Reversible Metal-Mediated Molecular Switching of a Phosphaethene Polyaromatic Hydrocarbon

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This experimental and theoretical study illustrates how phosphaalkenes, which are isolobal to alkenes, can utilize a variety of external triggers for molecular switching. The E/Z isomerization of a truxene-based phosphaalkene, i.e. TruxC=P-Mes* (Mes*=2,4,6-tris-t-butyl-benzene), is accomplished by irradiation, metal coordination, or deprotonation of the truxene core. The reversible and quantitative Z/E double bond isomerization by gold(I) coordination/decoordination of the phosphorous lone pair represents a novel fuelling strategy for molecular switches.

Introduction

Molecular switches are compounds able to interconvert reversibly between a stable and one or more metastable forms by means of external stimuli.[1–3] One of the key reactions at the heart of molecular switches is the E/Z isomerization of unsaturated bonds, with reports dating back to the beginning of the 1900s.[4–5] Consequently, substituted alkenes,[6–8] imines,[9] or azo motifs[2,10–11] have been studied extensively both for the fundamental and the applicative consequences linked to the large molecular motion of the associated substituents and the different properties of the isomers. Well-established triggers used for these processes are either light or electrochemistry.[12]

Recently, the introduction of a peripheral phosphorus center allowed for a unidirectional biaryl rotation via the Appel reaction, i.e. interconversion of the phosphine oxide to a phosphonium substituent.[13] However, systematic studies regarding the direct incorporation of a heavier pnictogen into the isomerizing bonds are significantly less explored. E/Z isomerization of diphosphenes (R–P=P–R), i.e., heavier analogs of azo compounds, remained almost unexplored due to their inherent instability.[14–16] Only recently, a highly selective photo- and side-on gold(I) coordination-induced isomerization of a diphosphene

has been described by Li et al.[17] The diverse chemistry of main group motifs and transition metal-containing fragments has inspired a variety of molecular switches.[18–19]

Already in 1984, the first photoisomerization of an E-phosphaalkene (**A**) was reported to give a mixture of thermally stable E- and Z-isomers (Figure 1).[20] Further reports on photochemical isomerization of the C=P bond substantiate the isolobal relationship between phosphaethenes – or more generally of heavier pnictaethenes – and alkenes, despite notable dissimilarities.[20–21] In other cases, the E/Z isomerization is reported to be triggered at room temperature in the absence of light (E-/Z-**B**, Figure 1).[22] A completely different stimulus promoting the isomerization of a C-aryl phosphaalkenes is (acidic) silica, i.e., the stationary phase of column chromatography.[23] A more complex behavior was described by Gates et al., showing that the metastable isomer of phosphabutadienes could be populated either through light irradiation or reaction with n-BuLi. Interestingly, the compounds underwent irreversible gold(I)-mediated cyclo-isomerization.[24–25]

Further skeletal rearrangements involving phosphaalkenes have been observed for a variety of transition metals.[26–30] On the other hand, triphospha-radialene maintains the integrity of the phosphaalkene, but gives a complex photo-isomerization chemistry when coordinated by or in the presence of transition metal carbonyl fragments.[31] These examples illustrate that the

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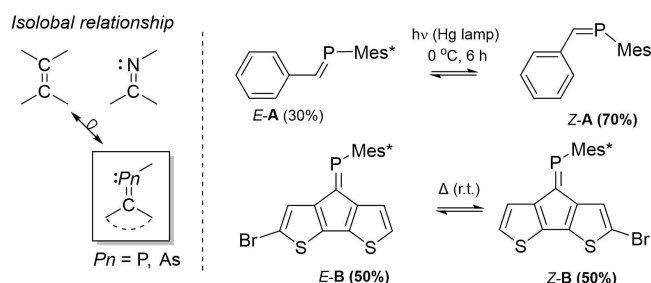Joseph Black Building, David Brewster Road, Edinburgh, UK

Figure 1. Unsaturated organic motifs at the core of molecular switches, highlighting the diagonal relationship of phosphorous & the heavier pnictogens and carbon (left); previous examples of photo- and thermal isomerization of P=C bonds (right).[21,22]

phosphaalkene moiety is highly susceptible to external triggers such as light or metal coordination.

In this communication, we report how the pnictogen lone pair of phosphaalkenes can be utilized via gold(I) coordination to trigger selective and quantitative inversion of the stereochemistry at the phosphaalkene of an ambiently stable truxene-based heteroalkene derivative.

Results and Discussion

As reported previously, the functionalization of truxene (TruxH$_6$) was achieved by a multi-step one-pot procedure to give the monosubstituted phosphaalkene as a single stereoisomer (Z-**P1**). However, upon further functionalization, the configuration of the P=C bond was inverted in its trisubstituted congener (E,E,E-**P3**), which triggered our interest (Figure 2 top).[32]

In order to further investigate this intriguing behavior of monofunctionalized truxenes, we prepared an arsenic analog (**As1**) and a tri-t-butylated phosphorus congener (**P1^{tBu}**) exploring how different pnictaalkene and substitution of the organic core impacts the geometric and electronic properties. The former, **As1**, requires in-situ formation of Mes*AsCl$_2$ to avoid the known arsaindole side reaction.[33] Despite the reduced number of steps in the synthesis of **P1^{tBu}**, the final product was only obtained in low yields (7% based on ^{tBu}TruxH$_6$), presumably due to the electron-donating substituents. Further synthetic details can be found in the supporting information. Interestingly, these derivatives are selectively formed as the E-pnictaalkenes (E-**As1** and E-**P1^{tBu}**), identified by single crystal X-ray diffraction and detailed NMR investigations (vide infra and Figure S14 & S27, SI).
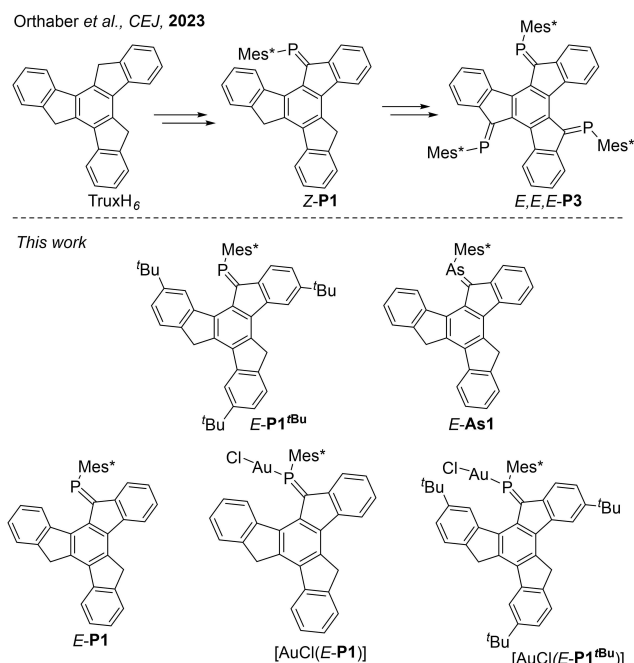
-In contrast, gold coordination gives a strong shift to lower frequencies. Derivative Z-**P1** cleanly converts into [AuCl(E-**P1**)], δ(^{31}P) of 180.6 ppm with inversion of the double bond geometry (vide infra). On the other hand, gold coordination to E-**P1^{tBu}** without double bond isomerization is evidenced by ^{31}P- and ^{1}H-NMR spectroscopy. The ^{31}P-NMR chemical shift of 174.5 ppm [AuCl(E-**P1^{tBu}**)], which is ca. 6 ppm more shielded than [AuCl(E-**P1**)] indicates a noticeable impact of the t-butyl groups on the metal coordination. Interestingly, gold(I) coordination to E-**As1** was unsuccessful, which is in line with the further increased s-character of the heavier pnictogen lone pair, rendering it less accessible to metal coordination.[34]

The higher affinity of gold complexes with tertiary phosphines than those with phosphaalkenes can be utilized for selective decomplexation.[35] The full sequence of coordination and decoordination induced switching is performed on NMR scales and monitored by ^{31}P{^{1}H}-NMR experiments. Quantitative complexation of Z-**P1** (δ^{31}P = 266.9 ppm) is evident from a shielded resonance at 180.6 ppm attributed to [AuCl(E-**P1**)]. Addition of 0.5 equiv. of PPh$_3$ leads to clean decomplexation and formation of Z-**P1** and [AuClPPh$_3$] (δ^{31}P = 33.4 ppm), which have distinct signals from the non-consumed [AuCl(E-**P1**)]. Full conversion is achieved using exactly one equivalent of the tertiary phosphine. Identical decomplexation is achieved using trialkylphosphine PMe$_3$, albeit more challenging to control exact equivalents due to its low boiling point (Figure 3a, R=Me or Ph). To the best of our knowledge, the herein-reported metal (de-) coordination-based switching of P=C double bonds is unprecedented. Attempts to recover and reuse the "AuCl" fragment in further switching cycles by exploiting the low reactivity of phosphaalkenes to nucleophiles (e.g. MeI) and the selective quaternization of the tertiary phosphine fragment have proven unsuccessful.
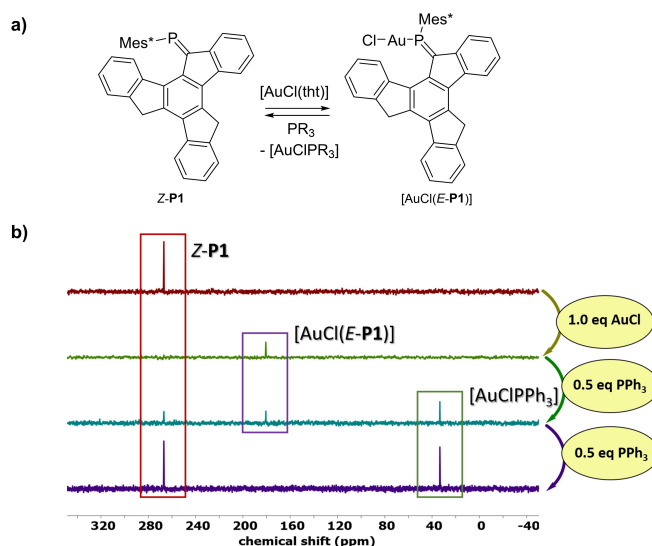

Figure 2. Top: Previous work on the synthesis of E,E,E-**P3** via Z-**P1**. Bottom: Pnictaalkenes and their gold(I) chloride complexes reported in this work.

Figure 3. a) Switching of the phosphaalkene moiety between Z-**P1** and [AuCl(E-**P1**)] by reversible coordination of an AuCl fragment. R=Me, Ph. b) Isomerization followed by ^{31}P{^{1}H}-NMR (ordered top to bottom): Z-**P1** followed by addition of 1.0 eq. AuCl, 0.5 eq. PPh$_3$ and 0.5 eq. PPh$_3$, respectively.

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Theoretical studies of the thermal and metal-triggered isomerization proceed via a biradical transition state where the C≡P bond is broken (see Figure S29). The isomerization barriers that we calculated ($\Delta G^{\ddagger} = 29.2$ kcal mol^{-1}) confirm the thermal bistability of the ligand and gold complexes. A detailed investigation of the PES for the free ligands and gold complexes of [AuCl(**P1**)] confirms the selectivity towards [AuCl(*E*-**P1**)] (see Figure S30). On the other hand, we have been unable to identify thermodynamic reasons for a preferential *Z*-**P1** formation in the free-ligand, which is 5.0 kcal/mol less stable than *E*-**P1**, based on our calculations.

From the UV–vis absorption spectra in Figure 4a, it is evident that substitution of the truxene core with *t*-butyl group did not affect the absorption behavior of the monophosphaalkene. Compounds *Z*-**P1**[32] and *E*-**P1**^{tBu} have almost superimposable absorption spectra with a maximum absorption at 427 nm. Arsenic derivative **As1** on the other hand shows a prominent red-shifted low energy absorption ($\lambda_{max} = 461$ nm), which is expected for the replacement of the phospha- by an arsaalkene moity. A very common way to tune the optical properties of pnictaalkenes significantly is achieved by functionalization of the pnictogen lone pair via coordination with a linear AuCl fragment.

[AuCl(*E*-**P1**)] and [AuCl(*E*-**P1**^{tBu})] show significantly further red-shifted absorption maxima at 480 nm and 486 nm, respectively, attributable to the acceptor nature of the AuCl fragment, giving a noticeable color shift from orange to red (Figure 4b). The metal coordination of **P1** results in an even more red-shifted low-energy band than *E*-**As1**.

As described previously, some phosphaalkenes are also prone to photochemical isomerization. Hence, we also investigated light-induced isomerization for this series of truxene-based pnictaalkenes. Irradiation of *Z*-**P1** in an NMR experiment (in C$_6$D$_6$) at 395 nm leads to a photostationary state (PSS) with ca. 15% of the *E*-isomer (δ^{31}P for *E*-**P1** = 272.9 ppm) being present based on ^{31}P{^{1}H}- and ^{1}H-NMR analysis (see Figures 4c, S5, S6). Irradiation with different light sources (395 nm and 455 nm) yielded similar PSSs, while extended irradiations led to untraceable decomposition products. Back isomerization to give the *Z*-**P1** isomer was studied at room temperature and 75 °C, which showed a complete conversion after 6 days at elevated temperature, and no change at room temperature (see Figures S11, S12). This reaction was also investigated by UV–Vis spectroscopy. Irradiation of *Z*-**P1** in DCM at 25 °C with 395 nm shows minute changes in the optical properties and clean
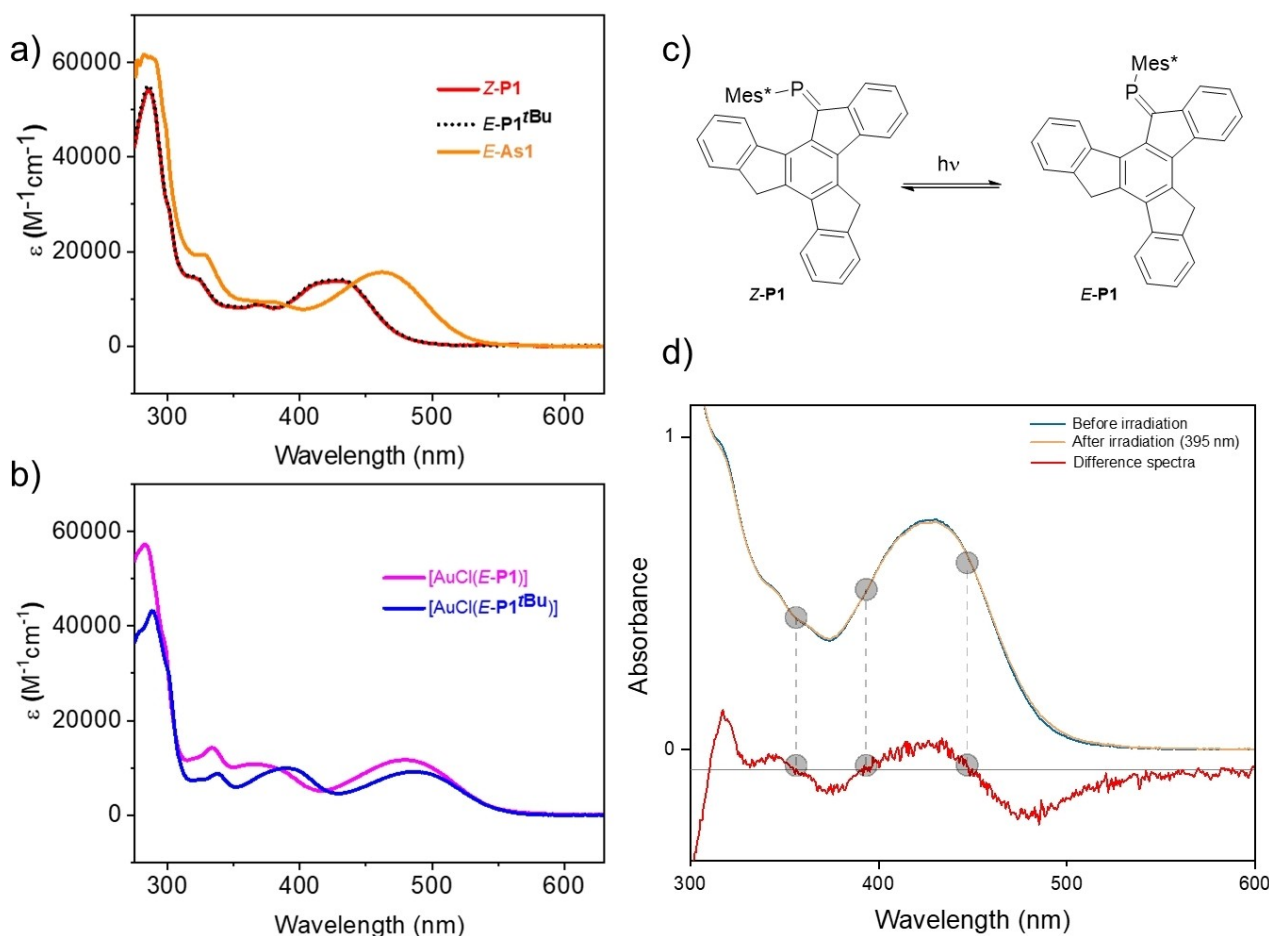

Figure 4. UV–Vis absorption spectra in chloroform a) *Z*-**P1**, *E*-**P1**^{tBu}, *E*-**As1**, b) [AuCl (*E*-**P1**)] and [AuCl(*E*-**P1**^{tBu})]. c) Photochemical *E/Z*-isomerization of **P1**. d) *Z*-**P1** in DCM (19.7 μM) at 25 °C before (blue) and after 395 nm irradiation (orange) for 10 min reaching a photostationary state (PSS); difference in absorbance after irradiation (red, rescaled).

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isomerization, as evidenced by the isosbestic points at 355 nm, 392 nm, and 449 nm (Figure 4d).

The low conversion to the metastable isomer can be attributed to the fact that the absorption features of the two isomers are very similar, which also explains the partial photochemical conversion. The thermal stability at room temperature is consistent with a large isomerization barrier for the P=C ($\Delta G^{\ddagger} = 29.2$ kcal mol^{-1}, see above).

These findings indicate that metal interaction as well as excitation leads to a temporarily reduced double bond strength via population of $\pi(P=C)$*-fulvenoid antibonding orbitals, which facilitates the isomerization at room temperature.

Crystallographic Studies

Single crystals have been obtained for *E*-**P1** (from the bulk irradiation experiments); *E*-**As1** (from the crude product), and [AuCl(*E*-**P1**)] (by slow evaporation from a saturated solution).[36] Crystal structure analysis shows that *E*-**As1** displays the same pnictaalkene configuration as observed in *E*-**P1** with a typical carbon phosphorus and carbon arsenic double bond distance of 1.693(2) Å and 1.814(3) Å, respectively (Figure 5).[37–38] Notably, upon gold coordination, the phosphaalkene double bond inverts and gives [AuCl(*E*-**P1**)]. The PC distance of 1.678(3) Å is slightly shorter compared to the uncoordinated *E*- and *Z*-isomers (*Z*-**P1** (1.695(2) Å), clearly showing that the reduced double bond character can occur only transiently during the coordination/decoordination process. The C—P=C angles are very similar for [AuCl(*E*-**P1**)]: 112.6(1)^0 and *Z*-**P1**: 111.2(1)^0), while the C—P=C angle in *E*-**P1** and *E*-**As1** is significantly reduced 105.7(1)^0 and 103.7(1)^0, respectively. In the previously described *Z*-**P1** structure, discrete dimeric motifs form a prominent cavity (centroid distance 4.186(1) Å).[32] A similar dimeric motif with a discrete cavity is also observed in [AuCl(*E*-**P1**)], with centroid distances of 3.695 Å, while *E*-**P1** and *E*-**As1** are better described as slipped columnar stacks. A notable difference in this series is the orientation and distortion of the aromatic plane of the Mes* and the two almost co-planar indenyl fragments. For all neutral *E*-isomers (*E*-**As1**, *E*-**P1**, and [AuCl(*E*-**P1**)]), this angle is in the range of 59.5° to 64.0°. However, it is significantly smaller in the case of *Z*-**P1** (38.6°), indicating a large influence on the

contortion of the entire system. Both stacking and orientation of the Mes* substituent is also reflected in the differently contorted truxene cores, which are highly relevant for these systems to achieve the observed structural and geometrical diversity.

Based on our previous observations, we hypothesized that the formation of anionic motifs is also related to the *E/Z*-isomerization of the phosphaalkene bond. To study this behavior, we reacted *Z*-**P1** with KC$_8$, giving a dark lustrous material (Figure 6). The high reactivity of this species precluded detailed characterization; however, single crystals were obtained from a saturated THF/pentane solution. The solid-state structure revealed the formation of a dianionic truxene derivative [K$_2$(18-crown-6)$_2$(*E*-**P1**)]. The compound crystallizes in the orthorhombic space group P2$_1$2$_1$2$_1$ with two independent molecules in the asymmetric unit (Figure 6). The potassium cations show strong potassium-π interactions at K—C distances ranging from 3.0 to 3.5 Å with the unsubstituted truxene arms, with η^2, η^4, and η^5 coordination at the bay and "cyclopentadienide" parts, respectively. The coordination environment of each K$^+$ is fully saturated with an 18-crown-6 molecule. Most notably, the P=C bond has been inverted and is represented as an (*E*-**P1**)$^{2-}$ motif. However, the bond distances of 1.704(3) and 1.696(3) Å are in the typical double bond range (e.g. [AuCl(*E*-**P1**)] 1.678 Å and *Z*-**P1** 1.695), indicating only a minor population of antibonding orbitals involving the phosphaalkene π* fragment and the dominant contribution from the carbon centers of the deprotonated methylene groups.

Conclusions

In conclusion, we reported complexation and decomplexation-fuelled isomer switching of a phosphaalkene, *Z*-**P1** with AuCl. Upon UV irradiation, a mixture of *E/Z*-**P1** (PSS 15:85) was observed. However, the absence of back isomerization at room temperature suggests the existence of a substantial kinetic barrier for the thermal processes. The facile isomer switching behavior assisted by changes in the P=C bond strength by metal coordination or irradiation is also plausible for the dianionic truxene derivative [K$_2$(18-crown-6)$_2$(*E*-**P1**)]. Our design opens up entirely new avenues to further explore contorted
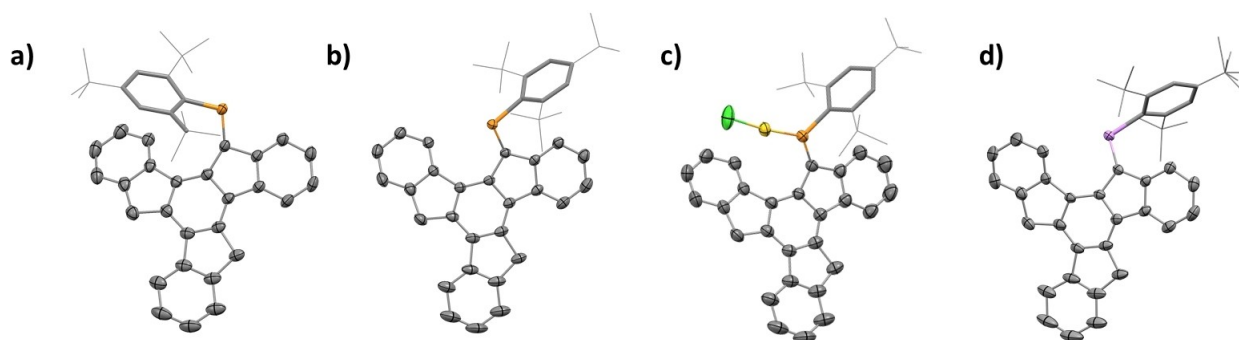
Figure 5. Solid-state structures of a) *Z*-**P1**,[32] b) *E*-**P1**, c) [AuCl(*E*-**P1**)] and d) *E*-**As1**. Thermal ellipsoids are plotted at a 50% probability level. Hydrogen atoms are omitted and the *t*-Bu groups are drawn as wire frames for clarity. Further crystallographic details can be found in the SI.
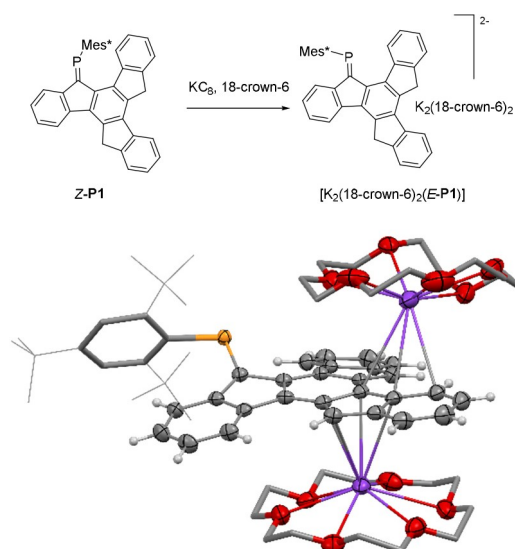
Figure 6. Synthesis and solid-state structure of [K$_2$(18-crown-6)$_2$(E-**P1**)]. Only one of the independent molecules of the unit cell is shown. Thermal ellipsoids are plotted at a 50% probability level.

scaffolds that exploit the unique coordinating properties of the lone pair at the phosphorus center. It is worth pointing out that the gold-mediated switching can be followed thanks to two readout parameters: the substantial ^{31}P-NMR shift difference and the hypso-/bathochromic shifted UV–Vis absorption upon de-/complexation, a property that is immediately recognizable even by visual inspection. Future studies will focus on understanding the substituent effects on the ligand structure, and unravelling why metal coordination and irradiation did not show any switching behavior in the case of the *t*-butyl substituted phosphaalkene, E-**P1**^{tBu}.

Supporting Information

The authors have cited additional references within the Supporting Information.[39,40–53]

Conflict of Interests

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.

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