

A Direct Synthesis of a Strongly Zwitterionic 6,6'-Diaminofulvalene

Dominic Schmid, Alexander Seyboldt and Doris Kunz

Institut für Anorganische Chemie, Eberhard Karls Universität Tübingen, Auf der Morgenstelle 18, 72076 Tübingen, Germany

Reprint requests to Prof. Dr. Doris Kunz. Fax: +49 7071 29-2436.

E-mail: Doris.Kunz@uni-tuebingen.de

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Upon reaction of the dipyrido-anellated guanidinium salt **1** with one equivalent of CpNa we were able to synthesize the dipyrido-anellated diaminofulvalene **4** in one step in 33% isolated yield. This shortens the initial route that applies a literature-known fulvalene synthesis *via* uronium salt **3** by two steps and avoids the need for a sacrificial equivalent of CpNa. Although the X-ray structure analysis reveals a shorter exocyclic double bond than observed in the diaminofulvalene **V**, a theoretical analysis based upon DFT calculations shows a stronger zwitterionic character for the dipyridofulvalene **4**.

Key words: Fulvene, Fulvalene, Imidazolium Salt, Guanidinium Salt, DFT

Introduction

Fulvenes and fulvalenes [1–4] are fascinating compounds as one mesomeric resonance form of these cross-conjugated π compounds is aromatic as in pentafulvene (**I**) and sesquifulvalene (**II**) (Fig. 1). It has recently been shown by calculations that the combination of one potentially aromatic and one antiaromatic cycle in fulvalenes still leads to an overall stabilization of the system [5]. Substitution of one or two ethylene moieties of the tropylium ring of sesquifulvalene (**II**) by a heteroatom leads to the π -isoelectronic pyridinium-fulvalenes **III** or 1,3-dithiafulvalenes **IV**. The very few examples of simple 1,3-dithiafulvalenes hitherto reported were found to polymerize easily or to be prone to protonation [6, 7]. We have recently managed to synthesize diaminofulvalene **VII** (Fig. 2) [8]. This compound reveals a much higher ylidic character than found for regular 6,6'-diaminofulvenes (**V**, **VI**), due to the high stability of the corresponding imidazolium salt. This strong zwitterionic character explains its reactivity towards air and moisture and the ready formation of ferrocenes with iron(II) salts as well as the long exocyclic “double” bond of 1.43 Å, as determined by single-crystal X-ray structure analysis. From earlier work on dipyrido-anellated carbenes [9–12] we concluded that a dipyrido moiety would provide an increased stabilization of the imidazolium moiety. There-

fore the corresponding dipyrido-anellated fulvalene **4** is expected to have an even higher ylidic character.

Results and Discussion

Synthesis of dipyridofulvalene 4

For the synthesis of the dipyrido-anellated fulvalene **4** we firstly applied the literature procedure for diaminofulvalene **VII** (Scheme 1) [8]: uronium salt **3**, that can be prepared in a two-step synthesis from the respective guanidinium salt **1** by basic hydrolysis to the urea **2** and subsequent alkylation with Meerwein's salt (triethyloxonium tetrafluoroborate) [13], is reacted with two equivalents of sodium cyclopentadienide [14]. This synthesis is based on a general fulvene synthesis by Meerwein [13] and Hafner [15]. We found that a second equivalent of CpNa is necessary as cyclopentadiene is formed during the reaction. This second equivalent of sodium cyclopentadienide serves as a sacrificial base and can be substituted by lithium diisopropylamide as was shown for fulvalene **VII**, however the reaction then became less clean [8]. We could synthesize the desired dipyridofulvalene **4** from the uronium salt in 57% yield, and in an overall yield of 44% over 3 steps starting from the guanidinium salt **1**. It however occurred to us that the synthesis of the dipyridofulvalene **4** could also be achieved

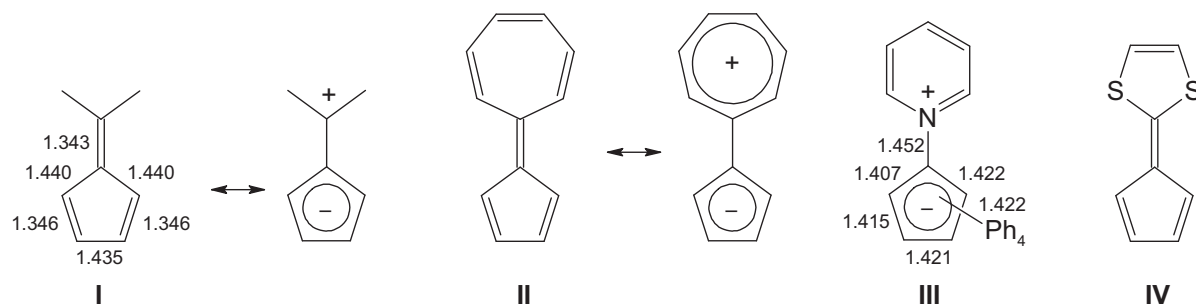


Fig. 1. Pentafulvene **I**, sesquifulvalene **II**, and the π -isoelectronic fulvalenes 1-pyridiniumfulvalene **III**, and 1,3-dithiafulvalene **IV**. Numbers refer to the bond lengths in Å.

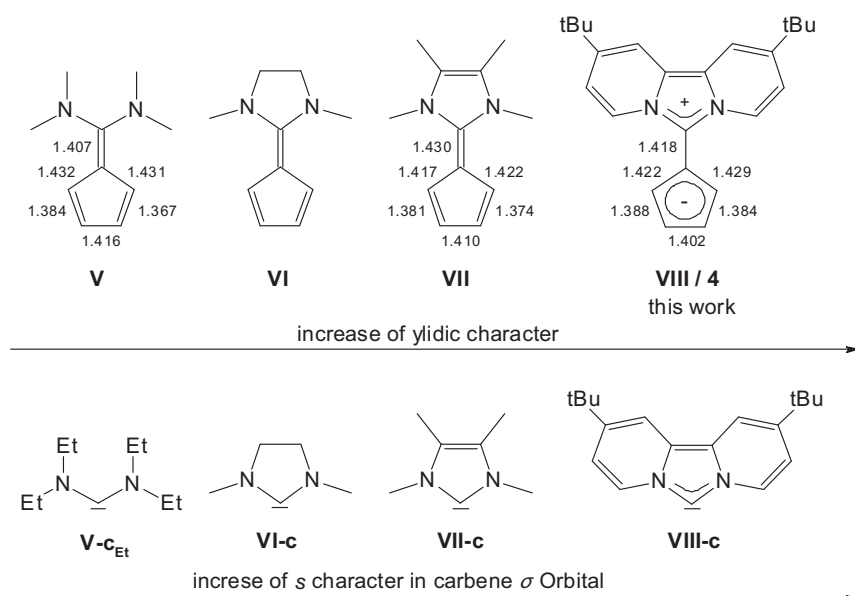


Fig. 2. Diaminofulvenes **V**, **VI** and -fulvalenes **VII**, **VIII** and their respective stable carbenes **V-c_{Et}**–**VIII-c**. Numbers refer to bond lengths in Å.

by direct reaction of the guanidinium salt **1** with CpNa, thus saving the two-step conversion into the uronium salt **3**. We found that the reaction proceeds straightforwardly and in addition, only one equivalent of CpNa is needed, as the dimethylamine released is less acidic than ethanol and does not lead to protonation of CpNa. After workup, we could isolate the desired dipyridofulvene **4** in 33% yield. In general, there are only very few examples of fulvenes synthesized by reaction of a guanidinium salt with metal cyclopentadienide.

The dipyridofulvene **4** was identified by its ^1H and ^{13}C NMR spectra. In the ^{13}C NMR spectrum (CD_2Cl_2) the signal of C6 at 131.2 ppm is strongly high-field shifted compared to the acyclic diamino-

fulvene **V** (164.5 ppm), the imidazolidine-derived **VI** (162.4 ppm) and the fulvalene **VII** (148.3 ppm). Such a high-field shift is also observed for the respective carbenes (252 ppm ($[\text{D}_8]\text{THF}$, **V-c_{Et}**) [16], 239.8 ppm (C_6D_6 , **VI-c**) [17], 213.7 ppm ($[\text{D}_8]\text{THF}$, **VII-c**) [18], 196.3 ($[\text{D}_8]\text{THF}$, **VIII-c**) [11]) or imidazolium salts (156.9 ppm (CDCl_3 , **V-imi**) [19], 159.75 (CDCl_3 , **VI-imi**) [20], 135.0 (CD_2Cl_2 , **VII-imi**) [18], 114.5 ($[\text{D}_6]\text{DMSO}$, **VIII-imi**) [11]). The signals of the cyclopentadiene ring are also high-field shifted compared to those of fulvenes **V**–**VII**, especially signal C-12 at 96.6 ppm.

The IR spectrum (KBr) of compound **4** shows a characteristic band for the exocyclic C=C vibration

Table 1 (color online). Structural parameters obtained by DFT calculations (TURBOMOLE 6.3 package) [25].

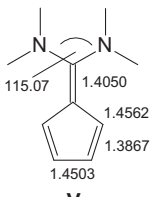
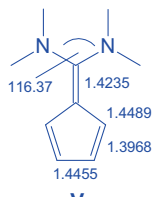
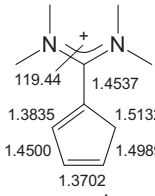
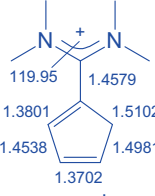
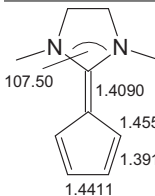
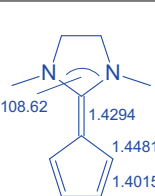
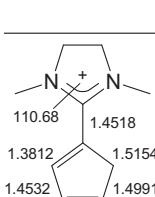
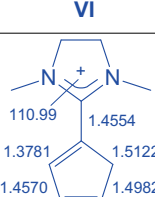
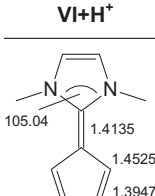
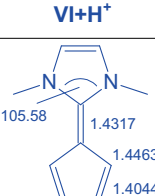
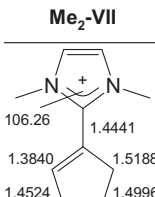
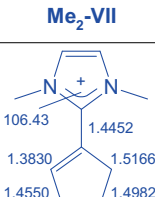
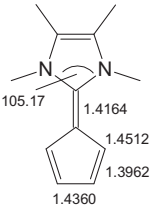
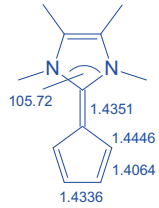
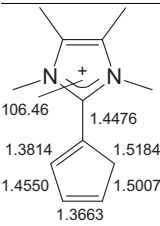
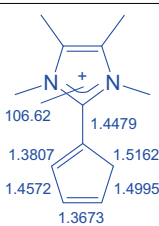
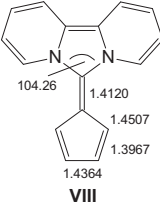
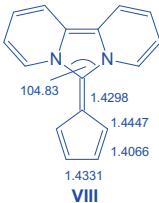
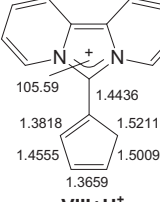
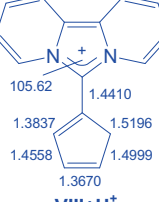
BP-86/def2-SVP ^a	$\Delta(\text{FH}^+ - \text{F})^b$ (C=C) (Å)	$\Delta(\text{FH}^+ - \text{F})^b$ (N-C-N) (deg)	BP-86/def2-SVP ^a , COSMO, $\epsilon = \infty$	$\Delta(\text{FH}^+ - \text{F})^b$ (C=C) (Å)	$\Delta(\text{FH}^+ - \text{F})^b$ (N-C-N) (deg)
 <p>V</p>	0.0487	4.37	 <p>V</p>	0.0344	3.58
 <p>V+H⁺</p>			 <p>V+H⁺</p>		
 <p>VI</p>	0.0427	3.18	 <p>VI</p>	0.0260	2.37
 <p>VI+H⁺</p>			 <p>VI+H⁺</p>		
 <p>Me₂-VII</p>	0.0306	1.25	 <p>Me₂-VII</p>	0.0135	0.85
 <p>Me₂-VII+H⁺</p>			 <p>Me₂-VII+H⁺</p>		

Table 1 (color online). Continued.

BP-86/def2-SVP ^a	$\Delta(\text{FH}^+ - \text{F})^b$ (C=C) (Å)	$\Delta(\text{FH}^+ - \text{F})^b$ (N-C-N) (deg)	BP-86/def2-SVP ^a , COSMO, $\epsilon = \infty$	$\Delta(\text{FH}^+ - \text{F})^b$ (C=C) (Å)	$\Delta(\text{FH}^+ - \text{F})^b$ (N-C-N) (deg)
 <p>VII</p>	0.0312	1.26	 <p>VII</p>	0.0128	0.90
 <p>VII+H⁺</p>			 <p>VII+H⁺</p>		
 <p>VIII</p>	0.0316	1.33	 <p>VIII</p>	0.0112	0.079
 <p>VIII+H⁺</p>			 <p>VIII+H⁺</p>		

^a Numbers refer to bond lengths (Å) or angles (deg); ^b $\Delta(\text{FH}^+ - \text{F})$: difference between the given dimension of the respective protonated fulvene (FH^+) and the fulvene (F).

at $\nu = 1541 \text{ cm}^{-1}$. This value is slightly lower than that for fulvalene **VII** (1547 cm^{-1}) [8] and a first indicator for a higher single bond character of this bond and therefore for a higher ylidic character of **4**.

From a saturated solution of dipyrifidofulvalene **4** in tetrahydrofuran we were able to obtain single crystals suitable for X-ray structure analysis [21]. The molecular structure (Fig. 3) shows that the plane of the dipyridoimidazolinyliidene moiety is twisted to that of the cyclopentadienyliidene moiety by $37.7(3)^\circ$ (defined by the torsion angle N5-C6-C12-C13). In

the imidazoline-derived fulvene **VII** this angle measures only 32° . It is not clear if the larger angle stems from a different electronic or steric situation. The exocyclic double bond whose length is an indicator for the zwitterionic character of the molecule, measures only $1.418(3) \text{ \AA}$. This is 0.012 \AA less than in fulvalene **VII** and could indicate a weaker zwitterionic character for fulvalene **4**. However, the carbon-carbon bonds in the cyclopentadienyliidene moiety measure $1.429(3)$ (C12-C13), $1.384(3)$ (C13-C14), $1.402(3)$ (C14-C15), $1.388(3)$ (C15-C16), and



Fig. 3. Molecular structure of dipyrifidofulvalene **4** in the crystal. Anisotropic displacement parameters are given at the 50% probability level, hydrogen atoms and one THF molecule have been omitted for clarity. Selected bond parameters (Å, deg) with estimated standard deviations in parentheses: 1.418(3) (C6–C12), 1.429(3) (C12–C13), 1.384(3) (C13–C14), 1.402(3) (C14–C15), 1.388(3) (C15–C16), 1.422(3) (C16–C12), 1.368(3) (C6–N5), 1.369(2) (C6–N7); 104.48(16) (N5–C6–N7); 37.7(3) (N5–C6–C12–C13).

1.422(3) Å (C16–C12), and in comparison with fulvalene **VII** the double bonds are slightly longer (1.381(3) and 1.374(3) Å, **VII**), and the single bond C14–C15 is slightly shorter (1.410(3) Å, **VII**). This indicates a larger cyclopentadienide character and therefore a stronger ylidic bonding situation for fulvalene **4**, whereas the slightly longer C16–C12 and C12–C13 bonds in **4** (compared to 1.417(3) and 1.422(3) Å in **VII**) account for a less aromatic character. Another structural feature is the more acute N7–C6–N5 angle (104.48(16)°) compared with **VII** (105.68(17)°). As it was found for carbenes (**Vc–VIIIc**) and their corresponding azolium salts (**V-imi–VIII-imi**), a more acute N–C–N angle is related to a stronger *s* character in the carbene σ orbital and the C–H or C–C bond-forming orbital in azolium salts, respectively [12]. As a consequence of the larger *s* character the C6–N bonds gain more *p* character and are therefore slightly elongated (1.369(2) and 1.368(3) Å in **4** vs. 1.359(2) and 1.351(2) Å in **VII**).

Given the higher *s* character of the orbital at C6, a shortening of the exocyclic bond (C6–C12) is expected already for a pure single bond. A measure for a pure single bond length (and therefore a pure

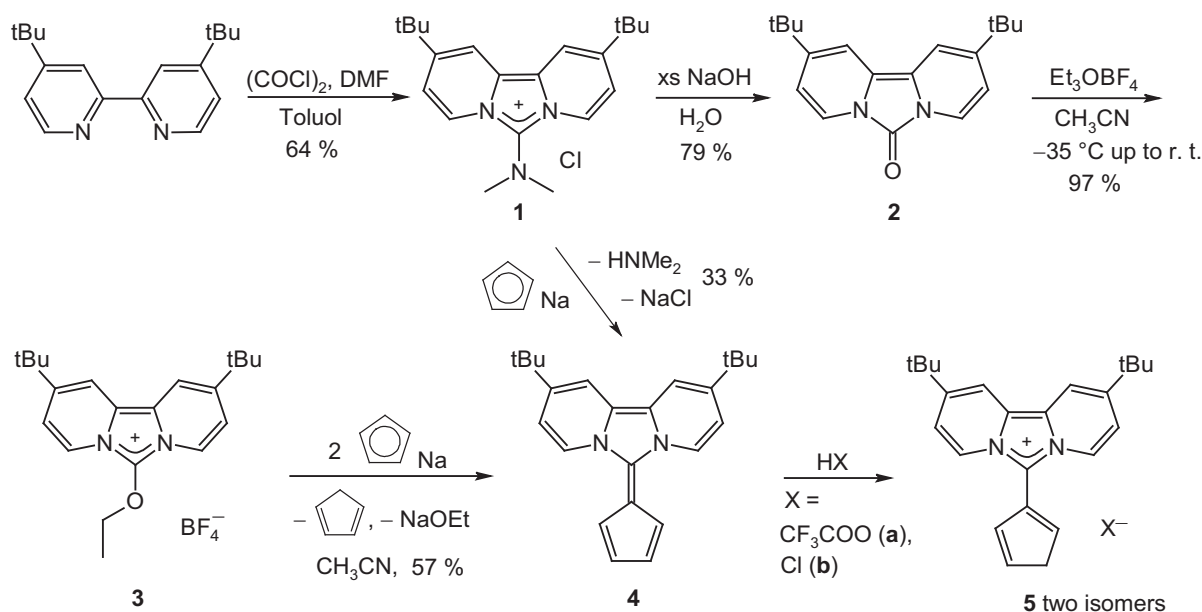
ylidic character) that takes into account also the hybridization character of the participating orbitals, would be the bond length of the respective protonated fulvene/fulvalene, *i. e.* a cyclopentadienyl-substituted imidazolium salt. It is known that heterofulvalenes, *e. g.* dithiafulvalenes, are very sensitive toward protonation [7], while protonated diaminofulvenes are not known due to the lower stabilization of the resulting azolium salts. In the case of diaminofulvalene **VII**, we also observed a protonated species **VII** + H⁺ and were able to determine its structure by X-ray diffraction. The exocyclic single bond (1.451(2) Å) is only 0.019 Å longer than the exocyclic “double bond” of the corresponding diaminofulvalene **VII** [8].

Protonation of dipyrifidofulvalene **4**

Upon addition of an excess of HCl in dioxane or *p*-toluenesulfonic acid to a solution of the fulvalene **4** in acetonitrile the protonated fulvalene **5** is generated *in situ* as a set of two out of three possible isomers in a 2 : 1 ratio (**5-A** : **5-B**). Unfortunately, we have not been able to isolate compound **5** so as to also obtain suitable single crystals of it. Therefore we decided to carry out a DFT analysis to elucidate the ylidic character of diaminofulvenes and -fulvalenes by comparing the bond length of their exocyclic double bond with the exocyclic single bond of the corresponding protonated diaminofulvenes and -fulvalenes.

Determining the zwitterionic character by DFT methods

Firstly, we calculated the structure of fulvene **VII** with TURBOMOLE 6.3 [25] applying the BP-86 functional with a def2-SVP basis set including a dispersion correction. However, the exocyclic double bond (1.416 Å in **VII**, 1.412 Å in **VIII**) was always calculated too short when compared to the experimental X-ray data (1.430(3) Å in **VII**, 1.418(3) Å in **VIII/4**). For the protonated species **VII** + H⁺, the calculated value (1.448 Å) for the exocyclic single bond fits quite well with the experimental one of 1.451(3) Å). As fulvenes and especially diaminofulvenes have a relatively large dipole moment of 5.4 D (**VI**) [1], it occurred to us that this influence is also present in the crystal and therefore would lead to a polar medium that stabilizes the zwitterionic resonance form and thus causes an elongation of the exocyclic double bond. Therefore,



Scheme 1. Two routes for synthesizing dipyrifolfulvene **4**, either *via* the uronium salt **3** and two equivalents of CpNa or in an improved way directly from guanidinium salt **1** with only one equivalent of CpNa.

we took the polar medium into account by applying the Conductor-like Screening Model (COSMO) [37]. To obtain the strongest stabilization of the zwitterionic species, we chose an infinite permittivity ϵ . Although the exocyclic double bond is now longer than the experimental value from the X-ray crystal structure analysis, this value is a good indicator for the longest possible exocyclic bond to be expected for the respective diaminofulvene/diaminofulvalene systems (V–VIII). Table 1 shows the structural parameters obtained from the DFT calculations including the difference of the exocyclic bond lengths of the protonated diaminofulvenes/fulvalenes and the diaminofulvene/-fulvalenes ($\Delta(\text{FH}^+ - \text{F})$) with (blue) and without (black) applying COSMO. It can also be recognized from the data that COSMO has a stronger influence on the bond lengths of the zwitterionic species but not on the exocyclic single bond of the azolium cyclopentadienes. By subtracting the value of the double bond from that of the single bond, the degree of the zwitterionic character can be obtained. Comparing this value for various systems (V–VIII) it becomes evident that the ylidic character is strongest (lowest difference between single and double bond) in the dipyrifolfulvalene VIII and lowest (largest difference between single and double bond) in 6,6'-bis(dimethylamino)fulvalene

V. Therefore we conclude that the dipyrifolfulvalene **4** has a stronger zwitterionic character than fulvalene III (additionally, this is indicated by the less alternating character of double and single bonds in the Cp ring). The reason for the shorter exocyclic double bond in the dipyrifolfulvalene **4** vs. the tetramethylfulvalene VII is therefore attributed to the higher *s* character of the azolium C-orbital in this bond and therefore to a shortening of the exocyclic bond in general. In the case of the fulvalene **4** this shortening is obviously not overcompensated by an increase of the ylidic character.

Conclusion

We have synthesized the highly ylidic fulvalene **4** by two routes from the dipyrifolguanidinium salt **1**. Applying a three-step literature procedure leads to an overall yield of 44%. In the second route, fulvalene **4** is directly formed from the guanidinium salt **1** in 33% isolated yield, and no additional cyclopentadienide is needed as a sacrificial base. Based on X-ray crystal structure analysis and DFT methods that calibrate the exocyclic double bond of fulvenes and fulvalenes to the exocyclic single bond of the corresponding protonated species, we come to the conclusion that dipyrifolfulvalene **4** has the highest ylidic character of

diaminofulvenes/-fulvalenes known so far. The slightly shorter exocyclic double bond of **4** can be explained with the higher *s* character of the bond-forming orbital which overcompensates a bond elongation by a higher ylidic character.

Experimental Section

Unless otherwise noted, all reactions were carried out under an atmosphere of dry argon using standard Schlenk techniques or were performed in an argon-filled glovebox. All solvents were dried using an MBraun MB-SPS Solvent Purification System and saturated with argon prior to use. Chemicals used were obtained from commercial suppliers and used without further purification. Filtrations were made using glass frits or *via* Teflon cannula with applied Whatman™ glass micro fiber filters. ¹H and ¹³C NMR spectra were recorded at room temperature using Bruker ARX 250 or AVII+400 spectrometers. ¹H and ¹³C chemical shifts are reported in ppm and calibrated to TMS on the basis of the residual proton signal of the solvent and the carbon signal of the deuterated solvent as internal standards (¹H NMR: 5.32 ppm [D₂]dichloromethane, 1.94 ppm [D₃]acetonitrile; ¹³C NMR: 53.84 ppm [D₂]dichloromethane and 118.26 ppm [D₃]acetonitrile). Assignments of peaks were made with the aid of 2D correlation spectra. The IR spectrum was recorded on a Bruker Vertex 70 instrument, and the elemental analysis was performed at the Institute of Inorganic Chemistry of the University of Tübingen. The starting materials 6-dimethylamino-2,10-di-*tert*-butylpyrido[1,2-*c*;2',1'-*e*]-imidazolium chloride (**1**) [14], 6-ethoxy-2,10-di-*tert*-butylpyrido[1,2-*c*;2',1'-*e*]-imidazolium tetrafluoroborate (**3**) [14], sodium cyclopentadienide [38], and lithium cyclopentadienide [39] were synthesized according to the reported procedures.

2,10-Di-*tert*-butyl-6-(cyclopenta-2,4-dien-1-ylidene)-dipyrido-[1,2-*c*;2'1'-*e*]-imidazole (**4**)

Route 1: At $-78\text{ }^{\circ}\text{C}$ a solution of 349 mg (4.85 mmol) lithium cyclopentadienide in 10 mL tetrahydrofuran was slowly added to a precooled solution of 1.00 g (2.43 mmol) of **3** in 10 mL tetrahydrofuran which is accompanied by an immediate color change to red. After 1 h, the mixture was allowed to warm up to $0\text{ }^{\circ}\text{C}$ and after another hour to room temperature. The solvent was removed *in vacuo* and the crude product purified by column chromatography on basic aluminum oxide with a mixture of pentane-THF (1 : 1), yielding 472 mg (57%) of **4** as a red-purple crystalline solid.

Route 2: To a solution of 1.00 g (2.90 mmol) of **1** in 16 mL acetonitrile 270 mg (3.07 mmol) of sodium cyclopenten-

tadienide was added at r. t. After stirring for 20 h, the yellow reaction mixture turned into a deeply red-purple suspension. The colorless precipitate was filtered off and the filtrate evaporated to dryness *in vacuo*. The crude product was recrystallized from small amounts of toluene yielding 226 mg (24%) of **4**. Further concentration of the mother liquor yielded additional 95 mg (9%) of **4** as red-purple crystals. M. p. $258\text{ }^{\circ}\text{C}$ (dec.). – IR (KBr): $\nu = 3079$ (w), 2960 (m), 2868 (w), 1654 (w), 1558 (w), 1541 (s), 1483 (m), 1367 (m), 1349 (m), 1270 (m), 1051 (m), 900 (w), 711 (m), 645 (m) cm^{-1} . – ¹H NMR (400.13 MHz, [D₂]dichloromethane): $\delta = 1.39$ (s, 18 H, C(CH₃)₃), 6.20 (m, $N = |^3J + ^4J| = 5.7\text{ Hz}$, 2 H, H-14/15), 6.51 (m, $N = |^3J + ^4J| = 5.7\text{ Hz}$, 2 H, H-13/16), 7.05 (dd, $^3J = 7.8\text{ Hz}$, $^4J = 1.8\text{ Hz}$, 2 H, H-3/9), 7.69 (s br, 2 H, H-1/11), 8.90 (br d, $^3J = 7.8\text{ Hz}$, 2 H, H 4/8) ppm. – ¹H NMR (400.13 MHz, [D₃]acetonitrile): $\delta = 1.38$ (s, 18 H, C(CH₃)₃), 6.09 (m, $N = |^3J + ^4J| = 5.7\text{ Hz}$, 2 H, H-14/15), 6.45 (m, $N = |^3J + ^4J| = 5.7\text{ Hz}$, 2 H, H-13/16), 7.15 (dd, $^3J = 7.8\text{ Hz}$, $^4J = 2.0\text{ Hz}$, 2 H, H-3/9), 7.92 (dd, $^4J = 2.0\text{ Hz}$, $^5J = 1.0\text{ Hz}$, 2 H, H-1/11), 8.85 (dd, $^3J = 7.8\text{ Hz}$, $^5J = 1.0\text{ Hz}$, 2 H, H 4/8) ppm. – ¹³C {¹H} NMR (100.61 MHz, [D₃]acetonitrile): 30.3 (C(CH₃)₃), 35.5 (C(CH₃)₃), 97.5 (C-12), 108.7 (C-13/16), 112.1 (C-1/11), 112.8 (C-14/15), 117.9 (C-3/9), 119.4 (C-11a/11b), 123.3 (C-4/8), 131.7 (C-6), 143.6 (C-2/10) ppm. – ¹³C {¹H} NMR (100.61 MHz, [D₂]dichloromethane): $\delta = 30.3$ (C(CH₃)₃), 35.2 (C(CH₃)₃), 96.6 (C-12), 108.2 (C-13/16), 111.6 (C-1/11), 112.0 (C-14/15), 117.1 (C-3/9), 118.8 (C-11a/11b), 123.3 (C-4/8), 131.2 (C-6), 143.3 (C-2/10) ppm. – C₂₄H₂₈N₂ (344.5): calcd. C 83.68, H 8.19, N 8.13; found C 83.23, H 8.36, N 8.06.

2,10-Di-*tert*-butyl-6-(cyclopenta-1,3-dien-1-yl)dipyrido-[1,2-*c*;2'1'-*e*]-imidazol-6-ium (**5a-CF₃COO⁻**) (Isomer A) and 2,10-di-*tert*-butyl-6-(cyclopenta-1,4-dien-1-yl)dipyrido-[1,2-*c*;2'1'-*e*]-imidazol-6-ium trifluoroacetate (**5a-CF₃COO⁻**) (Isomer B)

8 mg (23.2 μmol) of **4** was put into a Young NMR tube and dissolved in 0.5 mL of CD₃CN. 2 μL (26 μmol) of trifluoroacetic acid were added. The solution turned from red to yellow within minutes. At least two different isomers **5a-A** and **5a-B** were present in solution in an A : B = 2 : 1 ratio (NMR). – ¹H NMR (400.13 MHz, [D₃]acetonitrile): **5a-CF₃COO⁻** (**A**): $\delta = 1.44$ (s br, 18 H, C(CH₃)₃), 3.81 (s br, 2 H, H_A-14), 6.91–7.01 (m, 2 H, H_A-13/15), 7.49 (s br, 1 H, H_A-16), 7.53–7.61 (m, 2 H, H_A-3/9), 8.34 (s br, 2 H, H_A-1/11), 8.56 (d br, $^3J = 7.6\text{ Hz}$, 2 H, H_A-4/8) ppm. **5a-CF₃COO⁻** (**B**): $\delta = 1.44$ (s br, 18 H, C(CH₃)₃), 3.58 (s br, 2 H, H_B-13), 6.91–7.01 (m, 2 H, H_B-14/15), 7.37 (s br, 1 H, H_B-16), 7.53–7.61 (m, 2 H, H_B-3/9), 8.37 (s br, 2 H, H_B-1/11), 8.45 (d br, $^3J = 7.4\text{ Hz}$, 2 H, H_B-4/8) ppm.

2,10-Di-*tert*-butyl-6-(cyclopenta-1,3-dien-1-yl)dipyrido-[1,2-*c*;2'*1'*-*e*]-imidazol-3-ium (**5b-Cl⁻**) (Isomer **A**) and 2,10-di-*tert*-butyl-6-(cyclopenta-1,4-dien-1-yl)dipyrido-[1,2-*c*;2'*1'*-*e*]-imidazol-3-ium chloride (**5b-Cl⁻**) (Isomer **B**)

21 mg (61.0 μmol) of fulvalene **4** was put into a Young NMR tube and dissolved in 0.5 mL of CD₂Cl₂. 50 μL of a 5 M solution of HCl in dioxane were added, causing an immediate color change from red to yellow. Two out of three possible isomers are formed in an ratio **A** to **B** = 2 : 1. – ¹H NMR (400.13 MHz, CD₂Cl₂): **5b-Cl⁻** (**A**): δ = 1.45 (s br, 18 H, C(CH₃)₃), 3.92 (s br, 2 H, H_A-14), 6.91–7.05 (m, 2 H, H_A-13/15), 7.54 (s br, 1H, H_A-16), 7.58–7.64 (m, 2 H, H_A-3/9), 8.25 (s br, 2 H, H_A-1/11), 8.68 (d br, ³J = 7.4 Hz, 2 H, H_A-4/8) ppm. **5b-Cl⁻** (**B**): δ = 1.45 (s br, 18 H C(CH₃)₃), (H_B-13 not observed), 6.91–7.05 (m, 2 H, H_B-14/15), 7.45 (s br, 1 H, H_B-16), 7.58–7.64 (m, 2 H, H_B-3/9), 8.31 (s br, 2 H, H_B-1/11), 8.53 (d br, ³J = 7.3 Hz, 2 H, H_B-4/8) ppm. – ¹³C {¹H} NMR (100.61 MHz, CD₂Cl₂):

δ = 43.8 (C(CH₃)₃), 44.1 (C(CH₃)₃), 87.7 (C_B-12), 90.7 (C_A-12), 112.9 (C_A-1/11), 113.1 (C_B-1/11), 121.2 (C_A-3/9 and C_B-3/9), 121.3 (C_B-4/8), 121.5 (C_A-4/8), 129.3, 132.8, 138.3 (C_A-15, C_B-14, C_B-15), 139.2 (C_A-13), 141.6 (C_A-16), 141.7 (C_B-16), 147.4 (C_A-2/10), 147.9 (C_B-2/10) ppm. The signals for C6, C-11a/11b and C_A-14 could not be identified unambiguously for both isomers.

Supporting information

¹H, ¹³C{¹H} NMR and IR spectra of compound **4**, the ¹H NMR spectrum of compound **5a** and the ¹H and ¹³C{¹H} NMR spectra of **5b** are given as Supporting Information available online (DOI: 10.5560/ZNB.2014-4015).

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- [21] Crystal data of compound **4**: red crystal (irregular prism), dimensions 0.40 × 0.16 × 0.09 mm³, orthorhombic crystal system, space group *P2₁2₁2₁*, *Z* = 4, *a* = 10.4017(3), *b* = 13.2552(3), *c* = 17.3514(4) Å, *V* = 2392.35(10) Å³, *D*_{calcd.} = 1.16 g cm⁻³, *T* = 130(2) K, *θ*_{max} = 27.48°, MoK_α radiation, *λ* = 0.71073 Å, 0.5° *ω*- and *φ*-scans with a Bruker AXS APEX2 diffractometer equipped with a CCD area detector, 43 811 reflections measured, 5480 unique (*R*_{int} = 0.0532), 4476 observed (*I* > 2 *σ*(*I*)), an empirical absorption correction was applied using SADABS [22], *μ*(MoK_α) = 0.1 mm⁻¹, *T*_{min/max} = 0.92/0.96. The structure was solved by Direct Methods and refined using the SHELXLE software package [23, 24], 286 parameters refined, hydrogen atoms

- were treated using appropriate riding models, goodness of fit 1.036, final residual values $R1(F) = 0.0364$, $wR2(F^2) = 0.0951$, residual electron density -0.24 to $0.19 \text{ e } \text{Å}^{-3}$. CCDC 984026 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.
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