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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.

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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 [Cp2Ti(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 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.1 Almost 100 years later in 1964 the molecular structure of the product could be identified as P3Ph5 by X-ray crystal structure analysis.2 Although, Cowley et al. already mentioned the synthesis of P3(C2F5)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 P3Bu3 was reported by Baudler and co-workers in 1976,5,6 and various synthetic approaches towards triphosphiranes have since emerged.7 Reductive approaches starting from dihalophosphines RPX2 (X = Cl, Br) result in a mixture of oligophosphines of different ring sizes of PnRn (n = 3, 4, 5, 6) and are thus regarded as unspecific.8 The ratio of the different oligomers heavily depends on the steric demand of the substituent R.9 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.10 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 P3Cp*3 (Cp* = pentamethycyclopentadienyl), affording a mixture of cyclic selenotriphosphabutanes (Scheme 1, A) and cyclic selenodiphosphapropanes (Scheme 1, B).11 In contrast, thermolysis of P3Cp*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
formation of different phosphorus clusters, some of which are structurally related to Hit- torf’s-phosphorus (Scheme 1, C and D).11 Ring expansion reactions were reported by Uhl and Benter by the insertion of Ga(i) into a P–P bond of P3Bu3, thus establishing a way to prepare cyclic-galliumtriphosphabutanes (Scheme 1, E, M = Ga).13 A similar reactivity is observed when Al(i) compound (AlCP)* reacts with P3Bu3 (Scheme 1, E, M = Al).14 In addition, the reaction of P3Bu3 with PMe2Cl or PPh2Cl in the presence of Me3SiOTf or GaCl3, respectively, resulted in the selective ring expansion with insertion of [PMe2]− 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-triphenonoles in a click-type reaction (Scheme 1, G),17,18 underlining the value of triphosphiranes as synthons 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)(P3Bu3)(CO)2] with μ1− and μ2-bridging P3Bu3 ligands as well as a P3Bu3 chain, acting as a μ2(n3−n1−n0) ligand to three Ni atoms of the cluster.19

To the best of our knowledge, only four aryl-substituted triphosphiranes are reported in the literature. P3Ph3 was described as early as 1973 as a labile solid with respect to Ph3,20 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 Tokioto et al. synthesized (Anth = 9-arylanth, Bbt = 2,6-bis[bis-(trimethylsilyl)methyl]-4-[tri-(trimethylsilyl)phenyl]) in good yield by heating a mixture of AnthP=PBbt and 9BuP=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 phosphinidene were generated by reductive dechlorination of PRCl2 (R = Tipp, Mes).23–25 Moreover, Gaspar and co-workers reported on the photochemical-release of the triplet phosphinidene MesP from MesP(C6H4) in 1992.26 In the absence of a trapping reagent these triplet phosphinidenes oligomerize to give a mixture containing P3Mes3 and P3Mes4.

Using [W(PMe2)6] as a reducing agent the quantitative coupling of PRCl2 (R = Mes* = 2,4,6-iPr3C6H2; 2,4,6-(CF3)3C6H2) to the respective diphosphenes RP=PR was detected. Starting from TippPRCl2, 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 intermediary of W=PR species.27 Moreover, it was shown that the reductive degradation of P3 with mesityl-radicals (generated from MesBr and Ti(n)-based chlorine atom abstracting reagent [Ti(NBu3)(3,5-CH3C6H4Me)3]) yields P3Mes3 as the main product in good isolated yields.28

In 1998 Shah and Protasiewicz reported the formation of the triphosphirane P3Tipp (1a) by treatment of TippPRCl2 with PMe3 and Zn and subsequent reaction with benzaldehyde (Scheme 2).29 This so-called phospha-Wittig reaction afforded a mixture of P3Tipp and traces of the desired phosphaalkene Ph(Ph)C=PTipp.

In this contribution, we report on the synthesis of aryl substituted triphosphiranes using a modified synthesis on the basis of the studies by Protasiewicz et al.29 Furthermore, we report on the selective degradation of these P3Ar3 systems using [Cp2Ti(btmsa)] (Cp = cyclopentadienyl, btmsa = C2(SiMe3)2) as a Ti(n) synthon.

Results

In an attempt to prepare new variants of pyrindinophosphaalkenes,29 we utilized the phospha-Wittig protocol described by Protasiewicz et al. with DippPRCl2 (Dipp = 2,4,6-Pr3C6H2), 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 A2B 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 P3Dipp3 (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 2.2124(3), P3–P1 2.2124(3), P1–C1 1.8526(10), P2–C13 1.8594(10), P3–C25 1.8507(10), P1–P2 59.718(11), P2–P1 59.147(12), P1–P3 59.135(11).
singlet state is less stable by 26.01 kcal mol$^{-1}$.

We then utilized the sterically more demanding PET$_3$ to better stabilize the reactive phosphoryldiene phosphorane intermediate TippP$\equiv$PET$_3$. Phosphoryldiene phosphoranes have been identified as a source of the triplet phosphinidene Ar$\equiv$P$^\cdot$.\textsuperscript{14}

Additionally, we switched to TippPBr$_2$, as its reduction should be more facile. TippPBr$_2$, PET$_3$ (1.2 equiv.) and Zn (3 equiv.) were combined in THF at $-78 \, ^\circ$C and the formation of a deep yellow to orange suspension was observed, which again showed P$_2$Tipp$_2$ (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 P$_2$Tipp$_2$ (2) (Fig. 2), which has only been observed in solution in the $[W(PMe_3)_6]$ mediated coupling of ArPBr$_2$ (Ar = Tipp, Mes*, 2,4,6-(CF$_3$)$_3$C$_6$H$_2$) by $^{31}$P NMR experiments to date.\textsuperscript{27} The $^{31}$P NMR spectrum of isolated 2 showed P$_2$Tipp$_2$ ($\delta$($^{31}$P) = 517.4 ppm) to be the major species, whereas minor amounts of P$_3$Tipp$_3$ and P$_4$Tipp$_4$ were also detected. Monitoring a C$_6$D$_6$ solution of 2 over time at room temperature revealed that P$_2$Tipp$_2$ slowly coverts into P$_3$Tipp$_3$ and its dimer P$_4$Tipp$_4$, vide infra.\textsuperscript{28} 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) Å] (cf. d(P=P) P$_2$Mes$_2$ 2.034(2);\textsuperscript{35} P$_2$Ter$_2$ 2.029(1);\textsuperscript{36} P$_2$Bbt$_2$ 2.043(1)) is in the expected range for a diphosphene ($\sum$cos(P–P) = 2.04 Å),\textsuperscript{38} 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 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 DippPPMe$_3$ to P$_2$Dipp$_2$ 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(dichloro)phosphines ArPBr$_2$ (Ar = Mes, Dipp, Tipp) to elucidate whether treatment with PR$_3$ (R = Me, Et) and Zn gives general access to aryl-substituted triphosphiranes (Scheme 3).

The reaction of ArPBr$_2$ with PMe$_3$ (2.5 equiv.) and an excess of Zn (5 equiv.) in anhydrous THF afforded P$_2$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$_3$),\textsuperscript{39} 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 Et$_2$O in case of 1c. 1a–c show good thermal stability with melting points of higher than 167 °C.\textsuperscript{41} 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 TippPBr$_2$ 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

![Fig. 2](https://example.com/fig2.png)

**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 ArPCl$_2$ with a fivefold excess of PMe$_3$ afforded 1a–c in 43, 66 and 18% isolated yield, respectively. The potential of PMe$_3$ to act as a chloride abstracting reagent is documented in the literature and results in oxidation to the respective dichlorophosphorane.$^{46,41}$ or the homoleptic dication salt [Me$_2$P(PMe$_3$)$_2$]Cl$_2$. This concept has been used to access cyclo-tetra(stibinophosphonium) triflate salts of the type [Sb$_4$(PR$_3$)$_4$] [OTf]$_4$ (R = Me, Et, Pr, Bu), cationic antimony compounds related to the cyclic oligosphosphines.$^{42}$ To shed light on this proposition, we independently synthesized PMe$_3$Cl$_2$ and treated it with an excess of zinc dust in the presence of TippCl$_2$ in a mixture of MeCN/THF (3 : 1) over 24 h. A $^{31}$P NMR spectrum of the reaction mixture indeed showed 1a to be the main product of this reaction.$^{3}$ It can thus be concluded that PMe$_3$Cl$_2$ is a plausible by-product of the reduction with PMe$_3$ and zinc can reduce it back to PMe$_3$, vide infra. This opens the pathway for potential catalytic reduction of ArPCl$_2$ with PMe$_3$ and Zn as a sacrificial reductant. In another experiment DippPMe$_3$Cl$_2$ was reduced with an excess of PMe$_3$ and the white precipitate was carefully washed with benzene and n-hexane. Subsequently, the precipitate was treated with AgOTf in CH$_2$Cl$_2$. A spectroscopic study of the reaction mixture showed 1a to be the sole product of this reaction.$^{3}$

The synthetic approach using Zn/PMe$_3$ showed a high selectivity towards the respective triphosphiranes. In the case of 1a and 1b just little amounts of the corresponding cyclic tetraphosphines P$_3$Ar$_4$ were detected as side products by $^{31}$P NMR spectroscopy of the reaction mixture. When MesPCl$_2$ is applied in our approach, the selectivity decreases and the formation of little amounts of the cyclic tetraphosphine P$_3$Mes$_5$, and the cyclic pentaphosphine P$_3$Mes$_8$ 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 [Cp$_2$Ti(btmssa)] in order to access titanium phosphinidene complexes.

Titanocene-induced degradation of R$_3$P$_3$

Stephan and co-workers have shown the phospha-Wittig-type phosphinidene transfer for [Cp$_2$Zr=PMe$_3$][PMe$_3$] resulting in the formation of phosphaalkenes in the reaction with aldehydes along with the formation of [Cp$_2$ZrO]$_4$. Similar reactivity was observed by Cummins and Schrock for the terminal tantalum phosphinidene complexes, [(N$_3$N)Ta=PR] [N$_3$N = (Me$_3$Si–NCH$_2$CH$_2$)$_2$].$^{45}$

With the series of triphosphiranes 1a–c synthesized, we wanted to investigate the propensity to access monomeric, terminal Cp$_2$Ti=PR complexes, by reaction of 1 with the titanocene synthon [Cp$_2$Ti(btmssa)]. Cp$_2$Ti=PR has not been described in the literature. There are reports of neutral and zwitterionic terminal titanium phosphinidene complexes of the type [(Nacnac)Ti−PR](Ar) (Ar = Tipp, Mes*; R = CH$_2$Bu, CH$_3$, CH$_2$[C$_6$F$_5$]$_2$) by Minidola and co-workers with a bulky C–Si–Ph$_2$ group.

ORTEPs drawn at 30% probability, all H-atoms are omitted for clarity. Selected bond lengths (Å) and angles (°) of 3a: P1–P1’ 2.1826(7), P1–C1 1.8548(13), P1–Ti 2.5329(5), C1–P1–P1’ 108.39(5), P1–Ti1–P1’ 112.53(4), P1–Ti1–P2 50.725(12).

Fig. 3. 31P NMR spectrum of 3a (left) and 3b (right). Consequently, the reaction was repeated in the correct stoichiometry with [Cp$_2$Ti(btmssa)] 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 [Cp$_2$Ti(P$_2$Tipp$_2$)] (3a, Fig. 3, left) and [Cp$_2$Ti(P$_2$Mes$_2$)] (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.$^{43}$ Interestingly, in the $^1$H NMR spectrum three or two independent septets are detected for 3a and 3b, respectively. This indicates hindered rotation about the P−C$_{Ar}$ bond and the Me group of the isopropyl moiety in close proximity to the Cp$_2$Ti-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 $^1$H 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$_6$D$_6$ 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 ($\sum x_{\text{covalent}}(\text{P-P}) = 2.04$ 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$_2$Ph$_3$]] (ETBHI = ethylene-1,2-bis[5,4,5,6,7-tetrahydro-1-indenyl]), the only titanium diphosphene complex known to date.$^{29}$ It is worth noting that green [rac-(EBTHI)Ti[P$_2$Ph$_3$]] is insoluble in common non-halogenated organic solvents and thus, NMR data was not obtained. It is formed through the dehydrocoupling of PhP$_2$H in the presence of the Ti[n]-hydride dimer [rac-(EBTHI)-TiH]$_2$.$^{31}$

η$^2$-Diphosphene complexes of various transition metals have been known and were thoroughly reviewed by Weber.$^{32}$ Noteworthy, is the formation of [(P$_3$Ad)$_2$M(P$_2$Mes$_2$)$_2$] with an E-configured diphosphene ligand by the degradation of cyclic tetraphosphine P$_4$(C$_6$F$_5$)$_4$ in the presence of M(PPPh$_3$)$_2$ (M = Pt,$^{33}$ Pd). Other known diphosphene complexes of group 4 include the anionic species [Cp$_2$Zr(PPPh)$_2$Br]$^-$ with a P–P distance [2.145(3) Å] shorter than in 3a and 3b,$^{28}$ and the related Mes-substituted complex [Cp$_2$Zr(P$_2$Mes$_2$)$_2$] with a similar P–P distance [2.188(3) Å]. The Ti–P distances in 3a [2.5425(5), 2.5230(5) Å] and 3b [2.5329(5) Å], as well as the P–Ti–P angles (3a 50.725(12)$^\circ$; 3b 51.042(17)$^\circ$), are similar to that in [Cp$_2$Zr(PPPh)$_2$Br]$^-$(Ti–P–P 2.525(2) Å; Ti–P–P 51.00(6)$^\circ$) and point to a Ti(IV) center and an overall titanacyclo-propane, rather than a titanacyclo-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 [Cp$_2$Ti(btmusa)] 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$_2$Ph$_3$(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$_2$Dipp$_2$ and P$_2$Ph$_3$ can displace the btmsa molecule in [Cp$_2$Ti(btmusa)] to afford complexes 3b and [Cp$_2$Ti(P$_2$Ph$_3$)] (3Ph), respectively (Scheme 7, bottom). Interestingly, this reaction is also exergonic for P$_2$Dipp$_2$ and P$_2$Ph$_3$ 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$_2$P$_2$ (2) in hand, we treated 2 with [Cp$_2$Ti(btmusa)] in a 1 : 1 ratio at room temperature in C$_6$D$_6$. Having shown that the reaction of 1a with [Cp$_2$Ti(btmusa)] 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$_2$Ti(btmusa)]. Furthermore, this shows the drastic influences of the sterically demanding groups attached to phosphorus, as the diphosphene P$_2$Mes$_2$ was shown to not afford the respective diphosphene complex in the reaction with [Cp$_2$Ti(btmusa)].$^{37}$

To compare the reactivity of the aryl-substituted triphosphiranes with alkyl-substituted derivatives we treated [Cp$_2$Ti(btmusa)] with the known triphosphiranes P$_3$Bu$_3$ (1d) and P$_3$Ad$_3$ (Ad = adamantyl)$^{38,39}$ in a 1 : 1 ratio in benzene at 80 °C in C$_6$D$_6$ (Scheme 6). Interestingly, in the case of 1d full consumption of both starting materials was noted, with a new characteristic A$_2$B spin system in the $^{31}$P NMR spectrum. 1e also cleanly reacted in similar fashion, however full conversion 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
two identical P atoms and the formation of the triphosphanato-complexes \([\text{Cp}_2\text{Ti}(\text{P}_3\text{Bu}_3)] (4a)\) and \([\text{Cp}_2\text{Ti}(\text{P}_3\text{Ad}_3)] (4b)\). 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 \(\text{K}_2[\text{P}_4\text{Bu}_4]\) in a salt elimination reaction on the basis of NMR experiments.\(^\text{60}\) Extraction of the reaction mixture with \(\text{Et}_2\text{O}\) concentration to incipient crystallisation 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-titanatetriphosphine.

4a crystallizes in the orthorhombic space group \(P2_12_12_1\) with four molecules in the unit cell. The \(P\text-P\) distances \([P1-P2 2.1953(8), P2-P3 2.1840(8)]\) are shorter than a \(P\text-P\) single bond \(\sum \cos (P-P) = 2.22 \text{ Å}\) and the \(P\text-Ti\text-P\) angle \(90.34(2)^\circ\) is wider than in 3a and 3b and compares nicely with the \(P\text-Zr\text-P\) angle \(89.8(2)^\circ\) found in the related compound \([\text{Cp}_2\text{Zr}(\text{P}_3\text{Bu}_3)]\).\(^\text{55}\)

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.\(^\text{51}\) 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 \(\text{P}_3\text{Dipp}_2\) 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 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, while the two-electron transfer process is endergonic and thermodynamically not favored.\(^\text{51}\)

On the basis of these results, one can expect a stepwise reaction mechanism for the electron transfer reactions. Furthermore one of the \(P\text-P\) bonds in the radical anion species \([\text{P}_3\text{R}_3\text{]}^{-}\) is considerably elongated \([2.814 (R = \text{Dipp}), 2.973 \text{ Å (R = \text{Ph})}]\), which would allow for the liberation of a phosphinidene fragment or the recombination of two radical anions, under formal exchange of \(P\text-R\) 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. \(F_1/F_1^\text{c}\)), 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 \(a(\text{\text{^31}\text{P}}) = 72\) MHz and hyperfine coupling to titanium \(a(\text{\text{^49,\text{\text{^51}}}\text{Ti}}) = 22\) 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.\(^\text{64}\) In addition, there is an underlying signal stemming from \([\text{Cp}_2\text{Ti}(\text{btmsa})]\), which could be fitted to a species with \(g_{\text{iso}} = 1.973\) and \(a(\text{^1H}) = 32\) MHz.\(^\text{64}\) This could indicate a hydridic species such as \([\text{Cp}_2\text{Ti}(\text{\text{^1H}})]\), 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.\(^\text{65}\)

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 \(\text{P}_3\text{Ar}_3\text{R}\) should result in the formation of the mixed diphosphene complex.
Therefore, a 1:1 mixture of phosphinidenes P1 and P2 alongside [Cp2TiP2Ar2] and [Cp2TiP2Ar] (including an impurity (giso = 1.978, a(31P) = 72 MHz, and a(47,49Ti) = 22 MHz. Additionally, there are two doublets, indicating the formation of the mixed diphosphene complex 3ab in a scrambling experiment utilizing a 1:1 mixture of 3a and 3b in the presence of 1.5 equiv. [Cp2Ti(btmsa)].

The 31P NMR spectrum of the resulting product solution is shown in Fig. 6. For comparison the spectra of the pure compounds 3a and 3b are depicted as well. In the spectrum of the product mixture the singlet signals of the symmetric compounds 3a and 3b can be seen clearly at 283.8 and 290.7 ppm, respectively. Additionally, there are two doublets, indicating the formation of the mixed diphosphene complex [Cp2Ti[P2DippTipp]] (3ab). We conclude from this experiment that an exchange of P-R end groups or the intermediacy of phosphinidenes P-R are likely in the course of the reaction.

[Scheme] Transmetalation of 3a with TippPCl2, resulting in the formation of 1a.

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 TippPCl2 and found 1a as the product along with the formation of Cp2TiCl2 (Scheme 7),\textsuperscript{14} 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 P3Ar3 and identified PMe3 as the active reductant. These findings open the way for future studies to render these transformations catalytic with respect to PMe3. Moreover, we have shown that the Ti(n) synthon [Cp2Ti(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 diphosphines, authenticated by reaction of the elusive diphosphene P2Tipp2 (2) with [Cp2Ti(btmsa)]. In first reactivity studies we have shown that 3 can be utilized as a P2R2-transfer reagent in transmetalation protocols using TippPCl2. This opens the pathway to generate new P2R2-containing heterocycles.

Studies to further elucidate the reaction mechanism of the P3Ar3 degradation reaction are ongoing, to further investigate the nature of the paramagnetic intermediate. Additionally, application of the P3Ar3 systems in phosphinidene transfer reactions will be investigated.

### Conflicts of interest

There are no conflicts to declare.

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