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1,4-Additions of tricyclic 1,4-diphosphinines – a novel system to study σ-bond activation and π–π dispersion interactions

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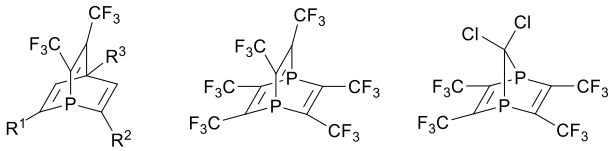
The dienic nature of the aromatic π-system in 1,4-diphosphinines remained largely unexplored to this day due to a lack of facile and efficient synthetic protocols. Recently reported stable, tricyclic 1,4-diphosphinines were used to explore the thermal reactivity of the π-system towards an array of dienophiles in [4π+2π]- and, for the first time, in [4π+2σ]-type cycloaddition reactions.

The discovery of phosphinines[1] by Märkl in 1966[2] was a landmark in the chemistry of low-coordinate phosphorus compounds, providing another good example of the isolobal analogy between CH and P.[3] This relationship holds even quantitatively in terms of the measured π ionization energies (energies of occupied π orbitals).[4] Consequently, aromaticities of $\sigma^2\lambda^3$-P containing compounds are only little less than their carbon counterparts,[4] when replacing carbon units by phosphorus. Due to the conjugated π-system and the presence of the P-center in the heterocyclic ring, phosphinines show two distinct reactivity features: a highly electrophilic P-center (i) and a dienic nature (double bond activation) of the π-system (ii).[5] The latter was used in the first synthesis of phosphabarrelenes **I** (Figure 1), obtained via [4+2]-cycloaddition of phosphinines with hexafluoro-2-butyne,[6] an electron-poor dienophile. This early success stimulated research on phosphabarrelenes which have become important ligands, e.g., in Rh-catalyzed hydroformylation[7, 8] and hydrogenation[9] of alkenes. Bidentate phosphabarrelene-based P,S-ligands[10] were also found to be highly effective in Pd-catalyzed Suzuki-Miyaura cross coupling.[11] In contrast to phosphinines, the low stability of the solitary case



I II III

Figure 1: Cycloaddition products of phosphinines (**I**) and a 1,4-diphosphinine (**II**,**III**).

of tetrakis(trifluoromethyl)-1,4-diphosphinine **II**[12, 13] and the lack of alternative and efficient synthetic protocols have barred a broad exploration of their chemistry including diene-type properties. Kobayashi and co-workers reported only preliminary results on cycloaddition reactions leading, e.g., to 1,4-diphosphabarrelene **II** and the 1,4-diphosphanorborna-diene derivative **III**,[12] but no further studies on the chemistry of **II** and **III** were reported.

Recently, we reported a facile access to stable, tricyclic imidazole-2-thione-based 1,4-diphosphinines[14] thus paving the way for broad reactivity studies. It is noteworthy that this protocol,[14] meanwhile, could be amended to other heterocyclic thiones.[15, 16] Since we have established that this compound can easily be oxidized, and reduced we expected that it will be rather reactive in bond activation reactions.

Herein, we present [4π+2π]-cycloaddition reactions of a tricyclic 1,4-diphosphinine with an alkyne and an alkene derivative along with novel [4π+2σ]-type cycloaddition reactions with diphenyldisulfane and –diselane yielding *trans* 1,4-addition products, selectively; the latter also represents an interesting new example of σ-bond activation.

Firstly, we studied the case of diphenylacetylene that was heated with the tricyclic 1,4-diphosphinine **1**[14] in toluene at 110 °C, but even after one week no reaction was observed. But when the dienophile was changed to an electron-deficient derivative such as dimethylacetylenedicarboxylate (DMAD) a clean conversion to the corresponding 1,4-diphosphabarrelene **2a** (Scheme 1) was already detected at 35 °C. In the same vein, reaction of *N*-phenyl maleimide with **1** resulted in the formation

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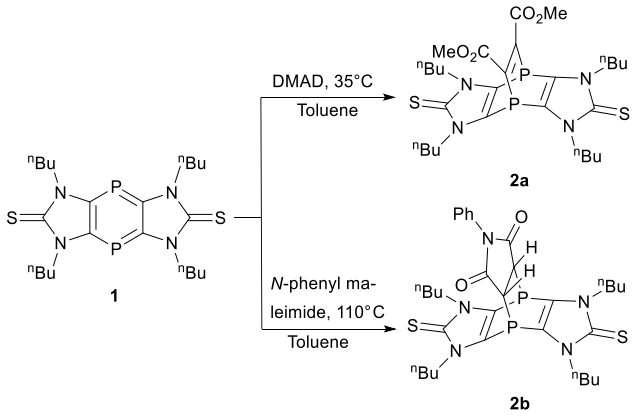


Scheme 1: [4+2]-Cycloaddition reactions of 1,4-diphosphinine **1** to yield **2a,b**.

of 7,8-dihydro-1,4-diphosphabarrelene **2b**. Compounds **2a,b** were isolated in excellent yields (95% for **2a** and 91% for **2b**) and fully characterized by spectroscopic and analytical methods (see ESI for details). The $^{31}P\{^{1}H\}$ NMR spectra showed resonance signals at -87.3 ppm (**2a**) and -86.3 ppm (**2b**), respectively, being in agreement with the presence of two bridgehead P-centers bearing three directly bound carbon atoms.[16, 17]

Single crystal X-ray structures of **2a** and **2b** (Figure 2) revealed that the P(1)-C(1) bond lengths are within the range of 1,4-diphosphatrypticenes.[17] For **2b** a slightly longer P(1)-C(23) bond can be explained by the presence of sp^3-hybridized carbon centers, instead of sp^2 as in **2a**. The sum of bond angles at the P-centers revealed strong pyramidal environments [$\Sigma\sphericalangle$ P = 280° (**2a**) and 284° (**2b**)] which are in good agreement with the value for 2,4,6-tri-phenyl[7,8]benzo-phospha-bicyclo-[2.2.2]octa-2,5,7-triene (283°).[7] This high extent of pyramidalization should result in high s-character of the P-lone pairs, resulting in reduced σ-donor properties of **2** type cage compounds.[18] In particular, it is of interest for the π-donating ability of such diphosphabarrelenes; studies on this property will be described in a future publication.

To have a better understanding of the reaction, M06-2X/6-311+G** DFT calculations were carried out. We considered the concerted pathway, which is preferred for [4π+2π]-cycloaddition reactions,[19] (Table S1 in ESI). In good agreement with the experimental results, the reaction with diphenylacetylene has a high activation barrier ($\Delta G^{\#}$ = 35.9 kcal/mol) along with an endergonic reaction Gibbs free energy (ΔG = 5.4 kcal/mol), thus hampering the reaction. On the other hand, reactions with DMAD and *N*-phenyl maleimide showed much lower activation barriers (25.3 and 18.2 kcal/mol, respectively, thus explaining the facile conversion of **1** during a slightly exergonic process (ΔG = -4.9 and -2,3 kcal/mol, respectively).

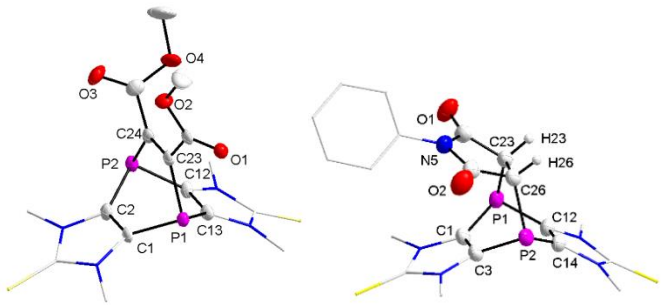
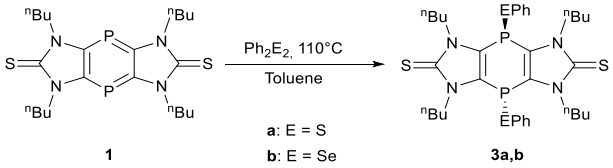


Figure 2: Reduced molecular structures of **2a** (left), **2b** (right). The ^{n}Bu chains and the H atoms (except H23 and H26) are omitted for clarity; (50% probability label). Selected bond distances (Å) and angles (°): for **2a**: P(1)-C(1) 1.820(6), P(1)-C(23) 1.878(7), C(1)-C(2) 1.353(9), C(23)-C(24) 1.329(9); C(1)-P(1)-C(23) 94.0(3), C(24)-C(23)-P(1) 122.2(5). For **2b**: P(1)-C(1) 1.826(3), P(1)-C(23) 1.897(4), C(1)-C(3) 1.363(4), C(23)-C(26) 1.532(5); C(1)-P(1)-C(23) 94.87(15), C(26)-C(23)-P(1) 117.5(2).



Scheme 2: Thermal 1,4-addition of PhE-EPh derivatives to 1,4-diphosphinine **1**.

Compound **1** showed no reaction with disulfane and diselane (dichalcogenides) Ph_2E_2 (E = S, Se, Te) in toluene at room temperature, but at 110 °C reactions occurred (Scheme 2). The $^{31}P\{^{1}H\}$ NMR spectra showed the slow consumption of compound **1** alongside with the fading of the dark red color, eventually turning bright yellow. The *trans* 1,4-dihydro-1,4-di-phosphinines **3a,b** were isolated as yellow powders in excellent yields (78% for **3a** and 75% for **3b**), and both compounds were unambiguously confirmed, including X-ray crystallography (Figure 3).

3a and **3b** showed ^{31}P chemical shift values at high field (-34.1 ppm for **3a**, -44.6 ppm for **3b**). The molecular structures, obtained by X-ray crystallography, confirmed that the 1,4-addition had occurred selectively to furnish the *trans* isomers of **3a,b**. According to the DFT studies, the *trans* isomer is by 15.4 (**3a**) and 12.5 (**3b**) kcal/mol more stable than the *cis* isomers, and the Gibbs free energy of the reaction being exergonic by 13.9 (S) and 7.0 (Se) kcal/mol for the two compounds (Figure S16 and S17 in the ESI). Under the same reaction conditions compound **1** showed (virtually) no reactivity towards Ph_2Te_2, which is in good agreement with the calculated positive (3.8 kcal/mol) reaction Gibbs free energy of the process.

To understand the mechanism and stereospecificity of the reaction, further M06-2X/6-311+G** DFT calculations provided a surprising result. (Figure S16 and S17). Our starting hypothesis was that the first step is a 1,1-addition of Ph_2E_2 at one of the phosphorus atoms resulting in a mixed-valence intermediate with one $\sigma^2\lambda^3$- and one $\sigma^4\lambda^5$-phosphorus atom. A further migration of one of the EPh units would then result in the formation of the product (Figure S17 in the ESI).

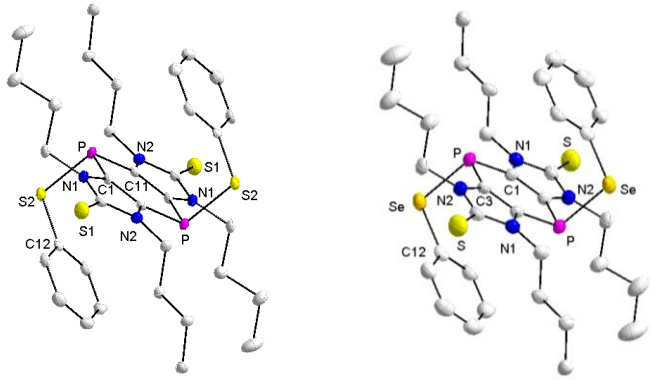


Figure 3: Reduced molecular structures of **3a** (left), **3b** (right). The H atoms are omitted for clarity; (50% probability label). Selected bond distances (Å) and angles (°): for **3a**: P-S(2) 2.1555(8), P-C(1) 1.803(2), S(2)-C(12) 1.781(2), C(1)-C(11) 1.369(3); C(1)-P-C(11) 96.54(9), P-S(2)-C(12) 102.86(7). For **3b**: P-Se 2.3098(7), P-C(1) 1.799(2), Se-C(12) 1.919(3), C(1)-C(3) 1.367(3); C(1)-P-C(3) 96.16(11), P-Se-C(12) 99.85(8).

The barrier for the first reaction step, however, turned out to be prohibitively high (63.5, and 61.6 kcal/mol for S and Se, respectively). Thus, we considered, the unusual [4π+2σ]-type cycloaddition producing the *cis* isomer, which should then invert thermally to the thermodynamically more stable *trans* isomer. The 41.4 kcal/mol barrier of the diphenyldisulfane addition (41.7 kcal/mol for the Se analogue) is considerably smaller than the TS of the alternative pathway (Figure S17 in the ESI). The inversion barrier between the *cis* and the *trans* structure (31.1 kcal/mol for SPh and 33.8 kcal/mol for SePh) is somewhat smaller. While the ca. 40 kcal/mol reaction barrier is too large for a reaction at room temperature, the reaction is enabled at 110 °C (Scheme 2).

The solid state structures of *trans* **3a,b** revealed that the two phenyl rings are folded inwards indicating some interaction between the Ph ring and the middle ring of the tricycle. This arrangement is facilitated by the usually near 90° bonding angle[22] about the heteroatoms phosphorus and sulfur. To reveal the strength of this interaction the different rotamers (in/in, in/out, out/out) were computed. The in/in rotamers of **3a** and **3b** (as shown in Figure 3 and Figure S18 in ESI) exhibit higher stability by 7.6 (S) and 5.9 (Se) kcal/mol than in/out and by 13.5 (S) and 13.8 (Se) kcal/mol than the out/out rotamer. It is noteworthy, that the energy of the *cis* isomer (S) – where the phenyl moieties are also not interacting with the tricyclic system – is by 16 kcal/mol higher than in case of the in/in *trans* structure. These evidences suggest that the interaction be-tween one phenyl and the middle ring of the tricycle amounts to 6-7 kcal/mol.

To understand the nature of this interaction, we have investigated the orbitals of **3a**, but did not find any occupied/ unoccupied pairs which could favourably interact to stabilize the observed structure. Also a second order perturbation theory investigation on the NBO basis, yielded again only small interactions (less than 2 kcal/mol). Thus, it seems that the stabilizing effect is mainly due to dispersive forces. Indeed, at the B3LYP/6-311+G** level, which provides a poor description of the dispersive effects, the Gibbs free energy difference between the in/in and out/out structures is reduced to 6.1 kcal/mol, while ωB97X-D/6-311+G** gave similar (14.3 kcal/mol) results to M06-2X.

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