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Specific Photochemical Dehydrocoupling of N-Heterocyclic Phosphanes and Their Use in the Photocatalytic Generation of Dihydrogen

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Dedicated to Professor Manfred Scheer on the occasion of his 60th birthday

Abstract: N-Heterocyclic phosphanes react under UV irradiation in a highly selective dehydrocoupling reaction to diphosphanes and H_2 . Computational studies suggest that the product formation is initiated by the formation of dimeric molecular associates whose electronic excitation yields H_2 and a diphosphane. Combining the dehydrocoupling of sterically demanding phosphanes with Mg-reduction of the formed diphosphanes allows constructing a reaction cycle for the photocatalytic reductive generation of H_2 from Et₃NH⁺.

Condensation of two element-hydrogen bonds to afford a new element-element (E-E) bond and dihydrogen is commonly denoted as "dehydrocoupling" (Scheme 1; the

> $R_nE-H + H-ER_n \xrightarrow{(cat.)} R_nE-ER_n + H_2 (a)$ $R_nE-H + H-E'R_n \xrightarrow{(cat.)} R_nE-E'R_n + H_2 (b)$

Scheme 1. a) Homo- and b) hetero- dehydrocoupling reaction.

E–E bond formed can be homo- or heteronuclear).^[1] The reaction is generally carried out with a catalyst, which permits to apply less forcing conditions and widens the scope of useable element–hydride substrates. Currently, dehydrocoupling routes draw growing attention in main-group chemistry as complement to established protocols (e.g., Wurtz-type reductions or dehydrohalogenation/salt elimination) for syntheses of E–E-bonded frameworks.^[1] Lately, they have also gained interest as a means to release H_2 from chemical storage materials.^[2]

Whereas early studies mainly focused on the bond formation between boron atoms or heavier Group 14 elements, catalyzed dehydrocoupling has meanwhile developed into a valuable approach for the selective formation of

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phosphorus–element bonds (including P–P bonds).^[3] Assembly of P–P bonds through uncatalyzed dehydrocoupling is also known, but has received little interest. Thermally induced reactions need high temperatures (175–200 °C), which is detrimental for selectivity and product stability.^[4] Photochemically induced dehydrocoupling seems to be limited to parent phosphane, which reacts upon UV photolysis to give H_2 and P_2H_4 as primary products.^[5] However, selectivity is likewise low, as diphosphane is photochemically unstable and decays to higher phosphanes and eventually elemental phosphorus.

During earlier syntheses of secondary N-heterocyclic phosphanes, we had noted that some of the formed products were converted to diphosphanes when the reaction mixtures were exposed to light (Scheme 2).^[6] Inspired by this observa-



Scheme 2. Reductive diphosphane synthesis via a spectroscopically detectable secondary phosphane intermediate. R = tBu, Xyl (2,6-Me₂C₆H₃).

tion, we have now carried out a detailed study of the photolysis of N-heterocyclic phosphanes and could establish that these species undergo photochemically induced dehydrocoupling which can be employed in a reaction cycle for photocatalytic generation of H_2 .

Photolysis experiments were carried out by irradiating solutions of isolated, pure N-heterocyclic phosphanes **1a–c/1'a,c** in inert solvents (THF, hexane) with a medium-pressure Hg-lamp. Monitoring the progress of the reactions by ³¹P NMR spectroscopy confirmed that a clean transformation to the diphosphanes **2/2'** took place (Scheme 3 and Figure 1).

The formation of dihydrogen as by-product was established by the direct observation of its characteristic signal $(\delta^1 H = 4.69)$ in the ¹H NMR spectrum of an irradiated solution of **1a** in [D₈]THF, and by trapping of the gas evolving from the reaction mixture through adsorption on palladium and elemental analysis.^[7] The ¹H and ³¹P NMR spectra of the reaction mixture showed no signals of transient intermediates or by-products. The reaction stopped when the photolysis was interrupted, and diphosphane formation was not at all detectable in control samples that were prepared and stored





Scheme 3. Photochemically induced dehydrocoupling of N-heterocyclic secondary phosphanes at ambient temperature ($Dipp=2,6-iPr_2C_6H_3$, Cy = cyclohexyl, tBu = tert-butyl); [a] determined by integration of ³¹P NMR signals. [b] The P-deuterated derivative (**1** a-D₁) gave 86% conversion after 28 h.



Figure 1. Photochemical conversion $1a \rightarrow 2a$ in THF at ambient temperature as monitored by ³¹P NMR spectroscopy.

under identical conditions, but protected from UV light. These findings confirm that P–P bond formation requires no other reactants (which may be present in the original reaction mixtures of Scheme 2) than the phosphanes 1/1', that the conversion is a photochemical reaction which does not go along with a thermal background process, and that the transformation proceeds as a selective, photochemically induced dehydrocoupling as shown in Scheme 3.

The reaction is amenable to diazaphospholenes (**1**'a,c) and diazaphospholidines (**1a–c**) with *N*-aryl and *N*-alkyl substituents (Scheme 3). Low-pressure Hg-lamps can also be used as radiation source. Preliminary studies indicate that the initial rate of diphosphane formation decreases with increasing concentration of the phosphane precursor, suggesting that the reaction does not follow a simple rate law. Unlike $P_2H_4^{[5]}$ and P_3H_5 ,^[8] the diphosphanes **2**/**2**' did not undergo detectable follow-up reactions and seem thus photochemically stable.

To gain insight into the electronic excitation and excitedstate characteristics of the N-heterocyclic phosphanes, we carried out DFT calculations on **1a**, **1'a**, and the *N*-Mesubstituted model compound **1'd**. Ground-state relative energies and geometries were computed at the $\omega B97xD/$ aug-cc-pVDZ level to account for the dispersion effects associated with the bulky substituents. Calculations of excited states were carried out at the TD-DFT CAM-B3LYP/aug-ccpVDZ level, which was selected after a performance study of different computational levels on **1'd** and allows a suitable modeling of Rydberg states.

For the electronic ground states of 1a and 1'a, three conformational isomers with different alignment of N-tBu and PH substituents were located. As the relative energies of these conformers differ by less than 2 kcal mol⁻¹, it is possible that all three contribute to the observed spectrum. The lowest (vertical) excitation is predicted to occur around 230 nm for 1a and at 280–300 nm for 1'a, depending on the conformation. In addition, each species may undergo several further excitations in the near UV region (7-9 out of the 15 lowest energy transitions for each conformer of 1a and 12-15 transitions for each conformer for 1'a are predicted to occur at wavelengths > 200 nm). Due to the high density of states and the coexistence of several conformers, the spectra are expected to exhibit rather little structure. This is in accord with the habit of the experimental UV-spectra of 1a and 1'a, which display an end-absorption with an inflection arising from an unresolved absorption band. The band maxima (1a: $\lambda_{\rm max} \approx 237 \,\rm nm; \, 1b: \, \lambda_{\rm max} \approx 274 \,\rm nm$ as inferred from spectral deconvolution) are red-shifted with respect to the spectral bands of PH₃ or simple trialkylphosphanes ($\lambda_{max} = 200$ -210 nm).^[9] Both the position of these bands and the ca. 40 nm redshift of the band onset of 1'a with respect to 1 a are in accord with the calculated wavelengths of the lowest energy transitions.

This lowest energy excitation is of specific importance because photochemical reactions originate from this state (Kasha's rule). Our calculations indicate that each conformer of 1a and 1'a exhibits two close-lying excited states which are of mixed valence/Rydberg character. Both excitations originate from the HOMO, which is a symmetrical combination of the nitrogen lone pairs with some hyperconjugative interaction with the σ_{PH} and (for 1'a) π_{CC} orbitals (for an illustration see the HOMO of 1'd in Figure 2a). The 8-10 lowest unoccupied orbitals of each conformer of 1a and 1'a are of diffuse nature. The LUMO is always an s-type and the LUMO + 1 a p-type diffuse orbital with similar symmetry as the lowest energy σ^* -valence orbital (LUvMO), which has NPN antibonding character (Figure 2b shows the appropriate orbital of 1'd). One of the two low-energy transitions is mainly of HOMO-LUMO (Rydberg) nature with small contributions from a valence excitation, whereas the other one involves a mixture of HOMO-LUvMO and HOMO-LUMO+1 excitations. For two conformers of 1a, the σ^*_{PH} orbital is only slightly higher than the LUvMO. It is note-



Figure 2. MOLDEN representation of a) the Kohn–Sham HOMO and b) the lowest-energy unoccupied valence MO (LUvMO) of **1'd**.

worthy that for all **1'a** conformers and for one **1a** conformer the HOMO–LUMO (pure Rydberg) excitation is not the one at lowest energy.

TD-DFT geometry optimization of the first two excited states of 1a and 1'a,d gave no evidence for a PH-dissociative nature which could explain the observed photochemical reactivity. Excitations with significant contribution from the HOMO-LUvMO electron configuration are accompanied by distinct PN bond lengthening (in accord with the PN antibonding character of this orbital),^[10] but even geometry optimization from a starting configuration with an extended P-H distance (1.6 Å) gave no indication for a possible decay through PH bond cleavage. In contrast, geometry optimization of the first excited state of PH3^[11] at the same computational level converged to a conical intersection which opened a pathway to PH bond fission, in accord with the known photochemical behavior of phosphine. It seems thus that the H-elimination channel in 1a and 1'a can only be reached from higher excited states.

In search for an alternative mechanism, we considered the formation of a phosphane dimer, either in the ground state or an excited state. During geometry optimization of dimeric structures $(\mathbf{1'd})_2$ at the ω B97XD/aug-cc-PVDZ level, we located one minimum with a stabilization energy of 5.2 kcal mol⁻¹ relative to the monomers and a P–P distance of 3.326 Å. RI-CC2/aug-cc-pVDZ geometry optimization gave a structure with a P–P distance of 3.089 Å and 8.9 kcalmol⁻¹ dimerization energy. Its LUvMO is a bonding combination of the LUvMOs of two monomers (Figure 3), and the first



Figure 3. MOLDEN representation of the CAM-B3LYP/aug-cc-PVDZ LUvMO of a dimeric structure $(1'd)_{2}$.

excited state has a significant contribution from the HOMO– LUvMO electron transition. The excitation energy of the dimer (at the RI-CC2/aug-cc-pVDZ geometry) is by 0.14 eV lower than that of the monomer, indicating a slight stabilization upon excimer formation. CC2 geometry optimization of this state converged to a conical intersection which enables the split of H₂ and formation of the diphosphane **2'd**. We conclude that photochemical excitation of a dimer provides thus a suitable explanation of the observed reaction behavior.

Since it is of interest whether the photochemically induced H_2 formation is reversible, we investigated computationally the thermochemistry of the dehydrocoupling reactions (Scheme 3) for 1'd and its saturated analogue 1d. The first

reaction was calculated to be weakly exergonic ($\Delta G_{298} = -1.5 \text{ kcal mol}^{-1}$) and the second one slightly endergonic ($\Delta G_{298} = 2.4 \text{ kcal mol}^{-1}$). NMR studies on solutions of **2c** and D₂ (which was used instead of H₂ in order to distinguish a possible bond activation product from species formed by diphosphane hydrolysis^[6]) in THF or [D₈]THF gave no evidence for the formation of D₂-activation products between ambient temperature and 60 °C. We conclude that the dehydrocoupling of **1c** is therefore indeed exergonic, or that reaction of H₂ with **2c** (or the phosphanyl radicals formed by P–P bond fission^[6,13]) is impeded by a substantial activation barrier.

As alternative to the direct activation of H_2 , regeneration of a secondary phosphane from a diphosphane is also feasible through a reductive pathway. The Et₃NHCl/Mg reduction of sterically strained N-heterocyclic diphosphanes with weak P– P bonds^[14] like **2c/2'c** seems particularly interesting for this purpose: the reaction proceeds at ambient temperature,^[6] and its combination with the photochemical dehydrocoupling of the phosphanes (**1c/1'c**) allows one to design a reaction cycle that should enable the reductive generation of H_2 from Et₃NH⁺ with a catalytic amount of the diphosphane (Scheme 4).



Scheme 4. Photocatalytic generation of H₂ from Et₃NH⁺ with magnesium as stoichiometric reductant and sterically demanding N-heterocyclic phosphanes/diphosphanes as photocatalysts. R = Dipp.

In line with this idea, we studied the reduction of Et₃NHCl with Mg in THF in the presence of $2c^{[6]}$ or *P*-bromodiazaphospholene $3'c^{[12]}$ which is reduced in situ to $2'c^{[6]}$ and may thus serve as precatalyst. In a first experiment, a mixture of the reactants in [D₈]THF was photolyzed in an NMR tube and the amount of liberated Et₃N monitored by ¹H NMR spectroscopy (Figure 4 a). The observed molar ratio $n(\text{Et}_3\text{N}):n(2'c) \approx 8.8$ clearly exceeds the value of two expected for the reaction^[6]

 $\mathbf{2'c} + 2\,\text{Et}_3\text{NHCl} + Mg \rightarrow 2\,\mathbf{1'c} + Mg\text{Cl}_2 + 2\,\text{Et}_3\text{N}$

which implies that the regeneration of 2'c by photolytic dehydrocoupling enables a turnover number (TON) > 1 and the reaction is thus catalytic in diphosphane. This was confirmed by further experiments which were conducted at higher dilution with 3'c or 2c as (pre)catalyst and monitored by measuring the volume of evolved H₂ (Figure 4b). The





Figure 4. a) Plot of mole of Et₃N per mole of diphosphane produced during photolysis of **2'c** (formed in situ from Mg and **3'c**) in the presence of excess Mg/Et₃NHCl versus reaction time. Data were derived from integration of ¹H NMR spectra recorded during the reaction. b) Plot of mole of H₂ generated per mole of diphosphane during photolysis of **2'c** (formed in situ by Mg reduction of **3'c**, blue circles) or **2c** (red diamonds) in the presence of excess Mg/Et₃NHCl versus reaction time. Grey areas indicate time periods when the irradiation was switched off and gas evolution ceased. Open green squares indicate the result of a control measurement without phosphane. The dashed horizontal lines mark the amount of Et₃N or H₂ formed in a stoichiometric reaction Mg + **2'c** + 2 Et₃NH⁺ \rightarrow **1'c** + 2 Et₃N + Mg²⁺ + H₂.

results illustrate that up to 18 turnovers (with $2^{\prime}c$ as catalyst) were reached, and that the activity of the phosphane– diphosphane pair acting as photocatalyst can be switched on and off by control of the radiation source. The higher conversion rate for the diazaphospholene-based photocatalyst indicates that the high tendency of $2^{\prime}c$ toward homolytic P–P bond cleavage^[13] may have some impact on its catalytic activity.

In conclusion, we have shown that functional phosphanes 1 and 1' undergo, unlike PH_3 or P_2H_4 , selective photochemically induced dehydrocoupling at room temperature. Computational studies suggest that the reaction is initiated by formation of phosphane dimers whose photochemical excitation yields H_2 and the diphosphane. This process can be implemented into a reaction cycle which enables photocatalytic generation of H_2 on demand upon irradiation with UV light. The feasibility of photolytic dehydrocoupling as specific reaction channel for functional phosphanes suggests that this transformation may also play a role in other photochemical processes (cf. the photolytic high-pressure reaction of red phosphorus with water to give H_2 and phosphorus oxyacids^[15]), and we are currently studying possible applications for further types of phosphanes.

Experimental Section

The starting materials $1a{-}c,^{[6]}$ $1'a{,}c,^{[16]}$ and $3c^{[12]}$ were prepared as described. Photolysis experiments with pure phosphanes were carried out in 3 mmol solutions in degassed and rigorously dried solvents (THF, [D₈]THF, hexane) in Pyrex NMR tubes, and the reactions were monitored by ³¹P and—where appropriate—¹H NMR spectroscopy. Photocatalytic reduction of Et₃NHCl was carried out a) by irradiating a mixture of magnesium powder (13.4 mg, 0.55 mmol), Et₃NHCl (140 mg, 1.02 mmol), and **3'c**: 5 mg, 1.13×10^{-2} mmol) in 0.6 mL [D₈]THF, or b) by irradiating a slurry of magnesium turnings (100 mg, 4.2 mmol), Et₃NHCl (700 mg, 5.1 mmol), and the phosphane (pre)catalyst (3'c: 100 mg, 0.20 mmol; 2c: 73 mg, 0.090 mmol) in THF (25 mL) with a medium-pressure Hg-lamp. The progress of the reaction was either monitored by ¹H NMR spectroscopy (reaction a, Figure 4a) or volumetric determination of H₂ (reaction b, Figure 4b). Further experimental details and characterization data (UV spectra) as well as a comprehensive account of the computational studies are given in the Supporting Information.

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Keywords: computational studies · dehydrocoupling · hydrogen · N-heterocyclic phosphanes · photolysis

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