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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.
Triphosphiranes are three-membered cyclo-phosphines, which are promising synthons 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 PP double bond. Almost 100 years later in 1964 the molecular structure of the product could be identified as $P_3PH_5$ by X-ray crystal structure analysis. Although, Cowley et al. already mentioned the synthesis of $P_3(C_2F_5)_3$ in 1970, it was later discussed that in fact the tetramer and pentamer were formed under the reaction conditions described. The first stable triphosphirane $P_3^tBu_3$ was reported by Baudler and co-workers in 1976, and various synthetic approaches towards triphosphiranes have since emerged. Reductive approaches starting from dihalophosphines $RPX_2$ ($X = Cl, Br$) result in a mixture of oligophosphines of different ring sizes of $P_nR_n$ ($n = 3, 4, 5, 6$) and are thus regarded as unspecific. The ratio of the different oligomers heavily depends on the steric demand of the substituent $R$. 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. 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 $P_3^tCp^*_3$ ($Cp^*$ = pentamethylocyclopentadienyl), affording a mixture of cyclic selenotriphosphabutanes (Scheme 1, A) and cyclic selenodiphosphapropanes (Scheme 1, B). In contrast, thermolysis of $P_3^tCp^*_3$ in xylene resulted in the

**Scheme 1** Selected reactivity modes of differently substituted triphosphiranes.
formation of different phosphorus clusters, some of which are structurally related to Hittorf’s-phosphorus (Scheme 1, C and D).12 Ring expansion reactions were reported by Uhl and Benter by the insertion of Ga(μ) into a P–P bond of P3Bu3, thus establishing a way to prepare cyclo-galliumtriphasphabutanes (Scheme 1, E, M = Ga).13 A similar reactivity is observed when Al(i) compound (AlCp*)2 reacts with P3Bu3 (Scheme 1, E, M = Al).14 In addition, the reaction of P3Bu3 with PMe2Cl or PhPMe2Cl in the presence of Me3SiOTf or GaCl3, respectively, resulted in the selective ring expansion with insertion of [PMe2]2 into the P–P bond between the two identical P atoms of P3Bu3 to afford [R2P(P3Bu3)] (Scheme 1, F; R = Me, Ph).15,16 More recently, Manners and co-workers showed the addition of P3Mes3 to organic nitriles after activation of the three-membered ring by electrophiles to yield differently substituted 1-aza-2,3,4-triphospholenes in a click-type reaction (Scheme 1, G),17,18 underlying the value of triphosphoranes as synths in synthetic inorganic chemistry. Fragmentation of P3Bu3 was observed by Fenske and Ahlrichs in the reaction with Ni(CO)4, resulting in the formation of [Ni2(P3Bu3)(P2Bu3)(CO)4] with μ1-and μ2-bridging P2Bu ligands as well as a P3Bu3 chain, acting as a μ3(n3, n1, n0) ligand to three Ni atoms of the cluster.19

To the best of our knowledge, only four aryl-substituted triphosphoranes are reported in the literature. P3Ph3 was described as early as 1973 as a labile solid with respect to P3Ph2,20 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, 6.21 Tokitoh et al. synthesized (Anth = 9-anthyl, Bbt = 2,6-bis[bis-(trimethylsilyl)methyl]-4-[tris(trimethylsilyl)phenyl]) in good yield by heating a mixture of AnthP = PBBt and 2,6-Bu2P = Te.22 P3Tipp (Tipp = 2,4,6-Pr3C6H2) and P3Mes3 (Mes = 2,4,6-Me3C6H2) were described as one of a mixture of products when free phosphinidenes were generated by reductive dechlorination of RPCl2 (R = Tipp, Mes).23-25 Moreover, Gaspar and co-workers reported on the photochemical release of the triplet phosphinidenes MesP from MesP(C6H4) in 1992.26 In the absence of a trapping reagent these triplet phosphinidenes oligomerize to give a mixture containing P5Mes3 and P5Mes4.

Using [W(PMe3)6] as a reducing agent the quantitative coupling of RPCl2 (R = Mes* = 2,4,6-iPr3C6H2; 2,4,6-(CF3)3C6H2) to the respective diphosphenes RP=PR was detected. Starting from TippPCl2, the initial formation of the diphosphene is detected by 31P NMR spectroscopy, however, the reaction continues to produce Tipp3P3 as the final product, clearly pointing to the intermediacy of W=PR species.27 Moreover, it was shown that the reductive degradation of P4 with mesityl-radicals (generated from Mes-Br and Ti(n)-based chlorine atom abstracting reagent [Ti(N[3-Bu][3,5-C6H3Mes])2]) yields P5Mes3 as the main product in good isolated yields.28

In 1998 Shah and Protasiewicz reported the formation of the triphosphirane P3Tipp3 (1a) by treatment of TippPCl2 with PMe3 and Zn and subsequent reaction with benzaldehyde (Scheme 2).29 This so-called phospha-Wittig reaction afforded a mixture of P3Tipp3 and traces of the desired phosphaalkene PhH[C]=PTipp.

In this contribution, we report on the synthesis of aryl substituted triphosphoranes using a modified synthesis on the basis of the studies by Protasiewicz et al. Furthermore, we report on the selective degradation of these P3Ar3 systems using [Cp,Ti(btmsa)] (Cp = cyclopentadienyl, btmsa = C5(SiMe3)2) as a Ti(n) synthon.

Results

In an attempt to prepare new variants of pyridinephosphaalkenes,30 we utilized the phospha-Wittig protocol described by Protasiewicz et al. with DippPCl2 (Dipp = 2,6-iPr3C6H2), PMe3 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 31P NMR spectrum of the reaction mixture displayed a major product with an A3B 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 P3Dipp1 (1b), in line with attempted synthesis of the phospha-Wittig reagent TippPPMe3 as discussed before.29 X-ray quality crystals of 1b were grown from a saturated n-hexane solution at 5 °C (Fig. 1). 1b crystallises in the monoclinic space group P21/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 P3 plane, with a minimally distorted central P3-ring [P1–P2 2.1991(4), P2–P3

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Scheme 2 Formation of Tipp3P3 (1a) 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\(^{-1}\) by density functional theory were carried out, assuming that angles at the dicoordinate P center are detected.

Minimal amounts (<0.01 g) of yellow needles suitable for single crystal X-ray analysis were obtained and identified as the elusive diphosphene \(\text{P}_2\text{Tipp}_2\) (Fig. 2), which has only been observed in solution in the \([\text{W}(\text{PMe}_3)_6]\) mediated coupling of \(\text{ArPCl}_2\) (Ar = Tipp, Mes, Dipp, Tipp) to elucidate whether treatment with \(\text{PR}_3\) (R = Me, Et) and Zn gives general access to aryl-substituted triphosphiranes (Scheme 3).

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(dichloro)phosphines \(\text{ArPCl}_2\) (Ar = Mes, Dipp, Tipp) to elucidate whether treatment with \(\text{PR}_3\) (R = Me, Et) and Zn gives general access to aryl-substituted triphosphiranes (Scheme 3).

The reaction of \(\text{ArPCl}_2\) with \(\text{PMe}_3\) (2.5 equiv.) and an excess of Zn (5 equiv.) in anhydrous THF afforded \(\text{P}_2\text{Ar}_3\) (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\(_2\) (Ar = Tipp, Dipp, Mes; X = Cl, Br; obtained through treatment of ArMgBr with PCl\(_3\)) with \(\text{PMe}_3\) 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 Et\(_2\)O in case of 1c. 1a–c show good thermal stability with melting points of higher than 167 °C. 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 \(\text{PMe}_3\) or Zn can act as reducing agents, we reduced \(\text{TippPCl}_2\) with each reductant separately (Scheme 3(iii) and (iv)). While there is no reaction observed, when \(\text{TippPCl}_2\) or \(\text{TippPBr}_2\) are stirred with an excess of Zn in THF over a period of 2 h at room temperature revealed that \(\text{P}_2\text{Tipp}_2\) slowly coverts into \(\text{P}_2\text{Tipp}_3\) and its dimer \(\text{P}_3\text{Tipp}_4\), vide infra. 2 crystallises as its trans-conformer in the triclinc space group P1 with one molecule in the unit cell. The P–P1’ distance [2.0290(5)] Å (cf. \(d(\text{P}=\text{P})\) \(\text{P}_2\text{Mes}_2\) 2.0342(2); \(\text{P}_2\text{Ter}_2\) 2.0291(1); \(\text{P}_2\text{Bbt}_2\) 2.0431(1)) is in the expected range for a diphosphene \((\sum \cos(\text{P}=\text{P}) = 2.04\) Å) and rather acute C–P–P’ [99.61(3)] angles 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 tetrimerization of Dipp-P with a triphosphate 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 DippPPMe\(_3\) to \(\text{P}_2\text{Dipp}_2\) and

![Fig. 2 POV-ray depiction of the molecular structure of 2. ORTEPs drawn at 30% probability. Selected bond lengths (Å) and angles (°): P1–P’1 2.0290(5), P1–C1 1.8439(10); C1–P1–P’t 99.61(3); P1’–P1–C1–C6 91.34(8), C1–C2–C3–C4 1.25(16).](image-url)

![Scheme 3](image-url) (i and ii) General procedure for the preparation of 1a–c (iii) identification of \(\text{PMe}_3\) 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 or the homeolytic dication salt [Me₆P₃PMe₃][OTf]₂. This concept has been used to access cyclo-tetra(stibinophosphonium) triflate salts of the type [Sb₄(PR₃)₄][OTf]₄ (R = Me, Et, Pr, Bu), cationic antimony compounds related to the cyclic oligophosphines.⁴⁴ To shed light on this proposition, we independently synthesized PMe₃Cl₃ and treated it with an excess of zinc dust in the presence of PippCl₂ in a mixture of MeCN/THF (3 : 1) over 24 h. A ³¹P NMR spectrum of the reaction mixture indeed showed 1a to be the main product of this reaction.³¹ It can thus be concluded that PMe₃Cl₂ is a plausible by-product of the reduction with PMe₃ and zinc that can reduce it back to PMe₃, vide infra. This opens the pathway for potential catalytic reduction of ArPCl₂ with PMe₃ and zinc 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 CD₂CN, allowing to unambiguously identify [Me₆P₃PMe₃][OTf]₂ (δ ³¹P(¹H) = 93.6 ppm),³⁴ and [Me₆P₃PMe₃][OTf]₂ (δ ³¹P(¹H) = 28.4 ppm)³⁴ among three unidentified PMe₃ containing species (Scheme 3(iii)).³¹

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 our approach, the selectivity decreases and the formation of little amounts of the cyclic tetraphosphine P₃Mes₄, and the cyclic pentaphosphine P₅Mes₅ species can be detected. We conclude that this is due to lesser steric bulk imposed by the mesityl substituent. The sterically more demanding substituents Tipp and Dipp promote the formation of the three-membered phosphorus ring more effectively.⁷

Having prepared 1a-c we wanted to explore their reactivity with the titanocene synthon [Cp₂Ti(btmlsa)] in order to access titanium phosphinidene complexes.

**Titanocene-induced degradation of R₃P₃**

Stephan and co-workers have shown the phospha-Wittig-type phosphinidene transfer for [Cp₂Zr=PMe₃(PMe₃)]⁵⁴ resulting in the formation of phosphaalkenes in the reaction with aldehydes along with the formation of [Cp₂ZrO].⁵⁴ Similar reactivity was observed by Cummins and Schrock for the terminal tantalum phosphinidene complexes, [(N₃N)Ta=PR] (N₃N = (Me₃Si-NCH₂CH₂CH₂)N).⁴⁴

With the series of triphosphiranes 1a-c synthesized, we wanted to investigate the propensity to access monomeric, terminal Cp₂Ti=PR complexes, by reaction of 1 with the titanocene synthon [Cp₂Ti(btmlsa)]. Cp₂Ti=PR has not been described in the literature. There are reports of neutral and zwitterionic terminal titanium phosphinidene complexes of the type [(³¹Nacnac)Ti=PAR’(R)] (Ar’ = Tipp, Mes*; R = CH₂Bu, CH₃, CH₃[B(C₆F₅)]₃) by Mindiola and co-workers with a bulky ³¹ diketiminate ligand [(³¹Nacnac=Ar’NC(Me)CH₂(Me)N)Ar, Ar = Dipp] on titanium.⁴⁷,⁴⁸ [Cp₂Ti(btmlsa)] is obtained by reduction of Cp₂TiCl₂ in the presence of btmlsa. In these complexes btmlsa acts as a spectator ligand and its facile release under the respective reaction conditions generates the highly reactive 14-electron [Cp₂Ti] fragment in situ.⁴⁹ Combination of three equivalents [Cp₂Ti(btmlsa)] with 1b in C₉D₉ at room temperature and monitoring by ³¹P NMR spectroscopy revealed slow, but selective, conversion into a phosphorus-containing species with a singlet resonance at 283.8 ppm. Heating this reaction mixture to 80 °C over a period of 16 h in a sealed NMR tube resulted in consumption of [Cp₂Ti(btmlsa)] according to ¹H NMR spectroscopy. However, unreacted P₃Ar₃ remained in the reaction mixture and thus, more [Cp₂Ti(btmlsa)] was added to the reaction mixture and heating to 80 °C was continued. Fractional crystallisation from C₉D₉ and determination of the molecular structure by single crystal X-ray analysis revealed the formation of the η¹-diphosphene complex [Cp₂Ti(P₂Dipp₂)] (3b) (Fig. 3, right). Consequently, the reaction was repeated in the correct stoichiometry with [Cp₂Ti(btmlsa)] and 1b in a 3 : 2 molar ratio in benzene, which allowed for full conversion into 3b after stirring at 80 °C over a period of 16 h. In analogy, 1a and 1c were converted into the respective titanocene diphosphene complexes [Cp₂Ti(P₂Tipp₂)] (3a, Fig. 3, left) and [Cp₂Ti(P₂Mes₂)] (3c) (Scheme 4). Filtration and subsequent concentration of the reaction mixtures and standing overnight at 5 °C resulted in the formation of deep yellow crystals of 3a suitable for X-ray analysis, whereas formation of 3c was authenticated by NMR spectroscopy, elemental analysis and HR-MS studies.⁴⁹ Interestingly, in the ¹H NMR spectrum three or two independent septets are detected for 3a and 3b, respectively. This indicates hindered rotation about the P-C₉ bond and the Me group of the isopropyl moiety in close proximity to the Cp₂Ti-fragment is significantly upfield-shifted, resonating at ~0.99 ppm in 3a and 3b. This hindered rotation is also evident in 3c, in which three ¹H NMR signals are detected for the Me groups of the Mes moiety.

3a crystallises in the monoclinic space group C2/c with four molecules in the unit cell as a benzene solvate. 3b crystallises in
the monoclinic space group $P2_1/c$ with four molecules of $3b$ and four $C_8D_6$ 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 $\left(\sum r_{cv}(P=P) = 2.04 \text{ Å}; (P-P) 2.22 \text{ Å}\right)$ and are in line with the $P$-$P$ distance [2.173(4) Å] in $[\text{rac-(EBTHI)}\text{Ti(P}_2\text{Ph}_2)]$ $[\text{ETBHI} = \text{ethylene-1,2-bis(5,4,5,6,7-tetrahydro-1-indenyl)}]$, the only titanium diphosphene complex known to date.\(^{39}\) It is worth noting that green $[\text{rac-(EBTHI)}\text{Ti(P}_2\text{Ph}_2)]$ is insoluble in common non-halogenated organic solvents and thus, NMR data was not obtained. It is formed through the dehydrocoupling of Ph$_2$H in the presence of the Ti[η]-hydride dimer $[\text{rac-(EBTHI)}\text{TiH}_2]$.$^{31}$

Diphosphene complexes of various transition metals have been known and were thoroughly reviewed by Weber.$^{35}$ Noteworthy, is the formation of $[[\text{Ph}_3P]_2M(\text{C}_6\text{F}_5)_{12}]$ with an $E$-configured diphosphene ligand by the degradation of cyclic tetraphosphine $P_4(\text{C}_6\text{F}_5)_{12}$ in the presence of $M(\text{Ph}_3)_{12}$ ($M = \text{Pt}^{52}, \text{Pd}^{54}$). Other known diphosphene complexes of group 4 include the anionic species $[\text{Cp}_2\text{Zr(PPH}_3)_2\text{Br}^-]$ with a $P$-$P$ distance [2.145(3) Å] shorter than in $3a$ and $3b$,\(^{25}\) and the related Mes-substituted complex $[\text{Cp}_2\text{Zr[P(Mes)_2]}]$ with a similar $P$-$P$ distance [2.188(3) Å].\(^{26}\) 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 $[\text{Cp}_2\text{Zr(PPH}_3)_2\text{Br}^-]$ $[d(\text{Ti-P}) 2.523(2) A; <(P$-$\text{Ti-P}) 51.00(6)°]$ and point to a $\text{T}(\text{i})$ center and an overall titana-cyclo-propene, rather than a titana-cyclo-propene type structure.

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 $[\text{Cp}_2\text{Ti(btmsa)}]$ with $1b$ in a 3 : 2 ratio was investigated. It is found that the gas phase reaction is exergonic by $-15.93 \text{ kcal mol}^{-1}$, 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 $P_2\text{Ph}_3$ ($1\text{Ph}$) the same exergonic character was calculated ($\Delta G = -18.32 \text{ kcal mol}^{-1}$) for this transformation. Additionally, we were interested to determine whether the free $\text{trans}$-diphosphenes $P_2\text{Dipp}_2$ and $P_2\text{Ph}_2$ can displace the btmsa molecule in $[\text{Cp}_2\text{Ti(btmsa)}]$ to afford complexes $3b$ and $[\text{Cp}_2\text{Ti}(P_2\text{Ph}_2)]$ ($3\text{Ph}$), respectively (Scheme 7, bottom). Interestingly, this reaction is also exergonic for $P_2\text{Dipp}_2$ and $P_2\text{Ph}_2$ by $-10.69$ and $-20.87 \text{ kcal mol}^{-1}$, respectively, illustrating that diphosphenes are potential intermediates along the reaction pathway (Scheme 5(iv)).

With minimal amounts of the free diphosphene $\text{Tipp}_2\text{P}_2$ ($2$) in hand, we treated $2$ with $[\text{Cp}_2\text{Ti(btmsa)}]$ in a 1 : 1 ratio at room temperature in $C_8D_6$. Having shown that the reaction of $1a$ with $[\text{Cp}_2\text{Ti(btmsa)}]$ 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 $^{31}\text{P}$ NMR shift of 290.7 ppm. This clearly shows, that diphosphenes are potential intermediates in the reaction of $1$ with $[\text{Cp}_2\text{Ti(btmsa)}]$. Furthermore, this shows the drastic influences of the sterically demanding groups attached to phosphorus, as the diphosphene $P_2\text{Mes}^*$ was shown to not afford the respective diphosphene complex in the reaction with $[\text{Cp}_2\text{Ti(btmsa)}]$.$^{37}$

To compare the reactivity of the aryl-substituted triphosphines with alkyl-substituted derivatives we treated $[\text{Cp}_2\text{Ti(btmsa)}]$ with the known triphosphiranes $P_3\text{Bu}_3$ ($1\text{d}$) and $P_3\text{Ad}_3$ ($\text{Ad} = \text{adamantyl}$)$^{38,59}$ in a 1 : 1 ratio in benzene at 80 °C in $C_8D_6$ (Scheme 6). Interestingly, in the case of $1\text{d}$ full consumption of both starting materials was noted, with a new characteristic $A_2B$ spin system in the $^{31}\text{P}$ NMR spectrum. $1\text{e}$ also cleanly reacted in similar fashion, however full consumption was not achieved due to the poor solubility of $1\text{e}$. Compared to $1\text{d}$ and $1\text{e}$ the $A_2$-part of the $^{31}\text{P}$ NMR signal is downfield-shifted, thus indicating selective insertion into the $P$-$P$ bond with the...
two identical P atoms and the formation of the triphosphanato-complexes \([\text{Cp}_2\text{Ti}(\text{P}_3\text{R}_3)]\) (4a) and \([\text{Cp}_2\text{Ti}(\text{P}_3\text{Ar}_3)]\) (4b). 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 \(\text{K}_2[\text{P}_3\text{Bu}_4]\) in a salt elimination reaction on the basis of NMR experiments.\(^{26}\) Extraction of the reaction mixture with \(\text{Et}_2\text{O}\), 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 \(\text{cyclo-} \text{titanatrophosphine}\).

4a crystallises 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 (\(\sum \cos (\text{P-P}) = 2.22\) Å)\(^{26}\) and the \(P-P\)-P angle [90.34(2)] is wider than in 3a and 3b and compares nicely with the \(P-Zr-P\) angle [89.82(2)] found in the related compound \([\text{Cp}_2\text{Zr}(\text{P}_3\text{Ph}_3)]\).\(^{33}\)

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 \(\text{Dipp}_2\text{P}_3\) 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 \(\text{P}_3\text{Bu}_3\) (3a) (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 \(\text{P}_3\text{Dipp}_2\) was also considered and is shown to be exergonic by \(-23.27\) kcal mol\(^{-1}\), whereas the same process is endergonic by +0.21 (+9.97 M062X) 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 \(\text{cyclo-} \text{P}_3\text{R}_3\) 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 \(\text{P}_3\text{R}_3\) that the single-electron transfer step is exergonic and favoured thermodynamically, whereas 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 \([\text{P}_3\text{Ar}_3]^-\) is considerably elongated [2.814 (R = Dipp), 2.973 Å (R = 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 \(-26.01\) (R = Dipp) and \(-33.71\) kcal mol\(^{-1}\) (R = 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 \(-3.09\) V (vs. \(F_2/\text{F}_2^+\)), 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 \(\varepsilon\)-factor of 1.978. This doublet signal shows strong coupling to one \(^{31}\)P nucleus with \(\alpha(\text{P}) = 72\) MHz and hyperfine coupling to titanium \(\alpha(\text{Ti}) = 22\) MHz. The rather large \(\varepsilon\)-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.\(^{64}\) In addition, there is an underlying signal stemming from \([\text{Cp}_2\text{Ti}(\text{btmsa})]\), which could be fitted to a species with \(\varepsilon_{\text{iso}} = \alpha(\text{P}) = 1.973\) and \(\alpha(\text{H}) = 32\) MHz.\(^{63}\) This could indicate a hydridic species such as \([\text{Cp}_2\text{Ti}(\text{m})-\text{H}]\), which has been discussed as resting state of \([\text{Cp}_2\text{Ti}\text{P}]=\) 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.\(^{63}\)

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 \(\text{P}_3\text{Ar}_3\) and \(\text{P}_3\text{Ar}_3\), 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{31} 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(n) 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} (2) with [Cp\textsubscript{2}Ti(btmsa)]. In first reactivity studies we have shown that 3 can be utilized as a P\textsubscript{2}R\textsubscript{2}-transfer reagent in transmetalation protocols using 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.

**Acknowledgements**

C. H.-J. thanks Prof. M. Beller for his support, the European Union for funding (H2020-MSCA-IF-2017 792177) and the Max Buchner-Foundation for a Scientific Fellowship. The CV studies were co-funded through the Leibniz Science Campus Phosphorous Research Rostock and the FCI (SK 202/22). We thank our technical and analytical staff for assistance, especially Dr Anke Spannenberg for her support regarding X-ray analysis. Dr Jonas Bresien is kindly acknowledged for help with vibrational spectroscopy.

**Notes and references**

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


7866 | Chem. Sci., 2019, 10, 7859–7867 This journal is © The Royal Society of Chemistry 2019


