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## Photoswitchable electron-rich phosphines: using light to modulate the electron-donating ability of phosphines<sup>†‡</sup>

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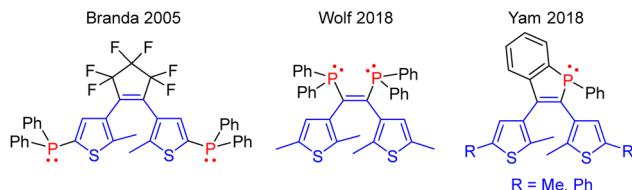
**The synthesis and properties of photoswitchable electron-rich phosphines containing N-heterocyclic imines equipped with a photochromic dithienylethene unit are reported. Heteronuclear NMR spectroscopy and UV/vis studies reveal that the imine substituents undergo reversible electrocyclic ring-closing and ring-opening reactions upon exposure to UV and visible light, respectively. The photoisomerization alters the electron-donating ability of the phosphines by up to  $\Delta\text{TEP} = 8 \text{ cm}^{-1}$ .**

Advances in modern transition metal and main group chemistry have been driven by the availability of strong donor ligands such as tertiary phosphines or N-heterocyclic carbenes (NHCs) with tuneable steric and electronic properties.<sup>1–6</sup> Using light to modulate the electron-donating character of these ligands is a particularly intriguing approach to remotely control properties of coordination compounds and the outcome of chemical reactions.<sup>7–14</sup> Dithienylethene (DTE) compounds, which were first introduced by Irie and co-workers,<sup>15–18</sup> have been proven most effective to alter the electron-donating ability of these ligands. Several photoresponsive phosphines with diazobenzene<sup>19–24</sup> and stiff-stilbene<sup>25–27</sup> chromophores have been reported. However, the photochemical *E/Z* isomerization mainly affects their steric properties and has negligible impact on their electronic properties.<sup>28</sup> Branda and co-workers reported the first photoswitchable DTE-based phosphine by attaching diphenylphosphino groups to the thiophene rings of

the chromophore (Chart 1).<sup>29,30</sup> Using the  $^1J_{\text{PSe}}$  coupling constant to probe the basicity,<sup>31</sup> they showed that the diphosphine is significantly more electron rich in the open form ( $^1J_{\text{PSe}} = 744 \text{ Hz}$ ) than in the closed form ( $^1J_{\text{PSe}} = 756 \text{ Hz}$ ), which corresponds to a change in basicity of  $\Delta\text{p}K_a = 1.6$  units. Subsequent studies showed that the variation of the phosphine basicity is less pronounced for the non-fluorinated DTE backbone.<sup>32</sup> The first chelating diphosphine which carries the phosphino groups at the central ethene unit of the chromophore was recently reported by Wolf and co-workers (Chart 1). The hydroboration of a styrene derivative is catalyzed by the corresponding phosphine-copper(i) complex at different rates, depending on the closed/open form of the DTE backbone.<sup>33</sup> The group of Yam incorporated the DTE unit into a phosphole and showed that the corresponding alkynylgold(i) complexes display photochromic and mechanochromic properties.<sup>34</sup>

A successful approach to photoswitchable NHCs was reported by the groups of Yam and Bielawski based on the incorporation of a photochromic DTE unit into the NHC-backbone.<sup>35–39</sup> The NHC

Previous work:



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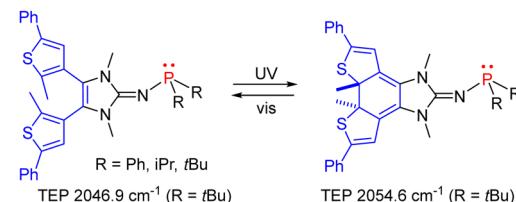


Chart 1 Examples of photoswitchable DTE-based phosphines.

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† Dedicated to Holger Braunschweig on the occasion of his 60th birthday.

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undergoes electrocyclic ring closure upon exposure to UV light leading to a significantly reduced donor strength as determined by the change of the Tolman electronic parameter (TEP)<sup>54</sup> from 2049 cm<sup>-1</sup> (open form) to 2055 cm<sup>-1</sup> (closed form).

The synthetic utilization of these NHCs was demonstrated by enabling photoswitchable Rh(i) catalyzed hydroborations,<sup>40</sup> transesterifications, amidations,<sup>41</sup> and the reversible activation of ammonia.<sup>42</sup> Recently, we converted Bielawski's NHC into N-heterocyclic imines (NHIs) which gave rise to photoswitchable nitrogen superbases exhibiting substantial pK<sub>a</sub> shifts of up to 8.7 units enabling light-driven reversible CO<sub>2</sub> fixation.<sup>43</sup> In 2015, we established that the electron-donating power of phosphines is considerably enhanced by substituents with strong  $\pi$ -donor ability such as NHI groups.<sup>44</sup> Changing the  $\pi$ -donor ability of the substituents thus directly affects the phosphine donor strength, which becomes particularly evident upon protonation of the exocyclic nitrogen atom of the NHI  $\pi$  system, changing the TEP of the phosphine by about  $\Delta$ TEP = 20 cm<sup>-1</sup> for each protonated substituent.<sup>45–47</sup> Small structural variations of the N-heterocyclic  $\pi$ -donor, such as the use of a benzimidazoline rather than an imidazoline backbone, have also been shown to alter the donor properties and reactivity of the corresponding phosphine.<sup>48–52</sup> Expanding on these results, we herein use a DTE-annulated NHI substituent to generate electron-rich phosphines with photoswitchable electronic properties (Chart 1).

For a selection of monosubstituted photoswitchable phosphines (PS-IAPs) with diverse donor abilities, we targeted the synthesis of **3-o**, **4-o** and **5-o** (Scheme 1). Henceforth, the notation o and c refer to the ring-opened and -closed form of the DTE unit in PS-IAPs, respectively. Following the reported synthesis of IAPs,<sup>44,46,53</sup> the phosphines were obtained as purple solids in yields of 93–97% by deprotonation of iminium salt **2** with *n*-butyllithium and subsequent treatment with the respective chlorophosphine. The phosphines, which can be stored in the absence of air and moisture for months, show good solubility in *n*-hexane, toluene, Et<sub>2</sub>O, THF and acetonitrile.

As the DTE unit in the backbone of **3-o**, **4-o** and **5-o** is expected to undergo a reversible electrocyclic photoisomerization reaction, the UV-vis and NMR spectroscopic properties of the phosphines were studied after exposure to UV and visible light, respectively. The UV-vis spectrum of the colorless solution of **3-o** in THF exhibits an intense absorption centered at 290 nm. Subsequent UV irradiation ( $\lambda_{\text{irr}} = 315$  nm) resulted in a purple solution and the decrease of the band centered at 290 nm concomitant with the appearance of new bands at 403

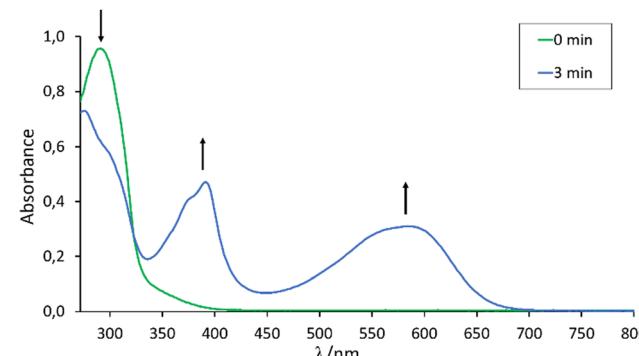


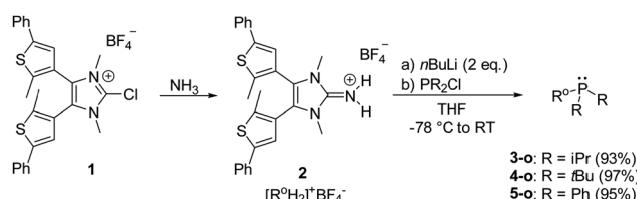
Fig. 1 UV/vis spectral changes of **3-o** in THF ( $[3\text{-o}]_0 = 10^{-4}$  M) upon UV irradiation ( $\lambda_{\text{irr}} = 315$  nm, 140 mW). The spectra were recorded after irradiation for 0 min (green line) and 3 min (blue line). The arrows indicate the evolution of the spectral changes.

and 590 nm (Fig. 1). The initial UV/vis spectrum can be restored by irradiation of the solution at 585 nm for 5 minutes. Similar behavior was observed for compounds **4-o** and **5-o** (see the ESI†).

<sup>31</sup>P NMR spectroscopy is a convenient tool to study small changes in the electronic properties of guanidine-substituted phosphines,<sup>44,46,53</sup> and thus to monitor the photocyclization reaction of PS-IAPs. In fact, upon irradiation of a THF-*d*<sub>8</sub> solution of **3-o** at 310 nm (140 mW) for 1 hour in a quartz NMR tube, a new signal appeared at 58.5 ppm in the <sup>31</sup>P NMR spectrum, which is shifted upfield compared to that of **3-o** (59.6 ppm) and corresponds to the ring-closed species **3-c**. In the <sup>1</sup>H NMR spectrum (in THF-*d*<sub>8</sub>), the two diagnostic resonances of the thiophen protons shift from 6.87 to 6.91 ppm and the methyl groups at the imidazole unit from 3.36 to 3.61 ppm.

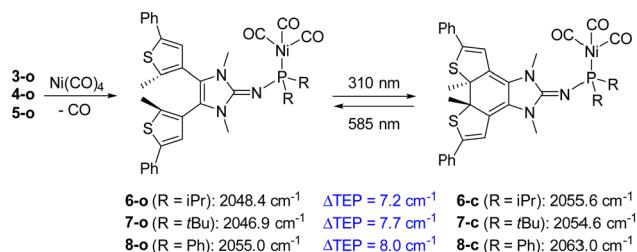
Quantitative <sup>31</sup>P and <sup>1</sup>H NMR spectroscopy reveal 86% conversion of **3-o** to **3-c** upon irradiation with UV light ( $\lambda_{\text{irr}} = 315$  nm, 140 mW) for 1 hour. Prolonged irradiation of the mixture by up to 12 h did not increase this value, which can be attributed to the superimposed UV/vis absorption bands of **3-o** and **3-c** (Fig. 1). The solution containing **3-o** and **3-c** can be stored in the dark for one week without noticeable changes in the <sup>31</sup>P and <sup>1</sup>H NMR spectra. However, full conversion back to **3-o** upon irradiation with visible light ( $\lambda_{\text{irr}} = 585$  nm, 140 mW) for one hour was accomplished. Similar spectral changes were observed for compounds **4-o** and **5-o** upon UV/vis-initiated ring-closing and ring-opening showing 88% and 90% photoconversion to the ring-closed form, respectively, and complete conversion to the ring-open form. The <sup>31</sup>P NMR resonances shift from 72.8 ppm (**4-o**) to 71.5 ppm (**5-c**) and from 33.8 ppm (**5-o**) to 31.9 ppm (**5-c**). For fatigue resistance testing, a concentrated solution of **5-o** was irradiated cyclically with UV and visible radiation for 1 and 3 hours, respectively. After 10 cycles, <sup>31</sup>P NMR analysis of the solution reveals about 14% degradation of the phosphine.

The effect of photoisomerization on the donor strength of the new phosphines was examined by determining their TEP values *via* IR spectroscopic characterization of the corresponding nickel complexes  $[(\text{PS-IAP})\text{Ni}(\text{CO})_3]$  (Scheme 2).<sup>§</sup> The electrocyclic ring closure of the NHI backbone upon UV



Scheme 1 Synthesis of iminium salt **2** and preparation of mono-substituted PS-IAPs **3-o**, **4-o**, and **5-o**.



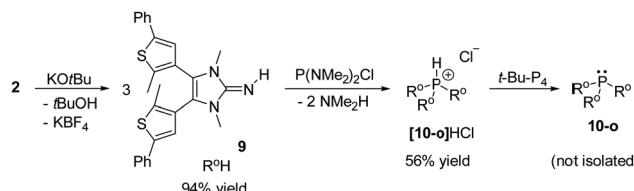


**Scheme 2** Preparation of the nickel complexes  $[(PS\text{-IAP})Ni(CO)_3]$  and the change of the TEP values upon light-induced photoisomerization of the DTE backbone.

irradiation leads to significantly reduced donor strength of the corresponding phosphines. The change in TEP values due to photocyclization of a single NHI group ( $\Delta TEP$  of  $7\text{--}8\text{ cm}^{-1}$ ) exceeds that of photochromic NHCs ( $\Delta TEP = 6\text{ cm}^{-1}$ ).<sup>40,41</sup> Taking the TEP values of phosphines 3, 4 and 5 into account, single substituent parameters of  $\chi = -9.5$  and  $\chi = -1.9$  can be derived for the open and closed state of the photochromic imine substituent, respectively. Similar substituent parameters were observed for NHIs with 4,5-dimethylimidazoline ( $\chi = -8.8\text{ cm}^{-1}$ ) and benzimidazoline ( $\chi = -3.9\text{ cm}^{-1}$ ) backbones,<sup>44,49</sup> showing that the photoisomerization of the DTE unit significantly affects the  $\pi$ -donor character of the NHI substituent.

The molecular structure of 7-o was established using single-crystal X-ray crystallography (Fig. 2). The thiophene rings are tilted from the plane of the imidazole ring ( $56^\circ/42^\circ$ ). Thus,  $\pi$  conjugation from the electron rich NHI unit into the thiophene rings is prevented, which is also evident by the C2–C6 and C3–C17 bond distances in the range of single bonds and explains the strong  $\pi$ -donor character of the substituent in the open state.

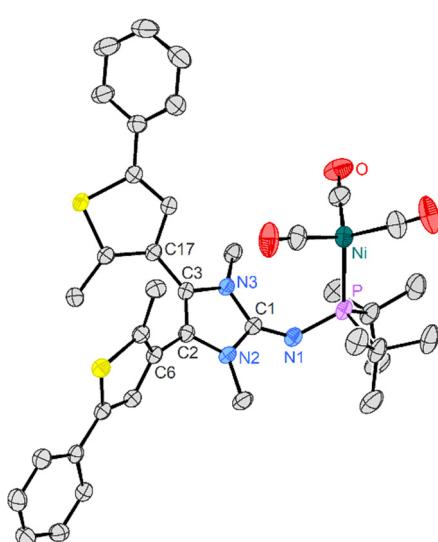
We previously demonstrated that the individual contribution of each  $\pi$  donor substituent to the overall donor ability of



**Scheme 3** Synthesis of the protonated tri-substituted PS-IAP **[10-o]HCl** and generation of the free phosphine **10-o** by *in situ* deprotonation.

IAPs are additive,<sup>44,51</sup> in agreement with Tolman's additivity rule.<sup>54</sup> A phosphine with three photoswitchable NHI substituents is therefore predicted to undergo photoinduced TEP changes of up to  $21.6\text{ cm}^{-1}$  in the range of  $2027.0\text{ cm}^{-1}$  (**10-o**) to  $2048.6\text{ cm}^{-1}$  (**10-c**). We attempted the synthesis of **10-o** by *in situ* deprotonation of 2 with nBuLi or KHMDS and reaction with  $PCl_3$ . However, an insoluble solid material was obtained, presumably due to the formation of stable coordination compounds *via* coordination of the sterically accessible exocyclic N atoms of the NHI moieties to alkali metal salts. Phosphonium salt **[10-o]HCl** was therefore prepared in an alkali metal-free route from the reaction of imine **9** with  $P(NMe_2)_2Cl$  (Scheme 3). **[10-o]HCl** was isolated as a white solid in 59% yield. However, treatment of **[10-o]HCl** with inorganic bases led to the same solubility issues. Using the nonionic *t*-Bu-P<sub>4</sub> Schwesinger base, the deprotonation of **[10-o]HCl** was successful. In the <sup>31</sup>P NMR spectrum of the reaction mixture, the signal for **[10-o]HCl** ( $-22.3\text{ ppm}$ ) had disappeared and a new resonance appeared at  $75.9\text{ ppm}$  with the expected ( $P(NiPr)_3$ :  $79.6\text{ ppm}$ )<sup>49</sup> chemical shift of the desired PS-IAP **10-o**. Despite several attempts, PS-IAP **10-o** could not be separated from  $[t\text{-}Bu\text{-}P_4]\text{-HCl}$  *via* extraction with *n*-hexane, *n*-pentane, diethyl ether or benzene, indicating that **10-o** is sparingly soluble in these solvents. Similar to the PS-IAPs with one NHI substituents, the UV/vis spectrum of the THF solution containing **10-o** and  $[t\text{-}Bu\text{-}P_4]\text{-HCl}$  in THF exhibits an absorption centered at  $290\text{ nm}$ . Exposure of the solution to UV light ( $\lambda_{irr} = 310\text{ nm}$ , 30 s) resulted in a deep purple solution and the decrease of the band centered at  $290\text{ nm}$  concomitant with the appearance of new bands at  $385$  and  $650\text{ nm}$  (Fig. S57, ESI<sup>†</sup>). These bands decrease upon prolonged irradiation and new absorption bands appear at  $355$  and  $580\text{ nm}$ . This observation suggests the stepwise photocyclization of the NHI substituents leading to several isomers. Indeed, the initial UV/vis spectra can be restored by exposure to light at  $585\text{ nm}$  for 5 minutes, confirming the reversibility of the photoreaction.

In conclusion, three photoswitchable phosphines (PS-IAPs) with electron donor ability in the range of NHCs were synthesized. Upon irradiation with UV and visible light, the photochromic DTE unit undergoes reversible photocyclization reaction with 85% conversion leading to changes in the TEP values of the corresponding phosphines of up to  $\Delta TEP = 8\text{ cm}^{-1}$ , which exceeds that of photochromic NHCs ( $\Delta TEP = 6\text{ cm}^{-1}$ ).<sup>40,41</sup> Photo-induced TEP changes of up to  $21.6\text{ cm}^{-1}$  are predicted for PS-IAPs with more than one photoswitchable NHI substituent. However, issues with the isolation of **10-o** indicate that sterically more



**Fig. 2** Solid-state structure of **7-o**. Hydrogen atoms and a disordered pentane solvent molecule are omitted for clarity. Ellipsoids are drawn at 50% probability. Selected bond lengths ( $\text{\AA}$ ): P–Ni 2.2717(5), P–N1 1.6624(16), N1–C1 1.306(2), N2–C1 1.376(2), N3–C1 1.378(2), N2–C2 1.395(2), N3–C3 1.405(2), C2–C3 1.357(2), C2–C6 1.468(2), C3–C17 1.464(2).



encumbered substituents are recommended to prevent the formation of stable coordination compounds and to increase the solubility of the PS-IAPs.

D. J.-M., M. D., M. F. and A. D. synthesized imidazolium salt 1. F. B. and A. S. synthesized the phosphines, supported by M. D. and L. F. B. W., and performed the photochemical experiments. M. S. performed the SCXRD study. F. D. and F. G. directed the investigation. F. B. and F. D. wrote the manuscript with contributions from all authors. All authors have given approval to the final version of the manuscript.

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## Conflicts of interest

There are no conflicts to declare.

## Notes and references

§ Note that complex **8-o** did not undergo the electrocyclic ring-closing reaction upon UV irradiation, presumably due to overlapping absorption bands. The ring-closed phosphine **5-o** was therefore reacted with  $\text{Ni}(\text{CO})_4$  to access **8-e**.

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