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Precursors for the Development of π-Conjugated Low-Coordinate Phosphorus Compounds

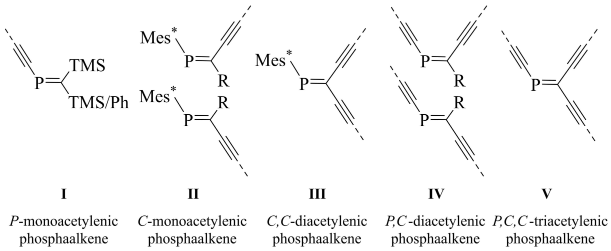
Keyhan Esfandiarfard, Anna I. Arkhypchuk, Andreas Orthaber, and Sascha Ott*[a]

The synthesis of a novel monomeric precursor and its butadiyne-bridged dimeric form for the preparation of novel π-conjugated organophosphorus compounds is presented. The precursors are synthesized from commercially available starting materials, and based on a Dmp (2,6-dimesitylphenyl) group for kinetic stabilization of the *P*-functionality, a bromo substituent for the introduction of the phosphorus center, and an acetylene unit at the *para* position of the Dmp moiety. Such acetylenic units are synthetically versatile, and can be explored for the construction of larger phosphorus-containing π-conjugates. The precursors are utilized to prepare Dmp-stabilized *C,C*-dibromophosphaalkenes, and butadiyne-bridged dimeric species thereof. The effect of the low-coordinate phosphorus centers and the extent of π-conjugation on the spectroscopic and electronic properties is evaluated by NMR and UV/Vis spectroscopy, as well as cyclic voltammetry. In addition to the phosphaalkenes, the successful syntheses of two new diphosphenes are presented, indicating a broad applicability of the precursor.

Introduction

Organophosphorus compounds are intriguing candidates for single molecule electronics or organic electronics applications as the phosphorous centers alter the electronic properties of appended π-conjugated systems.[1] At the same time, the inclusions of a phosphorus center in otherwise all-carbon scaffolds provides additional possibilities for subsequent synthetic manipulations.[2] Consequently, the design and exploration of new building blocks towards such compounds is of continued interest.

Examples of low-coordinate phosphorus compounds such as diphosphenes and phosphaalkenes with substituents at the phosphorus centers that both kinetically stabilize the compounds, while at the same time provide functional groups for further modifications, are limited.[3] The design of the precursors described herein was inspired by previous work on acetylenic phosphaalkenes. Such *P,C*-rich compounds have been reported by Appel and our group, and can be categorized into *P*-monoacetylenic (**I**),[4] *C*-monoacetylenic (**II**)[5] and *C,C*-diacetylenic (**III**)[6] structures. More elaborate *P,C*-diacetylenic (**IV**) and *P,C,C*-triacetylenic (**V**) phosphaalkenes have hitherto been synthetically elusive (Figure 1). The main reason is that a single acetylenic moiety at the *P*-center is insufficient in providing kinetic stabilization for the phosphaalkene when the *C*-center bears one or two acetylenic substituents at the same time.


TMS
TMS/Ph
P
Mes*
P
R
Mes*
P
R
Mes*
P
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R
P
R
P
I
II
III
IV
V
P-monoacetylenic phosphaalkene
C-monoacetylenic phosphaalkene
C,C-diacetylenic phosphaalkene
P,C-diacetylenic phosphaalkene
P,C,C-triacetylenic phosphaalkene

Figure 1. All possible forms of acetylenic phosphaalkenes. The phosphaalkenes of categories **IV** and **V** are synthetically elusive. Mes* = 2,4,6-^{t}Bu$_3$C$_6$H$_2$.

In order to overcome the stabilization problem, we decided to design a new phenyl-based stabilizing group with an acetylenic moiety at the *para* position relative to the *P*-center. With suitable bulky groups at the *ortho* positions, phosphaalkenes carrying this protection group would benefit from kinetic stability along with an acetylenic substituent that allows for further coupling chemistry. A Mes*-like group with two *ortho t*-Bu groups which would fulfill the criteria of kinetically stabilizing low-valent phosphorus compounds was however not further pursued due the lengthy pathway to a crucial starting material, 1-bromo-2,6-di-*t*-butylbenzene.[7] A *para*-acetylenic Dmp (=2,6-dimesitylphenyl) that is more readily available was targeted instead. Retrosynthetically, a bromo-substituted compound with a silyl protected acetylene moiety (**1$_{Br}$-Si**) seemed to be the most convenient synthetic target for our purpose (Figure 2). The iodo-analogue of **1$_{Br}$-Si** was deemed less suitable for the intended chemistry as the quantitative lithiation of **1$_I$-Si** has previously been found problematic,[8] resulting in difficulties in the purification process.

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Supporting information for this article is available on the WWW under https://doi.org/10.1002/cplu.202300067

Part of a Special Collection: "From Light to Heavy: Advancing the Chemistry of Pnictogen Compounds"

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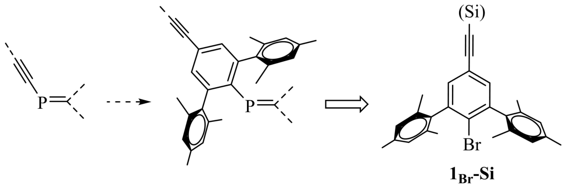
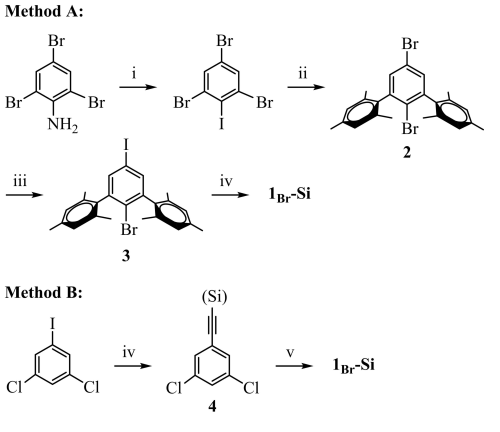


Figure 2. Design of the precursor 1_{Br}**-Si** suitable for the synthesis of π-conjugated low-valent phosphorus compounds; (Si) = silyl protecting group such as TMS or TIPS.

Results and Discussion

Previous work has shown that the direct bromination of the phenyl unit of the Dmp group is not possible and tetrabromination of the mesityl groups occurs instead, leaving the central phenyl ring unaffected.[9] A better strategy would then be to start the reaction sequence with a compound that already contains a bromide at its *para* position.

Two different methods towards 1_{Br}**-Si** were explored, both of which afford the desired precursor (Scheme 1). Method B was found more convenient as it is with fewer synthetic steps. For completion, both methods are described herein. As shown in Scheme 1, **Method A**[10] is based on the diazotization/iodination of the commercially available 2,4,6-tribromoaniline as the first step of the synthetic sequence. The Grignard reaction of the resulting 1,3,5-tribromo-2-iodobenzene with MesMgBr allows the incorporation of the mesityl groups on the molecule to form the *meta*-terphenyl **2**, upon quenching with Br_2. Compound **2** was unambiguously identified by single crystal structure analysis (see Supporting Information). A subsequent iodide-bromide exchange in position 4 gives *meta*-terphenyl **3** which can undergo a site-selective Sonogashira reaction to afford the desired compound 1_{Br}**-Si**. The selectivity in the final coupling step arises from the higher reactivity of the iodo-substituent and the greater steric accessibility compared to that of the bromide. In **Method B**, the selective Sonogashira coupling of 1,3-dichloro-5-iodobenzene affords the acetylene-substituted compound **4**.[11] Lithiation of **4** followed by the addition of MesMgBr, and subsequent quenching with Br_2 affords the desired 1_{Br}**-Si**.[12] Single crystals of 1_{Br}**-TIPS** were obtained by slow evaporation of an *n*-hexane solution (Figure 3). In the solid state, the two Mes groups are almost orthogonal to the central phenyl ring (twist of 88.7(3)° and 94.0(3)°) as expected. The opening bite angle of those flanking mesityl rings is around 121°.



Scheme 1. Synthesis of precursor 1_{Br}**-Si** via two different methods; (i) HCl, 0 °C, $NaNO_2$, H_2O, 30 min, KI, 1 h, 88 %. (ii) MesMgBr, THF, reflux, 16 h, 0 °C, Br_2, r.t., 2 h, 28 %. (iii) −78 °C, THF, BuLi, 1 h, I_2, −78 °C to r.t., 75 % (iv) $PdCl_2(PPh_3)_2$, CuI, NEt_3, (Si)-acetylene, THF, 1–2 h, 98 %. v) −78 °C, THF, BuLi, 1 h, MesMgBr, −78 °C to r.t., 16 h, reflux, 4 h, 0 °C, Br_2, 3 h. 1_{Br}**-TMS**: 35 %; 1_{Br}**-TIPS**: 43 %.

Deprotection of 1_{Br}**-Si** gives the acetylene 1_{Br}**-H** which can subsequently furnish the dimeric compound **5** via a Cu-catalyzed oxidative homocoupling reaction (Scheme 2). Compound **5** is a valuable precursor itself as it can, in theory, be used to make dimeric low-valent phosphorus compounds or even polymeric targets. Single crystals of **5** were obtained by slow crystallization from dichloromethane/acetone. The flanking Mes substituents are perpendicular to the central phenyl rings with a bite angle of 123.5(2)°, that is slightly wider compared to those in **2** (119.0°) and 1_{Br}**-TIPS** (121°). The diphenyl butadiene core is almost linear (C–C–C ranging from 175.3 to 178.8°), however the two phenyl end groups are rotated by ca. 80.1° relative to each other in the solid state (Figure 3).

Having precursors 1_{Br}**-Si** and **5** in hand, we decided to test their applicability for the preparation of low-valent phosphorus compounds, in the first instance diphosphenes. Symmetrical and unsymmetrical diphosphenes, mainly stabilized by Mes* or *meta*-terphenyl groups, have been reported in the literature during the last decades.[13] Symmetrical diphosphenes are

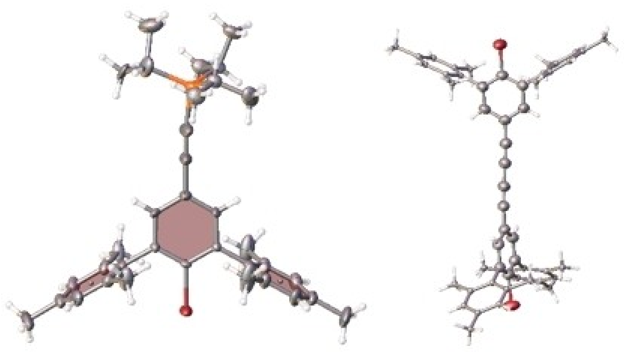
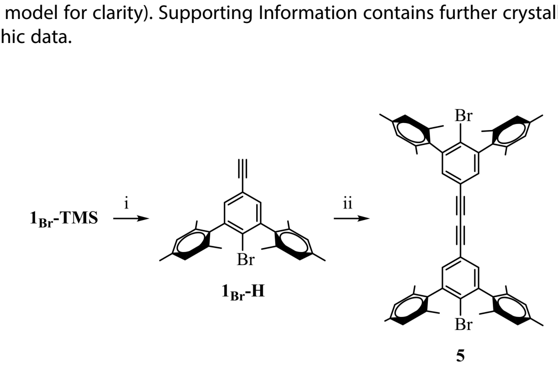


Figure 3. Solid state structure of 1_{Br}**-TIPS** (left) and **5** (right). Thermal ellipsoid plots at 50 % probability level. (The Mes groups in **5** are drawn as ball and stick model for clarity). Supporting Information contains further crystallographic data.

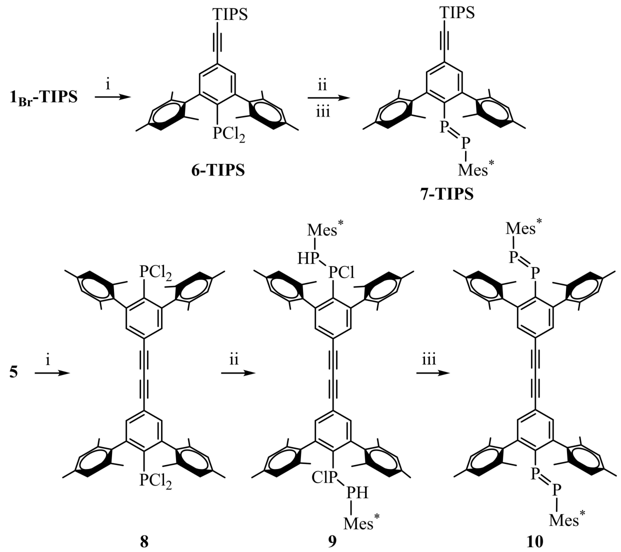


1_{Br}**-H**

5

Scheme 2. Synthesis of the dimeric precursor **5** from 1_{Br}**-TMS**. (i) THF/MeOH, r.t., K_2CO_3 or KOH, > 95 %. (ii) THF, 35 °C, $Cu(OAc)_2$, piperidine, 16 h, 91 %.

usually prepared by homocoupling of the corresponding dichlorophosphine in the presence of activated Mg (Mg*), while unsymmetrical diphosphenes are mainly obtained by the cross-coupling of a dichlorophosphine and a primary phosphine. An interesting synthetic target was an unsymmetrical diphosphene with a Mes* group on one *P*-centre and the designed para-acetylenic Dmp group on the other. Thus, lithiation of $\mathbf{1_{Br}}$**-TIPS** followed by quenching with PCl_3 gave the dichlorophosphine **6-TIPS** (Scheme 3). A solution of Mes*P(H)Li was prepared by the addition of BuLi to Mes^*PH_2 at −50 °C and added in situ to a solution of **6-TIPS** to form the P–P bond. Finally, addition of DBU and elimination of HCl led to the formation of diphosphene **7-TIPS**. The purification of **7-TIPS** by recrystallization from an acetonitrile/*n*-hexane solution afforded pure diphosphene, although in low yields. A highly π-conjugated "dimer" with two P=P termini was the next targeted compound. The dilithiation of precursor **5** followed by quenching with PCl_3 gave the bis(dichlorophosphine) **8**. The cross-coupling of **8** with two equivalents of Mes*P(H)Li resulted in the formation of intermediate **9** which could be converted to the desired bis(diphosphene) **10** by the DBU-promoted elimination of two equivalents of HCl. Unfortunately, attempts to isolate this compound failed due to decomposition during the purification process.



Scheme 3. Synthesis of diphosphene **7-TIPS** and bis(diphosphene) **10**. (i) −78 °C, THF, BuLi, 1 h, PCl_3, −78 °C to r.t., 16 h (ii) r.t., THF, Mes*P(H)Li, 1 h. (iii) r.t., DBU, 1 h. **7-TIPS**: 21 %; **10**: not isolated.

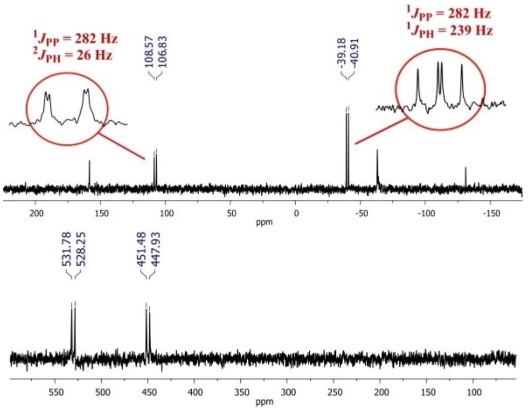
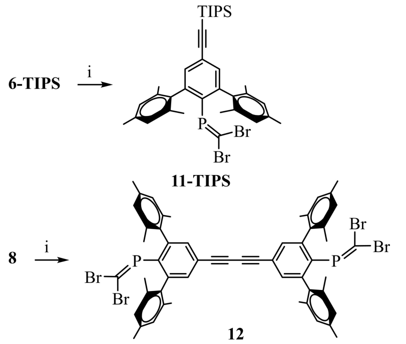


Figure 4. Monitoring the transformations to dimeric bis-diphosphene **10** (Scheme 3, *bottom*) by ^{31}P NMR spectroscopy. *Top:* H-coupled ^{31}P NMR showing the formation of intermediate **9**. *Bottom:* Full consumption of **9** and formation of the desired **10**.

The transformations depicted in Scheme 3 could however be monitored by ^{31}P NMR spectroscopy. The appearance of two distinct sets of doublets at 446 and 529 ppm with a coupling constant of 573 Hz confirms the successful synthesis of the desired diphosphene **7-TIPS**. In the second reaction, the full consumption of **8** with the disappearance of its singlet at 158 ppm is accompanied by the rise of two signals at −41 ppm and 108 ppm corresponding to the intermediate **9**. The H-coupled ^{31}P NMR (Figure 4) reveals two sets of doublet of doublets with different splitting patterns: one peak at −41 ppm with $^1J_{PP} = 282$ Hz and $^1J_{PH} = 239$ Hz assigned to P-*P*(H) and another peak at 108 ppm with $^1J_{PP} = 282$ Hz and $^2J_{PH} = 26$ Hz assigned to P-*P*(Cl). Transformation of these signals to two distinct doublets resonating at 450 and 530 ppm ($^1J_{PP} = 572.1$ Hz) confirms the successful synthesis of dimer **10**.

Next, *C,C*-dibromophosphaalkene products were targeted (Scheme 4) to further explore the chemistry of compounds $\mathbf{1_{Br}}$**-Si** and **5**. *C,C*-dibromophosphaalkenes are valuable precursors and have been widely used for the synthesis of many low-valent phosphorus compounds such as phosphaalkynes,[7,14] phosphaallenes,[15] phosphacumulenes,[16] or more elaborate phosphaalkenes.[17] These synthetic manipulations are expected to be applicable also on the *C,C*-dibromophosphaalkenes of $\mathbf{1_{Br}}$**-Si** and **5**. Consequently, such *C,C*-dibromophosphaalkenes are suitable precursors for the construction of "*P,C*-diacetylenic" or "*P,C,C*-triacetylenic" phosphaalkenes due to the presence of the bromo groups at the P=C and the *para*-acetylenic substituent of the Dmp. The reaction of **6-TIPS** with bromoform and two equivalents of LDA afforded, as expected, the desired dibromophosphaalkene **11-TIPS** (Scheme 4). Crystalline material suitable for X-ray structure elucidation was obtained by recrystallization from *n*-hexane solutions (Figure 5). The asymmetric unit contains two almost identical molecules of **2** with interesting methyl C–H···π non-covalent interactions (NCIs). The P=C bond



Scheme 4. Synthesis of *C,C*-dibromophosphaalkenes **11-TIPS** and **12** from their corresponding dichlorophosphine precursors **6-TIPS** and **8**. (i) −100 °C, THF, $CHBr_3$, LDA, −100 °C to r.t., 16 h **11-TIPS**: 42 %; **12**: 51 %.

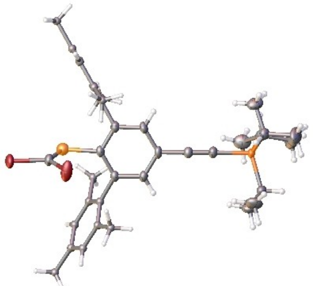


Figure 5. Solid state structure of **11-TIPS**. Thermal ellipsoid plots at 50 % probability level. Mes groups are drawn as ball and stick model for clarity. Only one of the two independent molecules is shown. Distances [Å] and angles [°]: P═C 1.660(4), C≡C 1.196(4), C–P═C 104.8(2). Supporting Information contains further crystallographic data.

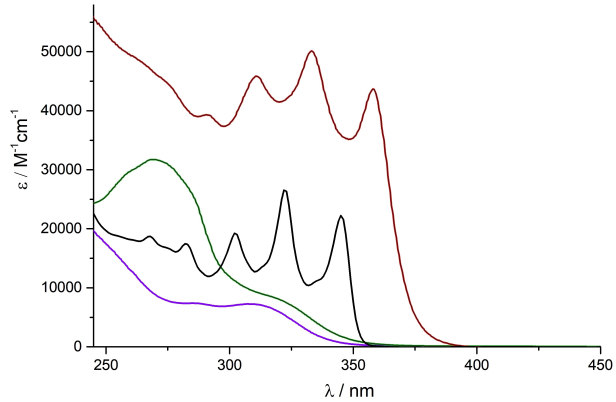


Figure 6. UV/Vis spectra of DmpP═CBr$_2$ (purple), bis(Dmp)butadiyne **5** (black), *C,C*-dibromophosphaalkenes **11-TIPS** (green) and **12** (red). All spectra were recorded for solutions of the analyte in CH$_2$Cl$_2$, 25 °C.

is in the expected range (1.660(4) and 1.557(3) Å). Unsurprising, the P═CBr$_2$ plane is almost orthogonal to the central phenyl ring of the Dmp motif (twist of 83.1° and 83.3°) due to the sterically demanding Mes substituents. The bite angle (125.2(1)°) is the widest within the series, also reflecting the increased size of the P═CBr$_2$ moiety compared to that of the Br-substituents in, for example, **5**.

In order to synthesize the dimeric phosphaalkene, two equivalents of bromoform and four equivalents of freshly-prepared LDA were added to a solution of bis(dichlorophosphine) **8** to give the pure dimer **12** in 51 % isolated yields. Single crystals, obtained of **12** were grown from a saturated *n*-hexane solution. Despite their poor quality, they could be used to confirm the connectivity between the atoms by X-ray crystallography (See Supporting Information for details).

NMR investigations – Signal broadening in the ^{1}H and ^{13}C NMR spectra of DmpP═CBr$_2$-type compounds is a frequently encountered feature,[9] and a similar spectroscopic behavior was also observed for *C,C*-dibromophosphaalkenes **11-TIPS** and **12**. Such a spectroscopic behavior stems from the restricted rotational freedom, as the mesityl rings of the Dmp group clash sterically with the –P═CBr$_2$ moiety. As a result, the *ortho*-methyl groups and *meta*-protons of the mesityl rings feature as two broad signals (see Supporting Information for details). Interestingly, such type of NMR behavior is absent in the spectra of similar *C,C*-dichlorophosphaalkenes,[18] indicating the influence of the size of the halogen.

UV/Vis investigations – UV/Vis absorption spectra of the synthesized *C,C*-dibromophosphaalkenes **11-TIPS** and **12**, bis(Dmp)butadiyne **5**, and previously reported monomeric phosphaalkenes DmpP═CBr$_2$[9] were recorded to investigate the effect of dimerization on the optical properties (Figure 6). As expected, the spectrum of dimeric **12** with the most extended π-system exhibits the most red-shifted absorptions of all the compounds. Interestingly, the fine structure that is observed in the lower energy part of the spectrum of **12** is also visible in that of precursor **5**, but at higher energy.

The electronic absorption spectra of DmpP═CBr$_2$ and **11-TIPS**, in contrast, are rather featureless, with the spectrum of **11-TIPS** showing a more intense band at 275 nm that is assigned to a π→π* transition on the acetylene extended Dmp. Apart from this difference, the longest wavelength absorption maximum of phosphaalkene DmpP═CBr$_2$ is quite similar to that of **11-TIPS**, indicating that a single acetylenic substitution on the Dmp group shifts this parameter only to a small extent.

Taken together, the similarities in shape of the spectra of **5** and **12** allow an assignment of the low-energy transitions in **12** to the common bis(Dmp)butadiyne portions of the compounds, but with contributions from the phosphaalkene portions which lead to the observed red-shift.

Cyclic voltammetry studies – Cyclic voltammograms of solutions of DmpP═CBr$_2$, *C,C*-dibromophosphaalkenes **11-TIPS** and **12** in CH$_2$Cl$_2$ are shown in Figure 7. No waves can be observed in the anodic scans, indicating that all oxidations occur at more positive potential than what is accessible within the solvent window. On the cathodic scans, irreversible reductions can be observed at a peak potential of −1.87, −2.07 and −2.13 V for **12**, **11-TIPS**, and DmpP═CBr$_2$, respectively. The CV of **5** (not shown) does not show a reduction within the solvent window, indicating that the redox features observed for **12**, **11-TIPS**, and DmpP═CBr$_2$ involve the phosphaalkene

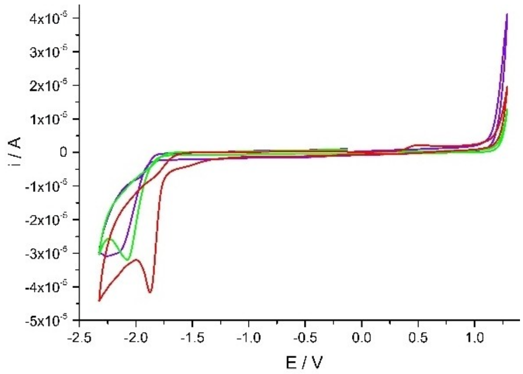


Figure 7. Cyclic voltammograms of DmpP═CBr$_2$ (purple),[9] and *C,C*-dibromophosphaalkenes **11-TIPS** (green) and **12** (red) (1 mM solutions of compounds in DCM, 0.1 M NBu$_4$PF$_6$, $\nu = 100$ mVs^{-1}, vs. Fc$^{+/0}$).

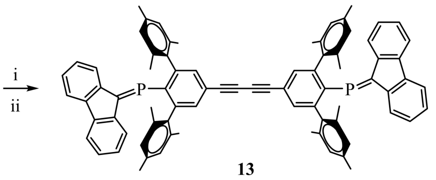
portions of the molecules. Moreover, the differences in reduction potential indicate that these processes are also impacted by the extended π-conjugated part of the compounds. As expected, dimeric phosphaalkene **12** with the largest π-system is easiest to reduce, followed by the extended acetylenic **11-TIPS**, and finally the unsubstituted DmpP=CBr$_2$.

In order to further investigate the communication between the two phosphorus centres in the dimeric compounds, a fluorene-containing analogue of **12** was synthesized. Compound **13** was prepared by adding a THF solution of lithiated fluorene to a solution of bis(dichlorophosphine) **8**, followed by the addition of DBU (Scheme 5). The bis-fluorene **13** was isolated in good yield (56%) simply by washing the crude reaction mixture with cold acetone and collecting the product by filtration.

Owing to the different *C*-substituents at the phosphaalkene portions of **12** and **13**, the ^{31}P NMR spectrum of compound **13** shows one signal at 249 ppm (C_6D_6, r.t.) that is shielded compared to that of dimer **12** (267 ppm). Unlike DmpP=CBr$_2$, **11-TIPS**, and **12** that exhibit no anodic waves in their CVs within the solvent window, the CV of **13** (Figure 8, *bottom*) shows an irreversible oxidation with a peak potential of 1.17 V. This higher HOMO level for **13** in comparison with those of the *C,C*-dibromophosphaalkenes is thus attributed to the fluorene cores of the compound. The cathodic scan shows two reductions at peak potentials of −1.88 and −2.12 V.

The first reduction is very close to that of dimer **12**, indicating that this process is localized at common portions of the molecules. The CV of compound **13** shows a certain degree of reversibility though when the cathodic scan is reversed at E = −1.90 V (Figure 8, *Top*). The half-wave potential deduced from this scan ($E_{1/2} = -1.81$ V) is considerably more positive than that of the previously reported Mes*P=C(fluorene) with $E_{1/2} = -1.99$ V,[19] suggesting that the lower-lying LUMO in **13** involves the butadiyne bridge. Interestingly, the $E_{1/2}$ of **13** at −1.81 V is identical to that of a Mes*-stabilized phosphaalkene with 2,7-diacetylenic fluorene substitution. This comparison reveals that the acetylenic extension on the "phosphorus side" of the P=C bond in **13** can have the same effect on the LUMO energy level as that imposed by the presence of acetylenes at the "carbon side" in the 2,7-diacetylenic fluorene phosphaalkene. In a more general outlook, highly π-conjugated systems with acetylenic substituents on both phosphorus and carbon sides of the P=C bond can be envisaged to tune LUMO levels in future compounds for organic electronics applications. Fabrication of such architectures is now possible with using the designed precursors reported in this work.

8



13

Scheme 5. Synthesis of bis(phosphaalkene) **13** from dichlorophosphine **8**. (i) −78 °C, THF, Fluorene-Li, 1 h. (ii) DBU, −78 °C to r.t., 1 h, 56%.

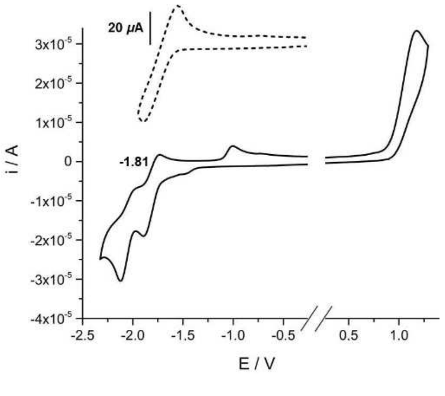


Figure 8. *Bottom:* Cyclic voltammogram of bis(phosphaalkene) **13** (1 mM solution in DCM, 0.1 M NBu$_4$PF$_6$, ν = 100 mVs^{-1}, vs. Fc$^{+/0}$). *Top:* Cathodic scan ν = 1.0 Vs^{-1} to E = −1.90 V showing the reversibility of the first reduction under these conditions.

Conclusion

In summary, we designed two precursors, **1$_{Br}$-Si** and **5**, which consist of three structural components: a Dmp-based stabilizing group, a bromo group which allows the incorporation of the P-centre, and a para-acetylene substituent that allows for further extensions of the structures through acetylene coupling reactions. Such precursors open up a variety of synthetic possibilities not only for low-coordinate phosphorus compounds but, in theory, also for compounds that contain other main group elements such as Si, As, Bi, etc. The dimeric precursor **5** is especially appealing as it can potentially be used to make polymeric targets. In the present work, compounds **1$_{Br}$-Si** and **5** were used to synthesize diphosphenes and phosphaalkenes. C,C-Dibromophosphaalkenes, **11-TIPS** and **12**, were synthesized and fully characterized including crystal structures of some of the key precursors. Owing to their para-acetylene and P=C(Br)$_2$ termini, the phosphaalkenes are suitable precursors for making acetylenic phosphaalkenes as well as other low-valent π-conjugated phosphorus compounds. The UV/Vis spectra show that the phosphaalkenes with the most elaborate π-system exhibit the smallest HOMO–LUMO gap, while CVs indicate that the reductions proceed mostly on the π-conjugated parts of the molecules. In addition to the developed C,C-dibromophosphaalkenes, we were able to synthesize two new unsymmetrical diphosphenes (**7-TIPS** and **10**), indicating a broad applicability of compounds **1$_{Br}$-Si** and **5**.

Experimental Section

Unless specified otherwise, all manipulations were carried out using standard Schlenk line or glovebox techniques, in order to exclude air and moisture. Glassware was flame-dried, diethyl ether, toluene, THF and pentane were freshly taken from solvent purification system under argon. Compounds **2**, **3** and **4** were prepared according to slightly modified literature procedures.[10–12] All analytical data were in agreement with the published values. NMR spectra were recorded on a JEOL (400YH magnet) Resonance

400 MHz spectrometer. Chemical shifts δ are reported in ppm and coupling constants J in Hz. ^{1}H NMR and ^{13}C NMR chemical shifts are referenced to the residual protic solvent signal and ^{31}P NMR spectra externally to 85% H_3PO_4(aq). High-resolution mass spectra (HR-MS) were recorded on a Thermo Scientific Orbitrap LTQ XL spectrometer.

Deposition Numbers 2238646-2238649 contain the supplementary crystallographic data for this paper. These data are provided free of charge by the joint Cambridge Crystallographic Data Centre and Fachinformationszentrum Karlsruhe Access Structures service.

Preparation of 1_{Br}-TMS (Method B) – MesMgBr was prepared in situ from the Grignard reaction of Mg (107.4 mmol, 2.6 g, 3 eq) and 1-bromomesitylene (93.1 mmol, 18.7 g, 2.6 eq) in THF (120 mL). To a solution of TMS-protected acetylene **4** (35.8 mmol, 8.7 g) in THF (100 mL) was added BuLi (2.5 M in hexanes, 14.3 mL, 1 eq) at −80 °C and the mixture was stirred for 1 h at the same temperature. The freshly-made Grignard reagent was then cooled to r.t. and added slowly to the lithiated solution via a cannula. The reaction mixture was stirred overnight and refluxed for 4 h afterwards. After cooling to 0 °C, bromine (3 eq) was added dropwise to the reaction mixture until it turned reddish. The reaction mixture was then stirred for 2 h to assure the completion of the reaction. THF was removed under reduced pressure and the residue was re-dissolved in pentane. White crystals of the product were obtained by slow evaporation of the solvent. The product was collected by filtration and obtained as a white solid in 35% yield. ^{1}H NMR ($CDCl_3$, 399.8 MHz): δ 7.24 (s, 2H), 6.94 (s, 4H), 2.33 (s, 6H), 2.00 (s, 12H), 0.23 (s, 9H). ^{13}C NMR ($CDCl_3$, 100.5 MHz): δ 143.1, 137.9, 137.5, 135.6, 132.7, 128.2, 127.0, 123.0, 104.2, 95.6, 21.3, 20.3, 0.0. HRMS: $C_{29}H_{33}BrSi$, $[M]^+$, calc. 490.15134, obs. 490.15125.

Preparation of 1_{Br}-TIPS – synthesized in analogy to **1_{Br}-TMS**, starting from TIPS-protected acetylene **4** (36.74 mmol, 12.0 g) to give the product as a white solid in 43% yield. ^{1}H NMR ($CDCl_3$, 399.8 MHz): δ 7.23 (s, 2H), 6.96 (s, 4H), 2.34 (s, 6H), 2.02 (s, 12H), 1.11 (s, 21H). ^{13}C NMR ($CDCl_3$, 100.5 MHz): δ 143.0, 138.0, 137.5, 135.7, 132.7, 128.2, 126.6, 123.5, 106.1, 92.0, 21.3, 20.4, 18.8, 11.4. HRMS: $C_{35}H_{45}BrSi$, $[M]^+$, calc. 574.24543, obs. 574.24576.

Preparation of the acetylene 1_{Br}-H – To a THF solution of **1_{Br}-TMS** (4.1 mmol, 2.0 g) was added a solution of K_2CO_3 (6.2 mmol, 0.86 g) in MeOH at room temperature. The reaction mixture was stirred for 2 h after which the volatiles were removed *in vacuo*. The product was extracted with Et_2O, washed with water and brine and dried over $MgSO_4$. Filtration and solvent removal afforded a white solid (1.7 g, 97%). ^{1}H NMR ($CDCl_3$, 399.8 MHz): δ 7.26 (s, 2H), 6.95 (s, 4H), 3.13 (s, 1H), 2.34 (s, 6H), 2.00 (s, 12H).

Synthesis of the dimer 5 – To a solution of **1_{Br}-H** (3.9 mmol, 1.6 g) in THF (150 mL) was added piperidine (3.9 mmol, 1 eq) and $Cu(OAc)_2$ (0.39 mmol, 78 mg, 10 mol%) at 35 °C. Air was bubbled into the solution for 1 h and the mixture was then left to stir overnight. THF was removed *in vacuo* and the residue was re-dissolved in DCM and washed with HCl(aq) (1 M), water and brine. The organic layer was dried over $MgSO_4$ and DCM was removed to give a crude product which was flash chromatographed (silica gel, pentane) to afford a white solid (1.5 g, 91%). ^{1}H NMR ($CDCl_3$, 399.8 MHz): δ 7.28 (s, 4H), 6.96 (s, 8H), 2.34 (s, 12H), 2.00 (s, 24H). ^{13}C NMR ($CDCl_3$, 100.5 MHz): δ 143.5, 137.7, 137.6, 135.6, 133.0, 128.3, 128.2, 121.6, 81.3, 75.0, 21.3, 20.3. HRMS: $C_{52}H_{48}Br_2Na$, $[M+Na]^+$, calc. 855.20011, obs. 855.20072.

Preparation of dichlorophosphine 6-TIPS – A solution of **1_{Br}-TIPS** in THF was lithiated at −78 °C by the addition of BuLi (2.5 M in hexanes, 1.1 eq) after which PCl_3 (2 eq) was added in one portion. The reaction was allowed to reach room temperature overnight. The volatiles were removed under reduced pressure using an extra cold trap to afford a white solid. The compound was used in subsequent steps without further purification. ^{31}P {^{1}H} NMR (C_6D_6, 161.8 MHz): δ 159.0.

Synthesis of diphosphene 7-TIPS – To a solution of **6-TIPS** (prepared from 0.6 mmol of **1_{Br}-TIPS**) in Et_2O (20 mL) was added a solution of freshly-made Mes*P(H)Li (0.6 mmol, 1 eq) in Et_2O (20 mL) at room temperature. After stirring for 40 min, the volume was reduced to half and DBU (1 M in THF, 1 eq) was added and the reaction stirred for 1 h until an orange color appeared. The precipitates were filtered off and the volatiles were removed from the filtrate to give an orange residue. The residue was dissolved in n-hexane and acetonitrile was added which resulted in the precipitation of a yellow solid. The precipitates were separated and washed with acetonitrile to afford the pure diphosphene **7-TIPS** in 21%. ^{1}H NMR ($CDCl_3$, 399.8 MHz): δ 7.24 (s, 2H), 7.15 (s, 2H), 6.84 (s, 4H), 2.28 (s, 6H), 2.10 (s, 12H), 1.25 (s, 9H), 1.11 (s, 21H), 0.97 (s, 18H). ^{13}C NMR ($CDCl_3$, 100.5 MHz): δ 153.6, 149.4, 146.9, 144.6, 138.5, 137.1, 135.8, 132.6, 128.8, 128.2, 124.5, 122.3, 106.9, 91.7, 38.2, 34.8, 33.9, 31.4, 21.6, 21.2, 18.8, 11.5. ^{31}P {^{1}H} NMR (C_6D_6, 161.8 MHz): δ 529.1 (d, $^1J_{PP} = 573.2$ Hz, Mes*$\underline{P}$), 446.3 (d, Dmp-$\underline{P}$).

Preparation of the bis-dichlorophosphine 8 – A solution of **5** (1.0 mmol, 0.83 g) in THF (80 mL) was di-lithiated with BuLi (2.5 M in hexanes, 0.88 mL, 2.2 eq) at −78 °C and stirred for 1 h. PCl_3 (4.4 mmol, 0.38 mL, 4.4 eq) was added quickly to the solution and the mixture was allowed to reach room temperature overnight. THF and excess of PCl_3 were removed under reduced pressure using a cold trap. The resulting residue was used for the next step without any further purification. ^{31}P {^{1}H} NMR (C_6D_6, 161.8 MHz): δ 158.9.

Synthesis of bis-diphosphene 10 – The same procedure as for **7-TIPS** was used starting with bis-dichlorophosphine **8** (0.8 mmol) prepared as described above, with this difference that *two* equivalents of Mes*P(H)Li and DBU were added in this case. The desired dimeric diphosphene was formed as an orange oil. ^{31}P {^{1}H} NMR (C_6D_6, 161.8 MHz): δ 530.1 (d, $^1J_{PP} = 572.1$ Hz, Mes*-$\underline{P}$), 449.7 (d, Dmp-$\underline{P}$).

Synthesis of *C,C*-dibromophosphaalkene 11-TIPS – To a solution of **6-TIPS** (prepared from 1.74 mmol of **1_{Br}-TIPS**) in THF (100 mL) was added bromoform (1.9 mmol, 1.1 eq). Freshly-prepared LDA (3.48 mmol, 2 eq) was added dropwise to the reaction solution at −78 °C and the reaction was allowed to reach room temperature overnight. Volatiles were removed *in vacuo* to afford a yellow residue. The residue was dissolved in pentane and the organic phase was washed with $HCl_{(aq)}$ 1 M, water and brine and dried over $MgSO_4$. Pentane was evaporated to give a concentrated solution. Slow evaporation of pentane afforded white-yellow crystals which were washed with acetonitrile and cold pentane to afford the product as a white solid in 42% yield. ^{1}H NMR ($CDCl_3$, 399.8 MHz): δ 7.28 (s, 2H), 6.93 (broad s, 4H), 2.32 (s, 6H), 2.16 (broad s, 12H), 1.12 (s, 21H). ^{13}C NMR ($CDCl_3$, 100.5 MHz): δ 144.6 (d, $^1J_{CP} = 7.7$ Hz), 142.7 (d, $^1J_{CP} = 44.6$ Hz), 137.6, 136.1, 132.8, 129.0 (broad s), 128.1, 127.3, 125.7, 106.5, 93.05, 21.5 (broad s), 21.3, 18.8, 11.5. ^{31}P {^{1}H} NMR ($CDCl_3$, 161.8 MHz): δ 269.0. HRMS: $C_{36}H_{45}PBr_2SiNa$, $[M+Na]^+$, calc. 719.12702, obs. 719.12828.

Synthesis of the dimeric phosphaalkene 12 – Bis-dichlorophosphine **8** (1.0 mmol) was dissolved in THF (20 mL) and bromoform (2.1 mmol, 0.18 mL, 2.1 eq) was added. The solution was cooled to −100 °C after which freshly-prepared LDA (4 mmol, 4 eq) was added dropwise. The mixture was allowed to reach room temperature overnight. THF was removed under vacuum and the organic phase was extracted with DCM, washed with HCl(aq) (1 M), water and brine and dried over $MgSO_4$. White crystals of the product (0.56 g, 51%) were obtained from a concentrated hexane solution of the crude product in the freezer. ^{1}H NMR ($CDCl_3$, 399.8 MHz):

δ 7.33 (s, 4H), 6.92 (broad s, 8H), 2.32 (s, 12H), 2.16 (broad s, 24H). ^{13}C NMR ($CDCl_3$, 100.5 MHz): δ 145.0 (d, $^1J_{CP}=7.8$ Hz), 144.3 (d, $^1J_{CP}=45.8$ Hz), 137.8, 135.8, 133.2, 129.1 (broad s), 128.3, 127.4, 123.8, 82.0, 75.6, 21.3 (broad s), 21.2. ^{31}P {^{1}H} NMR ($CDCl_3$, 161.8 MHz): δ 267.4.

Synthesis of the dimeric phosphaalkene 13 – Commercially available fluorene was lithiated with BuLi (2.5 M in hexanes, 0.25 mL, 2.1 eq) at −78 °C and stirred for 1 h. This solution was slowly added to a solution of bis(dichlorophosphine) **8** (0.3 mmol) in THF (30 mL) and stirred for 1 h, followed by the addition of DBU (2.2 eq). The reaction was allowed to reach room temperature and was stirred for 1 more hour. All the volatiles were removed and the organic phase was extracted with DCM and washed with HCl (1 M), water and brine. The solvent was removed under reduced pressure and cold acetone was added to the resulting residue. The solids were collected by filtration, and washed with cold acetone several times to afford the pure dimer **13** as a yellow solid (56 %). ^{1}H NMR ($CDCl_3$, 399.8 MHz): δ 7.71 (m, 2H), 7.53–7.43 (m, 8H), 7.21 (m, 4H), 7.04 (t, $J=7.49$ Hz, 2H), 7.00–6.90 (m, 4H), 6.83 (s, 4H), 6.67 (s, 4H), 2.20 (s, 12H), 2.17 (s, 12H), 1.94 (s, 12H). ^{13}C NMR ($CDCl_3$, 100.5 MHz): δ 175.3 (d, $^1J_{CP}=42.5$ Hz), 146.3, 143.2, 142.8 (d, $J_{CP}=17.4$ Hz), 139.4 (d, $J=10.1$ Hz), 138.0 (d, $J_{CP}=13.9$ Hz), 137.2 (d, $J_{CP}=8.9$ Hz), 136.9 (d, $J_{CP}=17.4$ Hz), 136.4, 135.7, 133.1, 129.5, 129.2 (d, $J_{CP}=5.2$ Hz), 128.7, 128.6, 126.7, 126.1, 123.1, 120.8 (d, $J_{CP}=23.4$ Hz), 119.3, 119.1, 82.3, 75.3, 21.4, 21.3, 21.0. ^{31}P {^{1}H} NMR ($CDCl_3$, 161.8 MHz): δ 251.2. HRMS: $C_{78}H_{64}P_2Na$, $[M+Na]^+$, calc. 1085.43755, obs. 1085.43776.

Acknowledgements

The Swedish Research Council (grant no. 2015-04640) is gratefully acknowledged for financial support, and Michelle Bedin for his help with the UV/Vis and CV measurements.

Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available in the supplementary material of this article.

Keywords: carbon-rich materials · diphosphenes · main group elements · phosphaalkenes · protecting groups

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Manuscript received: February 1, 2023
Revised manuscript received: March 20, 2023