Synthesis of 1-Azaspiro[2.4]hepta-1,4,6-trienes and Azaspiroconjugation Studied by Photoelectron Spectroscopy**

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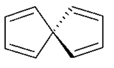
Dedicated to Prof. Dr. Adalbert Maercker on the occasion of his 70th birthday

Abstract: 1-Azaspiro[2.4]hepta-1,4,6-trienes **3a**–**c** have been prepared by photolysis or thermolysis of 6-azidofulvenes **5a**–**c**, which were accessible by nucleophilic substitution reactions of the precursors **4a**,**b** or by nucleophilic addition of hydrazoic acid to ethenylidenecyclopentadiene (**6c**). The UV photoelectron spectrum of 2-methyl-1-azaspiro[2.4]hepta-1,4,6-triene (**3c**) has been recorded and analyzed by making use of density functional theory (DFT) B3LYP calculations. Substantial homoconjugative interactions have been determined. The lone-pair orbital n(N) of the 2*H*-azirine nitrogen atom interacts with the π_1 orbital of the cyclopentadiene ring. The energies of these orbitals are lowered or increased by 0.95 or 0.91 eV with respect to the two parent compounds cyclopentadiene (**7**) and 3-methyl-2*H*-azirine (**9**), respectively. In addition, in compound **3c** the π(C=N) orbital of the three-membered ring interacts with a σ orbital of the cyclopentadiene unit and is destabilized by 0.47 eV by this effect.

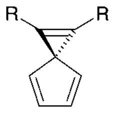
Keywords: azirines • density functional calculations • electronic structure • hyperconjugation • photoelectron spectroscopy

Introduction

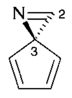
Spiro compounds which comprise of two orthogonal π electron systems ("spiro polyenes") exhibit a special form of homoconjugation, called spiroconjugation.[1, 2] This effect can be investigated by UV photoelectron (PE) spectroscopy as was shown for the first time by Schweig et al.[3–6] A showpiece for demonstrating the importance of spiroconjugation for spectroscopic properties is spiro[4.4]nonatetraene (**1**), for which UV and PE spectroscopic investigations have revealed the same splitting (1.23 eV) for the first two ionic states and the first two excited states resulting from homoconjugative spirointeraction between the two semilocalized π MOs $1a_2$ of the two cyclopentadiene rings.[7]



1



2
a R = H
b R = Et



3a

Spiro interaction between the two halves of a spiro compound is sizeable in symmetric compounds (D_{2d} symmetry). For other compounds, spiroconjugation is small and can be obscured by other effects. This has been shown for spiro[2.4]hepta-1,4,6-trienes **2** by the groups of Gleiter[8] and Billups.[9] Since 1-azaspiro[2.4]hepta-1,4,6-triene (**3a**) is π-isoelectronic with **2**, one might expect that also in this compound spiroconjugation can be neglected. However, in addition to the π(C=N) orbital of the three-membered ring, there is a high-lying n(N) orbital of the azirine nitrogen atom that might interact with the π electron system of the cyclopentadiene ring, although it is geometrically orthogonal to the π(C=N) orbital. In order to evaluate this effect, we have investigated derivatives of **3a** by PE spectroscopy and quantum-chemical calculations.

Results and Discussion

Treatment of compound **4b** (X = Cl)[10] with lithium azide in DMSO leads to 6-azidofulvene **5b** in 76% yield (Scheme 1).

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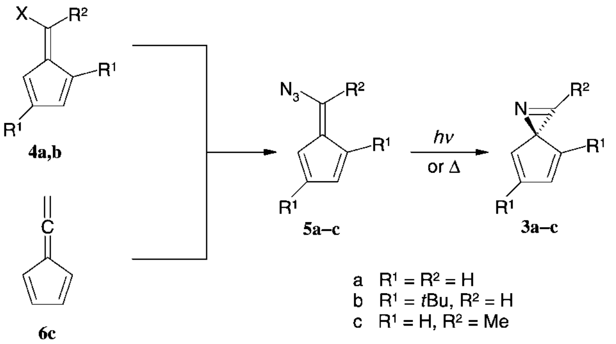

Scheme 1.

The parent compound **5a** has already been prepared by Hafner and co-workers[11] in an analogous way starting with **4a** (X = OTs). The azide **5c** is accessible by the reaction of the hydrocarbon **6c**[12] with lithium azide in methanol at low temperature. Even in solution at room temperature, **5c** tends towards cleavage of nitrogen, and photolysis at −50 °C or thermolysis completes these nearly quantitative transformations **5c** → **3c**. Since 2*H*-azirines that are unsubstituted in position 3 are notoriously reactive and unstable,[13] **3a,b** cannot be generated in acceptable yields by thermolysis in solution. However, irradiation of solutions of **5a,b** at low temperature (−40 to −60 °C) affords the spiro compounds **3a,b** in high yields (80–100 %). The structures of the title compounds **3a–c** were verified by their usual spectroscopic data (Figure 1), and, in the case of **3a,b**, the coupling constants $^1J(^{13}C,^1H)$ for the ^{13}C NMR signals of HC=N (245–250 Hz) give a further argument that supports the azirine structure.

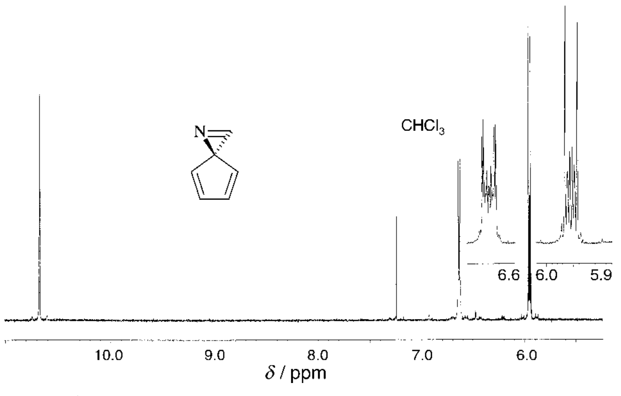

Figure 1. ^1H NMR spectrum (300 MHz) of compound **3a** in $CDCl_3$.

The PE spectrum of **3c**, the most stable spiro compound of type **3**, is depicted in Figure 2. The measured vertical ionization energies are summarized in Table 1 together with the relevant results of quantum-chemical calculations. The spectrum is characterized by four well-separated ionization bands of comparable intensity below 12 eV. In the remaining part of the spectrum (> 12 eV), superposition of several ionizations contributes to the bands. Since the compound was measured starting with a solution in dichloromethane, the *IP*s at 11.67 and 12.2 eV may be disturbed by signals from the solvent, which exhibits strong peaks at 11.40 and 12.22 eV.[14]

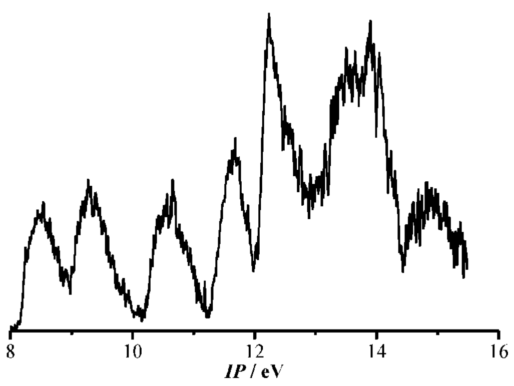

Figure 2. Photoelectron spectrum of compound **3c**.

Table 1. Ionization potentials *IP* [eV], orbital energies ε [eV] and total energies *E* [a.u.] of molecule M and radical cation $M^{\bullet+}$ for 2-methyl-1-azaspiro[2.4]hepta-1,4,6-triene (**3c**).

IP	$-\varepsilon^{PM3}$	$-\varepsilon^{AM1}$	$-\varepsilon^{B3LYP}$	$IP^{B3LYP[a]}$	MO	
8.51	9.39	9.18	6.08	8.17	7a″	π_2(diene)
9.31	10.25	10.15	7.08	9.17	13a′	n(N), π_1(diene)
10.61	11.07	10.95	8.31	10.40	6a″	π(C=N)
11.67	12.27	12.53	9.52	11.61	12a′	π_1(diene), n(N)
12.2	13.11	12.81	10.12	12.21	11a′	σ
	13.64	13.66	10.34		10a′	σ
	13.74	13.51	10.99		5a″	σ

[a] Calculation of first vertical *IP*: energy difference of molecule M (−325.635187 a.u.) and radical cation $M^{\bullet+}$ (−325.334788 a.u.) with identical geometry. Higher *IP*s: $IP_i = -\varepsilon_i + 2.09$ eV (see text).

Assignment of the *IP*s can be achieved by using the Koopmans theorem,[15] $IP_i = -\varepsilon_i$, by which vertical ionization energies and MO energies are related. Although Kohn–Sham orbitals obtained by DFT methods[15] are not molecular orbitals and their physical meaning is still debated, it has been shown that they can be used with high confidence for the interpretation of PE spectra.[17, 18] Much better agreement between experimental and theoretical values can be expected for the first vertical *IP* (IP_{1v}) when the energies of the molecule and the radical cation are calculated by the B3LYP method. For IP_{1v}, a single-point calculation is performed for the radical cation ($M^{\bullet+}$) by using the molecule's (M) geometry. The corresponding energy values are included in Table 1. We can now correct the other ε^{B3LYP} values by the difference $\Delta = 2.09$ eV between $-\varepsilon$(HOMO) and the calculated IP_{1v} in order to obtain higher IP_v values.[18] Whereas typical energy differences between IP_i and $-\varepsilon_i^{B3LYP}$ values are about 2 eV, experimental and calculated IP_i values differ only by 0.1–0.3 eV for the first three *IP*s. Furthermore, both $-\varepsilon_i^{B3LYP}$ and calculated IP_i(calcd) values are linearly correlated with the experimental IP_i(exp) values with correlation coefficients very close to 1.00. The correlation equation obtained for IP_i values is $IP_i(\text{calcd}) = 1.0681\, IP_i(\text{exp}) - 0.8460$ [eV] with $R = 0.999$. Also the orbital energies ε_i obtained by the semiempirical methods AM1 and PM3 (Table 1) correlate well with the experimental IP_i values ($R = 0.991$ for both methods).

Compound **3c** belongs to the symmetry point group C_s. The only symmetry element is a symmetry plane lying in the three-membered ring and bisecting the cyclopentadiene ring. Accordingly, the molecular orbitals factorize as symmetric (a′) or antisymmetric (a″) to this plane. In the numbering of the corresponding MOs (Table 1) the core orbitals (1s) of C and N atoms have been omitted.

In order to evaluate orbital interactions in **3c**, a correlation diagram of its *IP* values with those of related compounds is most useful. Such a diagram is displayed in Figure 3. The *IP*s related to the occupied π MOs (π_1 and π_2) of cyclopentadiene

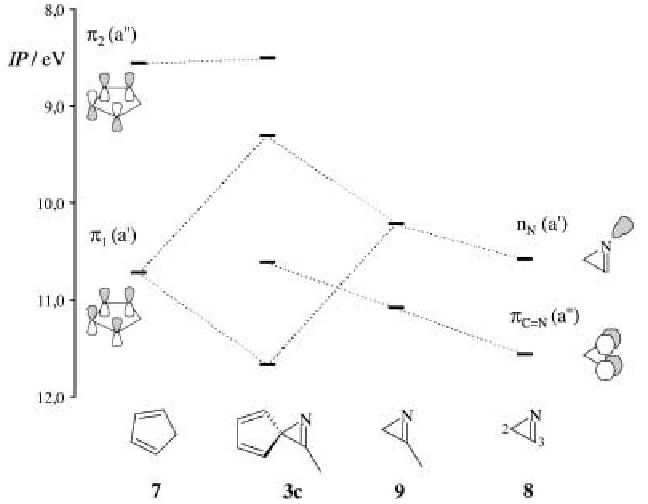

Figure 3. Correlation diagram for *IP* values of compounds **3c** and **7**–**9**. Symmetry properties (a′, a″) relate to the mirror plane of compound **3c**.

(**7**) are reported as 8.566 and 10.724 eV.[19] The PE spectrum of the highly unstable 2*H*-azirine (**8**) has been measured by Bock and Dammel,[20] and *IP* values of 10.58 and 11.56 eV were determined for the n(N) and π(C=N) ionizations, respectively. Experimental *IP* values for 3-methyl-2*H*-azirine (**9**) are not known, but the corresponding values can be estimated from those of the parent compound **8** with the aid of quantum-chemical calculations. By the B3LYP/6-31 + G**/method it is found that the n(N) and π(C=N) orbitals of **8** are destabilized by 0.36 and 0.48 eV, respectively. With these values the *IP*s of **9** are estimated as $10.58 - 0.36 = 10.22$ eV (n(N)) and $11.56 - 0.48 = 11.08$ eV (π(C=N)). In the same way, the first two *IP*s of 2,2,3-trimethyl-2*H*-azirine (**10**) are estimated as 9.66 eV (n(N)) and 10.86 eV (π(C=N)).

10

The most significant information to be obtained from Figure 3 is that the orbital $\pi_2(1a_2)$ of cyclopentadiene (**7**) is only very slightly destabilized in the spiro compound **3c** (7a″, $\Delta IP = 0.06$ eV); this indicates that it does not interact with orbitals of the 2*H*-arizine ring. (Alternatively, such interactions exactly compensate for each other.) On the other hand, $\pi_1(2b_1)$ of **7** is stabilized considerably in **3c** (12a′, $\Delta IP = 0.95$ eV) by interaction with n(N) of the 2*H*-arizine ring, which is simultaneously destabilized relative to that of **9** ($\Delta IP = 0.91$ eV). We can thus assign an energy value of 0.91–0.95 eV to azaspiroconjugation in compound **3c**. If only the two orbitals n(N) and π_1 interact with each other, one would expect that the antisymmetric combination is raised in energy more than the symmetric combination is lowered. Since actually the opposite is observed, it has to be concluded that interactions with other orbitals also contribute. In particular, interaction of n(N) with the lowest unoccupied molecular orbital $\pi_3(3b_1)$ has to be considered.

A substantial destabilization ($\Delta IP = 0.47$ eV) is also found for the π(C=N) (6a″) orbital of **3c**. The last observation has to be explained by interaction of π(C=N) with σ(C^3-C^4-C^7) of the same symmetry. According to quantum-chemical calculations, the corresponding orbitals are 5a″ in **3c** and $4b_2$ in **7**, which show an energy difference of 0.8 (PM3) or 1.1 eV (B3LYP/6-31 + G**). In the hydrocarbon analogue **2b**, the corresponding interaction is much smaller due to the fact that π(C=C) of the cyclopropene ring has a higher energy (−8.63 eV[8]).

A qualitative explanation of the observed orbital interactions[21] is possible with first-order perturbation theory, as indicated in Figure 4. Spiroconjugation is shown for three cases, including the two mentioned in the preceding sections. Only symmetric (stabilizing) interactions are shown, by which the lower of the interacting orbitals is lowered in energy. The corresponding antisymmetric (destabilizing) interactions, by which the energy of the higher orbital is increased, are obtained by inverting the phases of the orbitals in one of the two rings.

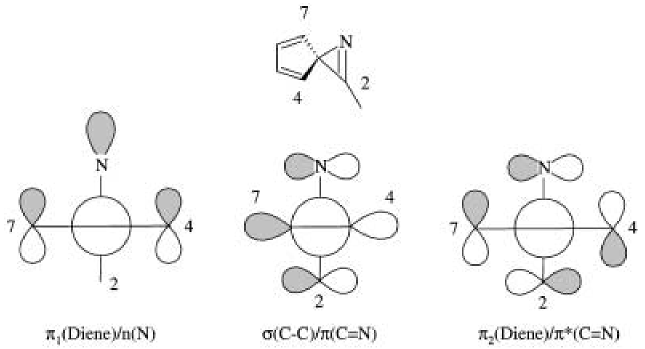

Figure 4. Three examples of spiroconjugation in compound **3c**. Atom numbering and relative phases of orbitals are indicated for atoms 1, 2, 4, and 7 in Newman projections. Only stabilizing interactions are shown.

As is evident from comparison of Figures 3 and 4, the first type of homoconjugation, termed azaspiroconjugation, is the most important case. It can be quantitatively determined by PE spectroscopy provided that the energies of the undisturbed partial orbital systems (**7** and **9**) have been estimated correctly. The second case illustrates the destabilizing interaction of π(C=N) with σ(C^3-C^4-C^7), and the third case shows stabilization of π_2 of **3c**, which is only of minor importance.

Conclusion

The results of this work can be summarized as follows. Spiroconjugation is an important feature in the electronic structure of 1-azaspiro[2.4]hepta-1,4,6-trienes **3**. By this effect, the nitrogen lone-pair orbital n(N) and the π_1 orbital of the diene system are substantially increased and lowered, respectively. These findings are in contrast to those for the isoelectronic hydrocarbons **2**, for which spiroconjugation is negligible.

Experimental Section

General: ^{1}H NMR and ^{13}C NMR spectra were recorded on a Varian Gemini 2000 spectrometer operating at 300 and 75 MHz, respectively. NMR signals were referenced to TMS ($\delta = 0$) or solvent signals recalculated relative to TMS. The multiplicities of ^{13}C NMR signals were determined with the aid of *gated* spectra and/or DEPT 135 experiments. IR and UV spectra were measured on Bruker IFS 28 and Zeiss MCS 400, respectively. Hewlett–Packard hp 5890 II and hp Engine 5989 A with helium as the carrier gas and HP 5 capillary column (5% phenylmethylsilicone gum) were used for GC-MS (EI). HR-MS (ESI) spectra were recorded on a Mariner 5229 from Applied Biosystems. Flash column chromatography was performed with 32–63 µm silica gel. Irradiation was conducted at −40 to −60 °C by using a high-pressure mercury lamp (TQ 150, Quarzlampengesellschaft Hanau) supplied with glass or quartz equipment and an ethanol cryostat. Most of these photolyses were monitored by NMR spectroscopy. Elemental analyses of potentially explosive azides and highly unstable azirines were not performed.

The PE spectrum was recorded on a UPG 200 spectrometer from Leybold–Heraeus equipped with a He(I) radiation source (21.21 eV). The sample of the unstable compound **3c** was obtained as a solution in dichloromethane. The solvent was removed under reduced pressure prior to measurement, and the residue was evaporated directly into the target chamber at ambient temperature. The spectrum was recorded repeatedly, and in the beginning there were strong signals from the solvent in the spectrum, which diminished slowly. The energy scale was calibrated with the xenon lines at 12.130 and 13.436 and argon lines at 15.759 and 15.937 eV. The accuracy of the measurements was approximately ±0.03 eV for ionization energies, for broad and overlapping signals it was only ±0.1 eV.

Semiempirical AM1[22] and PM3[23] calculations were performed with the MOPAC 93[24] program package, and ab initio B3LYP[25, 26] calculations were performed with the program GAUSSIAN 98.[27] For the latter methods, the basis set 6−31+G** was used, if not stated otherwise. Geometries were fully optimized at the respective levels of theory. Prior to quantum-chemical calculations, molecular geometries were preoptimized by molecular-mechanics calculations with the MMX[28] force field by using the program PCMODEL.[29]

1-Azaspiro[2.4]hepta-1,4,6-triene (3a): Solutions of **5a**[11] in $CDCl_3$, CD_2Cl_2, or [D$_6$]acetone at −60 °C or in CCl_4 or CD_3CN at −40 °C were irradiated until the evolution of nitrogen stopped. When these photolyses were performed with strict exclusion of air by dry argon, the reaction mixture changed from yellow–orange to light yellow, and the yields of **3a** measured by ^{1}H NMR spectroscopy with the aid of an internal standard reached 100%. Otherwise, degradation of **3a** was observed, with the reaction mixture turning red-brown. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 5.96$ (m, 2H; H-4/H-7), 6.64 (m, 2H; H-5/H-6), 10.70 (s, 1H; H-2), assignments based on ^{1}H NMR data of **3b**; ^{13}C NMR (75 MHz, $CDCl_3$, −20 °C, TMS): $\delta = 47.15$ (s, C-3), 134.6 (d, $^{1}J = 168$ Hz), 136.0 (d, $^{1}J = 174$ Hz), 171.1 (d, $^{1}J = 250$ Hz, C-2); IR (CCl_4): $\tilde{\nu} = 1676$ cm^{-1} (C=N); UV/Vis (CD_3CN): $\lambda_{max} = 229$, 264 nm; GC-MS (70 eV) *m/z* (%): 91 (100) [M^+], 64 (88), 63 (25), 39 (31), 38 (28).

4,6-Di-*tert*-butyl-1-azaspiro[2.4]hepta-1,4,6-triene (3b): A solution of **5b** in $CDCl_3$ was irradiated at −50 °C as described for the analogous reaction of **5a**. Yield (^{1}H NMR): 80%; ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 1.03$ (s, 9H; *t*Bu at C-4), 1.14 (s, 9H; *t*Bu at C-6), 5.23 (d, $^{4}J = 2.2$ Hz, 1H; H-7), 6.32 (d, $^{4}J = 2.2$ Hz, 1H; H-5), 10.52 (s, 1H; H-2), assignments based on NOE difference spectra; ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 29.22$ (q), 30.22 (q), 32.37 (s), 32.51 (s), 46.41 (s, C-3), 124.57 (d, $^{1}J = 167$ Hz), 127.80 (d, $^{1}J = 171$ Hz), 156.84 (s), 157.13 (s), 170.73 (d, $^{1}J = 245$ Hz, C-2); IR ($CDCl_3$): $\tilde{\nu} = 1670$ cm^{-1} (C=N); GC-MS (70 eV) *m/z* (%): 203 (11) [M^+], 147 (16), 146 (10), 132 (77), 57 (100), 41 (48), 39 (18); HR-MS (ESI): *m/z* (%): 204.1755 (100) [M^++H] (calcd for $C_{14}H_{22}N$: 204.1747), 407.3389 (25) [2M^++H] (calcd for $C_{28}H_{43}N_2$: 407.3421).

2-Methyl-1-azaspiro[2.4]hepta-1,4,6-triene (3c): Solutions of **5c** in $CDCl_3$ or CH_2Cl_2 (ca. 0.07 molar) were stored at room temperature for 40 h, heated at 40 °C for 3 h, or heated at 60 °C for 30 min to give a quantitative yield (^{1}H NMR) of **3c**. When CH_2Cl_2 was used, most of the solvent could be removed by distillation; however, there was a great loss of the product due to its volatility. All attempts to isolate **3c** by gas or liquid chromatography were unsuccessful. As described for the irradiation of **5b**, the quantitative transformation **5c** → **3c** was also possible by photolysis. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 2.66$ (s, 3H; Me), 5.98 (m, 2H; H-4/H-7), 6.62 (m, 2H; H-5/H-6), assignments based on ^{1}H NMR data of **3b**; ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 15.21$ (q, Me), 51.79 (s, C-3), 133.71 (d), 135.74 (d), 175.30 (s, C-2); IR ($CDCl_3$): $\tilde{\nu} = 1630$ cm^{-1} (C=N); GC-MS (70 eV) *m/z* (%): 105 (66) [M^+], 63 (100), 38 (60); HR-MS (ESI): *m/z*: 211.1220 [2M^++H] (calcd for $C_{14}H_{15}N_2$: 211.1230].

(*E*)-5-Azidomethylene-1,3-di-*tert*-butylcyclopenta-1,3-diene (5b): A solution of LiN_3 (0.13 g, 2.7 mmol) in DMSO (5 mL) was added to a solution of **4b**[10] (X = Cl, 0.50 g, 2.2 mmol) in DMSO (40 mL), and the resulting mixture was stirred at room temperature for 20 h. Thereafter, the reaction mixture was diluted with water (ca. 50 mL) and extracted with Et_2O (3 × 100 mL). The combined organic layers were washed with water (4 × 100 mL) and dried with $MgSO_4$. After removal of the solvent in vacuo, the residue was purified by flash chromatography (SiO_2, hexane) to give **5b** (0.39 g, 76%) as an orange oil. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 1.14$ (s, 9H; *t*Bu), 1.27 (s, 9H; *t*Bu), 5.97 (d, $^{4}J = 2.2$ Hz, 1H; H-2 or H-4), 6.12 (d, $^{4}J = 2.2$ Hz, 1H; H-2 or H-4), 7.08 (s, 1H; C=CHN$_3$); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 29.31$ (q), 32.26 (s), 32.32 (q), 32.96 (s), 109.07 (d), 126.77 (d), 129.72 (d), 134.22 (s), 146.66 (s), 155.79 (s); IR ($CDCl_3$): $\tilde{\nu} = 2107$ cm^{-1} (N_3).

5-(1-Azidoethylidene)cyclopenta-1,3-diene (5c): A solution of **6c**[12] (1.22 g, 13.5 mmol) in CH_2Cl_2 (20 mL) was added to a solution of LiN_3 (2.00 g, 40.8 mmol) in MeOH (100 mL), and the resulting mixture was stirred at −70 °C. The temperature of the reaction mixture was allowed to rise to −10 °C within 2 h. The subsequent workup had to be performed rapidly and at a temperature as low as possible since **5c** tended to cleave off nitrogen to produce **3c**, even at room temperature. The reaction mixture was poured into ice/water and extracted with Et_2O (3 × 150 mL). The combined organic layers were washed twice with cold water and dried with $MgSO_4$ at 0 °C. After removal of the solvent in vacuo, analysis of the crude product by ^{1}H NMR spectroscopy including an internal standard indicated that **5c** was formed with a yield of 81% along with 5-(1-methoxyethylidene)cyclopenta-1,3-diene[12] (6%) and small amounts of benzaldehyde resulting from the synthesis[12] of **6c**. The product could be purified by flash chromatography (SiO_2, CH_2Cl_2/hexane 1:3) to give **5c** as a yellow solid. M.p. < 30 °C; ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 2.40$ (s, 3H; Me), 6.39 (m, 2H), 6.46 (m, 1H), 6.52 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 16.72$ (q, Me), 118.25 (d), 120.75 (d), 130.27 (d), 131.45 (d), 133.39 (s), 142.69 (s); IR ($CDCl_3$): $\tilde{\nu} = 2101$ cm^{-1} (N_3).

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