Complete Defluorination of 1,2,3,4-Tetramethyl-5-(trifluoromethyl)cyclopentadiene by Titanium Tetrakis(dimethylamide)—Selective Formation of a Cyclic Hexanuclear Titanium Fluoroamide and 6,6-Dimethylaminotetramethylfulvene

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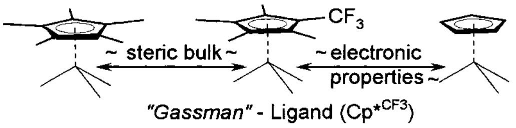
Abstract: 1,2,3,4-Tetramethyl-5-(trifluoromethyl)cyclopentadiene (Cp^{*CF3}-H, **1**) reacts with $[Ti(NMe_2)_4]$ (**2**) under mild conditions to give $[Ti(\mu\text{-}NMe_2)(NMe_2)(\mu\text{-}F)(F)]_6$ (**3**) in nearly quantitative yield. The molecular structure of **3** consists of a ring of six $[TiF_2(NMe_2)_2]$ edge-bridged octahedra. Titanium complexes containing the Cp^{*CF3} ligand, which was the primary intention of these investigations, were not observed. $C_5Me_4{=}C(NMe_2)_2$ (**4**) was isolated as a by-product. The complete defluorination of an aliphatic CF_3 group occurs during the reaction. The reaction mechanism involves the primary formation of a difluorofulvene intermediate $C_5Me_4{=}CF_2$ (**5**), which was monitored by NMR studies. Density functional theory calculations predict a highly charged C6 atom (+0.87) in **5**, which is discussed as the driving force of the reaction.

Keywords: amides · C–F bond activation · fluorine · titanium

Introduction

Cyclopentadienide (Cp) and pentamethylcyclopentadienide (Cp*) are two of the most commonly used ligands in organometallic chemistry.[1] Replacement of the hydrogen atoms on Cp by methyl groups results in major changes in both physical and chemical properties of the transition metal complexes.[2, 3] In order to understand steric and electronic effects of Cp and Cp* ligands, especially as a driving force in metallocene chemistry, Gassman et al. developed the 1,2,3,4-tetramethyl-5-(trifluoromethyl)cyclopentadiene ligand (Cp^{*CF3}, **1**).[4] The Cp^{*CF3} ligand shows the electronic properties of a Cp and the steric bulk of Cp* (Scheme 1).



Scheme 1. Electronic versus steric properties of Cp ligands.

The synthetic potential of this ligand is limited by the fact that corresponding lithium, potassium, or thallium salts, which can be used in further syntheses,[5] are unknown unlike nonmethylated $[C_5H_4(CF_3)Tl]$. Transition metal compounds of Cp^{*CF3} are accessible from the neutral 2,3,4,5-tetra-methyl-1-trifluoromethylcyclopentadiene (Cp^{*CF3}-H, **1**).[4] Additionally, tetramethyltrifluoromethylcyclopentadienide can be readily generated in gas phase, and it was proposed by Kass et. al. that under appropriate conditions it may be possible to form Cp^{*CF3} anions also in solution.[6] Based on this report, we have investigated the possibility of deprotonation of **1** by $[Ti(NMe_2)_4]$ (**2**) in order to replace one or two amide ligands by Cp^{*CF3} by amine elimination, as shown for metallocene complexes of early transition metals.[7]

Results and Discussion

Treatment of a solution of **2** in *n*-hexane with an equimolar amount of **1**[8] leads to the precipitation of orange crystals (98%). Surprisingly, the ^1H and ^{13}C NMR spectra of the isolated crystals (m. p. 202 °C (decomp)) each show only four signals in a 1:1:1:1 ratio, typical for resonances of methyl groups linked to nitrogen (^1H NMR $\delta = 2.64, 2.73, 3.53, 3.66$; ^{13}C NMR $\delta = 46.5$ (s), 50.3 (s), 50.6 (s), 52.2 (d, $^3J_{C,F} = 10.6$ Hz)). The spectra do not show signals of carbon-bonded methyl groups (^1H NMR: $\delta = 1.5-2.5$, ^{13}C NMR: $\delta = 9-11$) as expected for coordination of Cp^{*CF3} to the titanium center. The NMR spectra can be explained in terms of two sets of

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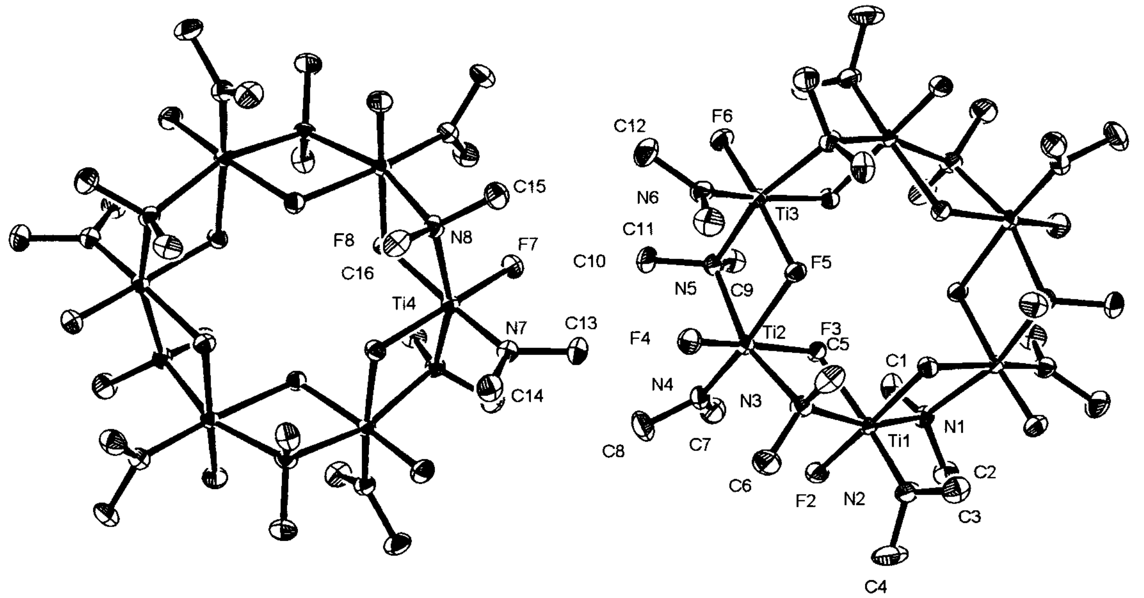


Figure 1. Molecular structure of the hexameric complex $[Ti(\mu\text{-}NMe_2)(NMe_2)(\mu\text{-}F)(F)]_6$ (**3**) (ORTEP drawing). Two types of molecules (**A**, left; **B**, right) are found in the unit cell. Selected distances [Å]: Ti–Ti **A**: 6.507; **B**: Ti1–Ti1′ 6.428, Ti2–Ti2′ 6.506, Ti3–Ti3′ 6.595.

signals corresponding to terminal and bridging NMe_2 groups, as found in the molecular structure of **3** (Figure 1).

Complex **3** is characterized as a cyclic hexanuclear structure which is formed from distorted octahedrally coordinated titanium centers.[9] The octahedrons are bridged by fluoride and amide groups. However, only atoms of the fluoride groups are located in the inner part of the hexameric unit. The structure of **3** represents a new type of $[Ti(NMe_2)_2F_2]$ oligomer. A tetranuclear species was discussed by Bürger et al. in the reaction of $[TiF_4]$ and $[Ti(NMe_2)_4]$,[10a] which was confirmed by X-ray structure analysis.[10b]

The complex **3** crystallizes in space group $R\bar{3}$. The unit cell contains two geometrically distinguishable molecules **A** and **B**. Type **A** occupies the highly symmetrical position $\bar{3}$ (site 3b), **B** is located on $\bar{1}$ (site 9d). The deviation from the threefold axis for **B** is small but significant (Ti–Ti distances see Figure 1). However, the average Ti–Ti distance in **B** (6.509 Å) is the same as the Ti–Ti distance in **A** (6.507 Å).

Abstract in German: *1,2,3,4-Tetramethyl-5-(trifluoromethyl)-cyclopentadien (Cp^{*CF3}-H, **1**) reagiert mit $[Ti(NMe_2)_4]$ (**2**) unter milden Bedingungen zu $[Ti(\mu\text{-}NMe_2)(NMe_2)(\mu\text{-}F)(F)]_6$ (**3**) in nahezu quantitativer Ausbeute. Die Molekülstruktur von **3** ist durch die Bildung eines sechsgliedrigen Ringes charakterisiert, der aus kantenverknüpfte $[TiF_2(NMe_2)_2]$ Oktaeder besteht. Ursprünglich angestrebte Titankomplexe mit Cp^{*CF3}-Liganden werden nicht beobachtet. Als weiteres Produkt wird $C_5Me_4{=}C(NMe_2)_2$ (**4**) isoliert. Der Reaktionsverlauf ist augenscheinlich durch die vollständige Defluorierung einer aliphatischen CF_3-Gruppe bestimmt. NMR Untersuchungen zeigen das Auftreten des Difluorfulvenintermediates $C_5Me_4{=}CF_2$ (**5**) als primären Schritt der Reaktion. Das hochgeladene C6 Atom (+0.87) in **5**, gefunden in DFT Rechnungen, wird als die Triebkraft der Reaktion angesehen.*

As a consequence, a more (**B**) or less (**A**) distorted octahedral gap is located in the center of **3**, defined by the six inner fluorine atoms. In type **A** equivalent distances from a fictive center (D_x) to fluorine atoms are found (2.238 Å), whereas in **B** different values are observed (D_x–F1: 2.279; D_x–F3: 2.165, D_x–F5: 2.2706 Å).

For further discussion of the octahedral moiety on each titanium center, the coordination geometry of Ti4 in Figure 1 is used (Figure 2). The average lengths of the terminal Ti–F bond (1.807 Å) is shorter than the Ti–F distances in the octahedrally coordinated titanium compounds $[K_2TiF_6]$ (1.916 Å), $[Cu(H_2O)_4]TiF_6$ (1.86 Å), and $[Cu(H_2O)_4)]TiF_6 \cdot NH_4F$ (1.88 Å),[11] as well as in most known tetrahedral titanocene fluorides.[12] The bridging Ti–μ-F distances are generally longer. In the F-Ti-μ-F axis, an average distance of 1.935 Å is measured, whereas an elongation to 2.138 Å (av) is found for the Me_2N-Ti-μ-F axis. This significant difference of 0.2 Å is evidence for the *trans* influence of the terminal Me_2N group. This results in asymmetric Ti-F-Ti bridges, in contrast

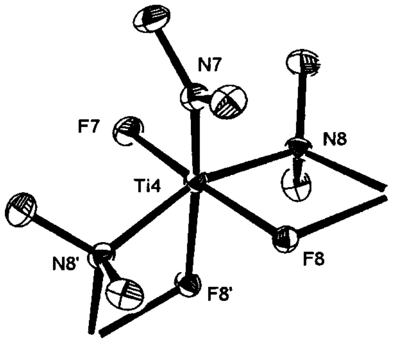


Figure 2. Selected bond lengths [Å] and angles [°] of a suboctahedron in **3** (**A**): Ti4–F8 2.138(11), Ti4–F8′ 1.9350(10), Ti4–F7 1.8064(11), Ti4–N8 2.1500(15), Ti4–N7 1.8899(16), Ti4–N8′ 2.1562(15); F7-Ti4-F8 88.61(5), F8-Ti4-F8′ 85.39(6), F8′-Ti4-N7 92.89(6), F7-Ti4-N7 94.61(6).

to the symmetric Ti-NMe$_2$-Ti units. Moreover, the terminal Ti–N distances (1.887 Å av) in **3** are shorter than those reported for other titanium amides.[13] The planar environment of the terminal nitrogen atoms can be discussed as a partial Ti–N double bond.[14] The bridging Ti–N distances (2.151 Å av) are in the expected range.[10b]

For the formation of the edge-bridged cyclic hexameric structure a distortion of the octahedral geometry at the titanium centers is necessary (Figure 3). The largest deviation from linearity for the diagonal in the octahedrons are detected for the μ-Me$_2$N-Ti-μ-NMe$_2$ axes (N8-Ti4-N8′: 159.89(7)°), while the terminal Me$_2$N-Ti-μ-F axes (N7-Ti4-F8′: 171.08(6)°) are close to 180°. The angle about the F-Ti-μ-F axis is between those discussed before (F7-Ti4-F8′: 167.92(5)°). In contrast to the case in [{Ti(Me$_2$N)$_2$F$_2$}$_4$], all the Ti-(μ-X)-Ti bond angles (X: F, NMe$_2$) are larger than 90° (Ti4′-F8-Ti4 106.51(5)°, Ti4′-N8-Ti4 98.45(6)°).

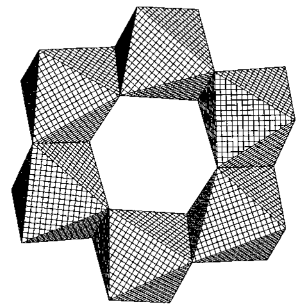
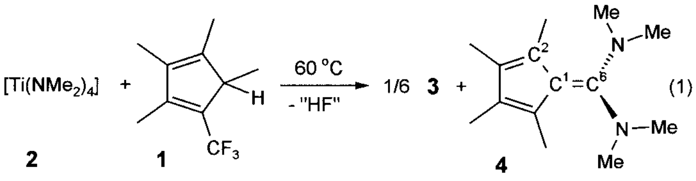


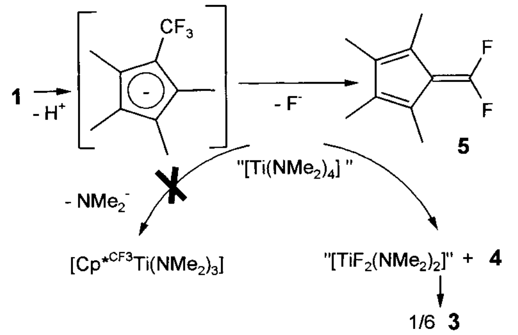
Figure 3. Coordination polyhedra in **3** (molecule type **A**).

In a [D$_1$]chloroform solution of **3** only one type of molecule is detected. No rearrangements to tetramers or open-chain oligomers are observed at room temperature. In the ^{19}F NMR spectra two pairs of signals appear at $\delta = 190.46$ (d, $J_{F,F} = 219$ Hz) for the terminal fluorine atoms and at higher field $\delta = -3.40$ (d, $J_{F,F} = 209$ Hz) assigned to the bridging fluorine atoms.[15] The EI mass spectrum reveals the fragment corresponding to the monomer unit, [Ti(NMe$_2$)$_2$F$_2$] (*m/z* 174, 50%). After the separation of **3** from the reaction mixture, orange needles are obtained from the remaining solution by cooling (−20 °C, 5 d), which were identified as 6,6-dimethylaminofulvene (**4;** 71%) by correct elemental analysis, EI mass spectra (*m/z* 220.1, 98%), and NMR spectra [Eq. (1)].



The ^{1}H NMR spectrum of **4** displays two signals assignable to the ring methyl groups ($\delta = 2.11$, 2.25), and two broad resonances at $\delta = 2.25$ and 2.67 (N(CH$_3$)$_2$). The ^{13}C NMR spectrum shows two signals at $\delta = 38.8$ and 42.1 for N(CH$_3$)$_2$, which become equivalent at 60 °C.[16] These data are in good agreement with density functional theory (DFT) calculations which show also nonequivalent amino groups ($\delta = 38.3$, 40.9), due to a twisting of the exocyclic double bond (C2-C1-C6-N 35.4°). In the molecular structure of C$_5$H$_4$=C(NMe$_2$)$_2$[17] a twist angle of 29° is found, compared to the DFT-calculated value of 26.0°.

The overall stoichiometry of the reaction shows that a total defluorination of the aliphatic CF$_3$ group has taken place. A vigorous reaction of **1** and **2** is found in the absence of solvents. The formation of free amine during the reaction was not detectable. To establish the mechanism for the formation of **3** and **4**, the reaction was monitored by ^{1}H NMR spectroscopy in C$_6$D$_6$ solution. As the reaction progresses, a rapid consumption of both starting materials is observed, together with the growth of the signals corresponding to the 6,6-disubstituted pentafulvene **4** (Scheme 2). This immediate consumption of the double bond isomeric mixture[8] of **1** is consistent with the formation of Cp*^{CF3} anion; however, complexation with titanium is not observed. Alternatively, the anion can be stabilized by fluoride elimination to give 6,6-difluorofulvene (**5**).[18] Accordingly, a low fluoride affinity of **5** (171 kJ mol^{-1}, gas phase) is found.[6] In addition to the signals of **4**, a further set of two singlets in a 1:1 ratio appears at $\delta = 1.50$ and 1.81, which are assigned to the proposed 6,6-difluorofulvene **5** (^{19}F NMR $\delta = -65.51$ (s)). Finally, the destiny of one molecule HF in the overall stoichiometry remains unsolved, a reaction with glassware as well as nitrogen-containing products besides **3** seems plausible.[19] The appearance of intermediate **5** explains the formation of **4** in terms of nucleophilic substitution of fluoride by amide at the =CF$_2$ center.



Scheme 2. Proposed reaction mechanism of the formation of **3** and **4**.

DFT calculations of **5** show a unusually highly charged C6 atom (+0.87; Figure 4). Owing to the negative charge present in the ring moiety, this positive charge is even higher than that for H$_2$C=CF$_2$ (+0.79) and makes the unexpected nucleophilic substitution more feasible.[20, 21]

Conclusion

With regard to the general interest in C–F bond activation processes,[22] the reaction of **1** and **2** represents an example of a complete defluorination gradation of a CF$_3$[23] group by titanium complexes.[24] The search for alternative synthetic routes to **3** from common starting materials is in progress with the aim of forming inclusion compounds.

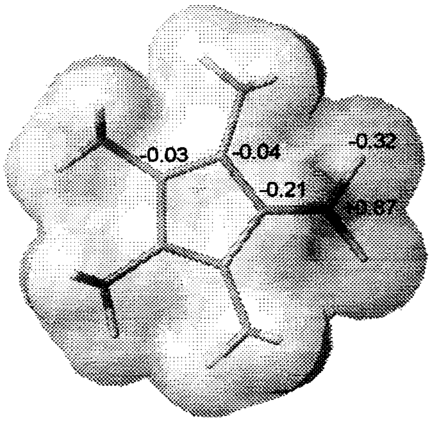


Figure 4. Partial charges of **5**, obtained from DFT calculations.

Experimental Section

General procedures: All manipulations of the described compounds were carried out under the exclusion of air and moisture using Schlenk-line or glovebox techniques. Solvents were distilled prior to use. C, H, and N analyses were performed at the Analytischen Laboratorien in Lindlar (Germany). ^{1}H NMR and ^{13}C NMR spectra were recorded on a 500 MHz Bruker AVANCE spectrometer. Residual protons of the solvent were used as reference ($CDCl_3$: $\delta = 7.24$; C_6D_6: $\delta = 7.15$), while a sealed tube containing $CFCl_3$ in C_6D_6 was used as the external reference for the ^{19}F NMR spectra.

Electron impact (EI) mass spectra were recorded on a Finnigan MAT 212 spectrometer. IR spectra were taken with a BIO-RAD FTS-7 spectrometer. $Ti(NMe_2)_4$ is commercially available (STREM) and was used without further purification. Cp^{*CF3} was prepared according to the literature procedure.[8]

3: $C_5Me_4CF_3H$ (0.85g, 4.47 mmol) was added to a solution of $[Ti(NMe_2)_4]$ (**1**) (1.0 g, 4.46 mmol) in *n*-hexane (50 mL) at room temperature. The reaction mixture was heated at 60 °C for 17 h. The orange-reddish solution was left at room temperature to give a first fraction of orange crystals of **3**, which were collected by filtration. A second fraction was obtained from the filtrate after cooling at −20 °C. The combined yield was 0.76 g (98%). ^{1}H NMR (500 MHz, $CDCl_3$, 27 °C): $\delta = 2.64$, 2.73 (s, 18H; μ-NMe_2), 3.53, 3.66 (s, 18H; NMe_2); $^{13}C\{^1H\}$NMR (125 MHz, $CDCl_3$, 27 °C): $\delta = 46.5$, 50.6 (s; μ-NMe_2), 50.3 (s; NMe_2), 52.2 (d, $^3J_{C,F} = 10.6$ Hz; NMe_2); ^{19}F NMR (282.4 MHz, $CDCl_3$, 27 °C): $\delta = -3.40$ (d, $J_{F,F} = 209$ Hz; μ-F), 190.46 (d, $J_{F,F} = 219$ Hz; $F_{terminal}$); IR (KBr, cm^{-1}): $\tilde{\nu} = 300$ (m), 392 (m), (δ framework), 490 (s), 515 (s), (vTiFTi), 584 (m) 637 (vs) (vTiN, TiF), 802 (s), 905 (s), 963 (s), 1032 (s), 1107 (s), 1262 (s), 1464 (s); MS (EI, 70 eV): *m*/*z*: 174.0 ($[TiF_2(NMe_2)_2]^+$, 50%); elemental analysis calcd (%) for $C_{24}H_{72}N_{12}F_{12}Ti_6$ (1044.10): C 27.61, H 6.95, N 16.09; found: C 27.63, H 6.84, N 16.17.

The remaining orange-reddish solution was concentrated (ca. 5 mL) to give a red oil from which the complex **4** was crystallized as orange-reddish needles (m. p. ca. 5 °C) by cooling to −20 °C for 5 days. Yield: 0.70 g, 71%. ^{1}H NMR (500 MHz, C_6D_6, 27 °C): $\delta = 2.11$, 2.25 (s, 6H; $C_5Me_4(=C(NMe_2)_2)$), 2.25, 2.67 (brs, 6H; $C_5Me_4(=C(NMe_2)_2)$); $^{13}C\{^1H\}$NMR (125 MHz, C_6D_6, 27 °C): $\delta = = 11.9$, 12.7 ($C_5Me_4(=C(NMe_2)_2)$), 38.8, 42.1 ($C_5Me_4(=C(NMe_2)_2)$), 109.3, 118.5, 126.0, 161.0 ($C_5Me_4(=C(NMe_2)_2)$); IR (KBr, cm^{-1}): $\tilde{\nu} = 640$ (m), 903 (m), 941 (s), 1032 (s), 1092 (s), 1134 (s), 1213 (s), 1350 (s), 1391 (s), 1452 (s), 1472 (s), 1520 (s), 1551 (s), 1620 (m), 2849 (m), 2915 (m); MS (EI, 70 eV): *m*/*z* (%): 220.1 ($[M^+]$, 98); elemental analysis (%) calcd for $C_{14}H_{24}N_2$ (220.33): C 76.31, H 10.98, N 12.71; found: C 76.35, H 10.70, N 12.67.

Crystal structure of 3: Intensity data collections were carried out on a STOE-IPDS diffractometer with $Mo_{K\alpha}$ radiation, 222 exposures Θ_{incr} 0.9°, $T = 193$ K. Crystal dimensions $0.38 \times 0.19 \times 0.19$ mm, $C_{16}H_{48}F_8N_8Ti_4$; $M_r = 696.22$, trigonal, space group $R\bar{3}$, $a = 43.3158(13)$, $c = 8.4952(2)$ Å, $V = 13803.7(7)$ Å^3, $Z = 18$, $\rho_{calcd} = 1.508$ g cm^{-3}, $\mu(Mo_{K\alpha}) = 1.072$ mm^{-1}, $F(000) = 6480$, $\Theta_{max} = 25.96°$. A total of 36458 reflections were collected, of which 5657 were unique ($R_{int} = 0.047$). Structure solution with SHELXS-97 by direct phase determination and refinement against F^2 (SHELXL-97)[25] with anisotropic thermal parameters for all non-hydrogen atoms. Calculated hydrogen positions with riding isotropic thermal parameters. 4402 reflections $I > 2\sigma(I)$ and 325 parameters refined, GOF (F^2) 0.935, final *R* indices: $R_1 = 0.0255$, $wR_2 = 0.0605$ max./min. residual electron density 0.265 and −0.252 e Å^{-3}. Crystallographic data (excluding structure factors) have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-147118 (**3**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

Computational details: The DFT calculations were carried out using the hybrid functional Becke3LYP[26] with 6–31G(d) and 6–311G(3df,2p) basis sets, employing the program package Gaussian 98.[27] The population analysis is based on the integrated NBO 3.1 module.[28] All structures were optimized and verified as local minima at the B3LYP/6–31G(d) level of theory. The NMR shifts with tetramethylsilane as reference were computed at the same level of theory as well as NPA charges. The obtained data did not improve significantly when 6,6-difluorofulvene was optimized by using the larger Becke3LYP/6–311G(3df,2p) basis set. Further details of the individual calculations are given in the Supporting Information.

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