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A selective route to aryl-triphosphiranes and their titanocene-induced fragmentation

This image of historic harbor cranes in Rostock by Dr. Christian Hering-Junghans depicts the work of André Schumann, Dr. Fabian Reiß, Jan Erik-Siewert, Haijun Jiao, Jabor Rabeah, Ivo Krummenacher, Prof. Holger Braunschweig and Dr. Christian Hering-Junghans from the LIKAT Rostock and the University of Würzburg on the synthesis of aryl-substituted triphosphiranes with a high selectivity. These three-membered phosphorus ring systems are then shown to be transformed into titanocene diphosphene complexes. The experimental work is supported by theoretical investigations to shed light on the mechanism of this titanocene-mediated fragmentation of triphosphiranes.

As featured in:

A selective route to aryl-triphosphiranes and their titanocene-induced fragmentation†

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Triphosphiranes are three-membered phosphorus cycles and their fundamental reactivity has been studied in recent decades. We recently developed a high-yielding, selective synthesis for various aryl-substituted triphosphiranes. Variation of the reaction conditions in combination with theoretical studies helped to rationalize the formation of these homoleptic phosphorus ring systems and highly reactive intermediates could be isolated. In addition we showed that a titanocene synthon \([\text{Cp}_2\text{Ti(btmsa)}]\) facilitates the selective conversion of these triphosphiranes into titanocene diphosphene complexes. This unexpected reactivity mode was further studied theoretically and experimental evidence is presented for the proposed reaction mechanism.

Introduction

Triphosphiranes are three-membered cyclo-phosphines, which are promising synths in inorganic chemistry (Scheme 1). As early as 1877 the first cyclic oligophosphine was synthesized by Köhler and Michaelis in an attempt to prepare a phosphorus analogue of azobenzene with a P–P double bond.1 Almost 100 years later in 1964 the molecular structure of the product could be identified as \(\text{P}_3\text{Ph}_5\) by X-ray crystal structure analysis.2 Although, Cowley et al. already mentioned the synthesis of \(\text{P}_3\text{(C}_2\text{F}_5)_3\) in 1970,3 it was later discussed that in fact the tetramer and pentamer were formed under the reaction conditions described.4 The first stable triphosphirane \(\text{P}_4\text{Bu}_3\) was reported by Baudler and co-workers in 1976,4,5 and various synthetic approaches towards triphosphiranes have since emerged.5 Reductive approaches starting from dihalophosphines \(\text{RPX}_2\) (X = Cl, Br) result in a mixture of oligophosphines of different ring sizes of \(\text{P}_n\text{R}_n\) \((n = 3, 4, 5, 6)\) and are thus regarded as unspecific.6 The ratio of the different oligomers heavily depends on the steric demand of the substituent \(\text{R}\).7 Cyclo-condensation reactions, which also allow the preparation of unsymmetrically substituted triphosphiranes, and cyclization by reductive dehalogenation of dihalotriphosphines have emerged as more selective synthetic pathways.8 Nevertheless, the presence of other cyclic oligophosphines as side products is often observed. Jutzi and co-workers have shown that selenium inserts into one P–P bond of \(\text{P}_3\text{Cp}^*3\) (\(\text{Cp}^* = \text{pentamethylenecyclopentadienyl}\)), affording a mixture of cyclic selenotriphosphabutanes (Scheme 1, A) and cyclic selenodiphosphapropanes (Scheme 1, B).11 In contrast, thermolysis of \(\text{P}_3\text{Cp}^*3\) in xylene resulted in the

Scheme 1 Selected reactivity modes of differently substituted triphosphiranes.

† Electronic supplementary information (ESI) available: Synthesis and characterization of compounds, NMR spectra, crystallographic, EPR and computational details. CCDC 1915056–1915060. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c9sc02322d
of different phosphorus clusters, some of which are structurally related to Hittorf’s-phosphorus (Scheme 1, C and D).\textsuperscript{12} Ring expansion reactions were reported by Uhl and Benter by the insertion of Ga(i) into a P–P bond of \( \text{P}_3\text{Bu}_3 \), thus establishing a way to prepare cyclo-galliumtriphosphabutanes (Scheme 1, E, M = Ga).\textsuperscript{14} A similar reactivity is observed when Al(i) compound (AlCp\textsuperscript{#}) reacts with \( \text{P}_3\text{Bu}_3 \) (Scheme 1, E, M = Al).\textsuperscript{14} In addition, the reaction of \( \text{P}_3\text{Bu}_3 \) with PMe\textsubscript{Cl} or PPh\textsubscript{Cl} in the presence of Me\textsubscript{3}SiOTf or GaCl\textsubscript{3}, respectively, resulted in the selective ring expansion with insertion of [PMe\textsubscript{3}]\textsubscript{2} into the P–P bond between the two identical P atoms of \( \text{P}_3\text{Bu}_3 \) to afford \([ \text{R}_2\text{P}(\text{P}_3\text{Bu}_3)] \) (Scheme 1, F; R = Me, Ph).\textsuperscript{15,26} More recently, Manners and co-workers showed the addition of \( \text{P}_3\text{Bu}_3 \) to organic nitriles after activation of the three-membered ring by electrophiles to yield differently substituted 1-aza-2,3,4-triphenylphosphinenes in a click-type reaction (Scheme 1, G),\textsuperscript{17,18} underlining the value of triphosphinenes as synthons in synthetic inorganic chemistry. Fragmentation of \( \text{P}_3\text{Bu}_3 \) was observed by Fenske and Ahrlich in the reaction with Ni(CO)\textsubscript{4}, resulting in the formation of \([ \text{Ni}_3\text{P}(\text{P}_3\text{Bu}_3)(\text{P}_3\text{Bu}_3)[\text{CO}_3]] \) with \( \mu_3 \)- and \( \mu_2 \)-bridging \( \text{P}^2 \)-ligands as well as a \( \text{P}_3\text{Bu}_3 \) chain, acting as a \( \mu_6(\text{n}^3\text{P},\text{n}^1\text{P},\text{n}^2\text{P}) \) ligand to three Ni atoms of the cluster.\textsuperscript{19}

To the best of our knowledge, only four aryl-substituted triphosphinanes are reported in the literature. \( \text{P}_3\text{Ph}_3 \) was described as early as 1973 as a labile solid with respect to \( \text{P}_3\text{Ph}_3 \),\textsuperscript{20} and it has been shown that this compound is part of an equilibrium mixture consisting of different oligomers with ring sizes of \( n = 3, 4, 5, 6 \).\textsuperscript{21} Tokitoh \textit{et al.} synthesized (Anth = 9-anthryl, Bbt = 2,6-dibis[bis-(trimethylsilyl)methyl]-4-[(tris(trimethylsilyl)phenyl)] in good yield by heating a mixture of DippPCl\textsubscript{2} (Dipp = 2,4,6-iPr\textsubscript{3}C\textsubscript{6}H\textsubscript{2}) and \( \text{P}_3\text{Mes}_3 \) (Mes = 2,4,6-Me\textsubscript{3}C\textsubscript{6}H\textsubscript{2}) were described as one of different oligomers with ring sizes of \( n = 1 \) to 7 and \( n = 3, 4, 5, 6 \).\textsuperscript{22} Moreover, Gaspar and co-workers reported on the photochemical release of the triplet phosphinidene MesP from MesP(C\textsubscript{5}H\textsubscript{2}) in 1992.\textsuperscript{26} In the absence of a trapping reagent these triplet phosphinidenes oligomerize to give a mixture containing \( \text{P}_3\text{Mes}_3 \) and \( \text{P}_3\text{Mes}_4 \).

Using [W(PMe\textsubscript{3})\textsubscript{6}] as a reducing agent the quantitative coupling of \( \text{RCl}_2 \) (R = Mes\textsuperscript{*} = 2,4,6-iPr\textsubscript{3}C\textsubscript{6}H\textsubscript{2}; 2,4,6-(CF\textsubscript{3})\textsubscript{3}C\textsubscript{6}H\textsubscript{2}) to the respective phosphinenes \( \text{RP} = \text{PR} \) was detected. Starting from TippPCl\textsubscript{2}, the initial formation of the diphosphene is detected by \( ^{31} \text{P} \) NMR spectroscopy, however, the reaction continues to produce Tipp\(_3\)P as the final product, clearly pointing to the intermediacy of \( \text{W} = \text{PR} \) species.\textsuperscript{27} Moreover, it was shown that the reductive degradation of \( \text{P}_3 \) with mesityl-radicals (generated from Mes-Br and Ti[\text{n}]-based chlorine atom abstracting reagent [Ti{N(Bu)}(3,5-C\textsubscript{6}H\textsubscript{3}Mes)]\textsubscript{3}) yields \( \text{P}_3\text{Mes}_3 \) as the main product in good isolated yields.\textsuperscript{28}

In 1998 Shah and Protasiewicz reported the formation of the triphosphirane \( \text{P}_3\text{Tipp}_2 \) (1a) by treatment of TippPCl\textsubscript{2} with PMe\textsubscript{3} and Zn in subsequent reaction with benzaldehyde (Scheme 2).\textsuperscript{29} This so-called phospha-Wittig reaction afforded a mixture of \( \text{P}_3\text{Tipp}_2 \) and traces of the desired phosphaalkene Ph(H)C=PTipp.

In this contribution, we report on the synthesis of aryl-substituted triphosphinanes using a modified synthesis on the basis of the studies by Protasiewicz \textit{et al.} Furthermore, we report on the selective degradation of these \( \text{P}_3\text{Ar}_3 \) systems using \([ \text{Cp}_{t}\text{Ti} (\text{btmsa}) ] \) (Cp = cyclopentadienyl, btmsa = C\textsubscript{2}(SiMe\textsubscript{3})\textsubscript{2}) as a Ti[\text{n}] synthon.

**Results**

In an attempt to prepare new variants of pyrindinophosphaalkenes,\textsuperscript{30} we utilized the phospha-Wittig protocol described by Protasiewicz \textit{et al.} with DippPCl\textsubscript{2} (Dipp = 2,6-Pr\textsubscript{3}C\textsubscript{6}H\textsubscript{2}), PMe\textsubscript{3} and excess of Zn powder in a strict low-temperature regime (\(-78 \) °C); after subsequent treatment with pyridine-2-carbaldehyde at that temperature and warming to room temperature the formation of the respective phosphaalkene was not observed. The \( ^{31} \text{P} \) NMR spectrum of the reaction mixture displayed a major product with an A\(_{2}\)B spin system with a doublet at \(-99.47 \) ppm and a triplet at \(-132.90 \) ppm with a coupling constant of 178.5 Hz, which was identified as \( \text{P}_3\text{Dipp}_2 \) (1b), in line with attempted synthesis of the phospha-Wittig reagent TippPME\textsubscript{3}, as discussed before.\textsuperscript{26,27} X-ray quality crystals of 1b were grown from a saturated n-hexane solution at 5 °C (Fig. 1). 1b crystallizes in the monoclinic space group \( \text{P}2_1/\text{c} \) with four molecules in the unit cell. The molecular structure of 1b shows the expected down-down-up orientation of the Dipp groups with respect to the central \( \text{P}_3 \) plane, with a minimally distorted central \( \text{P}_3 \)-ring (P1–P2 2.1991(4), P2–P3 2.1963(4), P1–P3 2.1963(4)).

\[ \textnormal{Scheme 2 \ Formation of Tipp}_3\text{P}_2 \text{(1a)} \text{and trace amounts of phosphaalkene H(Ph)C=PTipp in a so-called phospha-Wittig protocol.} \]
singlet state is less stable by 26.01 kcal mol\(^{-1}\) than the diphosphene P2Tipp2 (Table S1\(^{\dagger}\)).\(^{33,34}\) We then utilized the sterically more demanding PEt3 to better stabilize the reactive phosphinidene phosphorane intermediate TippP═PEt3. Phosphinidenephosphoranes have been identified as a source of the triplet phosphinidenes ArP═P.\(^{35}\)

Additionally, we switched to TippPBr2, as its reduction should be more facile. TippPBr2, PEt3 (1.2 equiv.) and Zn (3 equiv.) were combined in THF at \(-78^\circ\text{C}\) and the formation of a deep yellow to orange suspension was observed, which again showed P2Tipp2 (1a) as the major species in the \(^{31}\)P NMR spectrum.

After removal of the solvent and extraction with \(n\)-hexane minimal amounts (<0.01 g) of yellow needles suitable for single-crystal X-ray analysis were obtained and identified as the elusive diphosphene P2Tipp2 (2) (Fig. 2), which has only been observed in solution in the \([W(PMe_3)_6]\) mediated coupling of ArP.Br (Ar = Tipp, Mes*, 2,4,6-(CF\(_3\))\(_2\)C\(_6\)H\(_2\)) by \(^{31}\)P NMR experiments to date.\(^{27}\) The \(^{31}\)P NMR spectrum of isolated 2 showed P2Tipp2 (\(\delta^{(31}\)P = 517.4 ppm) to be the major species, whereas minor amounts of P3Tipp3 and P4Tipp4 were also detected. Monitoring a C\(_6\)D\(_6\) solution of 2 over time at room temperature revealed that P2Tipp2 slowly coverts into P3Tipp3 and its dimer P4Tipp4, vide infra.\(^{23}\) 2 crystallises as its trans-conformer in the triclinic space group P1 with one molecule in the unit cell. The P1–P1’ distance \(2.029(5)\ \text{ Å}\) (cf. d(P=P) P2Mes* = 2.034(2);\(^{5}\) P2Ter2 = 2.029(1);\(^{46}\) P2Bbt2 = 2.043(1))\(^{77}\) is in the expected range for a diphosphene \((\sum r_{\text{co}}(P=P) = 2.04\ \text{ Å})^{38}\) and rather acute C–P–P angles [99.61(3)\(^{\dagger}\)] at the dicoordinate P center are detected.

Theoretical investigations at the M062X/TZVP level of density functional theory were carried out, assuming that transient phosphinidenes are formed. The gas-phase trimerization of Dipp-P with a triplet ground state (the corresponding singlet state is less stable by 26.01 kcal mol\(^{-1}\)) is exergonic (−91.39 kcal mol\(^{-1}\)). In addition, we computed the transfer reaction of a Dipp-P fragment (which may be formed immediately at low temperatures) via DippPMe\(_3\) to P2Dipp2 and found this reaction to be exergonic by −15.74 kcal mol\(^{-1}\) (energy barriers were not calculated). This is in line with the isolation of 2.

Since there are only few high-yielding, selective methods for the preparation of aryl-substituted triphosphiranes outlined in the literature, we decided to take a closer look at this synthetic approach. We therefore tested different aryl(dichlorophosphines ArP.Cl (Ar = Mes, Dipp, Tipp) to elucidate whether treatment with PR3 (R = Me, Et) and Zn gives general access to aryl-substituted triphosphiranes (Scheme 3).

The reaction of ArP.Cl with PMe\(_3\) (2.5 equiv.) and an excess of Zn (5 equiv.) in anhydrous THF afforded P2Ar3 (Ar = Tipp (1a), Dipp (1b), Mes (1c)) as expected (Scheme 3, reaction (i)).

Purification by recrystallisation from a saturated \(n\)-hexane solution at 5 °C yielded 1a-c as colourless crystalline solids in 47, 50 and 10% isolated yield, respectively.

Starting from the easily accessible mixed dihalophosphines ArPX (Ar = Tipp, Dipp, Mes; X = Cl, Br; obtained through treatment of ArMgBr with PCl\(_3\))\(^{29}\) with PMe\(_3\) and Zn in a 1/2/2.5 molar ratio in THF at room temperature (Scheme 3, reaction (ii)), 1a, 1b and 1c could be obtained in up to 72%, 75% and 52% isolated yield, respectively, after extraction with benzene or EtO\(_2\) in case of 1c. 1a–c show good thermal stability with melting points of higher than 167 °C.\(^{31}\) Heating a solution of 1a in C\(_6\)D\(_6\) for 36 h at 80 °C showed no decomposition or rearrangement products in the \(^{31}\)P NMR spectrum.

Since either PMe\(_3\) or Zn can act as reducing agents, we reduced TippPCl\(_2\) with each reductant separately (Scheme 3(iii) and (iv)). While there is no reaction observed, when TippPCl\(_2\) or TippPBr\(_2\) are stirred with an excess of Zn in THF over a period of

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**Fig. 2** POV-ray depiction of the molecular structure of 2. ORTEPs drawn at 30% probability. Selected bond lengths (Å) and angles (°): P1–P1’ 2.029(5), P1–C1 1.8439(10); C1–P1–P1’ 99.61(3); P1’–P1–C1–C6 91.34(8), C1–C2–C3–C4 1.25(16).

**Scheme 3** (i and ii) General procedure for the preparation of 1a–c; (iii) identification of PMe\(_3\) as the active reductant; (iv) Zn can be excluded as active reductant.
24 h, treatment of ArPCl₂ with a fivefold excess of PMe₃ afforded 1a–c in 43, 66 and 18% isolated yield, respectively. The potential of PMe₃ to act as a chlorine abstracting reagent is documented in the literature and results in oxidation to the respective dichlorophosphorane.⁴⁴,⁴⁵ or the homoleptic dication salt [Me₂P³PMe₃]Cl₂. This concept has been used to access cyclic tetra(stibinophosphonium) trflate salts of the type [Sb₄(PR₃)₄][OTf]₄ (R = Me, Et, Pr, Bu), cationic antimony compounds related to the cyclic oligophosphoranes.⁴⁶ To shed light on this proposition, we independently synthesized PMe₃Cl₂ and treated it with an excess of zinc dust in the presence of TippPCl₂ in a mixture of MeCN/THF (3:1) over 24 h. A ³¹P{¹H} NMR spectrum of the reaction mixture indeed showed 1a to be the main product of this reaction.⁴³ It can thus be concluded that PMe₃Cl₂ is a plausible by-product of the reduction with PMe₃ and zinc can reduce it back to PMe₃, vide infra. This opens the pathway for potential catalytic reduction of ArPCl₂ with PMe₃ and Zn as a sacrificial reductant. In another experiment DippPCl₂ was reduced with an excess of PMe₃ and the white precipitate was carefully washed with benzene and n-hexane. Subsequently, the precipitate was treated with AgOTf in CH₂Cl₂. After filtration a colourless solid was obtained, which was dissolved in CD₃CN, allowing to unambiguously identify [Me₃PCl]OTf (δ = 93.6 ppm),¹⁹ and [Me₃P·PMe₃][OTf]δ = 31P{¹H} = 28.4 ppm) among three unidentified PMe₃ containing species (Scheme 3(iii)).¹¹

The synthetic approach using Zn/PMe₃ showed a high selectivity towards the respective triphosphiranes. In the case of 1a and 1b just little amounts of the corresponding cyclic tetraphosphines P₃Ar₄ were detected as side products by ³¹P NMR spectroscopy of the reaction mixture. When MesPCl₂ is applied in combination with an excess of zinc dust in the presence of TippPCl₂ in a mixture of MeCN/THF (3:1) over 24 h. ³¹P NMR spectrum of the reaction mixture showed 1a to be the main product of this reaction.

Having prepared 1a–c we wanted to explore their reactivity with the titanocene synthon [Cp₂Ti(btmisa)] in order to access titanium phosphinidene complexes.
the monoclinic space group P2_1/c with four molecules of 3b and four C_6D_6 molecules in the unit cell. 3a is located on a special position and thus shows C_2 symmetry in the solid state. The P-P distances in 3a [2.1826(7) Å] and 3b [2.1699(5) Å] are intermediate between a P-P single and double bond (\( \sum P=P = 2.04 \) Å; (P-P) 2.22 Å\(^{28} \)) and are in line with the P-P distance [2.173(4) Å] in [rac-EBTHI]Ti[P_2Ph_3] \(^{31} \). The Ti-P distances in 3a [2.5425(5), 2.5230(5) Å] and 3b [2.5239(5) Å], as well as the P-Ti-P angles (3a 50.725(12); 3b 51.042(17)), are similar to that in [Cp^2-Zr(PPh)_3] \(^{29} \) with a P-P distance [2.145(3) Å] shorter than in 3a and 3b,\(^{28} \) and the related Mes-substituted complex [Cp^2Zr[P Mes]] \(^{30} \) with a similar P-P distance [2.188(3) Å].\(^{28} \) The Ti-P distances in 3a [2.5425(5), 2.5230(5) Å] and 3b [2.5239(5) Å], as well as the P-Ti-P angles (3a 50.725(12); 3b 51.042(17)), are similar to that in [Cp^2-Zr(PPh)_3] \(^{29} \) with a P-P distance [2.145(3) Å]. Interestingly, in the case of [Cp^2Ti(btmsa)] in the gas phase.

The surprising selective formation of the titanocene diphosphene species 3, prompted us to study the reactivity by DFT calculations on the M062X/TZVP level of theory. The calculated gas phase structure of 1b and 3b and the metric parameters derived from X-ray crystallography are in good agreement. In a next step the reaction of [Cp^2Ti(btmsa)] with 1b in a 3 : 2 ratio was investigated. It is found that the gas phase reaction is exergonic by \(-15.93\) kcal mol\(^{-1} \)), indicating that the reaction is accessible thermodynamically, even though energy barriers for this transformation could not be determined (Scheme 5(i)). Using the truncated model compound P_2Ph_3 (1Ph) the same exergonic character was calculated (\( \Delta G = -18.32\) kcal mol\(^{-1} \)) for this transformation. Additionally, we were interested to determine whether the free trans-diphosphenes P_2Dipp_2 and P_2Ph_2 can displace the btmsa molecule in [Cp^2Ti(btmsa)] to afford complexes 3b and [Cp^2Ti(P_2Ph_2)] (3Ph), respectively (Scheme 7, bottom). Interestingly, this reaction is also exergonic for P_2Dipp_2 and P_2Ph_2 by \(-10.69\) and \(-20.87\) kcal mol\(^{-1} \)), respectively, illustrating that diphosphenes are potential intermediates along the reaction pathway (Scheme 5(iv)).

With minimal amounts of the free diphosphene Tipp_2P_2 (2) in hand, we treated 2 with [Cp^2Ti(btmsa)] in a 1 : 1 ratio at room temperature in C_6D_6. Having shown that the reaction of 1a with [Cp^2Ti(btmsa)] is slow at room temperature and full conversion is only achieved at 80 °C, we were delighted to see the disappearance of the diagnostic diphosphene signal at 517.4 ppm and formation of 3a with a characteristic \(^{31}P\) NMR shift of 290.7 ppm. This clearly shows, that diphosphenes are potential intermediates in the reaction of 1 with [Cp^2Ti(btmsa)]. Furthermore, this shows the drastic influences of the sterically demanding groups attached to phosphorus, as the diphosphene P_2Mes* was shown to not afford the respective diphosphene complex in the reaction with [Cp^2Ti(btmsa)].\(^{37} \)

To compare the reactivity of the aryl-substituted triphosphoranes with alkyl-substituted derivatives we treated [Cp^2Ti(btmsa)] with the known triphosphoranes P_3Bu_3 (1d) and P_3Ad_3 (Ad = adamantyl) in a 1 : 1 ratio in benzene at 80 °C in C_6D_6 (Scheme 6). Interestingly, in the case of 1d full consumption of both starting materials was noted, with a new characteristic A_2B spin system in the \(^{31}P\) NMR spectrum. 1e also cleanly reacted in similar fashion, however full consumption was not achieved due to the poor solubility of 1e. Compared to 1d and 1e the A_2-part of the \(^{31}P\) NMR signal is downfield-shifted, thus indicating selective insertion into the P-P bond with the

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**Scheme 4** Selective degradation of P_3Ar_3 (1a-c) into [Cp^2Ti(P_3Ar_3)] (3a-c) complexes using [Cp^2Ti(btmsa)] as a synthon for [Cp^2Ti].

**Scheme 5** M062X/TZVP (i and iv) and BP86/TZVP (ii and iii) (M062X) for R = 1^8Bu computed reaction free energies for possible paths of formation of [Cp^2Ti(P_2R_2)] in the gas phase.
two identical P atoms and the formation of the triphosphanato-complexes \([\text{CP}_2\text{Ti}(\text{P}_3\text{Bu}_3)]\) (4a) and \([\text{CP}_2\text{Ti}(\text{P}_3\text{Ad}_3)]\) (4b).\(^{31}\)

Complex 4a among other \([\text{CP}_2\text{Ti}(\text{P}_3\text{R}_3)]\) species has been described before by Köpf and co-workers in the reaction of \(\text{CP}_2\text{TiCl}_2\) with the salt \(K_2[\text{P}_4\text{Bu}_4]\) in a salt elimination reaction on the basis of NMR experiments.\(^{30}\) Extraction of the reaction mixture with EtO\(_2\) concentration to incipient crystallization and standing at 5 °C overnight, afforded deeply coloured brown crystals of 4a suitable for X-ray analysis (Fig. 4) in 64% yield. To the best of our knowledge this is the first structural characterization of a cyclo-titanatrophosphine.

4a crystallizes in the orthorhombic space group \(P2_12_12_1\) with four molecules in the unit cell. The P–P distances [P1–P2 2.1953(8), P2–P3 2.1840(8)] are shorter than a P–P single bond \((\sum \cos(P-P)=2.22\,\text{Å})\)\(^{34}\) and the P–Ti–P angle \(90.34(2)^\circ\) is wider than in 3a and 3b and compares nicely with the P–Zr–P angle \(89.8(2)^\circ\) found in the related compound \([\text{CP}_2\text{Zr}(\text{P}_3\text{Ph}_3)]\).\(^{35}\)

To rationalize the contrasting reactivity of alkyl- and aryl-substituted triphosphiranes noted in this study, we calculated the free enthalpies for the gas phase reaction of \([\text{CP}_2\text{Ti}(\text{btmsa})]\) with Dipp\(_3\)P to afford the insertion product \([\text{CP}_2\text{Ti}(\text{P}_3\text{Dipp}_3)]\) under liberation of btmsa at the BP86/TZVP/LANL2DZ level of theory.\(^{31}\) This transformation was found to be endergonic by 11.41 kcal mol\(^{-1}\), whereas this insertion process was computed to be almost thermo-neutral for \(\text{P}_3\text{Bu}_3\) (+1.64 (+4.20 M062X) kcal mol\(^{-1}\)) to give 4a (Scheme 5(ii)). The selective degradation of \([\text{CP}_2\text{Ti}(\text{P}_3\text{Dipp}_3)]\) to yield 3b and half an equivalent of \(\text{P}_3\text{Dipp}\) was also considered and is shown to be exergonic by \(-23.27\,\text{kcal mol}^{-1}\), whereas the same process is endergonic by \(+0.21\,(+9.97\,\text{M062X})\,\text{kcal mol}^{-1}\) for 4a (Scheme 5(iii)). These results are in line with the observed difference in reactivity of alkyl- and aryl-substituted triphosphiranes and that the reactions only take place at elevated temperatures. We then wanted to determine whether single electron transfer (SET) is preferred over reduction of the cyclo-P\(_3\)R\(_3\) in two electron steps by comparison of the free energies of the reduction products. It is noted from successive theoretical one-electron addition to triphosphiranes P\(_3\)R\(_3\) that the single-electron transfer step is exergonic and favoured thermodynamically, while the two-electron transfer process is endergonic and thermodynamically not favored.\(^{31}\)

On the basis of these results, one can expect a stepwise reaction mechanism for the electron transfer reactions. Furthermore one of the P–P bonds in the radical anion species \([\text{P}_3\text{R}_3^-]\) is considerably elongated \([2.814\,(\text{R}=\text{Dipp}), 2.973\,\text{Å}(\text{R}=\text{Ph})]\), which would allow for the liberation of a phosphinidene fragment or the recombination of two radical anions, under formal exchange of P–R groups. If arylphosphinidenes were formed in this transformation these would be triplet species, with the triplet state being thermodynamically favored by \(-26.01\,(\text{R}=\text{Dipp})\) and \(-33.71\,\text{kcal mol}^{-1}\,(\text{R}=\text{Ph})\), respectively. With these insights we set out to generate experimental evidence for these assumptions.

On the basis of these results, one can expect a stepwise reaction mechanism for the electron transfer reactions and the possible intermediary formation of a titanocene phosphinidene species. Electrochemical studies revealed an electrochemically irreversible reduction of 1b in THF at a potential of \(-3.09\,\text{V}\) (vs. \(F_2/F_2^+\)), which is in line with degradation of the aryl-substituted triphosphiranes into diphosphene fragments upon treatment with \([\text{CP}_2\text{Ti}(\text{btmsa})]\). Investigation of the reaction mixture of \([\text{CP}_2\text{Ti}(\text{btmsa})]\) and 1a (3 : 2 ratio, after heating to 80 °C for 1 h) at room temperature by electron paramagnetic resonance (EPR) spectroscopy revealed the occurrence of an EPR-active intermediate (Fig. 5) with an isotropic g-factor of 1.978. This doublet signal shows strong coupling to one \(^{31}\text{P}\) nucleus with \(a^{(31)}\text{P}=72\,\text{MHz}\) and hyperfine coupling to titanium \(a^{(49/48)}\text{Ti}=22\,\text{MHz}\). The rather large g-value and small hyperfine coupling to Ti indicates a species with a high spin density on phosphorus, in which only one phosphorus is attached to titanium, as a more complex EPR-signal would be expected otherwise.\(^{44}\) In addition, there is an underlying signal stemming from \([\text{CP}_2\text{Ti}(\text{btmsa})]\), which could be fitted to a species with \(g_{\text{iso}}=1.973\) and \(a^{(1)}\text{H}=32\,\text{MHz}\).\(^{44}\) This could indicate a hydric species such as \([\text{CP}_2\text{Ti}(\text{H})]\), which has been discussed as resting state of \([\text{CP}_2\text{Ti}]\) in solution. In this case hydrogen release would generate the free titanocene and subsequent addition of \(\text{H}_2\) regenerates the \([\text{CP}_2\text{TiH}]\) species.\(^{43}\)

We then wanted to generate more evidence for the end group liberation and formation of free phosphinidenes during the reaction. If this is the case, starting from a 1 : 1 mixture of differently substituted triphosphiranes P\(_3\)Ar\(_3\) and P\(_3\)Ar\(_3\) should result in the formation of the mixed diphosphene complex.
Moreover, titana- and zirconacycles are regularly applied in the formation of main group element substituted heterocycles.\textsuperscript{64,65} We wanted to probe this reactivity by treating isolated 3a with TippPCl\textsubscript{2} and found 1a as the product along with the formation of Cp\textsubscript{2}TiCl\textsubscript{2} (Scheme 7),\textsuperscript{11} which clearly shows the potential of complexes 3 for the formation of small inorganic ring systems.

**Conclusions**

We have shown in here a simple and selective synthetic protocol for the formation of aryl-substituted triphosphiranes 1 of the type P\textsubscript{3}Ar\textsubscript{3} and identified PMe\textsubscript{3} as the active reductant. These findings open the way for future studies to render these transformations catalytic with respect to PMe\textsubscript{3}. Moreover, we have shown that the Ti(II) synthon [Cp\textsubscript{2}Ti(btmsa)] reacts with 1 to yield the respective titanocene diphosphene complexes 3 in straightforward fashion. Combined theoretical and experimental studies suggest the intermediate formation of a paramagnetic titanium phosphorus species, indicating single electron transfer steps. Moreover, experimental evidence is presented for the intermediacy of free diphosphenes, authenticated by reaction of the elusive diphosphene P\textsubscript{2}Tipp\textsubscript{2} (1 equiv.) with TippPCl\textsubscript{2}. This opens the pathway to generate new P\textsubscript{2}R\textsubscript{2}-containing heterocycles.

Studies to further elucidate the reaction mechanism of the P\textsubscript{3}Ar\textsubscript{3} degradation reaction are ongoing, to further investigate the nature of the paramagnetic intermediate. Additionally, application of the P\textsubscript{3}Ar\textsubscript{3} systems in phosphinidene transfer reactions will be investigated.

**Conflicts of interest**

There are no conflicts to declare.

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**Notes and references**


31 Experimental and computational details, and details on the X-ray diffraction studies are included in the ESL†


