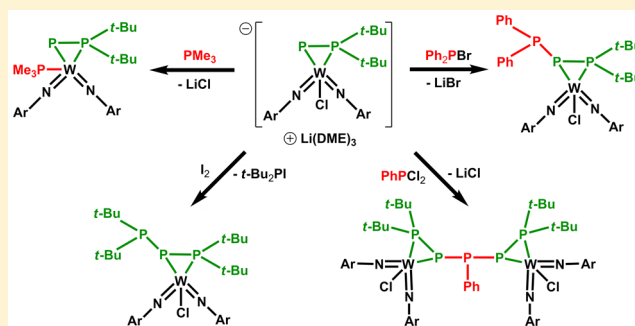


Reactivity of Phosphanylphosphinidene Complex of Tungsten(VI) toward Phosphines: A New Method of Synthesis of *catena*-Polyphosphorus LigandsRafał Grubba,^{*,†} Anna Ordyszewska,[†] Kinga Kaniewska,[†] Łukasz Ponikiewski,[†] Jarosław Chojnacki,[†] Dietrich Gudat,[‡] and Jerzy Pikies[†][†]Chemical Faculty, Department of Inorganic Chemistry, Gdansk University of Technology, G. Narutowicza St. 11/12, PL-80-233 Gdansk, Poland[‡]Institut für Anorganische Chemie, Universität Stuttgart, Pfaffenwaldring 55, 70550 Stuttgart, Germany

Supporting Information

ABSTRACT: The reactivity of an anionic phosphanylphosphinidene complex of tungsten(VI), $[(2,6\text{-}i\text{-Pr}_2\text{C}_6\text{H}_3\text{N})_2(\text{Cl})\text{-W}(\eta^2\text{-}t\text{-Bu}_2\text{P}=\text{P})]\text{Li}\cdot 3\text{DME}$ toward PMe_3 , halogenophosphines, and iodine was investigated. Reaction of the starting complex with Me_3P led to formation of a new neutral phosphanylphosphinidene complex, $[(2,6\text{-}i\text{-Pr}_2\text{C}_6\text{H}_3\text{N})_2(\text{Me}_3\text{P})\text{W}(\eta^2\text{-}t\text{-Bu}_2\text{P}=\text{P})]$. Reactions with halogenophosphines yielded new *catena*-phosphorus complexes. From reaction with Ph_2PBr and Ph_2PBr , a complex with an anionic triphosphorus ligand $t\text{-Bu}_2\text{P}-\text{P}^{(-)}-\text{PPh}_2$ was isolated. The main product of reaction with PhPCl_2 was a tungsten(VI) complex with a pentaphosphorus ligand, $t\text{-Bu}_2\text{P}-\text{P}^{(-)}-\text{P}(\text{Ph})-\text{P}^{(-)}-\text{P}-t\text{-Bu}_2$. Iodine reacted with the starting complex as an electrophile under splitting of the P–P bond in the $t\text{-Bu}_2\text{P}=\text{P}$ unit to yield $[(1,2\text{-}\eta\text{-}t\text{-Bu}_2\text{P}-\text{P}-\text{P}-t\text{-Bu}_2)\text{W}(2,6\text{-}i\text{-Pr}_2\text{C}_6\text{H}_3\text{N})_2\text{Cl}]$, $t\text{-Bu}_2\text{PI}$, and phosphorus polymers. The molecular structures of the isolated products in the solid state and in solution were established by single crystal X-ray diffraction and NMR spectroscopy.



INTRODUCTION

Phosphinidene complexes with RP ligands can be considered as phosphorus analogues of carbene complexes with R_2C ligands¹ which can be classified as electrophilic (Fischer type)² or nucleophilic (Schrock type) ones.³ For phosphinidene complexes, the donor properties of spectator ligands at the transition metal center exert likewise an essential impact on the “philicity” of the P atom.⁴ Complexes with strongly σ -donating spectator ligands show nucleophilic properties of the RP unit and are often sufficiently stable to be isolated,^{1,5} while complexes with strongly π -accepting spectator ligands (i.e., CO) exhibit electrophilic phosphinidene units and are often only generated as transient species.^{1,6} The electrophilic phosphinidene complexes can be stabilized if the P-substituent R is a strong π -donor.⁷ For example, introduction of aminosubstituents enabled the isolation of thermally stable and sterically unprotected molybdenum and tungsten complexes with terminal aminophosphinidene ligands, which display, however, weaker electrophilic reactivity⁸ than that of closely related transient alkyl phosphinidene complexes of molybdenum.⁹

Our group develops the chemistry of phosphanylphosphinidenes (heavier analogues of aminophosphinidenes) and phosphanylphosphides,¹⁰ especially as ligands in transition metal chemistry. Altogether, we elaborated the synthesis of

three types of compounds containing phosphanylphosphinidene groups ($\text{R}_2\text{P}-\text{P}$): (a) relatively stable neutral, side-on complexes $[\text{L}_2\text{Pt}(\eta^2\text{-R}_2\text{P}=\text{P})]$ (L = tertiary phosphine; $\text{R} = t\text{-Bu}$, $i\text{-Pr}$, $i\text{-Pr}_2\text{N}$, Et_2N)¹¹ whose reactions with $[(\text{OC})_5\text{M}\cdot\text{THF}]$ ¹² ($\text{M} = \text{Cr}$, W) and $t\text{-Bu}_2\text{P}=\text{P}(\text{Me})t\text{-Bu}_2$ ¹³ suggest nucleophilic character of the $\text{R}_2\text{P}-\text{P}$ unit, (b) very reactive complexes $[(\text{Me}_2\text{PhP})\text{Zr}(\eta^1\text{-P}-\text{P}-t\text{-Bu}_2)]$ ¹⁴ and $[\text{Cp}_2\text{Zr}\{\mu_2\text{-PP}(\text{NEt}_2)_2\}_2\text{ZrCp}_2]$ ¹⁵ with terminal and bridging $\text{R}_2\text{P}-\text{P}$ units, and (c) relatively stable anionic side-on complexes $[(\text{ArN})_2(\text{Cl})\text{W}\eta^2\text{-R}_2\text{P}=\text{P}]$ ($\text{Ar} = 2,6\text{-}i\text{-Pr}_2\text{C}_6\text{H}_3$; $\text{M} = \text{Mo}$ and W ; $\text{R} = t\text{-Bu}$ and $i\text{-Pr}$).^{16,17} Complexes that are related to group c were prepared by Cummins et al. using nucleophilic terminal phosphide complexes of niobium $\text{Na}[(\text{P})\text{Nb}\{\text{N}(3,5\text{-Me}_2\text{C}_6\text{H}_3)\text{-Np}\}_3]$ ¹⁸ and tungsten $[(\text{P})\text{W}\{\text{N}(3,5\text{-Me}_2\text{C}_6\text{H}_3)i\text{Pr}\}_3]$ ¹⁹ as platforms for electrophilic phosphonium synthons. However, chemical properties of such complexes have not been investigated at all. Recently, metal complexes bearing terminal phosphido and phosphinidene ligands were introduced as important tools for the preparation of phosphorus–element bonds.²⁰ Thus, we undertook an investigation of the reactivity of $[(2,6\text{-}i\text{-Pr}_2\text{C}_6\text{H}_3\text{N})_2(\text{Cl})\text{M}(\eta^2\text{-}t\text{-Bu}_2\text{P}=\text{P})]\text{Li}\cdot 3\text{DME}$ toward tertiary phosphines and halogenophosphines, and report here

Received: May 12, 2015

our results leading to new complexes with *catena*-phosphorus ligands.

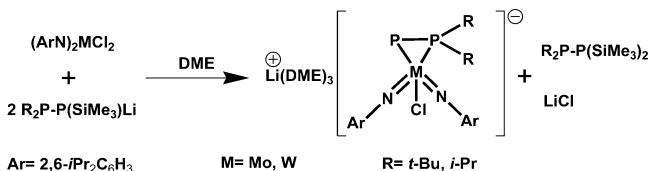
In contrast to *cyclo*-polyphosphorus compounds and ligands,^{21,22} catenated polyphosphorus species are relatively rare, and synthetic access to this class of phosphorus derivatives is limited.²³ Acyclic polyphosphorus ligands with three or more phosphorus atoms can be divided into two main classes, *catena*-polyphosphane and *catena*-polyphosphanido ligands. Transition metal complexes with acyclic polyphosphane ligands can be obtained in reactions of the corresponding triphosphanes or tetraphosphanes with iron or molybdenum carbonyl complexes.²⁴ A ruthenium complex with a P(OH)₂PHPPH(OH) ligand was synthesized via a hydrolysis reaction of complexed P₄ molecules.²⁵ As precursors of *catena*-polyphosphido ligands in syntheses of the transition metal complexes, di-^{10b,26} and triphosphanides^{17,27} or tetraphosphane-diides^{23b,28} were used. Several *catena*-polyphosphido complexes were synthesized via cleavage of a P–P bond in cyclophosphines,²⁹ or the cyclo-P₃ unit of the ferrocene analogue [Cp*FeP₃]³⁰ which occurs when the phosphorus substrates react with transition metal fragments. Additionally, chlorophosphines R₂NPCl₂ (R = Et, *i*-Pr)³¹ or the complex tetrakis(methyldichlorophosphine)nickel(0)³² was used as a source of polyphosphido ligands in reactions with Na₂Fe(CO)₄ and Re₂(CO)₁₀, respectively.

In this Article, we present a simple new method for the synthesis of acyclic polyphosphanido ligands starting from a phosphanylphosphinidene complex of tungsten(VI).

RESULTS AND DISCUSSION

Recently, we described the synthesis of a series of anionic phosphanylphosphinidene complexes of molybdenum(VI) and tungsten(VI)^{16,17} by reactions of diimido-dichlorido metal complexes with appropriate lithium diphosphanides³³ in DME (Scheme 1).

Scheme 1. Synthesis of Phosphanylphosphinidene Complexes [Li⁺·3DME][Cl(ArN)₂M(η²-R₂P=P)[−]]



For an investigation of the reactivity of these species, we selected the tungsten(VI) complex with a *t*-Bu₂P–P ligand (**1**). This compound is the most stable species in the series and can be easily isolated in high yield in crystalline form. Having previously derived the constitution of **1** only from spectroscopic data in solution,¹⁶ we have now obtained X-ray quality crystals of **1** which make it possible to discuss the geometry of the complex also in the solid state. The red tetrasolvate [Li⁺·3DME][Cl(ArN)₂W(η²-*t*-Bu₂P=P)[−]].DME¹⁶ (**1**·DME) crystallized from toluene as a red trisolvate [Li⁺·3DME][Cl(ArN)₂W(η²-*t*-Bu₂P=P)[−]] (**1**). The solid state structure of the anion of **1** is shown in Figure 1.

The η² binding mode of the *t*-Bu₂PP group is clearly evident. The short P1–P2 distance of 2.1065(17) Å is almost identical with the P–P distance of 2.101(3) Å in [Cl(ArN)₂W(η²-*i*-Pr₂P=P)[−]],¹⁶ and resembles the values of 2.0973(12) Å in [(3,5-Me₂C₆H₃)(*i*-Pr)N₃W(η²-Ph₂P=P)⁺]¹⁹ and 2.114 Å in [μ-(1,2:2-η-*t*-Bu₂P–P){Mo(CO)₂Cp^{fbu}}]₂.³⁴ The values of the

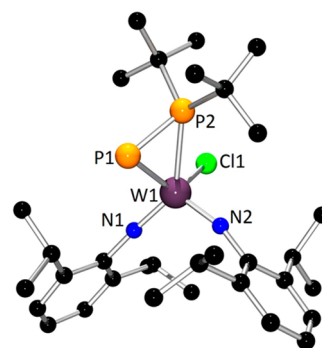
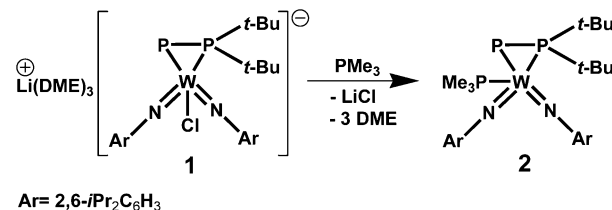


Figure 1. Ball-and-stick representation of the structure of the anion of crystalline [Li⁺·3DME][Cl(ArN)₂W(η²-*t*-Bu₂P=P)[−]] (**1**) showing the atom-numbering scheme; H atoms have been omitted for clarity. Important bond lengths (Å) and bond angles (deg): P1–P2 2.1065(17), P1–W1 2.4056(11), P2–W1 2.5713(11), W1–Cl 2.4150(10), W1–N1 1.793(4), W1–N2 1.785(4), P2–W1–P1 49.94(4), N1–W1–N2 108.89(16), W1–N1–Cl 176.3(3), C25–P2–C29 110.2(2).

shorter P1–W1 (2.4056(11) Å) and longer P2–W1 distances (2.5713(11) Å) in **1** are similar to those reported by Cummins et al. for [(3,5-Me₂C₆H₃)(*i*-Pr)N₃W(η²-Ph₂P=P)⁺].¹⁹ Formally, the tungsten atom is pentacoordinated, but the coordination geometry can also be described as distorted pseudotetrahedral (ligation by N1, N2, Cl1, and the P1–P2 bond).

In view of the strong σ- and π-donor properties of the imido spectator ligands and the π-donor properties of the R₂P moiety within the R₂P–P group,³⁵ nucleophilic properties for the phosphinidene phosphorus atom in **1** should be expected. As a part of our studies of the reactivity of phosphanylphosphinidene complexes, we therefore studied reactions with nucleophilic Me₃P and electrophilic Ph₂PCl, Ph₂PBr, PhPCl₂. The outcome of the reaction of **1** with Me₃P indicates that the phosphinidene P atom in **1** does not exhibit any significant Lewis acidity. Rather, the Me₃P ligand substitutes the chlorido ligand at tungsten to yield at ambient temperature the new neutral phosphanylphosphinidene complex **2** (Scheme 2).

Scheme 2. Synthesis of the Phosphanylphosphinidene Complex **2**



Complex **2** crystallizes as a red microcrystalline solid from pentane. The molecular structure of **2** is shown in Figure 2. The substitution of Cl by PMe₃ exerts substantial impact on the spatial alignment of the ligands around the tungsten atom and on the NMR data of the *t*-Bu₂PP group. The geometry around the W1 atom can still be seen as distorted pseudotetrahedral, but the PMe₃ ligand is now adjacent to the unsubstituted P1 atom of the P1–P2 bond, whereas the Cl atom in **1** was situated close to the P2 atom. Moreover, the distances P1–P2 of 2.066(3) Å and W1–P2 of 2.462(2) Å are shortened, and the distance W1–P1 of 2.493(2) Å is lengthened compared to

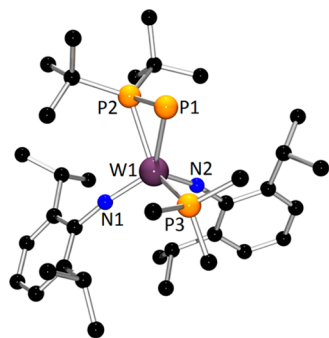
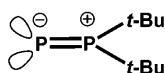


Figure 2. Ball-and-stick representation of the molecular structure of **2** in the crystal showing the atom-numbering scheme. H atoms have been omitted for clarity. Important bond lengths (Å) and bond angles (deg): P1–P2 2.066(3), P1–W1 2.493(2), P2–W1 2.462(2), W1–P3 2.479(2), W1–N1 1.820(6), W1–N2 1.796(6), P2–W1–P1 49.27(7), N1–W1–N2 114.8(3), W1–N1–C1 164.7(6), W1–N2–C13 169.9(6), C29–P2–C25 111.1(4).

1. The ligand displacement also changes the chemical shift of the phosphinidene-P atom and the value of $^1J_{PP}$ within the *t*-Bu₂P2–P1 moiety (62.8 ppm (P2), 17.6 ppm (P1), and $^1J_{P1-P2}$ = 454 Hz in **1** compared to 53.3 ppm (P2), –29.6 ppm (P1), and $^1J_{P1-P2}$ = 529 Hz in **2**). In contrast to **1**, in **2** we observed all P–W couplings, which nicely support the X-ray results. The value of $^1J_{PW}$ to the PMe₃ ligand (396 Hz) is typical for tertiary phosphine complexes of tungsten.³⁶ The $^1J_{PW}$ coupling to the P(*t*-Bu)₂ group is smaller (246 Hz) since the incorporation of the P and W atoms into a 3-membered ring induces presumably an increased p-character in the PW bond, and hence decreases J_{PW} . The still smaller coupling to the naked P atom ($^1J_{PW}$ = 48 Hz) is due to the fact that the P atom still carries a lone pair (with high s-character), and the PW bond is thus formally a σ -bond which exhibits a lower degree of s-character than a dative bond.³⁷ Small P–M couplings to the naked phosphorus atom were also observed for phosphanylphosphinide Pt(0) complexes.¹¹ Altogether, the ^{31}P NMR and X-ray data indicate that the bonding situation in **2** resembles that in [L₂Pt(η^2 -*t*-Bu₂P= P)] (L = tertiary phosphine).^{11a}

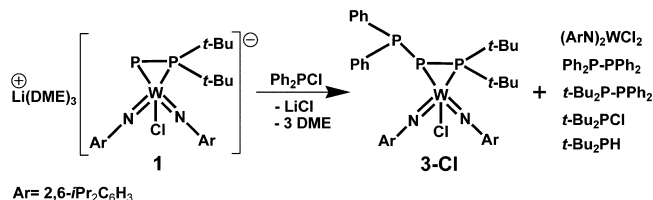
The electronic structure of the *t*-Bu₂P–P group was investigated by theoretical methods.^{11a} The results obtained suggest that the P–P bond in the phosphanylphosphinidene group is short: depending on the computational method, the bond length varies from 1.97 Å (RI-DFT) to 2.052 Å (*ab initio* calculations),^{11a} compared to 1.945 Å for singlet Me₂P–P (*ab initio* calculations).³⁸ The lengthening of the P–P bonds in **1** and **2** (2.11 and 2.07 Å) is a result of the η^2 -coordination of the singlet phosphinidene to the metal center. The calculations indicate that the P–P bond in the phosphanylphosphinidene ligand has a significant ionicity, with the positive charge being located on the substituted and the negative charge on the naked P atom.^{11a} Taking into account the computational results and the experimental data for complexes **1** and **2**, the best representation of phosphanylphosphinidene ligands in side-on complexes is given by the Lewis structure shown in Scheme 3.

Scheme 3. Lewis Structure of *t*-Bu₂P–P Ligand in Complex **1** and **2**



To our surprise, the reactivity of nucleophilic phosphinidene complexes toward phosphorus electrophiles was almost unexplored. Stephan et al. studied reactions of [Cp₂Zr(PMe₃)-PMe₃]⁺ with Me₂SiCl₂, Me₂GeCl₂, and Me₂SnCl₂, and observed a transfer of the PMe₃⁺ moiety to Si, Ge, and Sn with formation of four-membered E₂P₂ rings (E = Si, Ge, Sn).³⁹ Protasiewicz et al. studied reactions of [Cp₂Zr(PMe₃)PDmp] (Dmp = 2,6-Me₂C₆H₃) with Ph₂P–PPh₂ and observed formation of Ph₂P–PDmp–PPh₂.⁴⁰ In contrast to these reports, reaction of **1** with Ph₂P–PPh₂ produced [(2,6-*i*-Pr₂C₆H₃N)₂WCl₂], a small amount of the P1-substitution product [(1,2- η -*t*-Bu₂P–P–PPh₂)W[(2,6-*i*-Pr₂C₆H₃N)₂Cl]] (**3-Cl**), and a mixture of products which do not contain tungsten atoms (Ph₂P–PPh₂, *t*-Bu₂P–PPh₂,³¹ *t*-Bu₂P–PPh₂, and *t*-Bu₂PH, Scheme 4). We did not

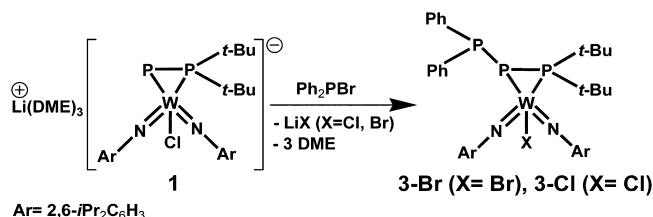
Scheme 4. Reaction of Complex **1** with Ph₂P–PPh₂



observe (in the ^{31}P NMR spectrum of the reaction mixture) any traces of the tetraphosphane (Ph₂P)₂P(P-*t*-Bu),⁴² which might be anticipated in view of the results of Protasiewicz.⁴⁰ The observed product distribution strongly suggests a participation of radical side processes. The absence of (Ph₂P)₂P(P-*t*-Bu) among the products suggests that **3-Cl** does not react with Ph₂P–PPh₂. Indeed, reaction of **1** with an excess of Ph₂P–PPh₂ does not produce (Ph₂P)₂P(P-*t*-Bu).

According to ^{31}P NMR studies, the reaction of Ph₂PBr with **1** proceeded much more selectively and yielded a significant amount of **3-Cl** together with a moderate amount of [(1,2- η -*t*-Bu₂P–P–PPh₂)W[(2,6-*i*-Pr₂C₆H₃N)₂Br]] (**3-Br**) (Scheme 5). In addition, a significant amount of Ph₂P–PPh₂ was formed.

Scheme 5. Reaction of Complex **1** with Ph₂PBr



The formation of **3-X** as major product is in line with the expected nucleophilic attack of the phosphinidene P atom on the electrophile Ph₂PBr. The successful isolation of the complexes is attributable to a lower chlorophilicity of the W-center which results in the low reactivity of **3-X** toward Ph₂PX (X = Cl, Br), contrarily to Protasiewicz' zirconium complexes. Figure 3 shows the X-ray structure of **3-Cl** which crystallizes as orange solid.

The molecular structure of **3-Cl** is similar to those of the complexes [(1,2- η -*t*-Bu₂P–P–P-*t*-Bu)₂M(2,6-*i*-Pr₂C₆H₃N)₂Cl] (M = Mo, W) recently published by us.¹⁷ Typical for this class of compounds is the side-on bonding of the *t*-Bu₂P–P fragment of a *t*-Bu₂P–P–PR₂ unit (R = *t*-Bu or Ph) which can be seen as η^2 -triphosphanido ligand. The geometry around the W1 atom is

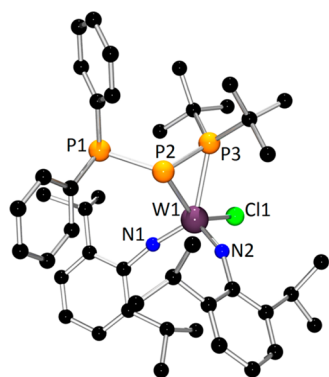
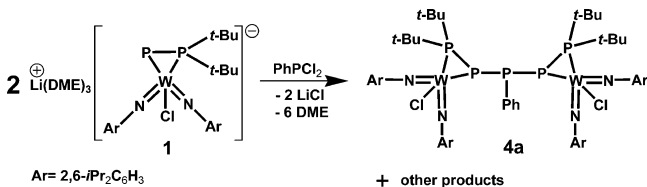


Figure 3. Ball-and-stick representation of the molecular structure 3-Cl in the crystal showing the atom-numbering scheme. H atoms have been omitted for clarity. Important bond lengths (Å) and bond angles (deg): P1–P2 2.2432(15), P2–P3 2.1801(15), P2–W1 2.5216(11), P3–W1 2.6130(10), W1–Cl1 2.4154(9), W1–N1 1.787(3), W1–N2 1.775(3), P2–W1–P3 50.21(3), N1–W1–N2 111.85(15), C13–N1–W1 170.7(3), C25–N2–W1 155.7(3), P1–P2–P3 112.22(6), P3–P2–W1 67.07(4), P1–P2–W1 115.17(5), P2–P1–C1 98.43(14), P2–P1–C7 95.75(19), C1–P1–C7 103.41(19), C37–P3–C41 114.01(19), C37–P3–P2 105.51(14), P2–P3–C41 120.44(14).

similar to that in **1** and can be described as pseudotetrahedral. The P2–P3 distance of 2.1801(15) Å is somewhat longer than the corresponding distance in [(1,2-*η*-*t*-Bu₂P–P–P-*t*-Bu₂)W(2,6-*i*-Pr₂C₆H₃N)₂Cl] (2.158 Å).¹⁷ Moreover, we observed P–P bond lengthening in phosphanylphosphido complexes (*t*-Bu₂P–P–PR₂) compared to the P–P bond in the appropriate parent phosphanylphosphinidene complex **1**. The P–P distance in **3-Cl** indicates partial multiple bond character when compared to the pure uncoordinated single P–P bond distance of 2.20–2.24 Å. The coordination geometry at P2 (sum of angles ∑P2 = 294.97°) and P1 (∑P1 = 297.59°) is distinctly pyramidal. The P3-atom exhibits a distorted tetrahedral coordination in which the “intraligand” angles are somewhat widened (∑P3 = 339.96° under neglect of the P3–W1 bond).

We have further checked the reactivity of **1** toward PhPCl₂ (molar ratio 2:1) and have observed the formation of [Cl(ArN)₂W(η²-*t*-Bu₂P–P)–P(Ph)–(η²-P–P-*t*-Bu₂)W(NAr)₂(Cl)] (**4a**) together with small amounts of *t*-Bu₂PCl, *t*-Bu₂PH, [(1,2-*η*-*t*-Bu₂P–P–P-*t*-Bu₂)W(2,6-*i*-Pr₂C₆H₃N)₂Cl] (**5-Cl**),¹⁷ and two hexaphosphorus compounds which give rise to higher order ³¹P NMR spectra of AA'MM'X₂ type and will be denoted as **4b**, **4c** (Scheme 6). Complex **4a** was isolated from

Scheme 6. Reaction of Complex **1** with PhPCl₂



the reaction mixture as orange crystals and its solid state structure determined by X-ray diffraction. The remaining compounds were only identified in solution by NMR spectroscopy (see Experimental Section). Although **4b** and **4c** could not be isolated and unmistakably identified, we assign them, on the basis of an analysis of the observed coupling patterns tentatively as complexes featuring a hexaphosphanido

ligand *t*-Bu₂P–P^(–)–P(Ph)–P(Ph)–P^(–)–P-*t*-Bu₂. The formation of **5-Cl** indicates intermediate generation of *t*-Bu₂PCl as a product of a radical side reaction, and its subsequent trapping by **1** according to Scheme 4.

Complex **4a** was isolated as orange solid by crystallization from pentane. Figure 4 shows the X-ray structure of **4a**. The

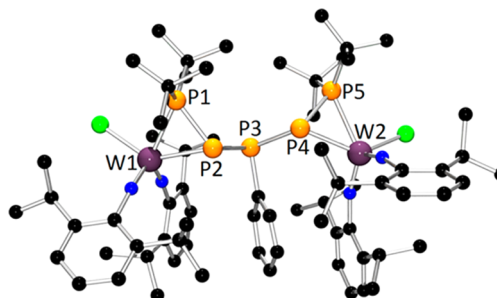


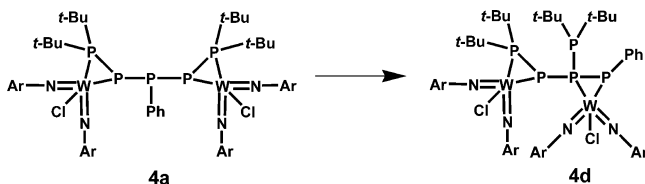
Figure 4. Ball-and-stick representation of the molecular structure **4a** in the crystal showing the atom-numbering scheme. H atoms have been omitted for clarity. Important bond lengths (Å) and bond angles (deg): P1–P2 2.176(5), P2–P3 2.247(5), P3–P4 2.238(5), P4–P5 2.168(5), P1–W1 2.556(4), P2–W1 2.552(4), P3–C33 1.850(14), W1–Cl1 2.368(4), W1–N1 1.726(11), W1–N2 1.774(12), P1–W1–P2 50.73(12), P1–P2–P3 112.7(2), P1–P2–W1 63.81(13), P3–P2–W1 106.22(18), P3–P4–P5 112.9(2), N1–W1–N2 113.6(5), P2–P3–P4 95.4(12), P2–P3–C33 92.7(5), P4–P3–C33 99.3(5), C21–N2–W1 170.0(11), C9–N1–W1 164.6(10), C1–P1–C5 114.9(6), P2–P1–C5 118.6(4), P2–P1–C1 106.1(7).

molecule consists of two [(*t*-Bu₂P–P)W(2,6-*i*-Pr₂C₆H₃N)₂Cl] parts connected by a bridging PPh group. The spatial alignment in the terminal fragments resembles the structure of **3-Cl**. The *t*-Bu₂P–P distances of 2.176(5) and 2.168(5) Å indicate partial double bond character of the P1–P2 and P4–P5 bonds. The average P2/P4–P3(Ph) distance of 2.242 Å is longer and suggests single bond character for the central P2–P3 and P3–P4 bonds. The coordination geometries at the P1/P5 and P2/P4 atoms are likewise similar as in **3-Cl**. The geometry around P3(PPh) (sum of angles ∑P3 = 282.7°) is even more pyramidal than in **3-Cl** (287.4°). Moreover, the planes of the phenyl rings at P3 and the 2,6-isopropylphenyl ring at N3 deviate from coplanarity by only 3.8° and have a centroid–centroid distance of 3.838 Å, suggesting a possible π–π stacking interaction.

Isolated **4a** was found to be unstable in solution and decayed in C₆D₆ within a few weeks at ambient temperature to a complicated product mixture which shows complex signal patterns most of which exhibit higher order splittings. Structural assignment is based on the analysis of ³¹P spectra by spectral simulation, and on the analysis of ¹H, ³¹P HMQC spectra which allowed us to distinguish between the P atoms of P-*t*-Bu₂, P(naked), and PPh moieties. NMR spectroscopic monitoring revealed that the initial stage of the reaction was dominated by formation of a new pentaphosphorus tungsten complex **4d**, which was identified by its first order ³¹P{¹H} spectrum and is a product of rearrangement of complex **4a** (Scheme 7). Moreover, the formation of small amounts of complex **4b** and a product assigned as a complex **4e** with an anionic tetraphosphorus ligand *t*-Bu₂P–P^(–)–P^(–)–P-*t*-Bu₂ was observed.

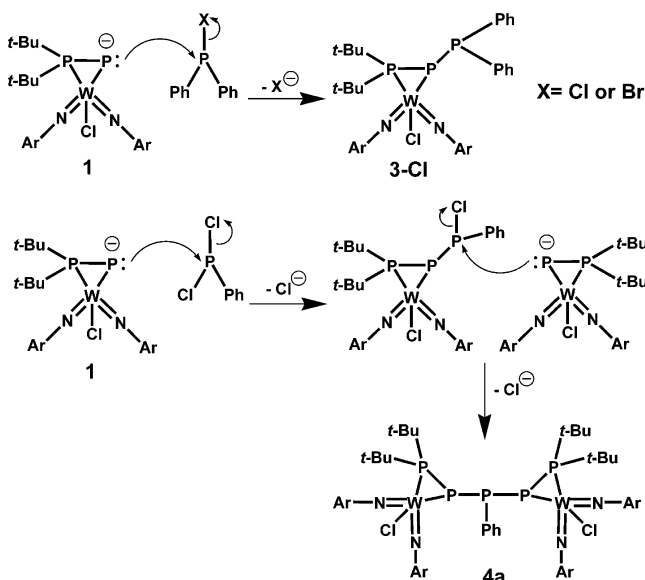
NMR spectra recorded after complete conversion of **4a** indicate the presence of significant amounts of complexes **4d**, **4b**, and a further hexaphosphorus compound (**4f**) which

Scheme 7. Rearrangement of Complex 4a



exhibits presumably a similar hexaphosphorus skeleton as **4b** and can possibly be regarded as a rearrangement product of this species. In addition, a minor quantity of **4e** was still present.

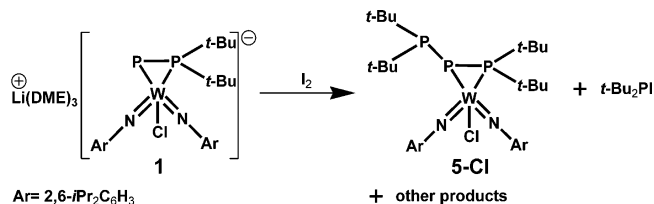
We suggest that reactions of the anionic phosphinidophosphinidene complex **1** with halogenophosphines proceed via a nucleophilic substitution mechanism (Scheme 8). In the

Scheme 8. Suggested Mechanism of the Reaction of **1** with (Di)halogenophosphines

formation of **3-Cl**, the nucleophilic phosphinidene phosphorus atom attacks the more electrophilic diphenylhalogenophosphine to form a new P–P bond under halide displacement. The reaction with dichlorodiphenylphosphine serves as a route to pentaphosphorus compounds. Probably, the first step of this synthesis proceeds via formation of a transient triphosphanido complex with a $t\text{-Bu}_2\text{P}=\text{P}^-(\text{Cl})\text{Ph}$ ligand. Then, the phosphinidene P atom of a second equivalent of **1** attacks the P(Cl)Ph group to give the pentaphospha-diido ligand.

Tertiary phosphines react with iodine to give iodophosphonium compounds $\text{R}_3\text{P}-\text{I}^+-\text{I}^-$.⁴³ Taking into account the nucleophilic properties of **1**, we have also tested its reactivity toward I_2 . ^{31}P NMR investigations of the reaction solution revealed formation of $t\text{-Bu}_2\text{PI}$ and a complex assigned as $[(1,2-\eta\text{-}t\text{-Bu}_2\text{P}-\text{P}-\text{P}-t\text{-Bu}_2)\text{W}(2,6\text{-}i\text{-Pr}_2\text{C}_6\text{H}_3\text{N})_2\text{Cl}]$ (**5-Cl**) as main products, together with small amounts of $[(1,2-\eta\text{-}t\text{-Bu}_2\text{P}-\text{P}-\text{P}-t\text{-Bu}_2)\text{W}(2,6\text{-}i\text{-Pr}_2\text{C}_6\text{H}_3\text{N})_2\text{I}]$ (**5-I**), $t\text{-Bu}_2\text{P-Cl}$, and $[(\eta^2\text{-}t\text{-Bu}_2\text{P}-\text{PH})\text{W}(2,6\text{-}i\text{-Pr}_2\text{C}_6\text{H}_3\text{N})_2\text{Cl}]$ (**6**) (Scheme 9).

These results indicate that the electrophile I_2 reacts with **1** predominantly under cleavage of the P–P bond of the $t\text{-Bu}_2\text{P}=\text{P}$ unit to yield $t\text{-Bu}_2\text{PI}$ and presumably insoluble phosphorus compounds. To our surprise, we did not find any traces of PI_3 . The formation of **5-I** and $t\text{-Bu}_2\text{P-Cl}$ arises obviously from halide metathesis between **5-Cl** and $t\text{-Bu}_2\text{PI}$

Scheme 9. Reaction of Complex **1** with Iodine

similar to Scheme 5. The complex **5-Cl** can also be independently prepared by direct reaction of $t\text{-Bu}_2\text{P}-\text{P}(\text{Li})-\text{P}-t\text{-Bu}_2$ with $[(2,6\text{-}i\text{-Pr}_2\text{C}_6\text{H}_3\text{N})_2\text{WCl}_2]$.¹⁷

EXPERIMENTAL SECTION

DME was dried over K/benzophenone and distilled under argon. Toluene was dried over Na/benzophenone and distilled under argon. Pentane was dried over Na/benzophenone/diglyme and distilled under argon. All manipulations were performed in flame-dried Schlenk type glassware on a vacuum line. Solution ^{31}P , ^{13}C , and ^1H spectra were recorded on Bruker AV300 MHz, Bruker AV400 MHz, and Varian 500 MHz spectrometers (external standard TMS for ^1H , ^{13}C ; 85% H_3PO_4 for ^{31}P) at ambient temperature. We determined the composition of reaction solutions by integration of the R_2P signals in the $^{31}\text{P}\{^1\text{H}\}$ NMR spectra. We compare the signals of similar groups. Me_3P , $\text{Ph}_2\text{P-Cl}$, and PhP-Cl_2 were purchased from Aldrich and used as received. A literature method was used to prepare $\text{Ph}_2\text{P-Br}$.⁴⁴ Coupling constants and chemical shifts of species giving rise to higher order splittings were determined by spectral simulation using the WIND-AISY module as implemented in the TopSpin software.

Crystallization of 1·DME from Toluene. A literature method was used to prepare complex **1·DME**.¹⁶ Solid **1·DME** (500 mg, 0.42 mmol) was then dissolved in ca. 5 mL of toluene. This solution was stored at $-20\text{ }^\circ\text{C}$, and red crystals of **1** suitable for X-ray analysis were deposited within 1 week. The yield of crystallization was 110 mg, 0.100 mmol, 24%. For NMR data of **1** see ref 16.

Reaction of **1 with PMe_3 . Synthesis of $[(2,6\text{-}i\text{-Pr}_2\text{C}_6\text{H}_3\text{N})_2(\text{Me}_3\text{P})\text{W}(\eta^2\text{-}t\text{-Bu}_2\text{P}=\text{P})]$ (**2**).** PMe_3 (0.076 g, 1 mmol) was added dropwise to a solution of **1** (512 mg, 0.50 mmol) in 5 mL of toluene at -30 to $-40\text{ }^\circ\text{C}$. During the reaction the color of the solution changed from red to purple. The mixture was then kept at ambient temperature for 24 h. The volume of the mixture was reduced to one-half under reduced pressure, and the remaining solution was analyzed by $^{31}\text{P}\{^1\text{H}\}$, ^{31}P , and ^1H NMR. Solvent and excess of PMe_3 were then evaporated under reduced pressure, and the residue was extracted with pentane. After a few minutes, crystalline **2** precipitated (320 mg, yield 81%). Results of the examination of the $^{31}\text{P}\{^1\text{H}\}$ NMR of the reaction solution: **2** (88%); PMe_3 (excess); $t\text{-Bu}_2\text{PP}(\text{SiMe}_3)_2$ (6%, contamination of starting complex **1**); $t\text{-Bu}_2\text{PH}$ (4%); $t\text{-Bu}_2\text{PP}(\text{SiMe}_3)_2\text{H}$ (2%, contamination of starting complex **1**).¹⁶

Data for **2** follow. $^{31}\text{P}\{^1\text{H}\}$: δ 54.9 (dd, $^1J_{\text{PP}} = 529\text{ Hz}$, $^2J_{\text{PP}} = 22\text{ Hz}$, $^1J_{\text{PW}} = 246\text{ Hz}$, $t\text{-Bu}_2\text{P}$); -4.3 (dd, $^2J_{\text{PP}} = 22$, $^2J_{\text{PP}} = 47\text{ Hz}$, $^1J_{\text{PW}} = 396\text{ Hz}$, PMe_3); -26.3 (dd, $^1J_{\text{PP}} = 529\text{ Hz}$, $^2J_{\text{PP}} = 47\text{ Hz}$, $^1J_{\text{PW}} = 48\text{ Hz}$, PW). ^1H : δ 6.95–6.70 (m, overlapped, 6 H, C_6H_3), 3.73 (sept, $^3J_{\text{HH}} = 6.8\text{ Hz}$, 4 H, CH), 1.40 (d, $^2J_{\text{PH}} = 10.0\text{ Hz}$, 9 H, Me_3P), 1.22 (d, $^3J_{\text{PH}} = 16.4\text{ Hz}$, 18 H, $t\text{-Bu}_2\text{P}$), 0.98 (d, $^3J_{\text{HH}} = 6.8\text{ Hz}$, 6 H, CH_3), 0.86 (d, $^3J_{\text{HH}} = 6.8\text{ Hz}$, 6 H, CH_3). $^{13}\text{C}\{^1\text{H}\}$: δ 155.4 (s, C), 140.9 (s, C_o), 124.0 (s, C_p), 123.3 (s, C_m), 38.1 (d, $J = 18.1\text{ Hz}$, H_3CCP), 33.1 (d, $J = 4.2\text{ Hz}$, H_3CCP), 27.5 (s, H_3CCP), 25.5 (s, CHCH_3), 24.9 (s, CHCH_3).

Reaction of **1 with $\text{Ph}_2\text{P-Cl}$. Formation of **3-Cl**.** $\text{Ph}_2\text{P-Cl}$ (110 mg, 0.50 mmol) was added dropwise to a solution of **1** (512 mg, 0.50 mmol) in 3 mL of DME at -30 to $-40\text{ }^\circ\text{C}$. During the reaction, the color of the solution changed from red to orange. The solution was then held at ambient temperature for 24 h. The volume was reduced to one-half under reduced pressure and the resulting solution analyzed by $^{31}\text{P}\{^1\text{H}\}$, ^{31}P , and ^1H NMR. Results of the examination of the $^{31}\text{P}\{^1\text{H}\}$ NMR of the reaction mixture follow: **3-Cl** (9%); $\text{Ph}_2\text{P-PPH}_2$ (41%);⁴¹

$t\text{-Bu}_2\text{P-PPh}_2$ (17%);⁴¹ $t\text{-Bu}_2\text{PCL}$; ⁴⁵ (8%) Ph_2PCL (8%);⁴⁶ $t\text{-Bu}_2\text{PH}$ (8%).

Data for **3-Cl** follow. $^{31}\text{P}\{^1\text{H}\}$: δ 48.5 (d, $^1J_{\text{PP}} = 377$ Hz, $^1J_{\text{PW}} = 26$ Hz, $t\text{-Bu}_2\text{P}$); -12.0 (d, $^1J_{\text{PP}} = 204$, Ph_2P); -132.1 (dd, $^1J_{\text{PP}} = 204$ Hz, $^1J_{\text{PP}} = 377$ Hz, $^1J_{\text{PW}} = 74$ Hz, P).

Reaction of 1 with Ph_2PBr . Formation of 3-Cl and 3-Br. Ph_2PBr (132 mg, 0.50 mmol) was added dropwise to a solution of **1** (512 mg, 0.50 mmol) in 3 mL of DME at -30 to -40 °C. During the reaction, the color of the solution changed from red to orange. The solution was then held at ambient temperature for 24 h. The volume was reduced to one-half under reduced pressure, and the resulting solution was analyzed by $^{31}\text{P}\{^1\text{H}\}$, ^{31}P , and ^1H NMR. The solvent was then evaporated under reduced pressure and the residue extracted with 5 mL of pentane. The extract was filtrated, reduced to one-half under reduced pressure, and stored at room temperature. Orange crystals of **3-Cl** deposited within 24 h (250 mg, yield 54%). Results of the examination of the $^{31}\text{P}\{^1\text{H}\}$ NMR of the reaction mixture: **3-Cl** (48%), **3-Br** (14%), $\text{Ph}_2\text{P-PPh}_2$ (19%), $t\text{-Bu}_2\text{PH}$ (19%).

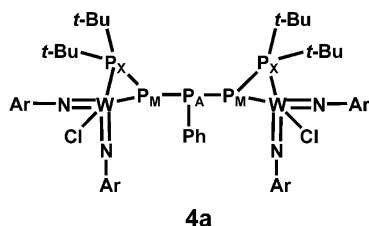
Data for **3-Cl** follow. $^{31}\text{P}\{^1\text{H}\}$: δ 48.9 (d, $^1J_{\text{PP}} = 377$ Hz, $^1J_{\text{PW}} = 25$ Hz, $t\text{-Bu}_2\text{P}$); -10.4 (d, $^1J_{\text{PP}} = 206$ Hz, Ph_2P); -130.2 (dd, $^1J_{\text{PP}} = 206$ Hz, $^1J_{\text{PP}} = 377$ Hz, $^1J_{\text{PW}} = 74$ Hz, P). ^1H : δ 7.55–7.45 (m, 5 H, C_6H_5), δ 7.15–6.90 (m, 6 H, C_6H_5), 3.95 (sept, $^3J_{\text{HH}} = 6.8$ Hz, 4 H, CH), 1.51 (d, $^3J_{\text{PH}} = 16.4$ Hz, 18 H, $t\text{-Bu}_2\text{P}$), 1.19 (d, $^3J_{\text{HH}} = 7.0$ Hz, 12 H, CH_3).

Data for **3-Br** follow. $^{31}\text{P}\{^1\text{H}\}$: δ 46.2 (d, $^1J_{\text{PP}} = 382$ Hz, $^1J_{\text{PW}} = 26$ Hz, $t\text{-Bu}_2\text{P}$); -12.3 (d, $^1J_{\text{PP}} = 204$ Hz, Ph_2P); -139.4 (dd, $^1J_{\text{PP}} = 204$ Hz, $^1J_{\text{PP}} = 382$ Hz, $^1J_{\text{PW}} = 72$ Hz, P).

Reaction of 1 with PhPCl_2 . Synthesis of 4a. PhPCl_2 (45 mg, 0.25 mmol) was added dropwise to a solution of **1** (512 mg, 0.5 mmol) in 3 mL of DME at -30 to -40 °C. During the reaction, the color of the solution changed from red to orange. The solution was then held at ambient temperature for 24 h. The volume was reduced to one-half under reduced pressure, and the resulting solution was analyzed by $^{31}\text{P}\{^1\text{H}\}$, ^{31}P , and ^1H NMR. The solvent was then evaporated under reduced pressure, and the residue was extracted with 5 mL of pentane. Orange crystals of **4a** deposited within 24 h (95 mg, yield 24%). Results of the $^{31}\text{P}\{^1\text{H}\}$ NMR examination of the reaction solution after a few weeks at room temperature: **4a** (47%), $t\text{-Bu}_2\text{PH}$ (22%), **4b** (12%), **4c** (12%), $t\text{-Bu}_2\text{PCL}$ (5%), [(1,2- η - $t\text{-Bu}_2\text{P}=\text{P}-\text{P}-t\text{-Bu}_2$)W(2,6- $i\text{-Pr}_2\text{C}_6\text{H}_3\text{N}_2$)Cl] (**5-Cl**)¹⁷ (2%).

The decay of **4a** in C_6D_6 solution was monitored by NMR spectroscopy within a few weeks. A 30 mg portion of crystalline **4a** was dissolved in 0.7 mL of C_6D_6 and stored in a flame-sealed NMR tube. This solution was analyzed by ^{31}P and ^1H , ^{31}P HMQC NMR. The analysis of signal patterns with high order splittings was accomplished by spectral simulation, and the results were used to propose a constitution for the phosphorus ligands in **4b**, **4c**, **4e**, and **4f**. Results of the examination of the $^{31}\text{P}\{^1\text{H}\}$ NMR of a freshly prepared C_6D_6 solution of crystalline **4a**: **4a** (54%), **4d** (29%), **4b** (14%), **4e** (3%). Results of the examination of the $^{31}\text{P}\{^1\text{H}\}$ NMR of a C_6D_6 solution of **4a** after a few weeks at room temperature: **4d** (44%), **4b** (40%), **4f** (14%), **4e** (2%).

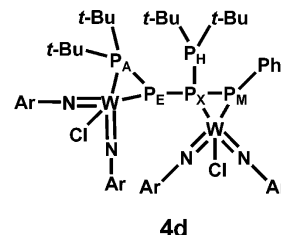
Data for **4a** follow. $^{31}\text{P}\{^1\text{H}\}$ (simulated as AMM'XX' spin system): δ 41.8 (XX', $t\text{-Bu}_2\text{P}$); -1.3 (A, PhP); -104.5 (m, MM', P); $^1J_{\text{AM}} = -254$ Hz, $^2J_{\text{AX}} = 9$ Hz, $^2J_{\text{MM}} = 252$ Hz, $^4J_{\text{XX}} = 0.0$ Hz, $^1J_{\text{MX}} = -399$ Hz, $^3J_{\text{MX}} = -1$ Hz, $^1J_{\text{MW}} = 25$ Hz, $^1J_{\text{XW}} = 73$ Hz.



Data for **4b** follow. $^{31}\text{P}\{^1\text{H}\}$ (simulated as AA'MM'XX' spin system): δ 54.8 (A, $t\text{-Bu}_2\text{P}$); -44.9 (M, P); -61.6 (X, PPh); $^1J_{\text{AM}} = -210$ Hz, $^2J_{\text{AX}} = 50$ Hz, $^3J_{\text{AX}} = -7$ Hz, $^4J_{\text{AM}} = -36$ Hz, $^5J_{\text{AA}} = 14$ Hz, $^1J_{\text{MX}} = -112$ Hz, $^2J_{\text{MX}} = 7$ Hz, $^3J_{\text{MM}} = -26$ Hz, $^1J_{\text{XX}} = -141$ Hz.

Data for **4c** follow. $^{31}\text{P}\{^1\text{H}\}$ (simulated as AA'MM'X₂ spin system): δ 56.9 (A, $t\text{-Bu}_2\text{P}$); -36.3 (M, P); -68.9 (X, PPh); $^1J_{\text{AM}} = -317.4$, $^3J_{\text{AM}} = 26.7$ Hz, $^3J_{\text{AX}} = 92.1$ Hz, $^1J_{\text{MX}} = -118.7$ Hz, $^2J_{\text{MM}} = 199.0$ Hz, $^4J_{\text{MM}} = -5.0$ Hz.

Data for **4d** follow. $^{31}\text{P}\{^1\text{H}\}$ (AEHMX spin system): δ 47.7 (A, d, $^1J_{\text{AE}} = -438$ Hz, $^1J_{\text{P-W}} \approx 10$ Hz, $t\text{-Bu}_2\text{P}$); 47.6 (H, ddd, $^1J_{\text{HX}} = -256$, $^2J_{\text{HM}} = 37$, $^2J_{\text{EH}} = 20$ Hz, $t\text{-Bu}_2\text{P}$); -41.0 (M, ddd, $^1J_{\text{MX}} = -156$ Hz, $^2J_{\text{EM}} = 42$ Hz, $^2J_{\text{HM}} = 37$ Hz, $^1J_{\text{PW}} \approx 11$ Hz, PPh); -30.2 (X, ddd, $^1J_{\text{EX}} = -378$ Hz, $^1J_{\text{HX}} = -256$ Hz, $^1J_{\text{MX}} = -156$ Hz, $^1J_{\text{PW}} \approx 19$ Hz, P); -96.4 (E, dddd, $^1J_{\text{AE}} = -438$ Hz, $^1J_{\text{EX}} = -378$ Hz, $^2J_{\text{EM}} = 42$ Hz, $^2J_{\text{EH}} = 20$ Hz, $^1J_{\text{PW}} \approx 10$ Hz, P).



Data for **4e** follow. $^{31}\text{P}\{^1\text{H}\}$ (simulated as AA'XX' spin system): δ 56.7 (A, $t\text{-Bu}_2\text{P}$); -121.3 (X, P); $^1J_{\text{AX}} = -383$, $^3J_{\text{AA}} = 9$ Hz, $^1J_{\text{XX}} = -220$ Hz.

Data for **4f** follow. $^{31}\text{P}\{^1\text{H}\}$ (simulated as AA'MM'XX' spin system): δ 54.9 (A, $t\text{-Bu}_2\text{P}$); -16.4 (M, PPh); -146.5 (X, P); $^5J_{\text{AA}} = 0$ Hz, $^1J_{\text{MM}} = -270$ Hz, $^3J_{\text{XX}} = 5$ Hz, $^1J_{\text{AX}} = -374$ Hz, $^4J_{\text{AX}} = 0$ Hz, $^2J_{\text{AM}} = 0$ Hz, $^3J_{\text{AM}} = 0$ Hz, $^1J_{\text{MX}} = -383$ Hz, $^2J_{\text{MX}} = 0$ Hz.

Reaction of 1 with I_2 . Synthesis of 5-Cl. I_2 (64 mg, 0.25 mmol) was added to a solution of **1** (512 mg, 0.50 mmol) in 3 mL of DME at -30 to -40 °C. During the reaction, the color of the solution changed from red to dark brown. The solution was then held at ambient temperature for 24 h. The volume was reduced to one-half under reduced pressure and the resulting solution analyzed by $^{31}\text{P}\{^1\text{H}\}$, ^{31}P , and ^1H NMR. Results of the examination of the ^{31}P NMR of the reaction solution: $t\text{-Bu}_2\text{PI}$ (59%);⁴⁰ **5-Cl** (35%);¹⁷ [(η^2 - $t\text{-Bu}_2\text{P}-\text{PH}$)W(2,6- $i\text{-Pr}_2\text{C}_6\text{H}_3\text{N}_2$)Cl] (**6**) (6%);¹⁶ [(1,2- η^2 - $t\text{-Bu}_2\text{P}-\text{P}-\text{PtBu}_2$)W(2,6- $i\text{-Pr}_2\text{C}_6\text{H}_3\text{N}_2$)I] (**5-I**) (W).

Data for **5-I** follow. $^{31}\text{P}\{^1\text{H}\}$: δ 44.3 (dd, $^1J_{\text{PP}} = 276$ Hz, $^2J_{\text{PP}} = 13$ Hz, $t\text{-Bu}_2\text{P}$); 16.9 (dd, $^1J_{\text{PP}} = 428$, $^2J_{\text{PP}} = 13$ Hz, $^1J_{\text{PW}} = 45$ Hz, $t\text{-Bu}_2\text{PW}$), -163.9 (dd, $^1J_{\text{PP}} = 428$, $^1J_{\text{PP}} = 276$ Hz, P).

Crystal Structure Determinations for 1, 2, 3-Cl, and 4a.

Good-quality single crystal specimens of **1**, **2**, **3-Cl**, and **4a** were selected for X-ray diffraction experiments carried out at 120 K. The diffraction data for **1**, **3-Cl**, and **4a** were collected with a KM4CCD kappa geometry diffractometer equipped with a Sapphire2 CCD detector. An enhanced X-ray Mo $K\alpha$ radiation source with a graphite monochromator was used. Diffraction data of **2** was collected on a STOE diffractometer equipped with an imaging plate detector system IPDS 2 using the same radiation and monochromatization. The structures were solved by direct methods and refined against F^2 by least-squares techniques using the SHELXS-97 and SHELXL-97 programs.⁴⁷ Non-hydrogen atoms were refined with anisotropic displacement parameters; hydrogen atoms were usually refined using the isotropic model with $U_{\text{iso}}(\text{H})$ values fixed to be 1.5 times U_{eq} of C atoms for CH_3 or 1.2 times U_{eq} for CH groups and aromatic H. Voids found in the structure of **1** were examined by the PLATON/SQUEEZE program.⁴⁸ Empty space of volume 204 Å³ was found at position (0 1/2 1) with residual electron density of 6.0 electrons inside the cave.

Crystallographic data for the structures of **1**, **2**, **3-Cl** and **4a** reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication No. CCDC 1054762, CCDC 1054763, CCDC 1054764 and CCDC 1054765. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

SUMMARY

A comprehensive reactivity study of the stable anionic phosphanylphosphinidene complex $[(2,6\text{-}i\text{-Pr}_2\text{C}_6\text{H}_3\text{N})_2(\text{Cl})\text{W}(\eta^2\text{-}t\text{-Bu}_2\text{P}=\text{P})]\text{Li}\cdot 3\text{DME}$ (**1**) was carried out. The nucleophilic properties of this complex were demonstrated by reactions with halogenophosphines Ph_2PCl , Ph_2PBr , or PhPCl_2 to give compounds with new anionic catenapolyphosphorus ligands $t\text{-Bu}_2\text{P}-\text{P}^--\text{PPh}_2$ or $t\text{-Bu}_2\text{P}-\text{P}^--\text{P}(\text{Ph})-\text{P}^--\text{P}-t\text{-Bu}_2$, respectively, as main products. The formation of these products is readily explained as resulting from nucleophilic attack of the phosphinidene P atom on the electrophilic phosphorus atom of the halogenophosphine. The complex with the pentaphosphane-diido ligand $t\text{-Bu}_2\text{P}-\text{P}^--\text{P}(\text{Ph})-\text{P}^--\text{P}-t\text{-Bu}_2$ was found to be unstable in solution and decayed into a product mixture containing, among other products, complexes with tetra- and hexaphosphane-diido ligands. Moreover, in the reaction of **1** with nucleophilic Me_3P , we observed substitution of the chlorido ligand by the PMe_3 ligand to give a new neutral phosphanylphosphinidene complex.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.inorgchem.5b01063.

Crystallographic data (CIF)

List of compounds, crystallographic details, and spectroscopic data (PDF)

AUTHOR INFORMATION

Corresponding Author

*E-mail: grubba@pg.gda.pl.

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

R. G., A. O., and K. K. thank the Polish Ministry of Science and Higher Education (Grant Iuventus Plus no. IP2012 037772) for financial support. The authors thank KNMF (Karlsruhe Nano Micro Facility) KIT Karlsruhe for X-ray single crystal measurements.

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