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## Heavier group 15 elements: a new frontier in molecular switch development

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Molecular switches—compounds capable of reversibly interconverting between distinct states in response to external stimuli—are foundational to the design of dynamic functional materials. Classical switches based on carbon and lighter pnictogen frameworks, such as stilbenes, azobenzenes, and imines, have long dominated the field owing to their well-defined photophysical properties, synthetic accessibility, and reversible *E/Z*-isomerization or related transformations. In recent years, significant efforts have been devoted to designing molecular switches incorporating main-group elements—not only to harness the unique attributes of these elements in expanding the frontier of stimuli beyond light and heat, but also to unlock novel mechanistic pathways. In this context, heavier group 15 elements—particularly phosphorus—have emerged as promising platforms for designing responsive molecular frameworks. Advances over the past decade in the synthesis and stabilization of unsaturated phosphorus species—including phosphalkenes ( $P=C$ ), diphosphenes ( $P=P$ ), their heavier analogues ( $E=E$ ,  $P=E$ ;  $E = Sb, Bi$ ), a variety of hypervalent phosphorus compounds, and phosphorus-based (di)radicals—have opened new opportunities in this field. These systems are not limited to classical photo- or thermally induced *E/Z* isomerization, but also respond to alternative triggers such as metal coordination, redox inputs, and chemical stimuli. Moreover, reactivity modes such as tautomerism, ligand rearrangement, and conformational dynamics provide further avenues for structural interconversion, enriching the scope of pnictogen-based molecular motion. Building upon the well-established paradigms of  $C=C$ ,  $N=N$ , and  $C=N$ -based switching systems, this Perspective highlights the evolution and future potential of heavier pnictogen-based molecular switches, with a particular focus on phosphorus-containing frameworks. We examine how *E/Z*-isomerization, tautomerism, and coordination-driven transformations can be strategically harnessed to develop multifunctional, stimuli-responsive materials. Furthermore, we compare these systems with their lighter main-group analogues and showcase recent advances in their integration into molecular motors, photoresponsive ligands, and other related applications. In doing so, we outline a forward-looking roadmap for the rational design of main-group-based molecular switches and underscore the promise of heavier pnictogens in expanding the molecular design toolkit. We also highlight key challenges that must be addressed to enhance the efficiency of these systems and position them as viable alternatives to classical molecular organic switches.

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## Introduction

In recent decades, research on functional systems controlled by external stimuli has expanded significantly,<sup>1</sup> leading to advances in drug delivery,<sup>2</sup> photo-cleavable protecting groups<sup>3</sup> molecular switches and machines.<sup>4–8</sup> Among these, molecular switches are one of the simplest components that can be used to build molecular machines<sup>8,9</sup> and are especially notable for their ability to reversibly change between multiple configur-

ations, allowing precise control over geometry and electronic structure.<sup>10,11</sup>

These switches can be activated by a range of stimuli, including changes in temperature and pH,<sup>12</sup> electrochemical input,<sup>13,14</sup> mechanical force,<sup>15,16</sup> or light.<sup>17</sup> This versatility enables their use in applications such as sensors,<sup>18,19</sup> imaging,<sup>20</sup> smart optical materials,<sup>21</sup> and spin-controlled materials.<sup>22</sup>

Among those, photochromic compounds have been studied since the 19<sup>th</sup> century, beginning with the seminal discovery of the sunlight-driven dimerization of anthracene.<sup>23</sup> Since then, several molecular scaffolds have been developed with well-established synthetic routes and reversible transformations, such as those of diarylethene compounds.<sup>24</sup> In particular, we

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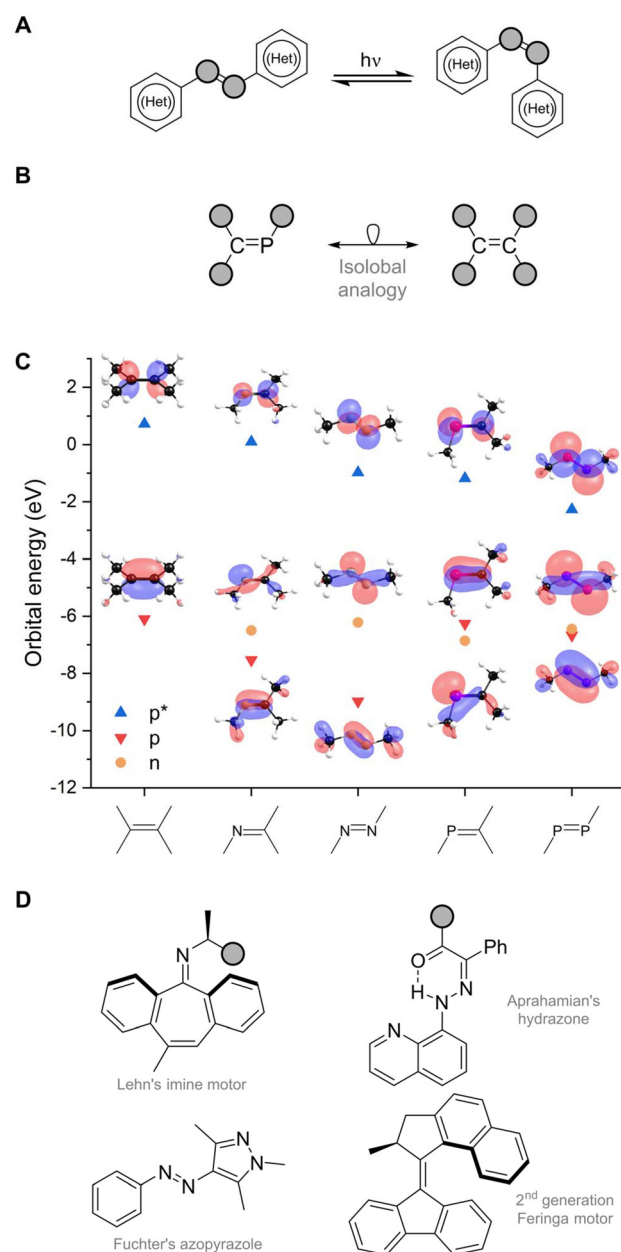


have witnessed the emergence of a subclass of switches that utilize light-induced isomerization about a double bond.<sup>17,25</sup> To be effective, photochromic switches should exhibit strong light absorption, efficient isomerization with high quantum yield, thermal stability, well-defined photo-stationary distributions, and resistance to photodegradation.<sup>17</sup>

Pnictogens, the group 15 elements (N, P, As, Sb, and Bi), are increasingly gaining attention in the field of functional materials. Their ability to engage in diverse bonding modes, participate in lone-pair interactions, and stabilize multiple oxidation states opens up new possibilities for switchable systems with unique structural and electronic features. Nitrogen-based switches have been extensively studied, but more recent efforts have started to explore the potential of the heavier congeners, including elements from period 3 and beyond. These heavier pnictogens can impart distinct reactivity, electronic properties, and tuneable switching behaviour, making them promising novel candidates for (photo-)responsive materials.<sup>26</sup>

In this perspective, we begin by introducing double bond isomerism focusing on nitrogen-based systems due to their group relationship with heavier pnictogens (Fig. 1A). Additionally, we include carbon-carbon double bond systems, based on their isolobal relationship with low valent and low coordinate organopnictogen compounds, featuring pnictogen-pnictogen and pnictogen-carbon bonds (Fig. 1B).<sup>26,27</sup> The isolobal analogy is a conceptual tool that relates molecular fragments based on their frontier orbitals, specifically, the number, symmetry properties, approximate energy, shape of the frontier orbitals, and the number of electrons in them.<sup>28,29</sup> Two fragments are thus considered isolobal if their frontier orbitals are similar—not identical—in these respects, even if they differ in atomic composition. This allows chemists to draw parallels between seemingly unrelated species. For example, a phosphorus-phosphorus double bond (RP=PR) can be considered isolobal to a carbon-carbon double bond (R<sub>2</sub>C=CR<sub>2</sub>), allowing the use of well-understood organic frameworks to rationalize the behaviour of less common main-group systems and, ultimately, utilize this analogy in a rational design of new switchable compounds with tailored properties.

The similarities due to isolobal analogy and dissimilarities due to electronegativity differences despite the group analogy are clearly illustrated in Fig. 1C, showing a comparison of the frontier molecular orbitals of C=C, C=N, P=C, and P=P containing systems. The highest molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) of alkenes and phosphalkenes consist of the bonding and antibonding  $\pi$ -orbitals, whereby the LUMO of the phosphalkene is significantly stabilized by the reduced C(2p)–P(3p) orbital overlap. The non-bonding lone pair of a phosphalkene is close in energy to the HOMO (–6.86 vs. –6.26 eV,  $\Delta_{\text{H/H-1}} = 0.6$  eV), providing a rich coordination chemistry involving mostly the lone pair. In contrast, imines and azo compounds are dominated by the non-bonding lone pairs as their HOMOs and significantly stabilized  $\pi$ -bonding orbitals ( $\Delta_{\text{H/H-1}} = 1.03$  eV and 2.76 eV, respectively). Diphosphenes show an even smaller HOMO–LUMO splitting and almost isoenergetic lone pair and



**Fig. 1** A. Pictorial representation of a photochemical *E/Z* double bond switch. B. Isolobal analogy of alkenes and phosphalkenes. C. Frontier molecular orbitals of common unsaturated main group fragments calculated at the B3LYP-D3ZERO/def2-TZVP level of theory. D. Examples of photochemically switching molecules.

$\pi$ -orbital energy levels, which promotes a more pronounced coordination chemistry *via* both orbitals, while maintaining a close isolobal analogy to alkenes and phosphalkenes. We should, however, note that non-aliphatic substituents can have a substantial impact on the frontier molecular orbitals.<sup>1,30</sup>

The following section on C=C and C=N containing molecular switches is not intended to be exhaustive, but rather aims to introduce the concepts and developments of organic switches relevant to their heavier main group congeners (Fig. 1D). Readers seeking a more detailed overview are encouraged to consult



several recent reviews that offer comprehensive insights into the field of molecular switches and machines.<sup>4–6,9,11</sup>

### Photosomerisation in compounds containing C=N, N=N and C=C bonds

The imine double bond between carbon and the lightest pnictogen atom, nitrogen, shows photoisomerization, with a precise motion that breaks the double bond upon population of the excited state (rotational motion) and reverts, usually thermally, back to the stable state *via* a linear transition state (inversion motion).<sup>31</sup> As for the majority of the systems, the switching and the stability of imines benefit from the substitution with an aryl or heteroaryl substituents.<sup>32</sup> Imines have recently come under the spotlight in systems such as the molecular motors designed by the group of Lehn,<sup>33</sup> iminothioindoxyl switches from Szymanski and co-workers<sup>1</sup> and the photo-switchable, bistable, aryliminopyrazoles by Greenfield and co-workers.<sup>32</sup> Hydrazones can be considered a separate class of switches from imines,<sup>34</sup> thanks to their remarkable thermal properties. Whilst maintaining the C=N isomerizing bond, hydrazones showcase a bistability which can reach over thousands of years.

By adding a second nitrogen in the isomerising bond, we obtain the class of azo compounds, with azobenzene being the more prominent example of this family.<sup>5,35</sup> Azobenzene's isomerism has been known since the beginning of the 1900s, but its isomerisation mechanisms, both at the excited and ground state, are still a source of debate.<sup>36</sup> Some azobenzenes and their heteroaromatic derivatives, especially azopyrazoles, have already been exploited in various applications thanks to their ease of synthesis, fatigue resistance and tunability. Surprisingly only few reports deal with light induced coordination mode changes involving the azo group.<sup>37</sup>

Moving from N=N to C=C bonds, we can identify the class of the alkene-based switches. C=C bonds isomerize *via* a rotational motion in their excited and ground state, with exceptions where a Hula Twist concerted isomerization was experimentally proven.<sup>38</sup> Undoubtedly, one of the cardinal examples of a molecule with light-responsive C=C double bonds is retinal, the chromophore of the scotopic protein, rhodopsin.<sup>39</sup> Two main classes of compounds take the lion's share of the research currently conducted on C=C bonds: stilbenes<sup>6</sup> and indigoids.<sup>40</sup> Stilbenes benefit from the bistability of their two forms, and are the platform that allowed the development of the first unidirectional molecular motors. Indigoids, spear-headed in the last years by the works of Dube and Hecht among others,<sup>41,42</sup> benefit from the intense coloration, the possibility to tune their lifetimes based on substitution pattern as well as being perfect scaffolds for the development of more complex motion patterns, like figure-of-eight<sup>43</sup> and mechanical threading.<sup>44</sup>

### Isomerisation in phosphalkenes ( $R_2C=PR$ )

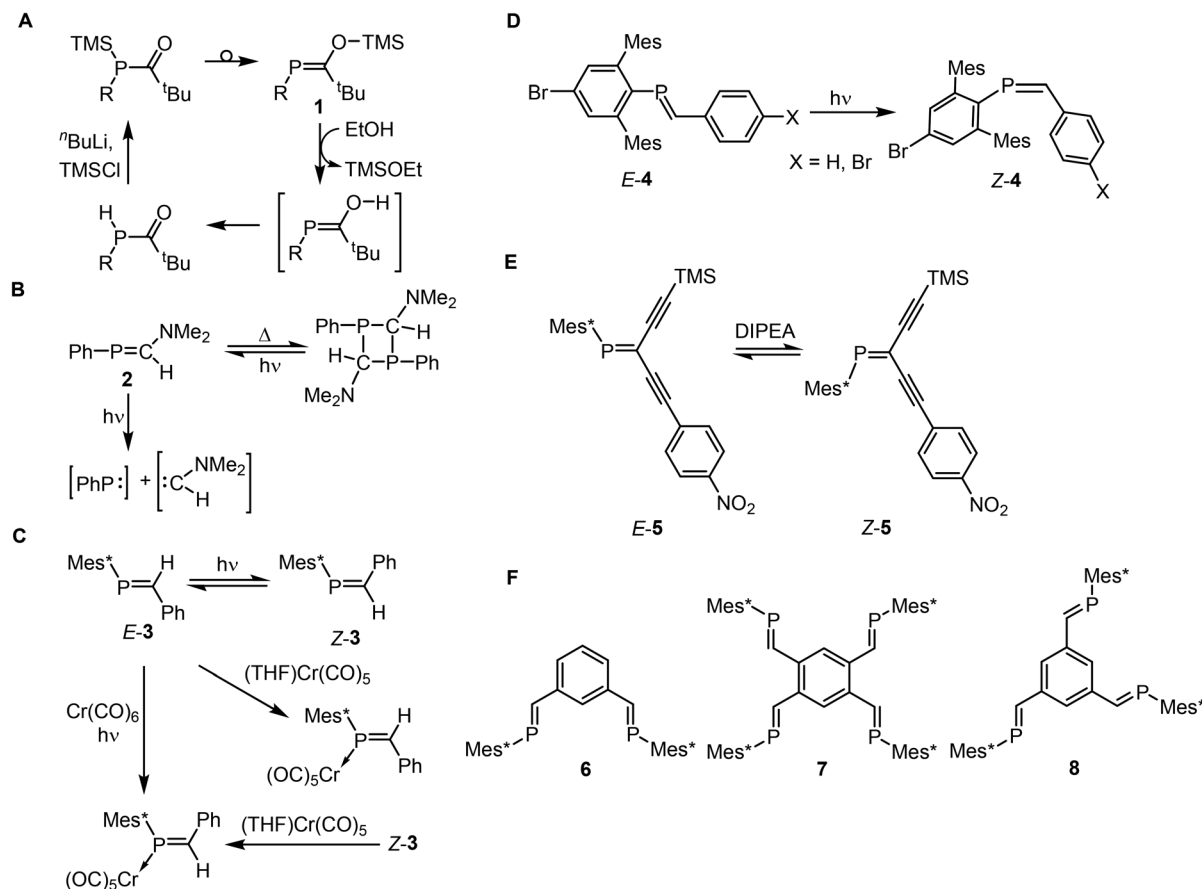
The foundation of low valent and low coordinated phosphorus chemistry was laid by Märkl in 1966,<sup>45</sup> with the synthesis of phosphabenzene, the heavier analogue of pyridine. This was

followed by significant breakthroughs in 1976 and 1978, when Becker and Bickelhaupt successfully isolated the first thermally stable inversely and normally polarized phosphalkenes, respectively—each featuring a localized P=C bond.<sup>46,47</sup> The synthetic route developed by Becker is particularly interesting, as it involves a 1,3-sigmatropic rearrangement of a silyl group at low temperatures, converting the acyl phosphine intermediate into the corresponding unsaturated phosphalkene (**1**) (Fig. 2A), resulting in a substantial alteration of its electronic structure and extension of the conjugated system.<sup>46</sup> The resulting phosphalkene reacts with alcohol leading to a 1,3-hydrogen shift of the acyl phosphane, which upon deprotonation and silylation undergoes again the 1,3-silyl shift to afford the original phosphalkene.<sup>48</sup> Expanding the sigmatropic rearrangement route to arsaalkenes illustrated the influence of the pnictogen atom on reaction kinetics, enabling short-term room-temperature stability of the acyl arsine and hinting at the possibility to tune reactivity, potentially achieving bistability under ambient conditions.<sup>49</sup>

The subsequent decade witnessed substantial progress, marked by the implementation of novel synthetic strategies and the introduction of a broad range of substituents at both the phosphorus and carbon termini, which together enabled greater structural diversity and significantly expanded the reactivity profile of phosphalkenes.<sup>50–52</sup> A notable development during this period was reported by Majoral and co-workers in 1983,<sup>53</sup> who illustrated the rich thermal and photochemical behaviour of inversely polarized phosphalkene Ph–P=C(NMe<sub>2</sub>)H (**2**) (Fig. 2B). While phosphalkene **2** was thermally unstable and yielded the head-to-tail [2 + 2] cycloaddition dimerized product, direct UV irradiation (254 nm) led to an inversion of polarity at the P=C bond in the excited state, resulting in transient phosphinidene and carbene species—evidenced by trapping experiments with and without methanol. Interestingly, the thermodynamically stable diphosphetane could be converted back to the metastable phosphalkene upon irradiation using the same light source. These findings provided early insights into the excited-state reactivity of phosphalkenes and paved the way for further light-driven reactivity studies. Albeit considerably fewer in number than their alkene counterparts, nearly 3000 C=P-containing compounds have been reported to date.<sup>54</sup> However, a significant portion of these remain inherently unstable, posing challenges for their broader exploration—particularly in the context of molecular switching and other advanced applications.

In 1985, Yoshifuji reported, for the first time, the detailed photolysis of a phosphalkene, Mes\*–P=CHPh (**3**).<sup>55</sup> Irradiation of the *E*-isomer (*E*-**3**) with a 100 W medium-pressure mercury lamp for 6 hours at 0 °C resulted in a photo-stationary state (PSS) with an approximate 3 : 7 (*E* : *Z*) ratio, as determined by <sup>31</sup>P NMR spectroscopy. A similar light-driven isomerization was observed for the *Z*-isomer (*Z*-**3**), yielding a mixture of both isomers (Fig. 2C). The isolated *E*- and *Z*-isomers exhibited high kinetic stability, showing no signs of isomerization upon heating at 100 °C for up to 24 hours. Coordination of these isomers with metal precursor [Cr





**Fig. 2** A. Isomerism in Becker phosphaaalkene **1**; B. photolysis of phosphaaalkene **2**; C–E. isomerisation in monophosphaaalkenes **3**–**5**; F. isomerisation in polyphosphaaalkenes **6**–**8**. Mes\* = 2,4,6- $\text{tBu}_3\text{C}_6\text{H}_2$ , Mes = 2,4,6- $\text{Me}_3\text{C}_6\text{H}_2$ , TMS =  $\text{SiMe}_3$ .

$(\text{CO})_5(\text{THF})$ ] proceeded with full retention of stereochemistry, however, reaction of the *E*-isomer with  $[\text{Cr}(\text{CO})_6]$  in the presence of light yielded the corresponding *Z*-isomeric complex. Although light-mediated isomerization of the isolated complexes was not investigated, the absence of the second isomer suggests a concerted coordination/isomerization mechanism.

Protasiewicz synthesized isomerically pure *E*-isomers of *meta*-terphenyl-based phosphaaalkenes (**E-4**), allowing for systematic spectroscopic studies. Upon irradiation, these derivatives isomerized to a mixture of *E*- and *Z*-isomers, reaching a PSS containing 76–81% of the *Z*-isomer (**Z-4**), illustrating the minimal influence of the *para*-substituent on the terphenyl group (Fig. 2D). Analysis of the PSS and the absorption spectra of both isomers indicated that the forward and backward processes have virtually identical quantum yields ( $\Phi_{E \rightarrow Z}$  and  $\Phi_{Z \rightarrow E}$ ). Notably, the *E*  $\rightarrow$  *Z* photoisomerization also occurred in the solid state resulting in partial conversion ( $\sim 30\%$ ) to the *Z*-isomer.<sup>56</sup> Despite the high kinetic barrier in most cases, some phosphaaalkenes undergo slow (hours) isomerization at room temperature,<sup>57</sup> while in other cases, the process is dramatically enhanced by silica gel.<sup>58</sup> Ott and co-workers further demonstrated in a thermally stable *C,C*-diacetylenic phosphaaalkene (**5**) bearing an electron-withdrawing nitrophenyl substituent on one of the acetylenic

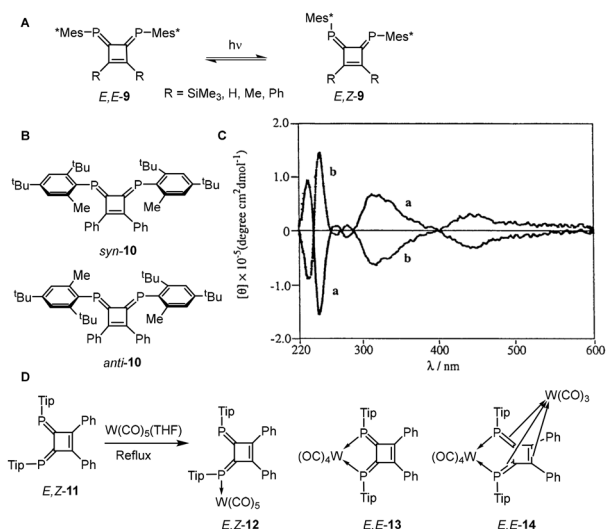
units that presence of *N,N*-diisopropylethylamine (DIPEA) promotes isomerization (Fig. 2E).<sup>59</sup>

In comparison to mono-phosphaaalkenes, compounds featuring multiple  $\text{C}=\text{P}$  units present a diverse and intriguing pattern of isomerization behaviour. A critical factor influencing the outcome is the degree of steric congestion, both around the phosphorus substituents and within the organic scaffold. For instance, Jouaiti and co-workers reported room-temperature *E,E*  $\rightarrow$  *E,Z*-isomerization in a bis-phosphaaalkene (**6**) (Fig. 2F). The presence of a *meta*-substituted phenylene linker, which increases the spatial separation between the  $\text{P}=\text{C}$  units and introduces greater conformational flexibility, enabled the formation of the *Z,Z*-isomer upon extended irradiation.<sup>60</sup> Detailed irradiation experiments of this compound and related tri- and tetra-phosphaaalkenes (**7** and **8**) revealed a thermodynamic preference for the all *E*-isomeric forms, while *Z*-containing isomers became dominant upon UV irradiation at 350 nm.<sup>61</sup>

Contrastingly, in geometrically constrained bis(phosphane-diy)cyclobutenes (**9**), only the *E,E*- and *E,Z*-isomer could be synthesized from the bis-phosphaaalkenic precursors *via* conrotatory rearrangements (Fig. 3A). Remarkably, despite the asymmetric structure of the *E,Z*-isomer ( $\text{R} = \text{SiMe}_3$ ), only a single







**Fig. 3** A and B. Configurational and conformational isomerism in diphosphinidenecyclobutenes **9** and **10**; C. CD-spectra of tungsten complex of *anti*-10; image is reproduced with permission from *Chem. Lett.*, 1990, **19**, 2195; D. coordination mediated isomerisation in **11**. Tip = 2,4,6-<sup>i</sup>Pr<sub>3</sub>C<sub>6</sub>H<sub>2</sub>, Mes\* = 2,4,6-<sup>t</sup>Bu<sub>3</sub>C<sub>6</sub>H<sub>2</sub>.

resonance was observed in the <sup>31</sup>P NMR spectrum—suggesting the presence of a rapid degenerate equilibrium mediated by an as-yet unidentified mechanism.<sup>62</sup> Irradiation of the *E,E*-bisphosphaalkenes yielded PSSs that were slightly influenced by the nature of the R substituents (R = H, Me, <sup>t</sup>Bu, and Ph), consistently favoring the (*E,Z*)-isomer with *E,E*:*E,Z* ratios ranging from 3 : 1 to 5 : 1.<sup>63–65</sup>

In addition to *E,Z*-configurational isomerism, diphosphinidenecyclobutenes also exhibit conformational isomerism when an asymmetrically substituted aryl protecting group is installed. This is attributed to restricted rotation about the exocyclic P=C bonds due to the sterically demanding nature of these substituents. Diphosphinidenecyclobutenes **10** were synthesized as an inseparable mixture of *syn* and *anti*-isomers in a 1 : 2 ratio (Fig. 3B). Upon complexation with [M(CO)<sub>5</sub>(THF)] (M = W, Co, Cr), <sup>31</sup>P NMR spectrum confirmed the presence of both *syn* and *anti*-isomers, with complete retention of their conformations during complexation. The *syn*-rotamer of the mononuclear tungsten complex was structurally characterized by single-crystal X-ray diffraction, while the *anti*-rotamers were separated by chiral HPLC, with each isomer displaying a mirrored circular dichroism (CD) spectrum (Fig. 3C).<sup>66</sup> These results demonstrate that this framework also enables the utilization of pseudo-atropisomerism as an additional means of distinguishing between different molecular states. Additionally, coordination of [W(CO)<sub>5</sub>THF] to the *E,Z*-bis(phosphanediyl) cyclobutene **11** initially gives coordination at the more accessible *Z*-phosphaalkene (*E,Z*-12), however results in a thermal/metal mediated *E,Z*-isomerization upon chelation (*E,Z*-13). Further coordination to the  $\pi$ -systems gives a dinuclear metal complex with an additional piano-stool coordination environment (*E,E*-14) (Fig. 3D).<sup>67</sup>

In 1996, Bickelhaupt introduced the isomerization of C-halophosphaalkenes (*E/Z*-15) using metal fragments (Fig. 4A),<sup>68</sup> involving formation of a three-membered metallacycle in case of Pt-group metals.<sup>69</sup> This process was subsequently used in highly regioselective C–C coupling affording functionalized phosphalkenes.<sup>70,71</sup> We recently explored a related metal-mediated isomerization in the case of a truxene-based phosphalkene (Fig. 4B). We have found that the *Z*-isomer (*Z*-18) undergoes light-driven isomerization, yielding 15% of the *E*-isomer (*E*-18) at the PSS. Surprisingly, quantitative formation of the corresponding *E*-isomer of the truxene core was observed upon metal coordination to an AuCl fragment [AuCl(*E*-18)], which could be reverted to the uncoordinated *Z*-isomer *Z*-18 by simple de-coordination using PPh<sub>3</sub>.<sup>72</sup> Furthermore, the oxidation of phosphalkenes with elemental sulfur—and to a lesser extent, selenium—offers a promising platform for the development of molecular switches. Mono-oxidation of phosphalkene **19**, results in the formation of a methylene(thioxo)phosphorane, **20**, which undergoes photochemical isomerization to the thermodynamically less favored thiaphosphirane, **21** (Fig. 4C). Additionally, direct oxidation of phosphalkene **19** with excess sulfur yields a thiaphosphirane sulphide **22**, which can be selectively converted to the corresponding thiaphosphirane **21** upon treatment with (Me<sub>2</sub>N)<sub>3</sub>P.<sup>73</sup>

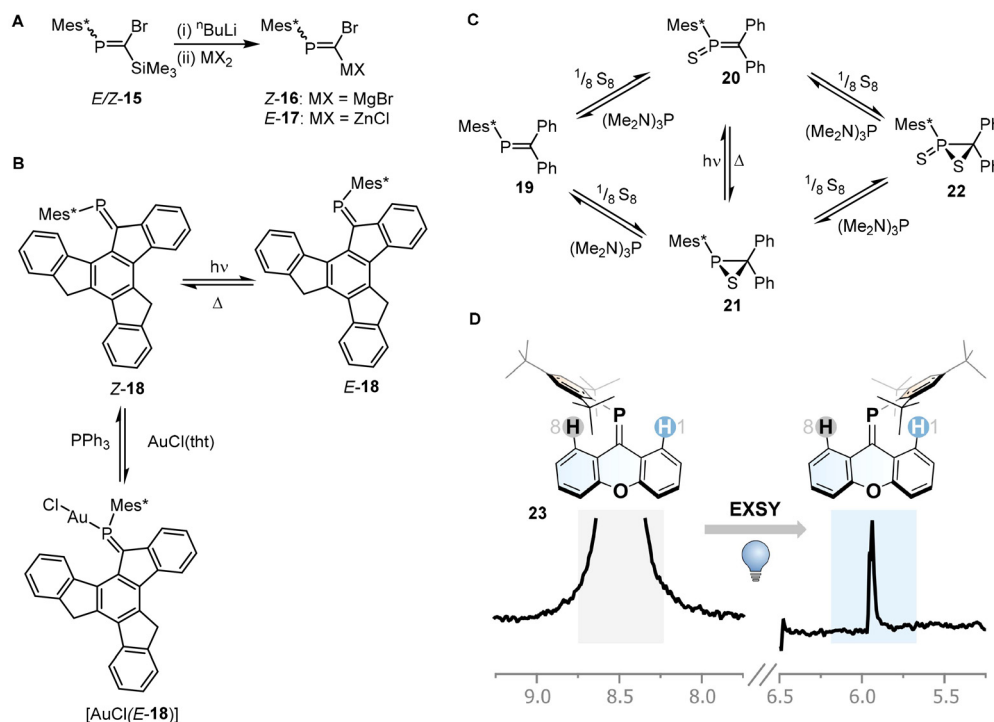
Recently, we have aimed to move beyond considering *E,Z*-isomerization in phosphalkenes as a mere chemical curiosity and instead sought to harness it as a functional property—specifically, in the design of molecular switches. To this end, we undertook a combined theoretical and spectroscopic investigation of simple, symmetric phosphalkene system (**23**) to gain a comprehensive understanding of the isomerization mechanism (Fig. 4D). Degenerate switching was experimentally confirmed through photochemical EXSY experiments, while the excited-state dynamics were elucidated using time-resolved spectroscopy. The measured time constants are consistent with the theoretical model in which isomerization proceeds *via* rotational motion on the excited-state potential energy surface (PES), ultimately relaxing to the ground state through a conical intersection.<sup>27</sup>

### Isomerisation in diphosphenes (RP=PR)

Diphosphenes are close analogues of diazo compounds, however, their significantly higher reactivity precluded their isolation until 1981, when Yoshifuji reported the first isolable diphosphene.<sup>74</sup> Only a few years later, Caminade observed the photoisomerization of the thermodynamically stable *E*-isomer (*E*-24, Fig. 5A) to the metastable *Z*-isomer (*Z*-24), achieving a photostationary state (PSS) containing approximately 70% of the *Z*-isomer upon irradiation at 515 nm at –80 °C. The kinetics of thermal back-isomerization were estimated based on <sup>1</sup>H, <sup>31</sup>P NMR, and UV/vis analyses at 0 °C, yielding unimolecular rate constants on the order of 3 × 10<sup>–4</sup> s<sup>–1</sup>.<sup>75</sup>

Several studies of unsymmetrical diphosphenes indicated that photolysis potentially involves dimerization to the corresponding cyclotetraphosphetanes (Fig. 5B), as evidenced by NMR spectroscopic data.<sup>76</sup> Notably, the ferrocenyl-containing





**Fig. 4** A and B. Metal mediated isomerisation in phosphalkenes **15** and **18**; C. sulfurization induced isomerisation in phosphalkene **19**; D. degenerate isomerism in phosphalkene **23**.  $\text{Mes}^* = 2,4,6\text{-tBu}_3\text{C}_6\text{H}_2$ ; image is reproduced from *Angew. Chem., Int. Ed.*, 2025, **64**, e202419943 under the CC-BY license.

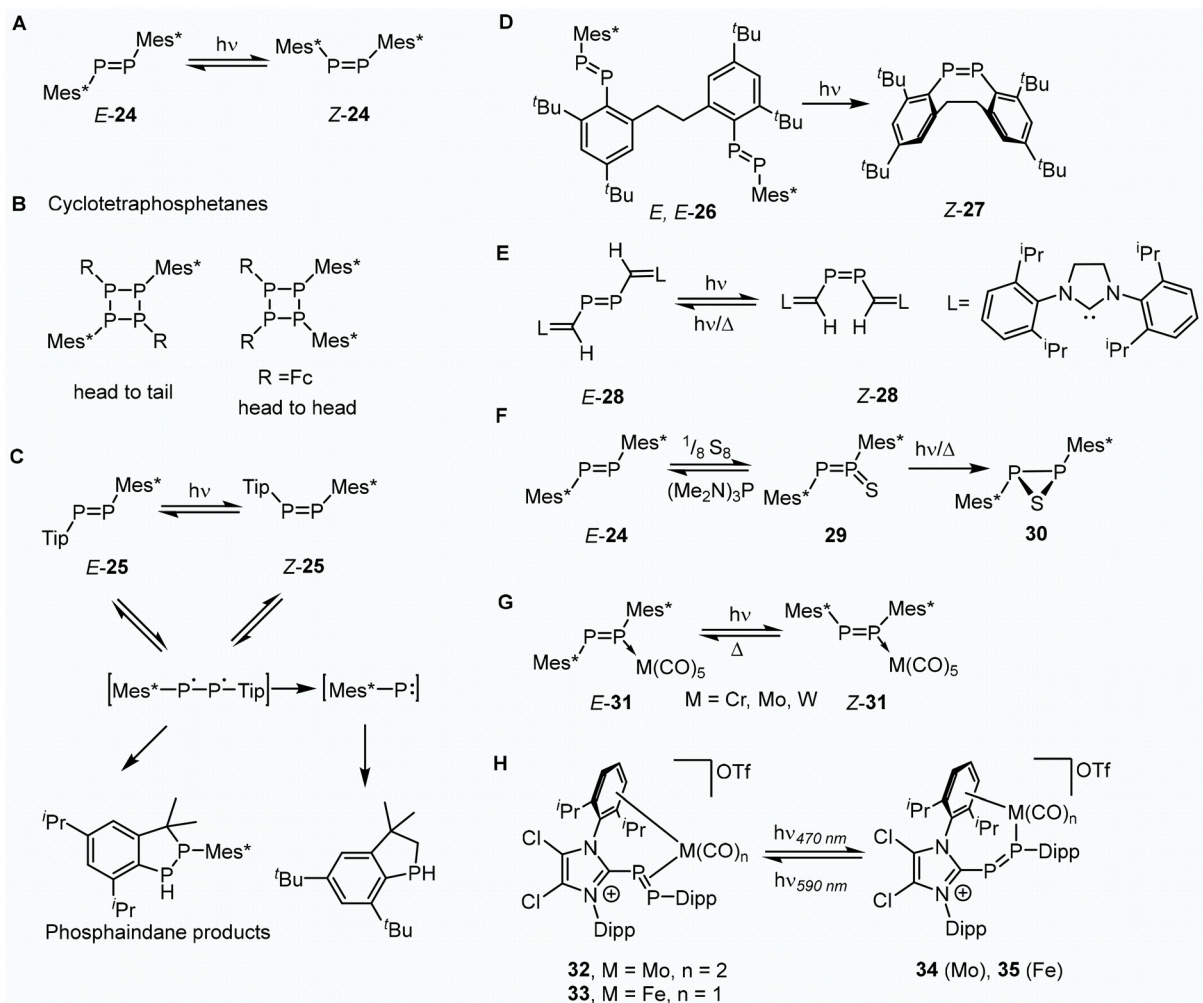
diphosphene ( $\text{FcP}=\text{PMes}^*$ ) was found to undergo slow dimerization at room temperature under ambient light to form the head-to-head dimerization product. Upon heating or UV irradiation, the dimer readily undergoes cycloreversion to regenerate the original *E*-diphosphene. It is proposed that this retro-transformation proceeds *via* the formation of an initial *cis*-diphosphene, followed by *cis/trans* isomerization to yield the *E*-isomer. Importantly, no evidence was found for the formation of phosphinidene intermediates or metathesis to  $\text{Mes}^*\text{P}=\text{PMes}^*$ .<sup>77</sup> The absence of phosphinidene intermediates has been supported by the lack of intramolecular trapping products—specifically, phosphaindane—at low temperatures ( $-40^\circ\text{C}$ ) when deep UV irradiation was excluded using a Pyrex®-filtered 100 W medium-pressure mercury lamp. In contrast, room-temperature irradiation without the filter led to formation of the phosphaindane product *via* C–H insertion of a phosphinidene species.<sup>78</sup> Bickelhaupt proposed the involvement of diradical intermediates in the *E,Z*-isomerization of diphosphene **25** (Fig. 5C).<sup>79</sup> Interestingly, prolonged irradiation led to rearrangement of the diradical species, yielding P-cyclized by-products. A similar phenomenon was observed for a  $\text{Cp}^*$ -stabilized phospharsene, where both head-to-tail and head-to-head  $[2 + 2]$  cycloaddition products (tetrapnictaphosphetanes) were detected, resulting in a complex mixture of stable and unstable photoproducts.<sup>80</sup>

Yoshifuji reported that, for an ethane-linked bis-diphosphene (*E,E*-**26**, Fig. 5D), irradiation led to intramolecular tetra-

raphosphetane formation followed by retro- $[2 + 2]$  cycloaddition, yielding a bridged *Z*-diphosphene system (**Z-27**).<sup>81</sup> Upon introduction of a secondary amine substituent,  $\text{R-NHP}=\text{PMes}^*$ , the *Z*-diphosphene is thermodynamically favoured, albeit, overall less kinetically stabilized, leading to facile cycloaddition and retro-cycloaddition decomposition pathways at mildly elevated temperatures.<sup>82</sup> This increased stability is reminiscent of hydrazone switches. Introducing a bis(trimethylsilyl)amine substituent rendered the *E* and *Z*-isomers nearly isoenergetic, but also significantly increased the thermal stability raising the barrier to  $\Delta G^\ddagger$ ,  $293 = 25.5 \text{ kcal mol}^{-1}$  (compared to  $\text{Mes}^*\text{P}=\text{PMes}^*$ , **24**  $\Delta G^\ddagger$ ,  $293 = 20.3 \text{ kcal mol}^{-1}$ ).<sup>83</sup> Introduction of N-heterocyclic vinyl (NHV) substituents preserved the high thermal stability of the photochemically generated *Z*-diphosphene (**Z-28**, Fig. 5E). The thermal barrier for the reverse isomerization was estimated at  $25.3 \pm 1.6 \text{ kcal mol}^{-1}$  ( $t_{1/2} > 200$  hours at room temperature), with a slight thermodynamic preference for the *Z*-isomer ( $\Delta G = -0.6 \text{ kcal mol}^{-1}$ ). Photolysis at 520 nm and 455 nm yielded PSS with *Z* : *E* ratios of 0.19 and 4.40, respectively, allowing for isolation of both isomers. The PSS at these wavelengths could be exclusively related to the differences in molar absorptivity, indicating very similar quantum yields for both events.<sup>84</sup>

As observed in the case of phosphalkene **19** (Fig. 4C), sulfurization can also induce isomerization in diphosphenes. Treatment of *E*-**24** with elemental sulfur yielded diphosphene 1-sulfide **29**, which undergoes isomerization under photother-





**Fig. 5** A. Isomerisation in symmetric diphosphene, **24**; B. cyclotetraphosphetanes; C–E. isomerisation and rearrangements of diphosphenes **25**–**28**; F. sulfurization induced isomerisation in diphosphene **24**; G and H: metal mediated isomerisation in compounds **31**–**33**. Dipp = 2,6- $\text{iPr}_3\text{C}_6\text{H}_3$ , Mes\* = 2,4,6- $\text{iBu}_3\text{C}_6\text{H}_2$ , Tip = 2,4,6- $\text{iPr}_3\text{C}_6\text{H}_2$ .

mal or thermal conditions to form the *E*-thiadiphosphirane **30** (Fig. 5F). Notably, **29** can be quantitatively reverted to the parent diphosphene *E*-**24** by treatment with  $(\text{NMe}_2)_3\text{P}$ .<sup>85,86</sup>

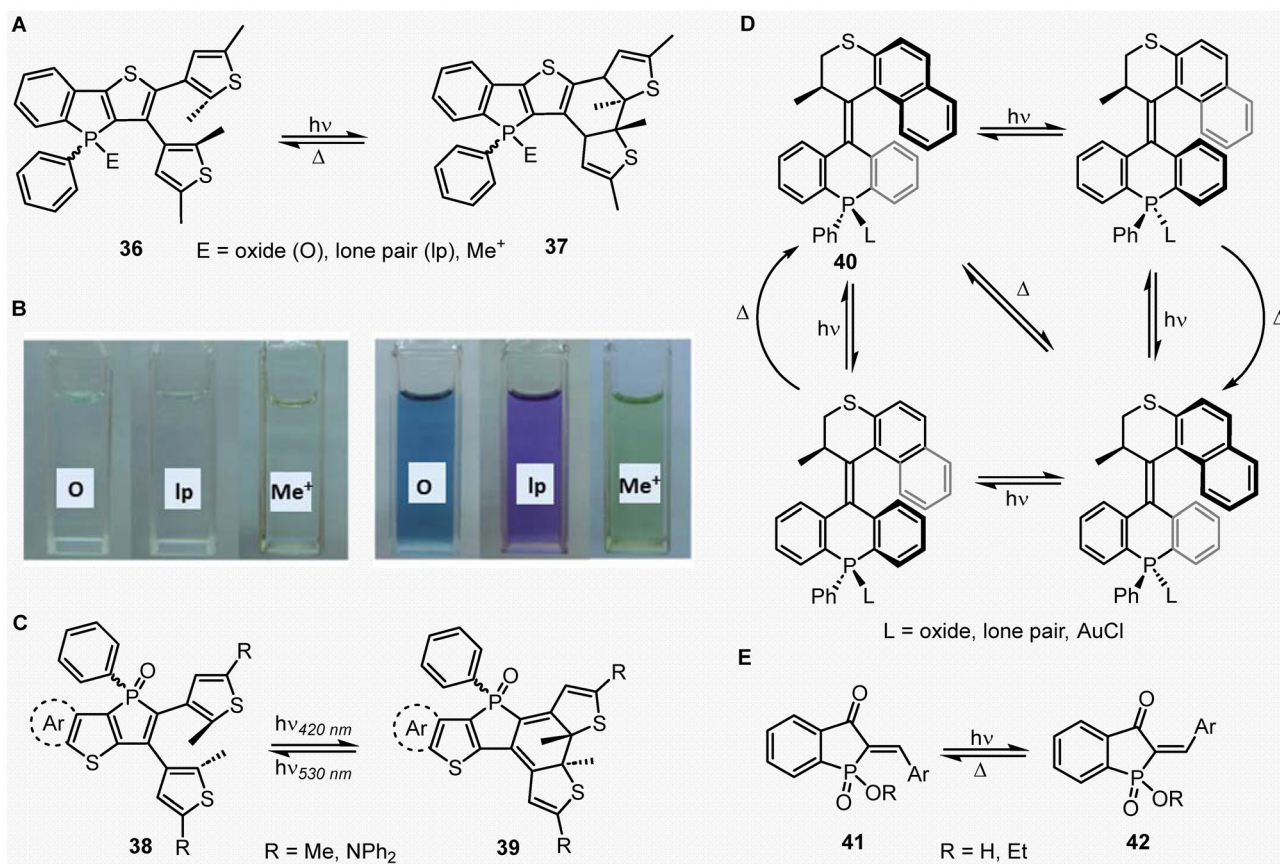
As early as 1985, it was discovered that metal complexation can profoundly influence the photochemical isomerization behaviour of diphosphenes. Yoshifuji demonstrated that reaction of *E*-isomer of  $\text{Mes}^*\text{P}=\text{P}\text{Mes}^*$  with a series of metal carbonyl complexes,  $[\text{M}(\text{CO})_5(\text{THF})]$  (M = Cr, Mo, W), afforded *E*-diphosphene complexes, *E*-**31** that could be cleanly photoisomerized to their *Z*-isomeric forms (*Z*-**31**) upon irradiation with a medium-pressure mercury lamp at 0 °C (Fig. 5G). The rate of photoisomerization was found to decrease systematically down the group (Cr  $\gg$  Mo > W).<sup>87</sup> Photochemical switching between  $\eta^1$ - and  $\eta^2$ -coordination modes was also reported for cationic diphosphene complexes of Fe(CO) and Mo(CO)<sub>2</sub> (**32**–**33**, Fig. 5H). These transitions involved substantial structural reorganization, including rotation about a single bond, and could be selectively triggered using different wavelengths of light—470/590 nm for Fe and 400/630 nm for Mo—taking

advantage of the pronounced color differences between the isomers. Notably, short irradiation times were sufficient to reach PSSs containing up to 96% of the photogenerated species.<sup>88</sup> In a similar fashion, gold coordination in NHV-based diphosphene systems can be switched between  $\eta^1$ - and  $\eta^2$ -binding modes, where metal migration is accompanied not only by bond rotation but also by *E*,*Z*-isomerization.<sup>84</sup>

### Miscellaneous phosphorous-containing molecular switches

Beyond phosphalkenes and diphosphenes, other phosphorus-containing molecules have recently garnered attention in the context of molecular switching. The Yam research group has investigated the highly tunable phosphole-based systems (**36**–**39**) as P-functionalized diarylethene photoswitches (Fig. 6A–C). Notably, benzannulated phosphole derivatives exhibited lower quantum yields than their dithienoannulated analogues, despite possessing similarly extended  $\pi$ -conjugated frameworks.<sup>89</sup> The latter displayed quantum yields of up to 0.87 for photocyclization and 0.44 for photocycloreversion pro-





**Fig. 6** Miscellaneous P-based molecular switches. A–C. P-functionalized diarylethene photoswitches **36–38**; B. schematic representation of colour change in the ring-opened and ring-closed diarylethene photoswitches; images are reproduced with permission from *Angew. Chem., Int. Ed.*, 2013, **52**, 11504; D. P-based molecular motor, **40**; E. hemiphosphoindigo photoswitches **41**.

cesses. Furthermore, the characteristic emission of the phosphole oxide core was significantly reduced upon cyclization, underscoring their potential as functional materials, especially imaging applications.<sup>90</sup> Building on these findings, further functionalization was achieved through alkynyl gold(i) complexation of the phosphole scaffold. In addition to the well-established photocyclization/cyclo-reversion behaviour, new metastable states—distinguished by their altered colour—could be accessed from both the open and closed forms through mechanical grinding, presumably *via* geometric changes in the triphenylamine moiety.<sup>91</sup>

Dielmann and co-workers reported the incorporation of a photoswitchable phosphine-based N-heterocyclic imine into a dithienylethene framework. The resulting molecule not only undergoes electrocyclic ring closure upon UV irradiation, but also exhibits modulation of the phosphine's donor strength between the ring-opened and ring-closed isomers, indicating that photoisomerization can effectively tune the electron-donating ability of the phosphine.<sup>92</sup> Subsequently, Hey-Hawkins and co-workers demonstrated that such photoresponsive modulation of electronic properties could be leveraged to tune the catalytic activity of palladium complexes derived from similar dithienylethene-based systems.<sup>93</sup>

Feringa and co-workers introduced a stereogenic phosphorus center into the backbone of overcrowded ethylene-based second-generation Feringa motor, **40** (Fig. 6D). While the gold-coordinated derivative ( $L = \text{AuCl}$ ) and the phosphine oxide ( $L = \text{O}$ ) exhibit the expected four-step unidirectional rotary cycle—comprising sequential photochemical *E,Z*-isomerization followed by thermal helix inversion—the tertiary phosphine variant ( $L = \text{lone pair}$ ) enables a shortcut isomerization pathway. This alternative cycle arises from thermal pyramidal inversion at the stereogenic phosphorus center, allowing direct epimerization between the two stable states at elevated temperatures.<sup>94</sup> Dube and co-workers recently reported a hemiphosphoindigo switch (**41**) as a water-soluble platform for chiroptical switching (Fig. 6E). Their high photofatigue resistance and tunable half-lives showcase the great potential of this class of compounds towards light activated drugs and other biological applications.<sup>95</sup>

The reactivity of low-coordinate phosphorus centres and their ability to stabilize biradicaloid species has been successfully exploited in a photochemical switching process. A phosphorus-based biradicaloid hetero-cyclopentane-1,3-diyl derivative (**43**) exhibits an absorption maximum at 643 nm, whereas its photoproduct, the corresponding hetero-housane, **44** shows

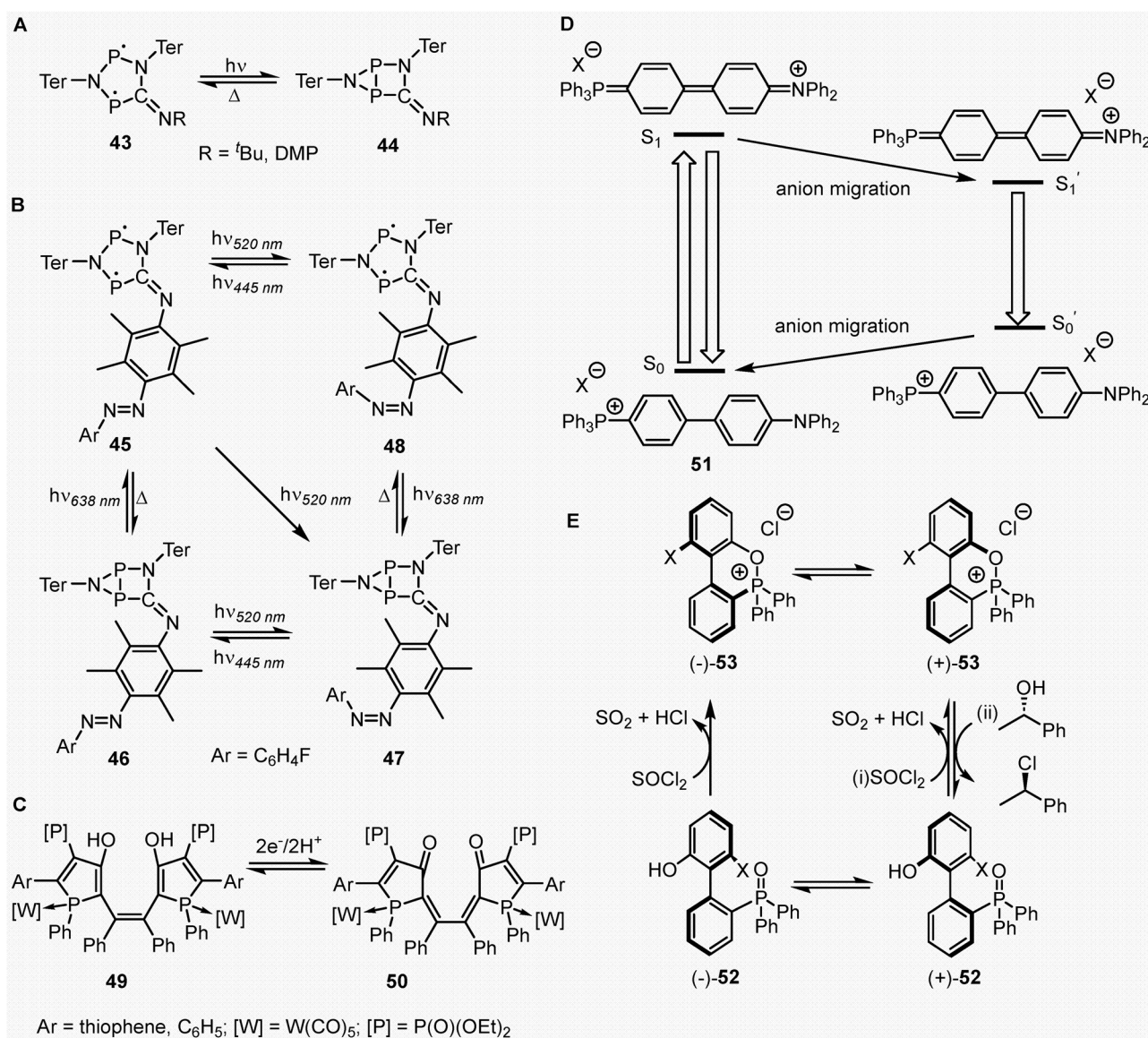




no absorption in the visible region (Fig. 7A). The photochemical switching is highly efficient, with a quantum yield of approximately 0.25 and complete conversion to the heterohousane. The thermal back-reaction follows first-order kinetics and results in quantitative recovery of the biradicaloid at room temperature ( $\tau_{1/2} = 7$  min,  $k = 1.73(3) \times 10^{-3} \text{ s}^{-1}$ ).<sup>96</sup> This concept was subsequently extended to the design of a visible-light-responsive dual photoswitch **45** that integrates both a constitutional switching unit (cyclopentenyl/hetero-housane) and a configurational switching unit *E,Z*-azobenzene (Fig. 7B). The biradicaloid/housane and azobenzene *E,Z*-isomerization processes could be independently triggered using red (638 nm) and green (520 nm)/blue (445 nm) light, respectively, providing orthogonal control over both switching units.<sup>97</sup> Ott and co-

workers presented an ethenyl bridged bisphosphole (**49**) which undergoes a reversible  $2e^-/2H^+$  proton coupled redox switching with a prominent electrochromic behaviour (Fig. 7C).<sup>98</sup>

Specifically designed, molecular and oligomeric motifs have been used for targeted sensing purposes. For example, Gabbaï and co-workers reported a phosphine decorated fluorescein derivative with high selectivity to Au(III) ions as turn-on fluorescence sensors.<sup>99</sup> On the other hand, Gates and co-workers reported selective fluorescence for both Au(I) and Au(III) ions of a phosphine-diyne polymer.<sup>100</sup> In contrast, the heavier pnictogens are also susceptible to interactions with Lewis bases, in particular Sb...F interactions, providing an interesting platform as responsive and smart materials<sup>101,102</sup>



**Fig. 7** Miscellaneous P-based molecular switches. A and B. Phosphorous-based diradicaloid switches; C. redox switching in bisphosphole; D. photoinduced anion migration in phosphonium fluorophore; E. phosphine oxide-based molecular rotor driven by Appel Reaction. Ter = 2,6-(2,4,6-Me<sub>3</sub>-C<sub>6</sub>H<sub>2</sub>)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>, DMP = 2,6-dimethylphenyl.

Another promising opportunity for phosphorus-based molecular switching lies in the use of stable hypervalent motifs. Koshevoy and co-workers incorporated phosphonium groups into spatially separated donor–acceptor dyes **51**, where photoexcitation induces a charge-transfer state that facilitates controllable counteranion migration (Fig. 7D). These materials represent a novel approach to ion-pairing-controlled property modulation, such as dual emission and other optoelectronic behaviours.<sup>103–105</sup> In a distinct context, a prochiral diphenylphosphine oxide installed on the rotor part of a molecular machine (–)**52** was converted into a phosphonium salt. Engaging that phosphonium chloride into a classical Appel reaction with a chiral secondary alcohol fuelled a uni-directional motion forming the basis for a molecular motor based on an external chiral agent and chirality transfer to the hypervalent P-centre (Fig. 7E).<sup>106</sup>

## Conclusion and outlook

*E/Z*-Isomerization in compounds featuring P=C and P=P double bonds has been recognized for over a decade as a fundamental chemical phenomenon. While double bond isomerization is a cornerstone of classical molecular switching, its application in the design of phosphorus-based molecular switches remains relatively underexplored. In recent years, however, the revival of interest in main-group element reactivity—especially through the lens of the “diagonal relationship” between phosphorus and carbon—has extended the relevance of unsaturated phosphorus chemistry into the realm of dynamic molecular systems. As a result, phosphorus-based molecular switches are now emerging as a distinct and versatile class, expanding the structural and mechanistic landscape beyond conventional carbon- or nitrogen-centered platforms such as azobenzenes and stilbenes.

In addition to conventional light-induced *E* → *Z* conversions (reminiscent of alkene or azo switches), phosphorus-based switches can respond to stimuli beyond light or heat—most notably metal coordination and chemical triggers. Recent literature offers several compelling proof-of-concept systems: for example, a phosphalkene embedded in a truxene was shown to isomerize not only under light irradiation but also upon metal coordination (Au(I) coordination triggers *Z* → *E* isomerization, reversed by decoordination). In the same system, chemical triggers such as deprotonation with KC<sub>8</sub> facilitate isomerization by generating an anionic *E*-isomer.<sup>72</sup> More recently, the incorporation of phosphalkene into an overcrowded ethylene framework has enabled redox-triggered conformational changes.<sup>107</sup> Likewise, diphosphene complexes have demonstrated visible-light-triggered *E/Z*-isomerization *via* haptotropic rearrangement of ligands—a novel mode of action rarely encountered in purely organic switches.<sup>84</sup> Similarly, Hadlington group reported a diphosphene-containing macrocycle capable of switching between endo- and exocyclic coordination modes.<sup>108</sup> These advances underscore that incorporating phosphorus enables switching mechanisms beyond the

photon-driven or thermal routes classically used, endowing main-group molecular switches with multi-responsive behaviour.

Beyond bond isomerization, introducing phosphorus into molecular switch designs opens broader opportunities. For instance, photoresponsive phosphine ligands appended with conventional switching motifs have been used in transition-metal complexes to reversibly modulate catalytic activity—a strategy that has been explored for some time.<sup>109</sup> Looking ahead, one can envision a light driven configurational changes of a phosphalkene or diphosphene ligand switching a catalyst from a dormant to an active state on demand *via E/Z* isomerization at the ligating atom. Similarly, phosphorus-driven molecular machines and actuators are on the horizon; indeed, embedding a P-atom in rotary motors has already imparted unique stereodynamic features. Thus far, stable hypervalent intermediates,<sup>106</sup> pnictogen specific rearrangements,<sup>48</sup> and substituent and coordination controlled tautomeric equilibria<sup>110–112</sup> have been observed, but not yet been utilized extensively as crucial components of molecular switches. By harnessing the susceptibility of heavier organopnictogen compounds to a wider array of stimuli compatibility—including low-energy visible light, coordination-induced motion, or redox stimuli—pnictogen-based frameworks may overcome some limitations of all-organic switches and enable operation under biocompatible or device-relevant conditions.<sup>95</sup>

Nonetheless, several challenges remain. Synthetic accessibility, once a hurdle for isolating reactive P=P and P=C compounds, has markedly improved with modern strategies, yielding air-stable, robust molecules. However, substantial steric bulk is often required to stabilize P=C/P=P bonds against oligomerization, and that very steric protection can impede efficient *E/Z*-isomerization; *Z*-isomers of heavier double bonds are notoriously hard to isolate due to steric congestion. Designing substituents that provide both electronic stabilization and geometric flexibility will be key to advancing the switchability of such systems.

Photophysical performance also warrants further optimization. While many phosphorus-based switches are responsive to light, achieving high photoisomerization quantum yields remains essential for practical implementation. Perhaps the most ambitious frontier is the realization of unidirectional motion in phosphorus-containing molecular motors. To date, no system has demonstrated directional rotary behaviour using a P=C or P=P bond as the central axle, and embedding these motifs into inherently asymmetrical frameworks (to bias directional rotation) poses significant design challenges. Yet the progress achieved thus far—from chemically and photochemically responsive phosphalkenes to visible-light-driven diphosphene switches—underscores the unique potential of phosphorus in dynamic molecular systems. With continued innovation in design, synthesis, and application, phosphorus-based switches and motors are poised to become a powerful and distinctive addition to the molecular switch toolkit.

Encouraged by progress with lighter pnictogens, researchers have begun to explore whether such isomerization behav-



our can be extended to heavier congeners. In the case of antimony and bismuth, stabilization of dipnictene ( $\text{Pn}=\text{Pn}$ ,  $\text{Pn} = \text{Sb, Bi}$ ) and pnictaalkene ( $\text{C}=\text{Pn}$ ,  $\text{Pn} = \text{Sb, Bi}$ ) frameworks demands extremely bulky substituents to prevent rapid decomposition and oligomerization. Consequently, all crystallographically characterized heavier distibenes and related analogues adopt *E*-geometries; isolable *Z*-isomers remain elusive. Tokitoh and co-workers reported that photolysis of  $\text{BbtSb}=\text{BiBbt}$  ( $\text{Bbt} = 2,6\text{-bis}[\text{bis}(\text{trimethylsilyl})\text{methyl}]\text{-4-[tris}(\text{trimethylsilyl})\text{methyl}]\text{phenyl}$ ) under medium-pressure mercury lamp irradiation led to bond cleavage rather than isomerization. Similar behaviour was observed for  $\text{Mes}^*\text{P}=\text{BiBbt}$ , underscoring the challenge of achieving *E/Z*-isomerization in these heavier main-group systems.<sup>113</sup> Despite these limitations, recent efforts offer glimpses of promise. For instance, Bismuto and co-workers demonstrated that blue-light irradiation of a distibene in the presence of  $\text{CpCo}(\text{CO})_2$  results in the formation of a cobalt–distibene complex featuring a metallacyclic  $\text{Co-Sb}_2$  motif.<sup>114</sup> Although this transformation represents bond reorganization rather than pure isomerization, it exemplifies the rich, photochemically induced reactivity accessible to heavy main-group double bonds. Looking forward, achieving reversible, stimulus-responsive *E/Z*-isomerization in antimony and bismuth systems will require innovative molecular designs that carefully balance steric demands and electronic effects. Drawing inspiration from the success of phosphorus-based systems, these efforts will not only broaden the scope of main-group molecular switches but also uncover new paradigms in photodynamic reactivity and responsive materials design.

## Author contributions

All authors have contributed to the writing, reviewing and editing of the manuscript.

## Conflicts of interest

There are no conflicts to declare.

## Data availability

No primary research results, software or code have been included and no new data were generated or analysed as part of this Perspective article.

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