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## COMMUNICATION

## The potassium hydride mediated trimerization of imines†

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A novel reaction, the potassium hydride mediated synthesis of fulvenes, is described. The synthesis utilizes *N*-aryl imines as an inexpensive starting material affording novel substituted amino-fulvenes. It is proposed that the presence of the metalated enamine as well as the imine (ratio 2 : 1) leads to the formation of an initial dimerization and a transient trimerization product, which cyclizes, giving rise to the aminofulvene.

Pentafulvenes, first described by Thiele at the beginning of this century,<sup>1</sup> attracted much interest due to their color,<sup>2</sup> reactivity (especially cycloadditions),<sup>3</sup> dipole moment<sup>4</sup> and questions regarding their aromatic or anti-aromatic<sup>5</sup> character. Furthermore they represent a class of very interesting organic ligands. Various organometallic compounds, being applied for instance as polymerization catalysts<sup>6</sup> or anticancer agents,<sup>7</sup> have been synthesized *via* fulvene routes.<sup>8</sup> Fulvenes can be obtained by condensation reaction<sup>9</sup> of aldehydes or ketones with cyclopentadienyl. Additionally, a few other methods can be utilized.<sup>10</sup> Herein we report a novel potassium hydride mediated approach towards 1,3,6-substituted 6-aminofulvenes. The imine trimerization reaction is based on tautomerization into metalated enamines and proceeds *via* C–H activation and multiple C–C bond formation steps.

Within experiments regarding the asymmetric hydrogenation<sup>11</sup> of **1a** (Fig. 1), the formation of a by-product was observed if KH was utilized as a base. A dark red material crystallized in one of the catalysis samples. It was identified as [(2,4-diphenyl-cyclopenta-2,4-dienylidene)-phenyl-methyl]-phenyl-amine **2a** (Fig. 1).

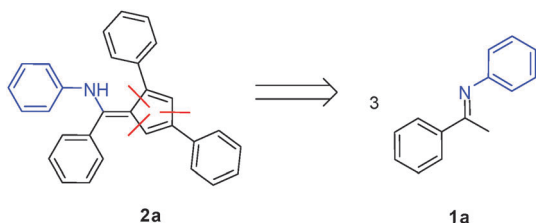


Fig. 1 Retrosynthetic approach towards novel fulvenes.

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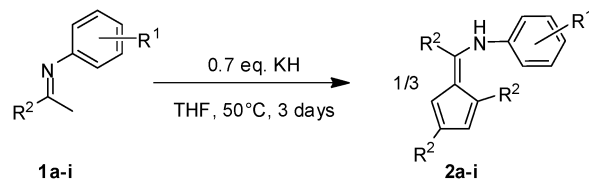


Fig. 2 Synthesis of fulvenes from *N*-aryl imines.

Upon this discovery, we were interested in understanding and using the side reaction. A precise reaction stoichiometry (imine : KH ratio) is crucial to yield fulvenes as the main product. Addition of a large excess of potassium hydride (3 eq.) led to amine formation, whilst using one equivalent mainly yielded the imine starting material (after workup). Upon utilization of 0.7 equivalents of potassium hydride, complete conversion of the imine to the corresponding 6-aminofulvene as the main product was observed (Fig. 2). The addition of several metal bases was investigated. Only the utilization of potassium hydride gave rise to fulvene **2a** with complete conversion of the starting material.

Upon the addition of potassium hydride to imines **1a–i** the color of the reaction solution changed quickly to green and then dark red, accompanied by hydrogen evolution. The corresponding fulvenes **2a–i** were obtained as dark red materials in moderate yields (Fig. 3).

A time-conversion plot was generated to gain additional insight into mechanistic details of this novel reaction (Fig. 4).

The isolated yield of the fulvene is consistent with the GC-yield, which was obtained in the kinetic experiment. Additionally, the formation of an intermediate (**3a**) and a by-product (**4a**) could be observed as well as the formation of imine. The key intermediate (1,3-diphenyl-but-3-enylidene)-phenyl-amine (**3a**) was independently synthesized. Reduction of **3a** gives rise (after aqueous workup) to the by-product (1,3-diphenyl-butylidene)-phenyl-amine (**4a**), which could be isolated from the reaction mixture and was characterized by NMR spectroscopy and EA.

The potassium cyclopentadienylimine complex **5a** was crystallized from the reaction mixture and was analyzed *via* X-ray crystal structure analysis to determine the molecular structure (Fig. 5).

In the dimeric complex **5a**, the potassium is coordinated by the N-atom and further stabilized by  $\pi$ -coordination of the electron rich phenyl substituents of **5a** and the cyclopentadienyl moiety of a second ligand molecule. The bond lengths of **5a**

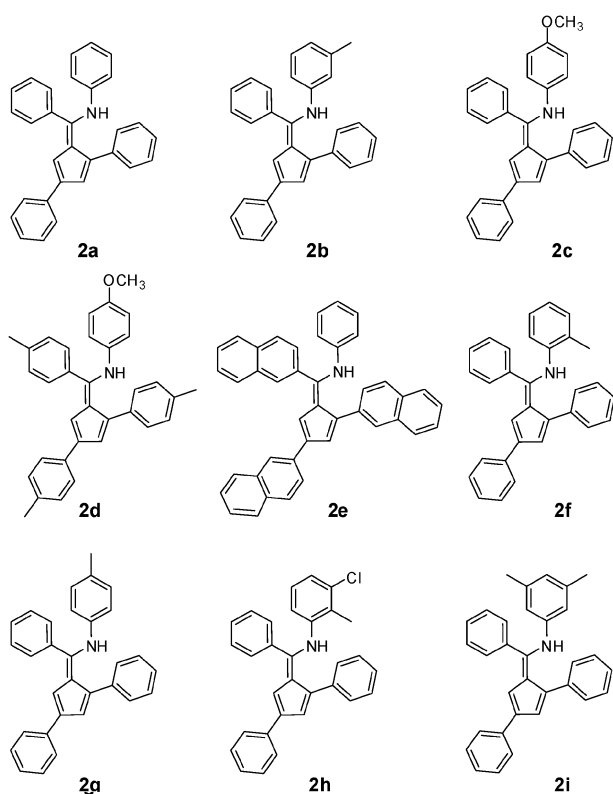


Fig. 3 6-Aminofulvenes **2a-i**.

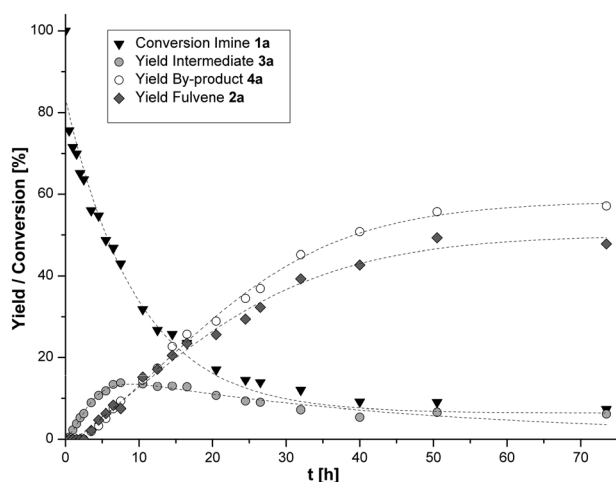


Fig. 4 Time-conversion plot; determined *via* GC with dodecane as an internal standard.

differ significantly from the bond lengths of the isolated fulvene **2a**. Whereas in **2a** the three double bonds (1.36–1.38 Å) are notably shorter than the sigma-bonds (1.45–1.47 Å), in **5a** only the C3–C4 bond length (1.39 Å) is in the supposed range. The other C–C bond lengths vary between 1.40 and 1.46 Å. The C–N bond length of only 1.30 Å indicates a C–N double bond. These data provide a consistent picture of the coordinated ligand as a cyclopentadienylimine rather than an amidofulvene. The deviation of the cyclopentadienyl plane is 0.005 Å. The nitrogen atom is out of this plane (distance 0.41 Å), because it coordinates the potassium atom.

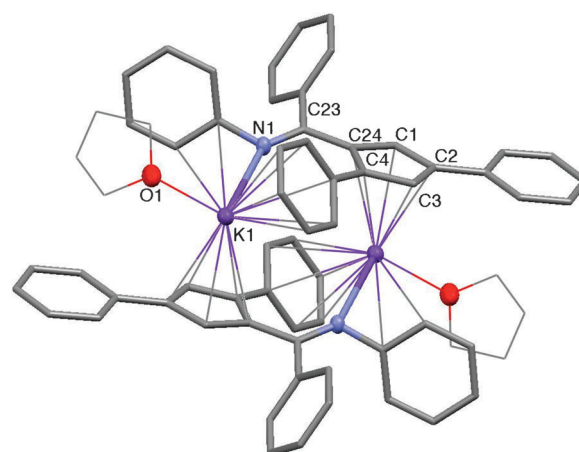


Fig. 5 Molecular structure of **5a**; selected bond lengths [Å] and angles [°]: C1–C2, 1.404(5); C1–C24, 1.416(6); C2–C3, 1.409(6); C3–C4, 1.386(6); C4–C24, 1.425(6); C17–K1, 3.208(4); C22–K1, 3.229; C23–N1, 1.304(5); C23–C24, 1.458(6); N1–K1, 2.814(4); N1–C22–K1, 60.4(2); N1–C23–C24, 120.1(4); N1–C23–C25, 122.5(4); C23–N1–C22, 121.4(4).

Since Knorr *et al.*<sup>12</sup> reported the formation of metastable secondary enamines *via* lithiation of imines with lithium diisopropylamide, we assumed that enamine-formation upon potassium hydride addition is a crucial reaction step in fulvene formation. The two olefinic hydrogen-atoms of the enamine **6a** were detected as doublets ( $J = 1.4$  Hz) at 4.29 and 4.12 ppm (solvent  $C_6D_6$  : THF- $d_8$  10 : 1). The presence of the imine as well as the enamine is necessary for the reaction to take place, which is supported by the results of the KH : imine ratio screening. As indicated in Fig. 6, the enamine species **6a**

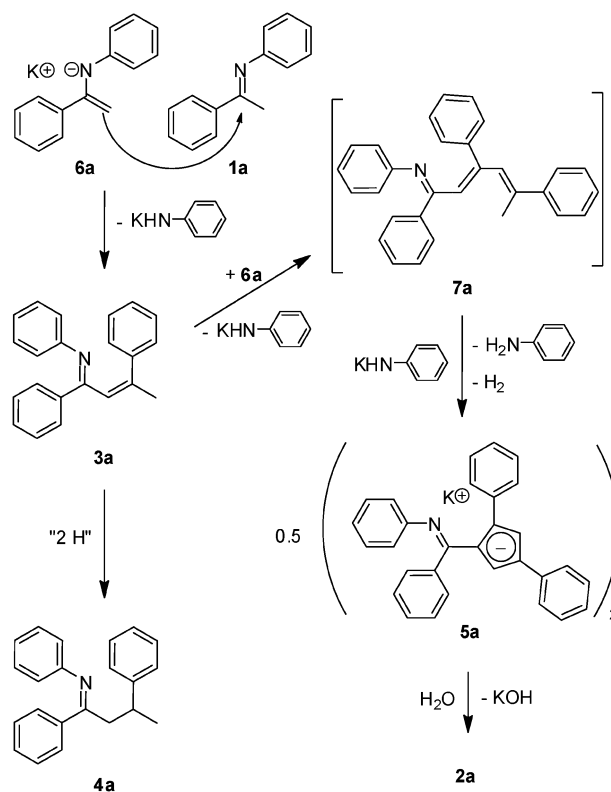


Fig. 6 Proposed reaction mechanism.

attacks the C-atom of the C=N bond<sup>13</sup> of **1a** to yield (1,3-diphenyl-but-3-enylidene)-phenyl-amine **3a**, thereby potassium anilide is eliminated. A second attack of **6a** at the imino-group of **3a** occurs and subsequently the trimerization product **7a** cyclizes to **5a**. The proposed mechanism is summarized in Fig. 6.

The reaction of *N*-alkyl imines, *N*-phenyl-(1-phenyl-propylidene)-amines, or *N*-phenyl-(1-alkyl-ethylidene)-amines with potassium hydride did not yield the corresponding fulvenes. NMR-experiments upon KH addition suggested that the tautomerization to aldimines or isomerization of the double bond into the alkyl-chain prevents the initial attack.

Heterocyclic substituted imines, which can form 5-membered chelates with potassium, for instance *N*-phenyl-(2-pyridylethylidene)-amine or *N*-phenyl-(thiophen-2-yl-ethylidene)-amine, do neither convert to fulvenes under the general conditions nor under harsh conditions (110 °C, diglyme or 1,4-dioxane). If higher temperatures are applied, an additional by-product was observed. This *N*-substituted 2,4-aryl-pyrrole is formed due to cyclization of the intermediate **3**.

The reaction of 3- or 4-substituted heterocyclic imines with potassium hydride under harsh conditions (110 °C, diglyme) was rather unselective leading to a mixture of various compounds.

In conclusion, a novel reaction was discovered. A series of novel 1,3,6-substituted 6-aminofulvenes was synthesized by a facile approach, which utilizes inexpensive and readily available imines as starting material. Furthermore, the mechanism of the reaction was investigated. We propose that the potassium-mediated trimerization reaction of *N*-aryl imines proceeds *via* an observed dimerization and a transient trimerization product, which subsequently cyclizes, thereby giving rise to novel fulvenes. In terms of organic synthesis a variety of fulvenes suited to stabilize constrained geometry type olefin polymerization catalysts is described.<sup>14</sup>

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