

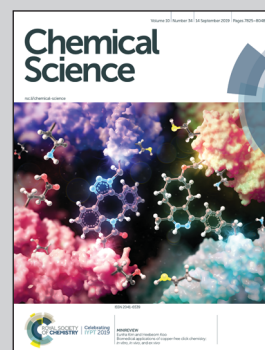


Showcasing research from Dr. Christian Hering-Junghans's laboratory, Leibniz Institute for Catalysis at the University of Rostock (LIKAT Rostock), Rostock, Germany.

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†

André Schumann,^a Fabian Reiß,^a Haijun Jiao,^a Jabor Rabeah,^a Jan-Erik Siewert,^a Ivo Krummenacher,^{bc} Holger Braunschweig^{id bc} and Christian Hering-Junghans^{id *a}

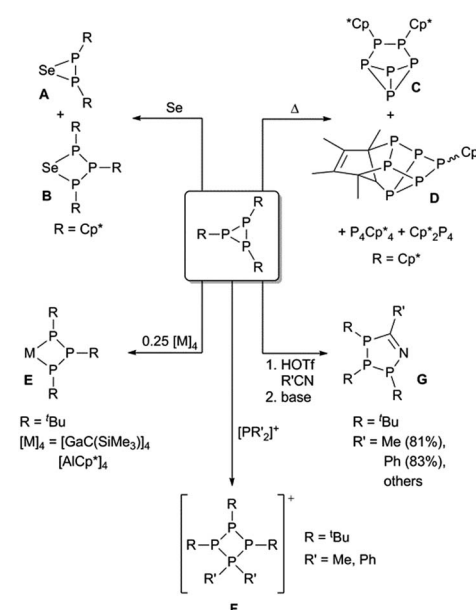
Triphosphiranes are three-membered phosphorus cycles and their fundamental reactivity has been studied in recent decades. We recently developed a high-yielding, selective synthesis for various aryl-substituted triphosphiranes. Variation of the reaction conditions in combination with theoretical studies 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 P₃Ph₃ 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 P₃^tBu₃ 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 of different ring sizes of P_nR_n (*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.^{5,9} 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* = pentamethylcyclopentadienyl), 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.

^aLeibniz-Institut für Katalyse e.V. an der Universität Rostock, Albert-Einstein-Straße 29a, 18059 Rostock, Germany. E-mail: christian.hering-junghans@catalysis.de

^bInstitut für Anorganische Chemie, Julius-Maximilians-Universität Würzburg, Am Hubland, 97074 Würzburg, Germany

^cInstitute for Sustainable Chemistry & Catalysis with Boron, Julius-Maximilians-Universität Würzburg, Am Hubland, 97074 Würzburg, Germany

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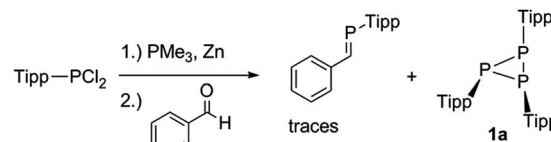
formation of different phosphorus clusters, some of which are structurally related to Hittorf's-phosphorus (Scheme 1, C and D).¹² Ring expansion reactions were reported by Uhl and Benter by the insertion of Ga(I) into a P–P bond of $P_3^tBu_3$, thus establishing a way to prepare cyclo-galliumtriphosphabutanes (Scheme 1, E, M = Ga).¹³ A similar reactivity is observed when Al(I) compound $(AlCp^*)_4$ reacts with $P_3^tBu_3$ (Scheme 1, E, M = Al).¹⁴ In addition, the reaction of $P_3^tBu_3$ with PMe_2Cl or PPH_2Cl in the presence of Me_3SiOTf or $GaCl_3$, respectively, resulted in the selective ring expansion with insertion of $[PMe_2]^+$ into the P–P bond between the two identical P atoms of $P_3^tBu_3$ to afford $[R_2P(P_3^tBu_3)]^+$ (Scheme 1, F; R = Me, Ph).^{15,16} More recently, Manners and co-workers showed the addition of $P_3^tBu_3$ 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} underlining the value of triphosphiranes as synthons in synthetic inorganic chemistry. Fragmentation of $P_3^tBu_3$ was observed by Fenske and Ahlrichs in the reaction with $Ni(CO)_4$, resulting in the formation of $[Ni_5(P^tBu)_3(P_3^tBu_3)(CO)_5]$ with μ_4 - and μ_3 -bridging P^tBu ligands as well as a $P_3^tBu_3$ chain, acting as a $\mu_4(\eta^2, \eta^1, \eta^2)$ 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. P_3Ph_3 was described as early as 1973 as a labile solid with respect to P_5Ph_5 ,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-anthryl, Bbt = 2,6-bis[bis(trimethylsilyl)methyl]-4-[tris(trimethylsilyl)phenyl]) in good yield by heating a mixture of AnthP=PBBt and $^nBu_3P=Te$.²² P_3Tipp_3 (Tipp = 2,4,6- $Pr_3C_6H_2$) and P_3Mes_3 (Mes = 2,4,6- $Me_3C_6H_2$) were described as one of a mixture of products when free phosphinidenes were generated by reductive dechlorination of RP_2Cl_2 (R = Tipp, Mes).^{23–25} Moreover, Gaspar and co-workers reported on the photochemical release of the triplet phosphinidene MesP from MesP(C₂H₄) in 1992.²⁶ In the absence of a trapping reagent these triplet phosphinidenes oligomerize to give a mixture containing P_3Mes_3 and P_4Mes_4 .

Using $[W(PMe_3)_6]$ as a reducing agent the quantitative coupling of RP_2Cl_2 (R = Mes* = 2,4,6- tBuC_6H_2 ; 2,4,6-(CF₃)₃C₆H₂) to the respective diphosphenes $RP=PR$ was detected. Starting from $TippP_2Cl_2$, the initial formation of the diphosphene is detected by ^{31}P NMR spectroscopy, however, the reaction continues to produce $Tipp_3P_3$ as the final product, clearly pointing to the intermediacy of $W=PR$ species.²⁷ Moreover, it was shown that the reductive degradation of P_4 with mesityl-radicals (generated from Mes-Br and Ti(III)-based chlorine atom abstracting reagent $[Ti\{N(^tBu)(3,5-C_6H_3Me_2)\}_3]$) yields P_3Mes_3 as the main product in good isolated yields.²⁸

In 1998 Shah and Protasiewicz reported the formation of the triphosphirane P_3Tipp_3 (**1a**) by treatment of $TippP_2Cl_2$ with PMe_3 and Zn and subsequent reaction with benzaldehyde (Scheme 2).²⁹ This so-called phospho-Wittig reaction afforded a mixture of P_3Tipp_3 and traces of the desired phosphoalkene $Ph(H)C=PTipp$.

In this contribution, we report on the synthesis of aryl substituted triphosphiranes using a modified synthesis on the



Scheme 2 Formation of $Tipp_3P_3$ (**1a**) and trace amounts of phosphoalkene $H(Ph)C=PTipp$ in a so-called phospho-Wittig protocol.

basis of the studies by Protasiewicz *et al.* Furthermore, we report on the selective degradation of these P_3Ar_3 systems using $[Cp_2Ti(btmsa)]$ (Cp = cyclopentadienyl, btmsa = $C_2(SiMe_3)_2$) as a Ti(II) synthon.

Results

In an attempt to prepare new variants of pyridinephosphoalkenes,³⁰ we utilized the phospho-Wittig protocol described by Protasiewicz *et al.* with $DippP_2Cl_2$ ($Dipp = 2,6-^iPr_2C_6H_3$), PMe_3 and excess of Zn powder in a strict low-temperature regime ($-78^\circ C$); after subsequent treatment with pyridine-2-carbaldehyde at that temperature and warming to room temperature the formation of the respective phosphoalkene was not observed. The ^{31}P NMR spectrum of the reaction mixture displayed a major product with an A_2B 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 P_3Dipp_3 (**1b**), in line with attempted synthesis of the phospho-Wittig reagent $TippPPMe_3$ as discussed before.²⁹ X-ray quality crystals of **1b** were grown from a saturated *n*-hexane solution at $5^\circ C$ (Fig. 1). **1b** crystallises in the monoclinic space group $P2_1/c$ 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 P_3 plane, with a minimally distorted central P_3 -ring [$P1-P2$ 2.1991(4), $P2-P3$

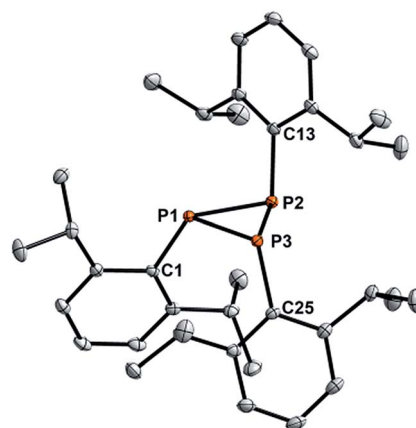


Fig. 1 POV-ray depiction of the molecular structure of **1b**. ORTEPs drawn at 30% probability, H atoms are omitted for clarity. Selected bond lengths (Å) and angles ($^\circ$): $P1-P2$ 2.1991(4), $P2-P3$ 2.2440(4), $P1-P3$ 2.2124(3), $P1-C1$ 1.8526(10), $P2-C13$ 1.8594(10), $P3-C25$ 1.8507(10); $P1-P2-P3$ 59.718(11), $P2-P1-P3$ 61.147(12), $P1-P3-P2$ 59.135(11).



2.2440(4); P1–P3 2.2124(3) Å] (Fig. 1). These metric parameters are in line with those detected for **1a** and **1c** (Table S1†),³¹ of which the molecular structures have been reported previously.^{32,33}

We then utilized the sterically more demanding PET_3 to better stabilize the reactive phosphanylidene phosphorane intermediate $\text{TippP}=\text{PET}_3$. Phosphanylidene phosphoranes have been identified as a source of the triplet phosphenes Ar-P .³⁴

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°C and the formation of a deep yellow to orange suspension was observed, which again showed P_3Tipp_3 (**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_2Tipp_2 (**2**) (Fig. 2), which has only been observed in solution in the $[\text{W}(\text{PMe}_3)_6]$ mediated coupling of ArPCl_2 ($\text{Ar} = \text{Tipp}, \text{Mes}^*, 2,4,6\text{-(CF}_3)_3\text{C}_6\text{H}_2$) by ^{31}P NMR experiments to date.²⁷ The ^{31}P NMR spectrum of isolated **2** showed P_2Tipp_2 ($\delta(^{31}\text{P}) = 517.4$ ppm) to be the major species, whereas minor amounts of P_3Tipp_3 and P_4Tipp_4 were also detected. Monitoring a C_6D_6 solution of **2** over time at room temperature revealed that P_2Tipp_2 slowly converts into P_3Tipp_3 and its dimer P_4Tipp_4 , *vide infra*.³¹ **2** crystallises as its *trans*-conformer in the triclinic space group $P\bar{1}$ with one molecule in the unit cell. The P1–P1' distance [2.0290(5) Å] (*cf.* d(P=P) $\text{P}_2\text{Mes}^* 2.034(2)$;³⁵ $\text{P}_2\text{Ter}_2 2.029(1)$;³⁶ $\text{P}_2\text{Bbt}_2 2.043(1)$ ³⁷) is in the expected range for a diphosphene ($\sum r_{\text{cov(P=P)}} = 2.04$ Å),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 phosphenes 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 intermediately at low temperatures) *via* DippPPMe_3 to P_2Dipp_2 and

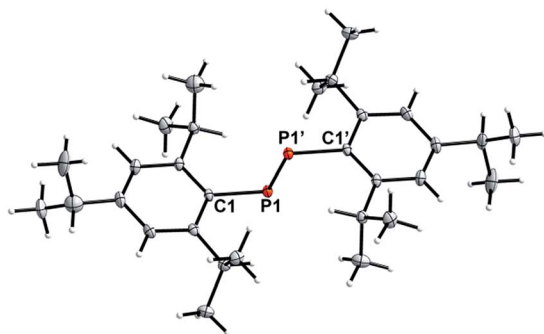


Fig. 2 POV-ray depiction of the molecular structure of **2**. ORTEPs drawn at 30% probability. Selected bond lengths (Å) and angles (°): P1–P1' 2.0290(5), P1–C1 1.8439(10); C1–P1–P1' 99.61(3); P1'–P1–C1 91.34(8), C1–C2–C3–C4 1.25(16).

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**.

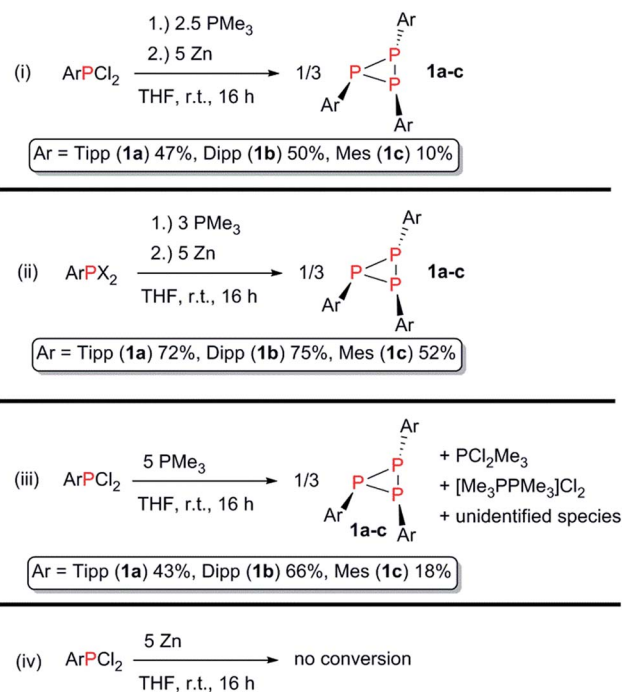
Since there are only few high-yielding, selective methods for the preparation of aryl-substituted triphosphiranes outlined in the literature, we decided to take a closer look at this synthetic approach. We therefore tested different aryl(dichloro)phosphines ArPCl_2 ($\text{Ar} = \text{Mes}, \text{Dipp}, \text{Tipp}$) to elucidate whether treatment with PR_3 ($\text{R} = \text{Me}, \text{Et}$) and Zn gives general access to aryl-substituted triphosphiranes (Scheme 3).

The reaction of ArPCl_2 with PMe_3 (2.5 equiv.) and an excess of Zn (5 equiv.) in anhydrous THF afforded P_3Ar_3 ($\text{Ar} = \text{Tipp}$ (**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 ($\text{Ar} = \text{Tipp}, \text{Dipp}, \text{Mes}$; $\text{X} = \text{Cl}, \text{Br}$; obtained through treatment of ArMgBr with PCl_3),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_2O 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_6D_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



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 chlorine abstracting reagent is documented in the literature and results in oxidation to the respective dichlorophosphorane,^{40,41} or the homoleptic dication salt $[\text{Me}_3\text{PPMe}_3]_2\text{Cl}_2$. This concept has been used to access cyclo-tetra(stibinophosphonium) triflate salts of the type $[\text{Sb}_4(\text{PR}_3)_4][\text{OTf}]_4$ ($\text{R} = \text{Me, Et, Pr, Bu}$), cationic antimony compounds related to the cyclic oligophosphines.⁴² To shed light on this proposition, we independently synthesized PMe_3Cl_2 and treated it with an excess of zinc dust in the presence of TippPCL_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.³¹ It can thus be concluded that PMe_3Cl_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 DippPCL_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_2Cl_2 . After filtration a colourless solid was obtained, which was dissolved in CD_3CN , allowing to unambiguously identify $[\text{Me}_3\text{PCL}]\text{OTf}$ ($\delta^{31}\text{P}\{^1\text{H}\} = 93.6$ ppm),⁴³ and $[\text{Me}_3\text{P–PMe}_3][\text{OTf}]_2$ ($\delta^{31}\text{P}\{^1\text{H}\} = 28.4$ ppm)⁴⁴ among three unidentified PMe_3 containing species (Scheme 3(iii)).³¹

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_4Ar_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_4Mes_4 , and the cyclic pentaphosphine P_5Mes_5 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 $[\text{Cp}_2\text{Ti}(\text{btmsa})]$ in order to access titanium phosphinidene complexes.

Titanocene-induced degradation of R_3P_3

Stephan and co-workers have shown the phospho-Wittig-type phosphinidene transfer for $[\text{Cp}_2\text{Zr}=\text{PMes}^*(\text{PMe}_3)]$ resulting in the formation of phosphalkenes in the reaction with aldehydes along with the formation of $[\text{Cp}_2\text{ZrO}]_n$.⁴⁵ Similar reactivity was observed by Cummins and Schrock for the terminal tantalum phosphinidene complexes, $[(\text{N}_3\text{N})\text{Ta}=\text{PR}]$ ($\text{N}_3\text{N} = (\text{Me}_3\text{Si–NCH}_2\text{CH}_2)_3\text{N}$).⁴⁶

With the series of triphosphiranes **1a–c** synthesized, we wanted to investigate the propensity to access monomeric, terminal $\text{Cp}_2\text{Ti}=\text{PR}$ complexes, by reaction of **1** with the titanocene synthon $[\text{Cp}_2\text{Ti}(\text{btmsa})]$. $\text{Cp}_2\text{Ti}=\text{PR}$ has not been described in the literature. There are reports of neutral and zwitterionic terminal titanium phosphinidene complexes of the

type $[(^{\text{Ar}}\text{Nacnac})\text{Ti}=\text{PAR}'(\text{R})]$ ($\text{Ar}' = \text{Tipp, Mes}^*$; $\text{R} = \text{CH}_2^t\text{Bu, CH}_3, \text{CH}_3[\text{B}(\text{C}_6\text{F}_5)_3]$) by Mindiola and co-workers with a bulky β -diketiminate ligand ($^{\text{Ar}}\text{Nacnac}=[\text{Ar}]\text{NC}(\text{Me})\text{CHC}(\text{Me})\text{N}[\text{Ar}]$, $\text{Ar} = \text{Dipp}$) on titanium.^{47,48} $[\text{Cp}_2\text{Ti}(\text{btmsa})]$ is obtained by reduction of Cp_2TiCl_2 in the presence of btmsa. In these complexes btmsa acts as a spectator ligand and its facile release under the respective reaction conditions generates the highly reactive 14-electron $[\text{Cp}_2\text{Ti}]$ fragment *in situ*.⁴⁹ Combination of three equivalents $[\text{Cp}_2\text{Ti}(\text{btmsa})]$ with **1b** in C_6D_6 at room temperature and monitoring by ^{31}P 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 $[\text{Cp}_2\text{Ti}(\text{btmsa})]$ according to ^1H NMR spectroscopy. However, unreacted P_3Ar_3 remained in the reaction mixture and thus, more $[\text{Cp}_2\text{Ti}(\text{btmsa})]$ was added to the reaction mixture and heating to 80 °C was continued. Fractional crystallisation from C_6D_6 and determination of the molecular structure by single crystal X-ray analysis revealed the formation of the η^2 -diphosphene complex $[\text{Cp}_2\text{Ti}(\text{P}_2\text{Dipp}_2)]$ (**3b**) (Fig. 3, right). Consequently, the reaction was repeated in the correct stoichiometry with $[\text{Cp}_2\text{Ti}(\text{btmsa})]$ 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 $[\text{Cp}_2\text{Ti}(\text{P}_2\text{Tipp}_2)]$ (**3a**, Fig. 3, left) and $[\text{Cp}_2\text{Ti}(\text{P}_2\text{Mes}_2)]$ (**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.³¹ 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–C_{Ar} bond and the Me group of the isopropyl moiety in close proximity to the Cp_2Ti -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

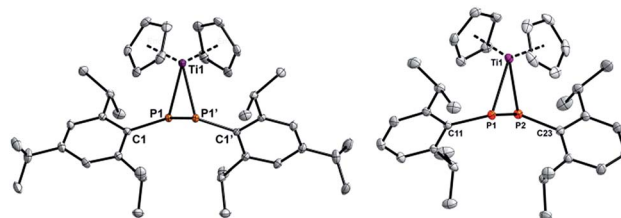
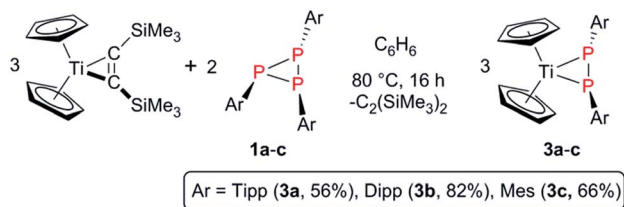


Fig. 3 POV-ray depiction of the molecular structure of **3a** and **3b**. ORTEPs drawn at 30% probability, all H-atoms are omitted for clarity. Selected bond lengths (Å) and angles (°) of **3a**: P1–P1' 2.1826(7), P1–C1 1.8548(13), P1–Ti1 2.5329(5); C1–P1–P1' 108.39(5), P1–Ti1–P1' 51.042(17). **3b**: P1–P2 2.1699(5), P1–Ti1 2.5425(5), P2–Ti1 2.5230(5), P1–C11 1.8548(13), P2–C23 1.8495(13); C11–P1–P2 108.88(4), C23–P2–P1 112.53(4), P1–Ti1–P2 50.725(12).

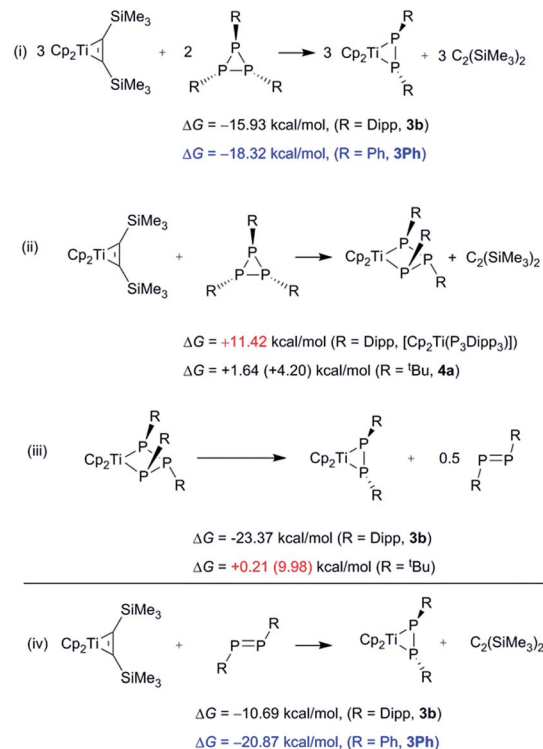




Scheme 4 Selective degradation of P_3Ar_3 (**1a–c**) into $[Cp_2Ti(P_2Ar_2)]$ (**3a–c**) complexes using $[Cp_2Ti(btmsa)]$ as a synthon for $[Cp_2Ti]$.

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 ($\sum r_{cov}(P=P) = 2.04$ Å; (P–P) 2.22 Å)³⁸ and are in line with the P–P distance [2.173(4) Å] in $[rac-(EBTHI)Ti(P_2Ph_2)]$ (ETBHI = ethylene-1,2-bis(5-4,5,6,7-tetrahydro-1-indenyl)), the only titanium diphosphene complex known to date.⁵⁰ It is worth noting that green $[rac-(EBTHI)Ti(P_2Ph_2)]$ is insoluble in common non-halogenated organic solvents and thus, NMR data was not obtained. It is formed through the dehydrocoupling of $PhPH_2$ in the presence of the $Ti(III)$ -hydride dimer $[rac-(EBTHI)-TiH]_2$.⁵¹ η^2 -Diphosphene complexes of various transition metals have been known and were thoroughly reviewed by Weber.⁵² Noteworthy, is the formation of $[(Ph_3P)_2M(P_2\{C_6F_5\}_2)]$ with an *E*-configured diphosphene ligand by the degradation of cyclic tetraphosphine $P_4(C_6F_5)_4$ in the presence of $M(PPh_3)_4$ ($M = Pt$,⁵³ Pd ⁵⁴). Other known diphosphene complexes of group 4 include the anionic species $[Cp_2Zr(PPh)_2Br]^-$ with a P–P distance [2.145(3) Å] shorter than in **3a** and **3b**,⁵⁵ and the related Mes-substituted complex $[Cp_2Zr(P_2Mes_2)]$ with a similar P–P distance [2.188(3) Å].⁵⁶ 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)°; **3b** 51.042(17)°), are similar to that in $[Cp_2Zr(PPh)_2Br]^-$ [d(Ti–P) 2.525(2) Å; <(P–Ti–P) 51.00(6)°] and point to a $Ti(IV)$ center and an overall titana-cyclo-propane, 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 $[Cp_2Ti(btmsa)]$ 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_3Ph_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



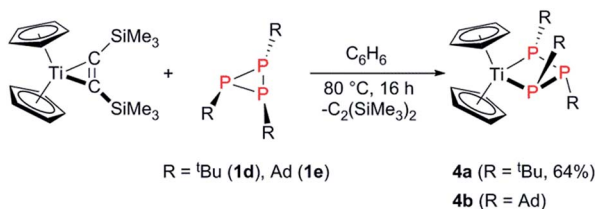
Scheme 5 M062X/TZVP (i and iv) and BP86/TZVP ((ii and iii) (M062X) for $R = {}^tBu$) computed reaction free energies for possible paths of formation of $[Cp_2Ti(P_2R_2)]$ in the gas phase.

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 ³¹P 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 $P_2Mes^*_2$ was shown to not afford the respective diphosphene complex in the reaction with $[Cp_2Ti(btmsa)]$.⁵⁷

To compare the reactivity of the aryl-substituted triphosphiranes with alkyl-substituted derivatives we treated $[Cp_2Ti(btmsa)]$ with the known triphosphiranes $P_3{}^tBu_3$ (**1d**) and P_3Ad_3 (Ad = adamantyl),^{58,59} 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 ³¹P 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 ³¹P NMR signal is downfield-shifted, thus indicating selective insertion into the P–P bond with the





Scheme 6 Formation of the *cyclo*-titanatraphosphabutanes [Cp₂-Ti(P₃R₃)] (R = ^tBu (**4a**), Ad (**4b**)) starting from [Cp₂Ti(btmsa)] and triphosphiranes **1d** and **1e**.

two identical P atoms and the formation of the triphosphanato-complexes [Cp₂Ti(P₃^tBu₃)] (**4a**) and [Cp₂Ti(P₃Ad₃)] (**4b**).³¹ Complex **4a** among other [Cp₂Ti(P₃R₃)] species has been described before by Köpf and co-workers in the reaction of Cp₂TiCl₂ with the salt K₂[P₄^tBu₄] in a salt elimination reaction on the basis of NMR experiments.⁶⁰ Extraction of the reaction mixture with Et₂O, 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*-titanatraphosphine.

4a crystallises in the orthorhombic space group P2₁2₁2₁ 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 (Σ_{cov}(P–P) = 2.22 Å)³⁸ and the P–Ti–P angle [90.34(2)°] is wider than in **3a** and **3b** and compares nicely with the P–Zr–P angle [89.8(2)°] found in the related compound [Cp₂Zr(P₃Ph₃)].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 [Cp₂Ti(btmsa)] with Dipp₃P₃ to afford the insertion product [Cp₂Ti(P₃Dipp₃)] 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 P₃^tBu₃ (+1.64 (+4.20 M062X) kcal mol^{−1}) to give **4a** (Scheme 5(ii)). The selective

degradation of [Cp₂Ti(P₃Dipp₃)] to yield **3b** and half an equivalent of P₂Dipp₂ 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*-P₃R₃ 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 P₃R₃ 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 [P₃R₃]^{•−} 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. Fc/Fc⁺), which is in line with degradation of the aryl-substituted triphosphiranes into diphosphene fragments upon treatment with [Cp₂Ti(btmsa)]. Investigation of the reaction mixture of [Cp₂Ti(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 ³¹P nucleus with *a*(³¹P) = 72 MHz and hyperfine coupling to titanium *a*(^{49/47}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.⁶¹ In addition, there is an underlying signal stemming from [Cp₂Ti(btmsa)], which could be fitted to a species with *g*_{iso} = 1.973 and *a*(¹H) = 32 MHz.⁶² This could indicate a hydridic species such as [Cp₂-Ti(III)-H], which has been discussed as resting state of [Cp₂Ti] in solution. In this case hydrogen release would generate the free titanocene and subsequent addition of H₂ regenerates the [Cp₂TiH] 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 P₃Ar₃ and P₃Ar'₃ should result in the formation of the mixed diphosphene complex

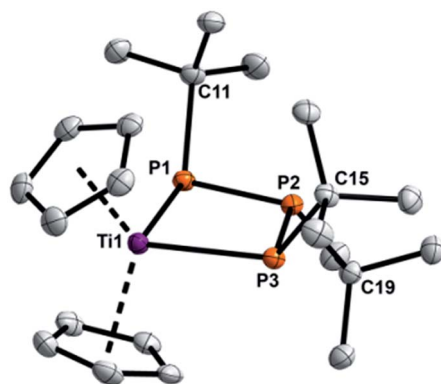


Fig. 4 POV-ray depiction of the molecular structure of **4a**. ORTEPs drawn at 30% probability, H atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): P1–P2 2.1953(8), P2–P3 2.1840(8), Ti1–P1 2.5354(6), Ti1–P2 3.0348(7), Ti1–P3 2.5480(7); P1–Ti1–P3 90.34(2).



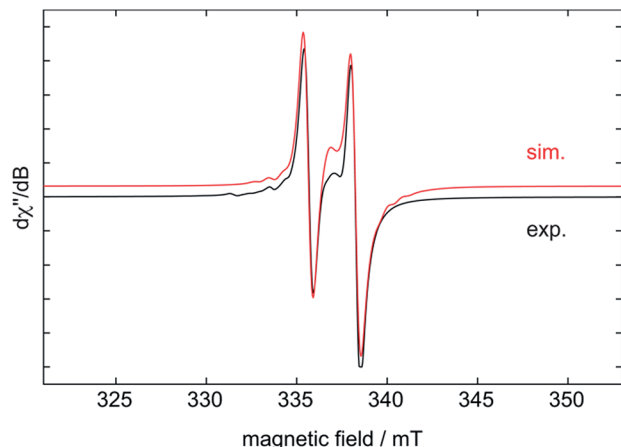


Fig. 5 Experimental (black) and simulated (red) X-band EPR spectra of the intermediate formed in the reaction of $[\text{Cp}_2\text{Ti}(\text{btmsa})]$ with Tippi_3P_3 to yield **3a** in benzene solution at room temperature. The simulation includes an impurity ($g_{\text{iso}} = 1.973$, $a(^1\text{H}) = 32$ MHz) which is present in the titanium precursor $[\text{Cp}_2\text{Ti}(\text{btmsa})]$. Simulation parameters: $g_{\text{iso}} = 1.978$, $a(^{31}\text{P}) = 72$ MHz, and $a(^{47,49}\text{Ti}) = 22$ MHz.

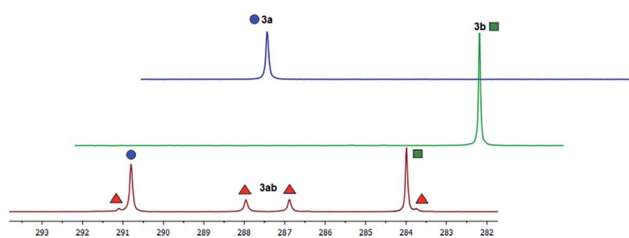
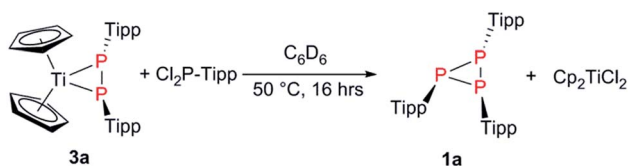


Fig. 6 Formation of the mixed diphosphene complex **3ab** in a scrambling experiment utilizing a 1 : 1 mixture of **3a** and **3b** in the presence of 1.5 equiv. $[\text{Cp}_2\text{Ti}(\text{btmsa})]$.

$[\text{Cp}_2\text{TiP}_2\text{ArAr}']$ (from recombination of differently substituted phosphinidenes) along with $[\text{Cp}_2\text{TiP}_2\text{Ar}_2]$ and $[\text{Cp}_2\text{TiP}_2\text{Ar}'_2]$. Therefore, a 1 : 1 mixture of **1a** and **1b** (1 equiv.) was mixed with 1.5 equiv. of $[\text{Cp}_2\text{Ti}(\text{btmsa})]$ in C_6D_6 in an NMR scale reaction.

The ^{31}P 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 $[\text{Cp}_2\text{Ti}(\text{P}_2\text{DippTipp})]$ (**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 7 Transmetalation of **3a** with Tipp-PCl_2 , resulting in the formation of **1a**.

Moreover, titana- and zirconacycles are regularly applied in the formation of main group element substituted heterocycles.^{64,65} We wanted to probe this reactivity by treating isolated **3a** with TippPCl_2 and found **1a** as the product along with the formation of Cp_2TiCl_2 (Scheme 7),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_3Ar_3 and identified PMe_3 as the active reductant. These findings open the way for future studies to render these transformations catalytic with respect to PMe_3 . Moreover, we have shown that the Ti(II) synthon $[\text{Cp}_2\text{Ti}(\text{btmsa})]$ 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_2Tipp_2 (**2**) with $[\text{Cp}_2\text{Ti}(\text{btmsa})]$. In first reactivity studies we have shown that **3** can be utilized as a P_2R_2 -transfer reagent in transmetalation protocols using TippPCl_2 . This opens the pathway to generate new P_2R_2 -containing heterocycles.

Studies to further elucidate the reaction mechanism of the P_3Ar_3 degradation reaction are ongoing, to further investigate the nature of the paramagnetic intermediate. Additionally, application of the P_3Ar_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

- 1 H. Köhler and A. Michaelis, *Ber. Dtsch. Chem. Ges.*, 1877, **10**, 807.
- 2 J. J. Daly and L. Maier, *Nature*, 1964, **203**, 1167.
- 3 A. H. Cowley, T. A. Furtch and D. S. Dierdorf, *J. Chem. Soc., Chem. Commun.*, 1970, 523.



- 4 P. S. Elmes, M. E. Redwood and B. O. West, *J. Chem. Soc. D*, 1970, 1120.
- 5 M. Baudler, B. Carlsohn, W. Böhm and G. Reuschenbach, *Z. Naturforsch., B: Anorg. Chem., Org. Chem.*, 1976, **31**, 558.
- 6 M. Baudler, B. Carlsohn, B. Kloth and D. Koch, *Z. Anorg. Allg. Chem.*, 1977, **432**, 67.
- 7 M. Baudler and K. Glinka, *Chem. Rev.*, 1993, **93**, 1623.
- 8 W. Mahler and A. B. Burg, *J. Am. Chem. Soc.*, 1957, **79**, 251.
- 9 M. Baudler, J. Hahn and E. Clef, *Z. Naturforsch., B: Anorg. Chem., Org. Chem.*, 1984, **39**, 438.
- 10 M. Baudler and J. Hellmann, *Z. Naturforsch., B: Anorg. Chem., Org. Chem.*, 1981, **36**, 266.
- 11 P. Jutzi, N. Brusdeilins, H.-G. Stammer and B. Neumann, *Chem. Ber.*, 1994, **127**, 997.
- 12 P. Jutzi and N. Brusdeilins, *Z. Anorg. Allg. Chem.*, 1994, **620**, 1375.
- 13 W. Uhl and M. Benter, *J. Chem. Soc., Dalton Trans.*, 2000, 3133.
- 14 C. Üffing, C. v. Hänisch and H. Schnöckel, *Z. Anorg. Allg. Chem.*, 2000, **626**, 1557.
- 15 C. A. Dyker, N. Burford, G. Menard, M. D. Lumsden and A. Decken, *Inorg. Chem.*, 2007, **46**, 4277.
- 16 M. H. Holthausen, D. Knackstedt, N. Burford and J. J. Weigand, *Aust. J. Chem.*, 2013, **66**, 1155.
- 17 S. S. Chitnis, R. A. Musgrave, H. A. Sparkes, N. E. Pridmore, V. T. Annibale and I. Manners, *Inorg. Chem.*, 2017, **56**, 4521.
- 18 S. S. Chitnis, H. A. Sparkes, V. T. Annibale, N. E. Pridmore, A. M. Oliver and I. Manners, *Angew. Chem., Int. Ed.*, 2017, **56**, 9536.
- 19 R. Ahlrichs, D. Fenske, H. Oesen and U. Schneider, *Angew. Chem., Int. Ed. Engl.*, 1992, **31**, 323–326.
- 20 M. Baudler and M. Bock, *Z. Anorg. Allg. Chem.*, 1973, **395**, 37.
- 21 K. Schwedtmann, R. Schoemaker, F. Hennersdorf, A. Bauzá, A. Frontera, R. Weiss and J. J. Weigand, *Dalton Trans.*, 2016, **45**, 11384.
- 22 N. Tokitoh, A. Tsurusaki and T. Sasamori, *Phosphorus, Sulfur Silicon Relat. Elem.*, 2009, **184**, 979.
- 23 C. N. Smit, T. A. van der Knaap and F. Bickelhaupt, *Tetrahedron Lett.*, 1983, **24**, 2031.
- 24 L. Weber, D. Bungardt, R. Boese and D. Bläser, *Chem. Ber.*, 1988, **121**, 1033.
- 25 D. G. Yakhvarov, E. Hey-Hawkins, R. M. Kagirow, Y. H. Budnikova, Y. S. Ganushevich and O. G. Sinyashin, *Russ. Chem. Bull.*, 2007, **56**, 935.
- 26 X. Li, D. Lei, M. Y. Chiang and P. P. Gaspar, *J. Am. Chem. Soc.*, 1992, **114**, 8526.
- 27 K. B. Dillon, V. C. Gibson and L. J. Sequeira, *J. Chem. Soc., Chem. Commun.*, 1995, 2429.
- 28 B. M. Cossairt and C. C. Cummins, *New J. Chem.*, 2010, **34**, 1533.
- 29 S. Shah and J. D. Protasiewicz, *Chem. Commun.*, 1998, 1585.
- 30 P. Le Floch, *Coord. Chem. Rev.*, 2006, **250**, 627.
- 31 Experimental and computational details, and details on the X-ray diffraction studies are included in the ESI.†
- 32 K. S. A. Motolko, D. J. H. Emslie, H. A. Jenkins and J. F. Britten, *Eur. J. Inorg. Chem.*, 2017, 2920.
- 33 C. Frenzel and E. Hey-Hawkins, *Phosphorus, Sulfur Silicon Relat. Elem.*, 1998, **143**, 1.
- 34 J. D. Protasiewicz, *Eur. J. Inorg. Chem.*, 2012, 4539.
- 35 M. Yoshifuji, I. Shima, N. Inamoto, K. Hirotsu and T. Higuchi, *J. Am. Chem. Soc.*, 1981, **103**, 4587.
- 36 J. D. Protasiewicz, M. P. Washington, V. B. Gudimetla, J. L. Payton and M. C. Simpson, *Inorg. Chim. Acta*, 2010, **364**, 39.
- 37 T. Sasamori, N. Takeda and N. Tokitoh, *J. Phys. Org. Chem.*, 2003, **16**, 450.
- 38 P. Pykkö and M. Atsumi, *Chem.–Eur. J.*, 2009, **15**, 12770.
- 39 D. Dhara, D. Mandal, A. Maiti, C. B. Yildiz, P. Kalita, N. Chrysochos, C. Schulzke, V. Chandrasekhar and A. Jana, *Dalton Trans.*, 2016, **45**, 19290.
- 40 A. Aistars, R. J. Doedens and N. M. Doherty, *Inorg. Chem.*, 1994, **33**, 4360.
- 41 R. Appel and H. Schöler, *Chem. Ber.*, 1977, **110**, 2382.
- 42 S. S. Chitnis, A. P. M. Robertson, N. Burford, J. J. Weigand and R. Fischer, *Chem. Sci.*, 2015, **6**, 2559.
- 43 J. J. Weigand, N. Burford, A. Decken and A. Schulz, *Eur. J. Inorg. Chem.*, 2007, 4868.
- 44 A. P. M. Robertson, S. S. Chitnis, H. A. Jenkins, R. McDonal, M. J. Ferguson and N. Burford, *Chem.–Eur. J.*, 2015, **21**, 7902.
- 45 T. L. Breen and D. W. Stephan, *J. Am. Chem. Soc.*, 1995, **117**, 11914.
- 46 C. C. Cummins, R. R. Schrock and W. M. Davis, *Angew. Chem., Int. Ed. Engl.*, 1993, **32**, 756.
- 47 F. Basuli, J. Tomaszewski, J. C. Huffman and D. J. Mindiola, *J. Am. Chem. Soc.*, 2003, **125**, 10170.
- 48 G. Zhao, F. Basuli, U. J. Kilgore, H. Fan, H. Aneetha, J. C. Huffman, G. Wu and D. J. Mindiola, *J. Am. Chem. Soc.*, 2006, **128**, 13575.
- 49 T. Beweries, M. Haehnel and U. Rosenthal, *Catal. Sci. Technol.*, 2013, **3**, 18.
- 50 S. Xin, H. G. Woo, J. F. Harrod, E. Samuel and A.-M. Lebus, *J. Am. Chem. Soc.*, 1997, **119**, 5307.
- 51 S. Xin, J. F. Harrod and E. Samuel, *J. Am. Chem. Soc.*, 1994, **116**, 11562.
- 52 L. Weber, *Chem. Rev.*, 1992, **92**, 1839.
- 53 P. S. Elmes, M. L. Scudder and B. O. West, *J. Organomet. Chem.*, 1976, **122**, 281.
- 54 J. Chatt, P. B. Hitchcock, A. Pidcock, C. P. Warrens and K. R. Dixon, *J. Chem. Soc., Dalton Trans.*, 1984, 2237.
- 55 J. Ho, T. L. Breen, A. Ozarowski and D. W. Stephan, *Inorg. Chem.*, 1994, **33**, 865.
- 56 S. Kurz and E. Hey-Hawkins, *J. Organomet. Chem.*, 1993, **462**, 203.
- 57 M. Schaffrath, A. Villinger, D. Michalik, U. Rosenthal and A. Schulz, *Organometallics*, 2008, **27**, 1393.
- 58 M. Baudler, K. Glinka, A. H. Cowley and M. Pakulski, Organocyclophosphanes, in *Inorg. Synth.*, ed. H. R. Allcock, 2007.
- 59 J. R. Goehrich and R. Schmutzler, *Z. Anorg. Allg. Chem.*, 1994, **620**, 173.
- 60 H. Köpf and R. Voigtländer, *Chem. Ber.*, 1981, **114**, 2731.



- 61 A. T. Normand, Q. Bonnin, S. Brandès, P. Richard, P. Fleurat-Lessard, C. H. Devillers, C. Balan, P. Le Gendre, G. Kehr and G. Erker, *Chem.–Eur. J.*, 2019, **25**, 2803.
- 62 J. Pinkas, R. Gyepes, I. Císařová, J. Kubišta, M. Horáček, N. Žilková and K. Mach, *Dalton Trans.*, 2018, **47**, 8921.
- 63 M. Polášek and J. Kubišta, *J. Organomet. Chem.*, 2007, **692**, 4073.
- 64 X. Yan and C. Xi, *Acc. Chem. Res.*, 2015, **48**, 935.
- 65 T. Baumgartner and R. Réau, *Chem. Rev.*, 2006, **106**, 4681.

