8.29-8.50 (br, 4H, *o*-**CH**); ^{31}P{^{1}H}NMR (THF-d$_8$, 162 MHz, δ): 118.9 ppm (d, $^1J_{P1\text{-}P2}$ = 143.9 Hz, $^2J_{P1\text{-}Pt}$ = 147.5 Hz, **P1**), 87.5 ppm (d, $^1J_{P1\text{-}P2}$ = 143.9 Hz, $^3J_{P2\text{-}Pt}$ = 10.6 Hz, **P2**), 42.6 ppm (s, $^1J_{P3,4\text{-}Pt}$ = 3201 Hz, **P3**, **P4**); ^{13}C{^{1}H}NMR (THF-d$_8$, 100 MHz, δ): 134.85 (**C*$_i$***), 132.49 (**C*$_i$***), 131.22 (**C*$_{m,p,}$***), 128.48 (**C*$_{m,p}$***), 43.39 (dd, $^1J_{CP}$ = 22.3 Hz, $^2J_{CP}$ = 11.2 Hz **C**(CH$_3$)$_3$), 29.64 (s, C(**C**H$_3$)$_3$), 28.42 (m, P**C**H$_2$); elemental analysis calculated for $C_{34}H_{42}P_4PtS_4 \cdot 0.5$ THF (M = 933.99 g/mol): 46.29 %C, 4.96 %H, 13.73 %S, found 46.38 %C, 5.12 %H, 13.33 %S (what is in line with the amount of THF present in the ^{1}H NMR spectrum).

NMR and UV-Vis spectra of **3** are presented in Figures S1-S7 and S15 in ESI.

[(*p*Tol$_3$P)$_2$Pt{S$_2$P(S)–P(S)*t*Bu$_2$}] (4)

A solution of [(*p*Tol$_3$P)$_2$Pt(η^2-*t*Bu$_2$P=P)] (0.392 g, 0.4 mmol) in 7 mL THF was added dropwise to solid sulfur (0.051 g, 1.6 mmol) at -20°C. The reacting mixture was warmed up to room temperature and stirred for 2 h. Then the resulting solution was concentrated to half of its volume and ^{31}P{^{1}H} NMR spectrum was measured. The solvent was then evaporated under reduced pressure, and the residue was washed with pentane and dissolved in 3 mL of toluene, further layered with 3 mL of pentane. White microcrystalline powders of product **4**, *p*Tol$_3$P=S, and *t*Bu$_2$PH(S) were obtained from toluene/pentane solution at room temperature. According to ^{1}H-NMR data, the powder has a molar composition of **4** (≈ 67%), *t*Bu$_2$PH(S) (≈ 7 %), *p*-Tol$_3$PS (≈ 26 %). Therefore, the residue dissolving in toluene further layered with pentane was repeated 4 times. Then the obtained residue was washed 7 times with pentane resulting in pure **4** (0.167 g, 0.148 mmol, yield 37%). Crystals of **4** suitable for X-ray analysis were grown from toluene/pentane solution with a few drops of C_6D_6 at room temperature.

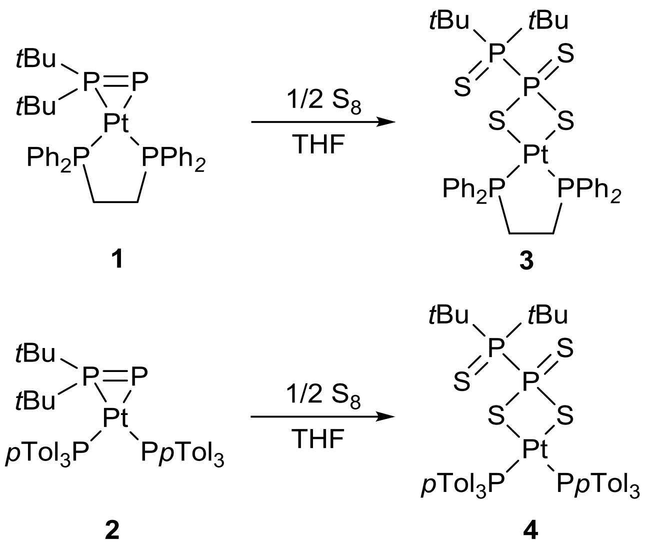
NMR data:

^{1}H NMR (C_6D_6, 400 MHz, δ): 1.82 ppm {d, 18H, $^3J_{PH}$ = 15.1 Hz, C(C$\mathbf{H_3}$)$_3$}, 1.93 ppm (s, 18H, C$\mathbf{H_3}$-C), 7.70(m, 12H, *o*-C**H**), 6.78 (m, 12H, *m*-C**H**); ^{31}P{^{1}H}NMR (C_6D_6, 162 MHz, δ): 106.7 ppm (d, $^1J_{P1\text{-}P2}$ = 146.4 Hz, $^2J_{P1\text{-}Pt}$ = 174.5 Hz, **P1**), 87.0 ppm (d, $^1J_{P1\text{-}P2}$ = 146.4 Hz, $^3J_{P2\text{-}Pt}$ = 10.6 Hz, **P2**), 17.2 ppm (s, $^1J_{P3,4\text{-}Pt}$ = 3289 Hz, **P3**, **P4**); ^{13}C{^{1}H}(C_6D_6, 100 MHz, δ): 140.48 ($\mathbf{C}_i$), 135.18 ($\mathbf{C}_o$), 128.39 ($\mathbf{C}_m$), 43.87 (dd, $^1J_{CP}$ = 21.9 Hz, $^2J_{CP}$ = 10.7 Hz **C**(CH$_3$)$_3$), 30.56 (s, C(**C**H$_3$)$_3$), 20.77 (s, **C**CH$_3$); elemental analysis calculated for $C_{50}H_{60}P_4PtS_4$ (M = 1108.25 g/mol): 54.19 %C, 5.46 %H, 11.57 %S, found 53.97 %C, 5.59 %H, 11.13 %S

NMR and UV-Vis spectra of **4** rea presented in Figures S8-S14 and S16 in ESI.

RESULTS AND DISCUSSION

The phosphanylphosphinidene complex [DppePt(η^2-P=P*t*Bu$_2$)] (**1**) reacts with elemental sulfur in THF in a 1:4 molar ratio under mild conditions. ^{31}P{^{1}H} NMR spectrum of the reaction solution revealed the quantitative formation of a single product **3** after 24 hours of stirring at room temperature (Scheme 2, Figure S1).



Scheme 2. Syntheses of **3** and **4**.

Complex **3** is the sole product of this reaction regardless the molar ratio of reagents. We have also tested the reaction of **1** with sulfur at molar ratio 1:2 and only the presence of **3** and unreacted **1** was detected. The $^{31}P\{^{1}H\}$ spectrum of **3** shows three resonances at 118.9 ppm (P1), 87.5 ppm (P2), and 42.6 (P3, P4) ppm (AMX_2 pattern), where signals of the P1 and P2 atoms can be attributed to a newly formed thiophosphorus ligand, whereas P3 and P4 signal can be assigned to Dppe ligand (Figure S2). The resonances of P1 and P2 atoms are significantly downfield shifted in comparison to the corresponding resonances of the parent **1** (-48.2 ppm (P1), 71.5 ppm (P2)). Moreover, in contrast to complex **1**, compound **3** displays a small value of $^{1}J_{P1\text{-}P2}$ (143.9 Hz (**3**) vs. 622.4 Hz (**1**)) and has no coupling between P-atoms of Dppe ligand (P3, P4) and P-atoms of new thiophosphorus ligand (P1, P2). All signals in the $^{31}P\{^{1}H\}$ spectrum of **3** possess platinum satellites with values of 147.5 Hz (P1), 10.6 Hz (P2) and 3201 Hz (P3). Relatively small first two absolute values of platinum-phosphorus couplings indicate that P1 and P2 atoms are not directly bonded to the platinum metal center. It is worth mentioning that the ^{1}H NMR spectrum of **3** at ambient temperature in THF-d_8 solution points to the dynamic behavior of the Dppe ligand. The resonances of *orto* C**H** at 8.25 and 7.62 ppm are broad multiplets and the same is observed for P-C**H**$_2$-C**H**$_2$-P hydrogens visible as broad signals at 2.50 and 2.31 ppm (Figure S3). Based on NMR data of **3**, we assumed that the phosphanylphosphinidene ligand was sulfurized in the coordination sphere of platinum. This hypothesis was fully confirmed by the single-crystal X-ray diffraction analysis.

The successful crystallization from THF/pentane yielded yellow crystals of **3**. The X-ray structure of **3** clearly shows the addition of four sulfur atoms to the phosphanylphosphinidene ligand which leads to the formation of a new phosphinothioyltrithiophosphonato ligand (Figure 1).

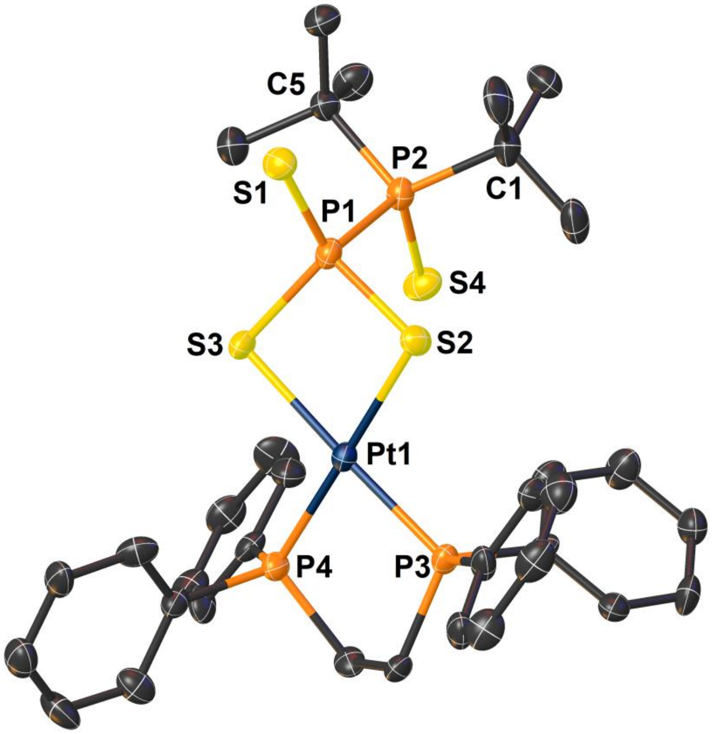


Figure 1. Molecular view and atom labeling scheme for **3**. Hydrogen atoms are omitted, displacement ellipsoids are drawn at 50% probability level. Selected bond lengths and angles [Å, °]: Pt1-P3 2.247(2), Pt1-P4 2.254(2), Pt1-S2 2.356(2), Pt1-S3 2.359(2), P1-S1 1.956(4), P1-S2 2.055(3), P1-S3 2.063(3), P1-P2 2.285(3), P2-S4 1.969(4); P3-Pt1-P4 85.72(8), S2-Pt1-S3 82.29(8), S1-P1-P2 116.1(1), P2-P1-S2 105.7(1), P2-P1-S3 106.2(1), P1-P2-S4 110.5(1).

The $t\mathrm{Bu}_2\mathrm{PP}$ moiety was split off from the Pt-center, however, the P-P bond is retained in the newly formed $[t\mathrm{Bu}_2\mathrm{P}(=\mathrm{S})\text{-}\mathrm{P}(=\mathrm{S})\mathrm{S}_2]^{2-}$ ligand. The geometry around Pt-atom in complex **3** is distorted square planar, where S2 and S3 atoms of $[t\mathrm{Bu}_2\mathrm{P}(=\mathrm{S})\text{-}\mathrm{P}(=\mathrm{S})\mathrm{S}_2]^{2-}$ anion and P3 and P4 atoms of Dppe ligand coordinate to the platinum atom. Interestingly, the flat fragment is extended to also include S2, S3, and P1 atoms of the trithiophosphonato moiety. The molecule of **3** displays a roughly mirror plane perpendicular to it along the Pt1-P1 vector. The P1 and P2 atoms exhibit distorted tetrahedral geometry. The P1-P2 bond is very long (2.285(3) Å), even longer than the expected value for the P-P single bond (2.22 Å)[44]. The P1-S2 and P2-S1 bond lengths with values of 2.055(3) Å and 2.063(3) Å respectively, are in between typical single and double bond distances, whereas short bond lengths of P1-S1 (1.956(4) Å), and P2-S4 (1.969(4) Å) confirm their double bond character (a sum of single covalent bond radii for P and S atoms is 2.14 Å; a sum of double covalent bond radii for P and S atoms is 1.96 Å)[44][45]. The terminal P1-S1 and P2-S4 bonds exhibit anti-periplanar orientation to each other with dihedral angle S1-P1-P2-S4 equal -166.12°. The Pt-S2 and Pt-S3 distances with values of 2.356(2) Å and 2.359(2) Å are very similar compared to those observed for $[(\mathrm{R}_3\mathrm{P})_2\mathrm{Pt}(\mathrm{S}_3\mathrm{PR'})]$[28].

The reaction of $[(p\mathrm{Tol}_3\mathrm{P})_2\mathrm{Pt}(\eta^2\text{-}\mathrm{P{=}P}t\mathrm{Bu}_2)]$ (**2**) with sulfur undergoes similarly yet not so cleanly as the reaction of **1** with sulfur (Scheme 2). The NMR examination of the reaction solution indicates a formation of $[(p\text{-}\mathrm{Tol}_3\mathrm{P})_2\mathrm{Pt}\{\mathrm{S}_2\mathrm{P}(\mathrm{S})\text{–}\mathrm{P}(\mathrm{S})t\mathrm{Bu}_2\}]$ (**4**), $p\text{-}\mathrm{Tol}_3\mathrm{P{=}S}$, and small amounts of $^t\mathrm{Bu}_2\mathrm{PH}(\mathrm{S})$, $p\mathrm{Tol}_3\mathrm{P}$, and $t\mathrm{Bu}_2\mathrm{PS}_2\mathrm{Li}(\mathrm{THF})_n$ [30] (Figure S8). A formation of $p\text{-}\mathrm{Tol}_3\mathrm{P{=}S}$ and $p\text{-}\mathrm{Tol}_3\mathrm{P}$ indicates that S_8 can split off the $p\text{-}\mathrm{Tol}_3\mathrm{P}$ ligand from the Pt center. The presence of $t\mathrm{Bu}_2\mathrm{PH}(\mathrm{S})$ and $t\mathrm{Bu}_2\mathrm{PS}_2\mathrm{Li}(\mathrm{THF})_n$ points to the P-P bond cleavage of the $t\mathrm{Bu}_2\mathrm{P{=}P}$ ligand during the reaction. A formation of $t\mathrm{Bu}_2\mathrm{PS}_2\mathrm{Li}(\mathrm{THF})_n$ is possible since LiCl is the contamination of **2**. The similarity of **4** and **3** NMR data supports its identification (for details see Experimental and Figures S8-S14).

The formation of **4** is preferred regardless of the molar ratio **2**: S. Nevertheless, we isolated compound **4** as an analytically pure white solid by fractional crystallization from toluene/pentane solution. The addition of few drops of C_6D_6 to toluene/pentane solution of **4** at room temperature gave colorless crystals of **4**·C_6D_6 suitable for X-ray analysis. The molecular structure of **4**, reminiscent to **3**, is presented in Figure 2.

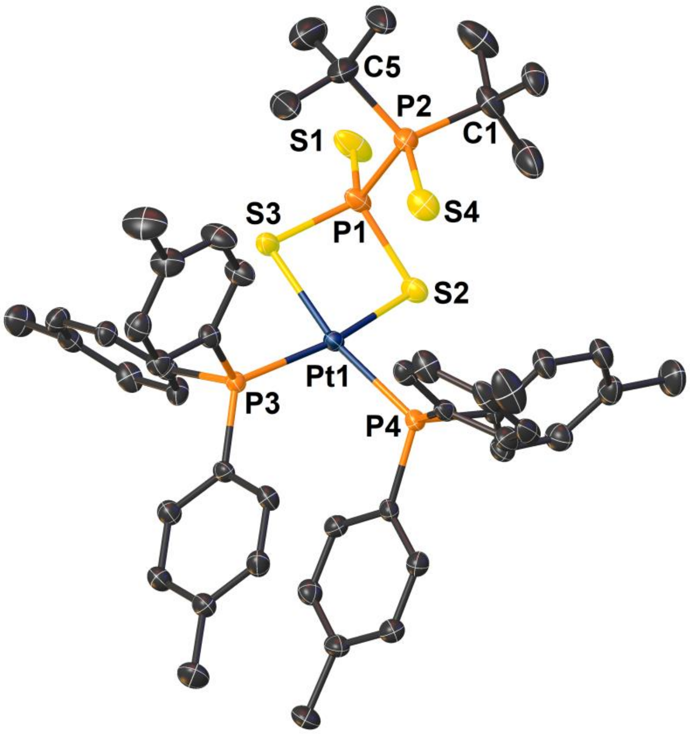


Figure 2. Molecular view and atom labeling scheme for **4**. Hydrogen atoms and are omitted, displacement ellipsoids are drawn at 50% probability level. Selected bond lengths and angles [Å, °]: Pt1-P3 2.297(1), Pt1-P4 2.273(1), Pt1-S2 2.339(1), Pt1-S3 2.374(1), P1-S1 1.948(2), P1-S2 2.056(2), P1-S3 2.059(2), P1-P2 2.285(2), P2-S4 1.967(2); P3-Pt1-P4 102.82(4), S2-Pt1-S3 81.17(4), S1-P1-P2 112.31(8), P2-P1-S2 103.63(7), P2-P1-S3 107.65(7), P1-P2-S4 107.97(7).

The reactivity of side-on phosphanylphosphinidene Pt complexes **1** and **2** toward sulfur differs significantly from the reactivity of their tungsten counterparts toward chalcogens[30]. The formation of chelate phosphinothioyltrithiophosphonato ligands is strongly preferred for the platinum complexes. To our knowledge, **3** and **4** are the first example of compounds bearing $R_2P(=S)$-$P(=S)S_2$ structural motif. On the other hand, the formation of phosphanylphosphinidene sulfide ligand tBu$_2$P–P=S and its side-on bonded complex i.e. [DppePt(2,3-η-tBu$_2$P–P=S], which is typical for anionic $[(DippN)_2W(Cl)(\eta^2\text{-P–P}t\text{Bu}_2)]^-$, is not visible[30]. Moreover, in the case of phosphanylphosphinidene ligand coordinated to the platinum metal center, reactions with an excess of sulfur did not produce a complex with tetrathiophosphate ligands $[PS_4]^{3-}$ as it was observed for analogous reactions involving $[(DippN)_2W(Cl)(\eta^2\text{-P–P}t\text{Bu}_2)]^-$ [30]. When it comes to stability, both solids **3** and **4** are stable in air, although **4** is slowly decomposing in a solution.

We have also studied the electronic structure of phosphinothioyltrithiophosphonato ligand using theoretical methods. The analysis of natural bond orbitals (NBOs) of complex **3** indicates sp^3 hybridization of both P atoms within the chelate ligand $[t\text{Bu}_2P(=S)\text{-}P(=S)S_2]^{2-}$. Each terminal S atom possesses three electron pairs: one displaying a dominated *s*-character and two with dominated *p*-character. The shortening of terminal P1-S1 and P2-S4 bonds can be explained by π-interactions between *p*-electron pairs at terminal sulfur atoms with antibonding σ*(P2-C1)/σ*(P2-C5) orbitals (Figure 3A), antibonding σ*(P1-P2) orbital (Figure 3B, 3C), and antibonding σ*(P1-S2)/σ*(P1-S3) orbitals (Figure 3D). The significant elongation of the P1-P2 bond observed in the molecular structure of **3** can be explained by π-donation to the σ*(P1-P2) orbital.

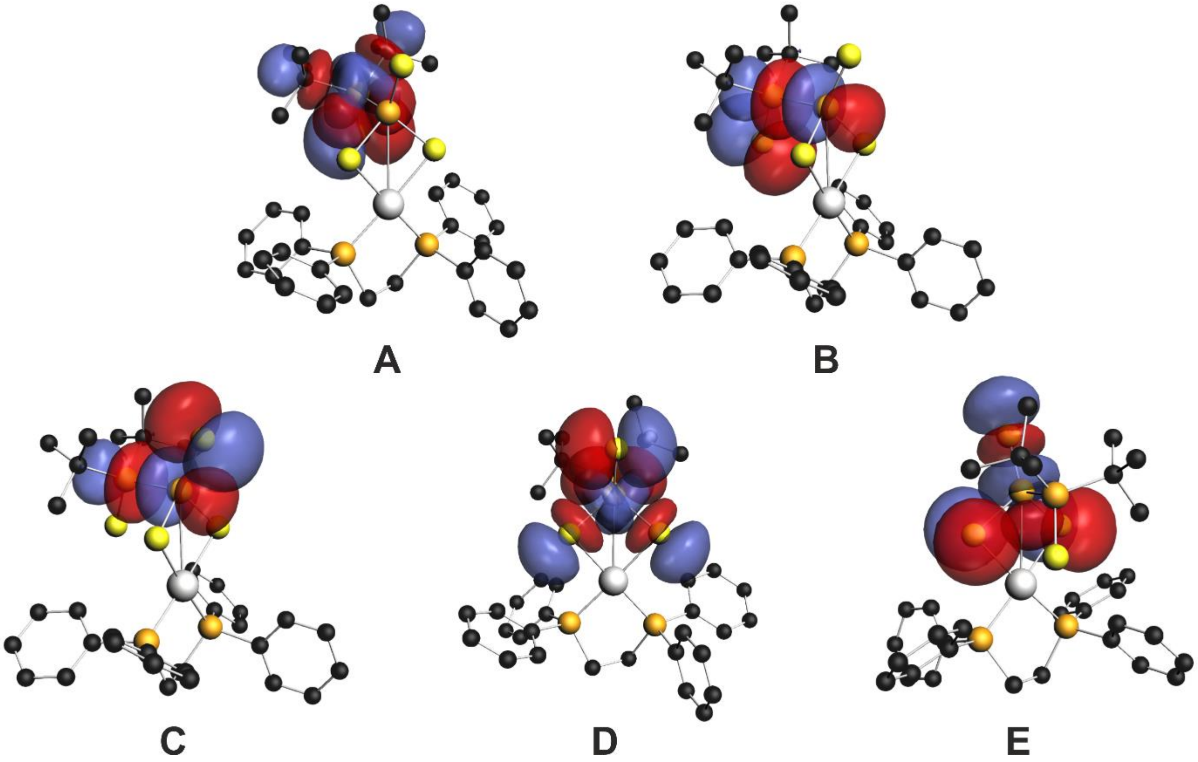


Figure 3. Graphical representation of NBOs of **3** associated with LP1(S4), σ*(P2-C1) and σ*(P2-C5) (**A**); LP2(S4) and σ*(P1-P2) (**B**); LP2(S1) and σ*(P1-P2) (**C**); LP1(S1), σ*(P1-S2) and σ*(P1-S3) (**D**); LP1(S2), LP1(S3), and σ*(P1-S1) (**E**).

The presence of mentioned π-interactions is additionally confirmed by decreased occupancies of NBOs associated with electron *p*-pairs at S1 and S4 atoms (1.70-1.82) and increased occupancies of antibonding orbitals: σ*(P2-C1)/σ*(P2-C5) (0.17/0.18), σ*(P1-P2) (0.42), and σ*(P1-S2)/σ*(P1-S3) (0.21/0.21). The Wiberg bond orders for P1-S1, P2-S4, and P1-P2 bonds with the values of 1.40, 1.33, and 0.61 respectively, are in line with their metric parameters. Additional π-interactions are also observed within the P1-S2-Pt-S3 cycle, where electron *p*-pairs of the bridging S2 and S3 atoms interact with the antibonding σ*(P1-S1) orbital (Figure 3E). The contribution of *d*-orbitals of P1 and P2 atoms in the mentioned above π-interactions is small but cannot be neglected. The S2-Pt and S3-Pt bonds can be seen as dative bonds and it is confirmed by the contribution of S atoms in NLMOs associated with these bonds (ca. 71%). Hirshfeld charge analysis shows that large positive charges are located at phosphorus atoms of [tBu$_2$P(=S)-P(=S)S$_2$]$^{2-}$ ligand (+0.172 (P1), +0.271 (P2)), whereas a small positive charge is present at Pt atom (+0.082). As expected, the largest negative charges are located on terminal S atoms (-0.234 (S1), -0.200 (S4)), and bridging S atoms (-0.150 (S2), -0.146 (S3)).

In conclusion, sulfurization of side-on phosphanylphosphinidene platinum(0) complexes yielded compounds with new phosphinothioyltrithiophosphonato ligands. Despite the addition of four sulfur atoms to the tBu$_2$PP moiety, the P-P bond is retained in the newly formed ligand. The outcomes of the mentioned reactions are in strong contrast with the reactivity of the side-on phosphanylphosphinidene tungsten(VI) complex toward chalcogens, where complexes of phosphanylphosphinidene chalcogenides or tetrachalcogenophosphates were formed. The obtained sulfur-rich anion with the formula [tBu$_2$P(=S)-P(=S)S$_2$]$^{2-}$ is an attractive building block for coordination chemistry which can act as a polydentate chelating or bridging ligand.

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REFERENCES

[1] G. Bucher, M.L.G. Borst, A.W. Ehlers, K. Lammertsma, S. Ceola, M. Huber, D. Grote, W. Sander, Infrared, UV/Vis, and W-band EPR Spectroscopic Characterization and Photochemistry of Triplet Mesitylphosphinidene, Angew. Chem. Int. Ed. 44 (2005) 3289–3293. https://doi.org/10.1002/anie.200462862.

[2] G. Fritz, T. Vaahs, H. Fleischer, E. Matern, tBu$_2$P-P=PBrtBu$_2$·LiBr and the Formation of

tBu_2P-P, Angew. Chem. Int. Ed. Engl. 28 (1989) 315–316. https://doi.org/10.1002/anie.198903151.

[3] O. Back, M. Henry-Ellinger, C.D. Martin, D. Martin, G. Bertrand, ^{31}P NMR Chemical Shifts of Carbene-Phosphinidene Adducts as an Indicator of the π-Accepting Properties of Carbenes, Angew. Chem. Int. Ed. 52 (2013) 2939–2943. https://doi.org/10.1002/anie.201209109.

[4] E. Matern, J. Olkowska-Oetzel, J. Pikies, G. Fritz, Die Reaktionen von $^tBu_2P$–P=P(Me)$^tBu_2$ und (Me_3Si)^{t}BuP–P=P(Me)$^tBu_2$ mit PR_3, Z. Anorg. Allg. Chem. 627 (2001) 1767–1770. https://doi.org/10.1002/1521-3749(200108)627:8<1767::AID-ZAAC1767>3.0.CO;2-4.

[5] J. Olkowska-Oetzel, J. Pikies, Chemistry of the phosphinophosphinidene $^tBu_2$P-P, a novel π-electron ligand, Appl. Organometal. Chem. 17 (2003) 28–35. https://doi.org/10.1002/aoc.387.

[6] K. Lammertsma, Phosphinidenes, Top. Curr. Chem. (2003) 95–119. https://doi.org/10.1007/b11152.

[7] F. Mathey, N.H.T. Huy, A. Marinetti, Electrophilic terminal-phosphinidene complexes: Versatile phosphorus analogues of singlet carbenes, Helv. Chim. Acta. 84 (2001) 2938–2957. https://doi.org/10.1002/1522-2675(20011017)84:10<2938::AID-HLCA2938>3.0.CO;2-P.

[8] C.C. Cummins, R.R. Schrock, D.W. M., Phosphinidenetantalum(V) complexes of the type [(N_3N)Ta=PR] as Phospha-Wittig reagents (R = Ph, Cy, tBu, N_3N = $Me_3SiNCCH_2CH_2)_3N$),

Angew. Chem. Int. Ed. Engl. 32 (1993) 756–759. https://doi.org/10.1002/anie.199307561.

[9] T.L. Breen, D.W. Stephan, Phosphinidene Transfer Reactions of the Terminal Phosphinidene Complex $Cp_2Zr(:PC_6H_2\text{-}2,4,6\text{-}t\text{-}Bu_3)(PMe_3)$, J. Am. Chem. Soc. 117 (1995) 11914–11921. https://doi.org/10.1021/ja00153a013.

[10] M. Zauliczny, A. Ordyszewska, J. Pikies, R. Grubba, Bonding in Phosphanylphosphinidene Complexes of Transition Metals and their Correlation with Structures, ^{31}P NMR Spectra, and Reactivities, Eur. J. Inorg. Chem. 2018 (2018) 3131–3141. https://doi.org/10.1002/ejic.201800270.

[11] M.M. Hansmann, R. Jazzar, G. Bertrand, Singlet (Phosphino)phosphinidenes are Electrophilic, J. Am. Chem. Soc. 138 (2016) 8356–8359. https://doi.org/10.1021/jacs.6b04232.

[12] P.P. Gaspar, H. Qian, A.M. Beatty, D. André D'Avignon, J.L.F. Kao, J.C. Watt, N.P. Rath, 2,6-Dimethoxyphenylphosphirane oxide and sulfide and their thermolysis to phosphinidene chalcogenides - Kinetic and mechanistic studies, Tetrahedron. 56 (2000) 105–119. https://doi.org/10.1016/S0040-4020(99)00779-6.

[13] L. Wang, R. Ganguly, F. Mathey, Revisiting the chemistry of phosphinidene sulfides, Organometallics 33 (2014) 5614–5617. https://doi.org/10.1021/om500828n.

[14] C.M.E. Graham, T.E. Pritchard, P.D. Boyle, J. Valjus, H.M. Tuononen, P.J. Ragogna, Trapping Rare and Elusive Phosphinidene Chalcogenides, Angew. Chem. Int. Ed. 56 (2017) 6236–6240. https://doi.org/10.1002/anie.201611196.

[15] M. Alonso, M.E. García, M.A. Ruiz, H. Hamidov, J.C. Jeffery, Chemistry of the phosphinidene oxide ligand, J. Am. Chem. Soc. 126 (2004) 13610–13611. https://doi.org/10.1021/ja045487g.

[16] M. Alonso, M.A. Alvarez, M.E. García, D. García-Vivó, M.A. Ruiz, Chemistry of the Oxophosphinidene Ligand. 1. Electronic Structure of the Anionic Complexes $[MCp\{P(O)R^*\}(CO)_2]^-$ (M = Mo, W; R* = 2,4,6-$C_6H_2{}^tBu_3$) and Their Reactions with H^+ and C-Based Electrophiles, Inorg. Chem. 49 (2010) 8962–8976. https://doi.org/10.1021/ic101261f.

[17] M. Alonso, M.A. Alvarez, M.E. García, M.A. Ruiz, H. Hamidov, J.C. Jeffery, Oxidation Reactions of the Phosphinidene Oxide Ligand, J. Am. Chem. Soc. 127 (2005) 15012–15013. https://doi.org/10.1021/ja054941t.

[18] M. Alonso, M.A. Alvarez, M.E. García, D. García-Vivó, M.A. Ruiz, Nucleophilic behaviour of dioxo- and thiooxophosphorane complexes $[MoCp(CO)_2\{E,P\text{-}EP(O)(2,4,6\text{-}C_6H_2{}^tBu_3)\}]^-$ (E = O, S), Dalton Trans. 43 (2014) 16074–16083. https://doi.org/10.1039/c4dt01942c.

[19] B. Alvarez, M.A. Alvarez, I. Amor, M.E. García, D. García-Vivó, J. Suárez, M.A. Ruiz, Dimolybdenum Cyclopentadienyl Complexes with Bridging Chalcogenophosphinidene Ligands, Inorg. Chem. 51 (2012) 7810–7824. https://doi.org/10.1021/ic300869z.

[20] T.W. Graham, K.A. Udachin, A.J. Carty, Synthesis of σ-π-phosphinidene sulfide complexes $[Mn_2(CO)_n(\mu\text{-}\eta^1,\eta^2\text{-}P(NR_2)S)]$ (n=8,9) via direct sulfuration of electrophilic μ-phosphinidenes and photochemical transformation to a trigonal prismatic $Mn_2P_2S_2$ cluster,

Inorganica Chim. Acta 360 (2007) 1376–1379. https://doi.org/10.1016/j.ica.2006.02.022.

[21] C.M. Alvarez, M.A. Alvarez, M.E. García, R. González, M.A. Ruiz, H. Hamidov, J.C. Jeffery, High-yield synthesis and reactivity of stable diiron complexes with bent-phosphinidene bridges, Organometallics 24 (2005) 5503–5505. https://doi.org/10.1021/om050617v.

[22] M.A. Alvarez, M.E. García, R. González, M. a Ruiz, Reactions of the phosphinidene-bridged complexes [Fe_2(η^5-C_5H_5)2(μ-PR)(μ-CO)(CO)2] (R = Cy, Ph) with electrophiles based on p-block elements, Dalton Trans. 41 (2012) 9005–9018. https://doi.org/10.1039/c2dt31506h.

[23] Y. Lv, C.E. Kefalidis, J. Zhou, L. Maron, X. Leng, Y. Chen, Versatile reactivity of a four-coordinate scandium phosphinidene complex: Reduction, addition, and CO activation reactions, J. Am. Chem. Soc. 135 (2013) 14784–14796. https://doi.org/10.1021/ja406413d.

[24] I. Kourkine, D. Glueck, Synthesis and reactivity of a dimeric platinum phosphinidene complex, Inorg. Chem. 36 (1997) 5160–5164. https://doi.org/10.1021/ic970730g.

[25] W. Henderson, R.D.W. Kemmitt, S. Mason, M.R. Moore, J. Fawcett, D.R. Russell, Thiadiazatrimethylenemethane and N,N′,P-triphenylphosphonothioic diamide complexes of platinum(II), J. Chem. Soc., Dalton Trans. (1992) 59–66. https://doi.org/10.1039/DT9920000059.

[26] G.A. Zank, T.B. Rauchfuss, Thiophosphoryl Complexes of Bis(cyclopentadienyl)titanium. 1. Syntheses, Interconversions, and Structures, Organometallics. 3 (1984) 1191–1199. https://doi.org/10.1021/om00086a009.

[27] M. Shafaei-Fallah, W. Shi, D. Fenske, A. Rothenberger, Synthesen und strukturen von übergangsmetall-komplexen mit dithiophosphinato- und trithiophosphonato-liganden, Z. Anorg. Allg. Chem. 632 (2006) 1091–1096. https://doi.org/10.1002/zaac.200600023.

[28] I.P. Parkin, M.J. Pilkington, A.M.Z. Slawin, D.J. Williams, J.D. Woollins, The preparation and characterization of $Pt(Se_3PPh)(PR_3)_2$; the X-ray crystal structure of $Pt(Se_3PPh)(dppe)\cdot CH_2Cl_2$, Polyhedron 9 (1990) 987–990. https://doi.org/10.1016/S0277-5387(00)84302-8.

[29] P.T. Wood, J.D. Woollins, The preparation of $M(PR_3)_2(S_2(S)PC_6H_4OMe)$ (M=Ni, Pd, Pt) from Lawessons reagent, Transition Met. Chem. 12 (1987) 403–405. https://doi.org/10.1007/BF01171647.

[30] A. Ordyszewska, N. Szynkiewicz, Ł. Ponikiewski, M. Scheer, J. Pikies, R. Grubba, Syntheses and Structures of Transition Metal Complexes with Phosphanylphosphinidene Chalcogenide Ligands, Inorg. Chem. 58 (2019) 7905–7914. https://doi.org/10.1021/acs.inorgchem.9b00594.

[31] H. Krautscheid, E. Matern, G. Fritz, J. Pikies, Einfluß der Chelatbildner dppe und dppp auf die Bildung und die Eigenschaften der Pt-Komplexe des $^tBu_2P–P$, Z. Anorg. Allg. Chem. 624 (1998) 501–505. https://doi.org/10.1002/(SICI)1521-3749(199803)624:3<501::AID-ZAAC501>3.0.CO;2-U.

[32] W. Domańska-Babul, J. Chojnacki, E. Matern, J. Pikies, Reactions of $R_2P–P(SiMe_3)Li$ with $[(R'_3P)_2PtCl_2]$. A general and efficient entry to phosphanylphosphinidene complexes of platinum. Syntheses and structures of $[(\eta^2\text{-}P{=}P^iPr_2)Pt(p\text{-}Tol_3P)_2]$, $[(\eta^2\text{-}P{=}P^tBu_2)Pt(p\text{-}$

$Tol_3P)_2$], [{η^2-P=P($N^iPr_2)_2$}Pt(*p*-$Tol_3P)_2$] and [{($Et_2PhP)_2Pt$}$_2P_2$], Dalton Trans. (2009) 146-151. https://doi.org/10.1039/B807811D.

[33] A.W. Ehlers, E.J. Baerends, K. Lammertsma, Nucleophilic or Electrophilic Phosphinidene Complexes MLn=PH; What Makes the Difference?, J. Am. Chem. Soc. 124 (2002) 2831–2838. https://doi.org/10.1021/ja017445n.

[34] H. Aktaş, J. Chris Slootweg, K. Lammertsma, Nucleophilic phosphinidene complexes: Access and applicability, Angew. Chem. Int. Ed. 49 (2010) 2102–2113. https://doi.org/10.1002/anie.200905689.

[35] K. Lammertsma, M.J.M. Vlaar, Carbene-like chemistry of phosphinidene complexes - Reactions, applications, and mechanistic insights, Eur. J. Org. Chem. (2002) 1127–1138. https://doi.org/10.1002/1099-0690(200204)2002:7<1127::AID-EJOC1127>3.0.CO;2-X.

[36] H. Krautscheid, E. Matern, G. Fritz, J. Pikies, Reaktionen des [η^2-{P-P^tBu_2}Pt($PPh_3)_2$] und [η^2-{P-PtBu2}Pt(dppe)] mit Metallcarbonylen. Bildung von [η^2-{($CO)_5M$ · PPtBu2}Pt($PPh_3)_2$] (M = Cr, W) und [η^2-{($CO)_5Cr$ · PP^tBu_2}Pt(dppe)], Z. Anorg. Allg. Chem. 624 (1998) 1617–1621. https://doi.org/10.1002/(SICI)1521-3749(199810)624:10<1617::AID-ZAAC1617>3.0.CO;2-A.

[37] R. Grubba, A. Ordyszewska, Ł. Ponikiewski, D. Gudat, J. Pikies, An investigation on the chemistry of the R_2P=P ligand: reactions of a phosphanylphosphinidene complex of tungsten(VI) with electrophilic reagents, Dalton Trans. 45 (2016) 2172–2179. https://doi.org/10.1039/C5DT03085D.

[38] R. Grubba, K. Baranowska, J. Chojnacki, J. Pikies, Access to Side-On Bonded Tungsten

Phosphanylphosphinidene Complexes, Eur. J. Inorg. Chem. 2012 (2012) 3263–3265. https://doi.org/10.1002/ejic.201200456.

[39] R. Grubba, A. Ordyszewska, K. Kaniewska, Ł. Ponikiewski, J. Chojnacki, D. Gudat, J. Pikies, Reactivity of Phosphanylphosphinidene Complex of Tungsten(VI) toward Phosphines: A New Method of Synthesis of catena-Polyphosphorus Ligands, Inorg. Chem. 54 (2015) 8380–8387. https://doi.org/10.1021/acs.inorgchem.5b01063.

[40] A. Ordyszewska, N. Szynkiewicz, J. Chojnacki, J. Pikies, R. Grubba, The Reactivity of Phosphanylphosphinidene Complexes of Transition Metals Toward Terminal Dihaloalkanes, Inorg. Chem. 59 (2020) 5463–5474. https://doi.org/10.1021/acs.inorgchem.0c00091.

[41] G.M. Sheldrick, Crystal structure refinement with SHELXL, Acta Cryst. C 71 (2015) 3–8. https://doi.org/10.1107/S2053229614024218.

[42] G.M. Sheldrick, SHELXT – Integrated space-group and crystal-structure determination, Acta Cryst. A 71 (2015) 3–8. https://doi.org/10.1107/S2053273314026370.

[43] O. V Dolomanov, L.J. Bourhis, R.J. Gildea, J.A.K. Howard, H. Puschmann, OLEX2: a complete structure solution, refinement and analysis program, J. Appl. Cryst. 42 (2009) 339–341. https://doi.org/10.1107/S0021889808042726.

[44] P. Pyykkö, M. Atsumi, Molecular single-bond covalent radii for elements 1-118, Chem. Eur. J. 15 (2009) 186–197. https://doi.org/10.1002/chem.200800987.

[45] P. Pyykkö, M. Atsumi, Molecular double-bond covalent radii for elements Li-E112, Chem.

Eur. J. 15 (2009) 12770–12779. https://doi.org/10.1002/chem.200901472.