Dibenzohomopyracylene, a Segment of Methanofullerene $C_{61}H_2$, Its Radical Ions and Dianion

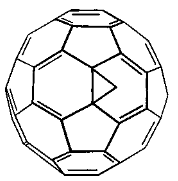
Fabian Gerson,*[a] Pascal Merstetter,[a] Frédérique Barbosa,[b] Emanuel Vogel,[c] Christoph König,[c] Johann Lex,[c] Klaus Müllen,[d] and Manfred Wagner[d]

Abstract: Dibenzohomopyracylene (**2**), the 12b,12c-homo derivative of indeno[1,2,3-*cd*]fluoranthene (**1**), has been synthesized. Both ^{13}C NMR and X-ray diffraction data suggest that **2** has a "closed" norcaradiene-like structure (**2cl**). The radical ions **2**$^{\bullet+}$ and **2**$^{\bullet-}$ were characterized by their ^{1}H coupling constants using ESR, ENDOR, and TRIPLE-resonance spectroscopy. In accord with UB3LYP/6-31G*//UHF/3-21G* calculations, the radical cation **2**$^{\bullet+}$ retains the "closed" structure (**2cl**$^{\bullet+}$), while the structure of the radical anion **2**$^{\bullet-}$ appears to be "intermediate" (**2int**$^{\bullet-}$) between the "closed" (**2cl**$^{\bullet-}$) and the "open" annulene-like (**2op**$^{\bullet-}$) forms. The ^{13}C NMR spectrum of dianion **2**$^{2-}$ is consistent with the "open" structure (**2op**$^{2-}$). The transition from the "closed" to the "open" form in the redox sequence **2cl**$^{\bullet+}$, **2cl**, **2int**$^{\bullet-}$, **2op**$^{2-}$ therefore occurs at the radical anion stage. Since **2cl** represents a segment of the "6-6-closed" methanofullerene ($C_{61}H_2$), the latter may also undergo corresponding structural changes in its radical ions and dianion.

Keywords: dibenzohomopyracylene · ENDOR spectroscopy · EPR spectroscopy · NMR spectroscopy · radical ions · structure elucidation

Introduction

An important and simple modification of the carbon framework in [60]fullerene is the addition of diazomethane to a formal C=C bond.[1] The final reaction product $C_{61}H_2$, obtained after extrusion of nitrogen, is either a methanofullerene with a "closed" σ-homoaromatic structure or a methanofulleroid with an "open" π-homoaromatic one. The former prevails when addition occurs at the junction between two six-membered rings ("6-6-closed"), whilst the latter dominates when addition takes place at the junction between a six- and a five-membered ring ("6-5-open").[2] The "6-6-closed" structure proved to be thermodynamically more stable than the "6-5-open" one. NMR spectroscopy, especially the chemical shift of the ^{13}C isotope in the methylene-carbon atom and the pertinent ^{13}C-^{1}H spin–spin coupling constant enables the two forms to be distinguished. No similar information is available for the corresponding radical ions. Although the $C_{61}H_2$ adduct readily accepts an electron to yield the radical anion, the ESR spectrum of $C_{61}H_2^{\bullet-}$ was void of hyperfine splittings and could not be studied by the ENDOR technique.[3]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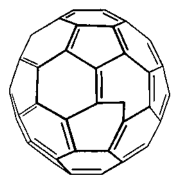
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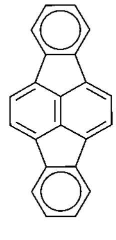
The nonalternant hydrocarbon indeno[1,2,3-*cd*]fluoranthene (dibenzopyracylene; **1**) represents a flattened segment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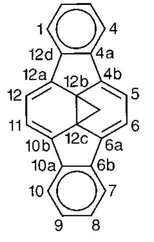
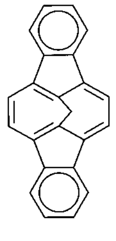


2cl


2op

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[a] Prof. Dr. F. Gerson, Dr. P. Merstetter
Institut für Physikalische Chemie
Universität Basel
Klingelbergstrasse 80, CH-4056 Basel (Switzerland)
Fax: (+41) 61-267-38-55
E-mail: gerson@ubaclu.unibas.ch

[b] Dipl. Chem. F. Barbosa
Institut für Organische Chemie
Universität Basel
St. Johanns-Ring 19, CH-4056 Basel (Switzerland)

[c] Prof. Dr. E. Vogel, Dr. C. König, Dr. J. Lex
Institut für Organische Chemie der Universität
Greinstrasse 4, D-50939 Köln (Germany)

[d] Prof. Dr. K. Müllen, Dr. M. Wagner
Max-Planck-Institut für Polymerforschung
Ackermannweg 10, D-55021 Mainz (Germany)

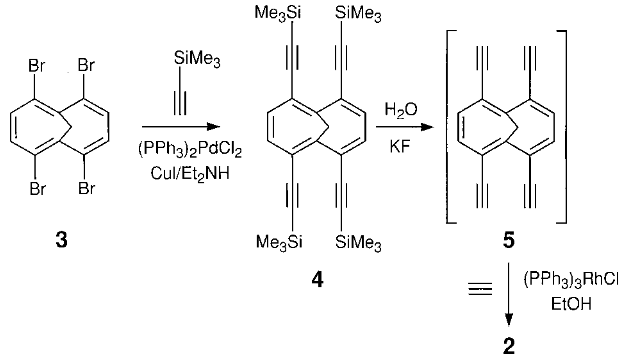
of [60]fullerene. Dibenzopyracylene was first synthesized in 1951[4] and studies involving its radical ions $\mathbf{1}^{\bullet+}$ and $\mathbf{1}^{\bullet-}$ [5] were carried out many years prior to the discovery of the fullerenes. In the present paper, we describe the synthesis, spectroscopic characteristics, and X-ray crystal structure of the hydrocarbon **2**, the bowl-shaped 12b,12c-homo derivative of **1**.[6] In addition, we report some studies involving the corresponding radical ions $\mathbf{2}^{\bullet+}$ and $\mathbf{2}^{\bullet-}$ which exhibit rich ESR-hyperfine patterns and give rise to well-defined ENDOR spectra. Interest is focussed on whether **2**, $\mathbf{2}^{\bullet+}$, and $\mathbf{2}^{\bullet-}$ prefer the "closed" norcaradiene-like (**cl**) or the "open" annulene-like (**op**) structure. Information relating to the structure of the dianion $\mathbf{2}^{2-}$ is readily obtained from NMR measurements. Notably, a homo derivative of **1** is a segment of $C_{61}H_2$ (cf. the pertinent formulae) and, in particular, the "closed" form **2cl** of dibenzohomopyracylene represents a segment of the "6-6-closed" methanofullerene $C_{61}H_2$.

Results and Discussion

Dibenzohomopyracylene (**2**) was synthesized from 2,5,7,10-tetrakis(trimethylsilylethynyl)-1,6-methano[10]annulene (**4**), which was prepared by a known procedure[7] from the tetrabromo compound **3** (Scheme 1). After removal of the protecting trimethylsilyl groups, tetraethynylmethano[10]annulene (**5**) was cyclized with acetylene in a Rh^{I}-catalyzed reaction to yield **2**. The ^{13}C NMR data (see below) clearly characterize the product as **2cl**, which was confirmed by an X-ray crystallographic structure analysis (Figure 1).

Oxidation of **2** with a freshly sublimed mirror of aluminum trichloride in dichloromethane at about 200 K led to the ESR and ENDOR spectra consistent with the radical cation $\mathbf{2}^{\bullet+}$ (Figure 2; $g = 2.0030 \pm 0.0001$). The ^{1}H coupling constants derived from the ENDOR spectrum are $|a_H| = 0.335 \pm 0.002$, 0.203 ± 0.002, 0.105 ± 0.001, and 0.019 ± 0.001 mT. As indicated by the computer simulation of the ESR-hyperfine

Abstract in German: *Dibenzohomopyracylen (**2**), das 12b,12c-Homo-Derivat von Indeno[1,2,3-cd]fluoranthen (**1**), wurde synthetisiert. ^{13}C-NMR-Spektrum und Röntgen-Kristallstruktur von **2** weisen auf eine „geschlossene" Norcaradien-ähnliche Form (**2cl**) hin. Die Radikalionen $\mathbf{2}^{\bullet+}$ and $\mathbf{2}^{\bullet-}$ wurden durch ihre ^{1}H-Kopplungskonstanten mittels ESR-, ENDOR- und TRIPLE-Resonanz-Spektroskopie charakterisiert. In Uebereinstimmung mit B3LYP/6–31G* -Rechnungen behält das Radikalkation $\mathbf{2}^{\bullet+}$ die „geschlossene" Form ($\mathbf{2cl}^{\bullet+}$), während die Struktur des Radikalanions $\mathbf{2}^{\bullet-}$ als „intermediär" ($\mathbf{2int}^{\bullet-}$) zwischen der „geschlossenen" ($\mathbf{2cl}^{\bullet-}$) und der „offenen" Annulen-ähnlichen Form ($\mathbf{2op}^{\bullet-}$) erscheint. Für das Dianion $\mathbf{2}^{2-}$ wird die „offene" Form ($\mathbf{2op}^{2-}$) durch sein ^{13}C-NMR-Spektrum belegt. In der Redox-Folge $\mathbf{2cl}^{\bullet+}$, **2cl**, $\mathbf{2int}^{\bullet-}$, $\mathbf{2op}^{2-}$ findet demnach der Uebergang von der „geschlossenen" zur „offenen" Form auf der Stufe des Radikalanions statt. Das „6-6-geschlossene" Methanofulleren $C_{61}H_2$, dessen Teilstück **2cl** darstellt, dürfte in seinen Radikalionen und Dianion die entsprechenden strukturellen Aenderungen durchlaufen.*



Scheme 1. Synthesis of **2** from **3** via **5**.

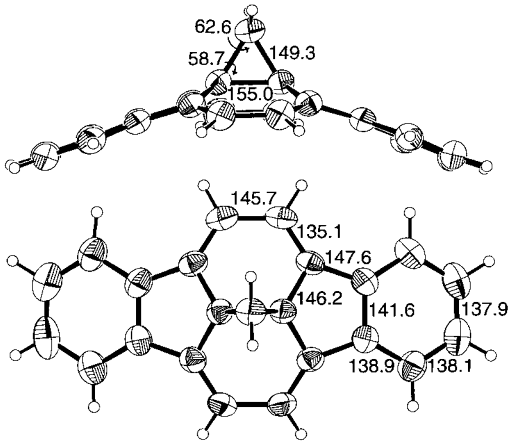


Figure 1. X-ray crystal structure of dibenzohomopyracylene (**2**). The selected C–C bond lengths [pm] and C-C-C bond angles [°] are average values of those parameters which are equivalent by C_{2v} symmetry.

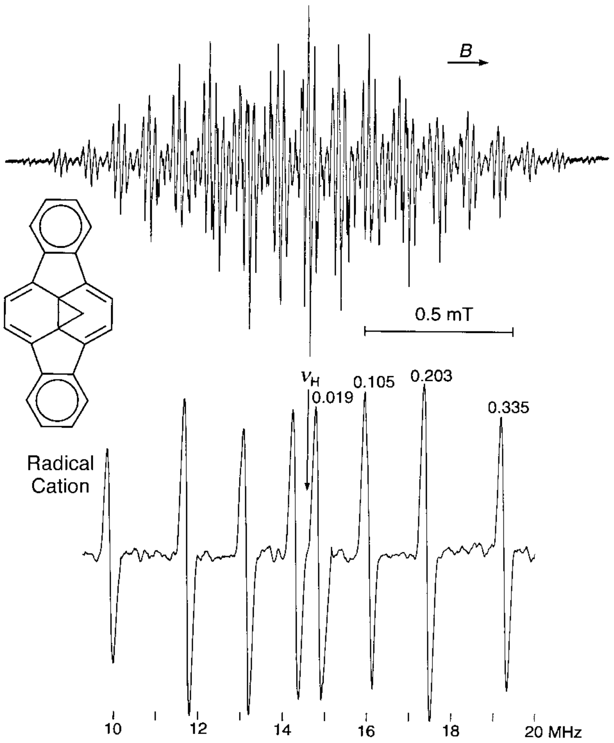


Figure 2. ESR (top) and ENDOR (bottom) spectra of $\mathbf{2}^{\bullet+}$. Solvent dichloromethane, counterion (presumably) $AlCl_3^-$; temperature 200 K. The numbers above the ENDOR signals are the associated $|a_H|$ values in mT.

pattern, the largest $|a_H|$ value is due to the two methylene protons, and the three smaller couplings result from the three sets of four α-protons[8] at the periphery of the π system. General-TRIPLE-resonance experiments[9] carried out on the ENDOR signals indicated the same sign for all coupling constants which must be negative, in accord with the theory for α-protons.[10] From calculations at the UB3LYP/6-31G*//UHF/3-21G* level[11] (performed with GAUSSIAN 94),[12] the "closed" form **2cl**$^{\bullet+}$ with a C(12b)–C(12c) bond length of 146 pm is 84 kJ mol^{-1} more stable than the "open" form **2op**$^{\bullet+}$ in which the analogous bond length is 218 pm. Moreover, the a_H values calculated for **2cl**$^{\bullet+}$ compare very favorably with the experimental data, whilst those calculated for **2op**$^{\bullet+}$ are markedly different (Table 1). This finding not only enables one to attribute the structure **2cl**$^{\bullet+}$ to the radical cation, but (Table 1) it also leads to an unequivocal assignment of the observed coupling constants to the α-protons.

Table 1. Calculated and observed ^{1}H coupling constants, a_H in mT, for the radical ions, $\mathbf{2}^{\bullet+}$ and $\mathbf{2}^{\bullet-}$, and relative energies E_{rel} in kJ mol^{-1}.

	Position 1,4,7,10	2,3,8,9	5,6,11,12	methylene	E_{rel}
2cl$^{\bullet+}$, calcd	0.001	– 0.102	– 0.219	– 0.389	0.0
2op$^{\bullet+}$, calcd	– 0.164	– 0.053	+ 0.231	– 0.111	84.1
$\mathbf{2}^{\bullet+}$, obsd	– 0.019	– 0.105	– 0.203	– 0.335	
2cl$^{\bullet-}$, calcd	– 0.004	– 0.116	– 0.062	+ 0.003	6.3
2op$^{\bullet-}$, calcd	– 0.031	– 0.062	+ 0.369	– 0.132	0.0
2int$^{\bullet-}$, calcd	– 0.028	– 0.070	+ 0.133	– 0.117	0.0
$\mathbf{2}^{\bullet-}$, obsd	– 0.031	– 0.064[a]	+ 0.069[a]	– 0.079	

[a] Assignment of the absolute value uncertain.

ESR and ENDOR spectra of the radical anion $\mathbf{2}^{\bullet-}$ were observed upon reduction of **2** with a potassium mirror in 1,2-dimethoxyethane at 200 K (Figure 3; $g = 2.0025 \pm 0.0001$). The coupling constants used for the computer simulation of the ESR-hyperfine pattern were derived from the ENDOR spectrum. The pertinent values are $|a_H| = 0.079$ mT for the two methylene protons and 0.069, 0.064, and 0.031 mT for the α-protons (experimental error: ±0.001 mT). As indicated by the general-TRIPLE-resonance method, the largest and the smallest coupling constants have the same sign (presumably negative), whereas the two very similar intermediate values, associated with the pair of the broadest ENDOR signals (0.067 mT in Figure 3), are of opposite sign. The energy of the "closed" form **2cl**$^{\bullet-}$, calculated at the same level of theory, is slightly higher (6.3 kJ mol^{-1}) than that of the "open" form **2op**$^{\bullet-}$. The a_H values for both forms, however, deviate considerably from the experimental data (Table 1). Better agreement between the experimental and calculated data can be achieved by invoking a structure "intermediate" between the two forms which is predicted to have the same energy as **2op**$^{\bullet-}$. It is therefore reasonable to assume that the the radical anion has such a structure (**2int**$^{\bullet-}$), in which the C(12b)–C(12c) bond length of 185 pm is almost the average of those in the "closed" (157 pm) and the "open" form (216 pm). The observed coupling constants for the α-protons were assigned by correlation with the values calculated for **2int**$^{\bullet-}$ (Table 1).

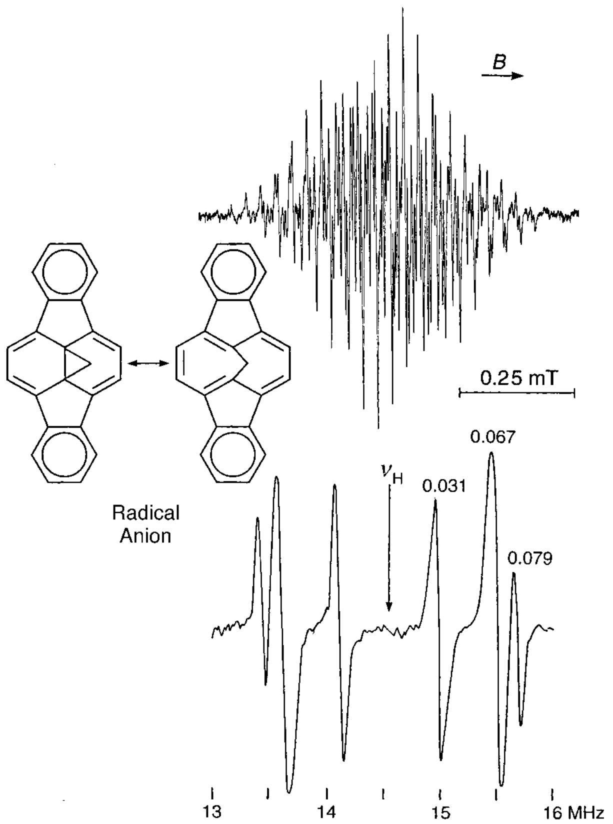


Figure 3. ESR (top) and ENDOR (bottom) spectra of $\mathbf{2}^{\bullet-}$. Solvent 1,2-dimethoxyethane, counterion K$^+$, temperature 200 K. The numbers above the ENDOR signals are the associated $|a_H|$ values in mT. The pair of broad signals, denoted 0.067 in the high-frequency portion, are two overlapping narrower signals with $|a_H|$ values of 0.064 and 0.069 mT (cf. text and Table 1).

The dianion $\mathbf{2}^{2-}$ was generated by prolonged contact of **2** with lithium wire in perdeuteriotetrahydrofuran at 253 K. Its ^{1}H NMR spectrum was markedly different from that of **2** and high-field shifts, expected for the conversion of a neutral compound to its dianion, were not observed (Table 2). The

Table 2. ^{1}H and ^{13}C NMR data, δ in ppm and $^1J_{C,H}$ in Hz, for **2** and its dianion $\mathbf{2}^{2-}$.[a]

	Position 1,4,7,10	2,3,8,9	5,6,11,12	4a,6b,10a,12d	4b,6a,10b,12a	12b,12c	methylene
2, δ (^{1}H)	6.95[b]	6.92[b]	5.60				2.55
2, δ (^{13}C)	120.88	128.81	112.73	138.20	138.73	59.08	15.75
2, $^1J_{C,H}$							169.0
$\mathbf{2}^{2-}$, δ (^{1}H)	6.99[b]	6.22[b]	6.50				4.56
$\mathbf{2}^{2-}$, δ (^{13}C)	113.06	117.79	121.19	135.73	145.82	98.32	34.69
$\mathbf{2}^{2-}$, $^1J_{C,H}$							138.0

[a] Experimental error: ±0.01 ppm in δ (^{1}H), ±0.05 ppm in δ (^{13}C), and ±0.05 Hz in $^1J_{C,H}$. [b] Assignment uncertain, AA′BB′ system.

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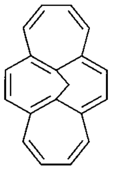
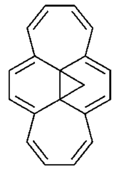
shift of the signals for protons in the positions 5,6,11, and 12 from $\delta = 5.60$ (**2**) to $\delta = 6.50$ ($\mathbf{2}^{2-}$) can be explained by a change from the "closed" norcaradiene-like form of the central nonaromatic moiety to the "open" form of an aromatic methano[10]annulene. Moreover, the low-field shift of the signal of the methylene protons from $\delta = 2.55$ (**2**) to $\delta = 4.56$ ($\mathbf{2}^{2-}$) is also consistent with the transformation of the three-membered ring into a methano-bridged form. Such a transition from the neutral compound **2cl** into the "open" structure, $\mathbf{2op}^{2-}$ of the dianion is supported by the ^{13}C NMR spectra. The signal of the ^{13}C isotope in the methylene-carbon atom shifts from $\delta = 15.75$ for **2cl** to $\delta = 34.69$ for $\mathbf{2op}^{2-}$, while associated spin–spin coupling constant $^{1}J_{\mathrm{C,H}}$ decreases from 169.0 to 138.0 Hz . Such changes mirror those observed in the ^{13}C NMR spectra of homodipleiadiene (12b,12c-homodicyclohepta[*de,ij*]naphthalene; **6**) and its dianion,[13] although in this instance the neutral molecule was identified as **6op** ($\delta = 39.08$ and $^{1}J_{\mathrm{C,H}} = 142.4$ Hz) and the dianion as $\mathbf{6cl}^{2-}$ ($\delta = 25.02$ and $^{1}J_{\mathrm{C,H}} = 157.5$ Hz).



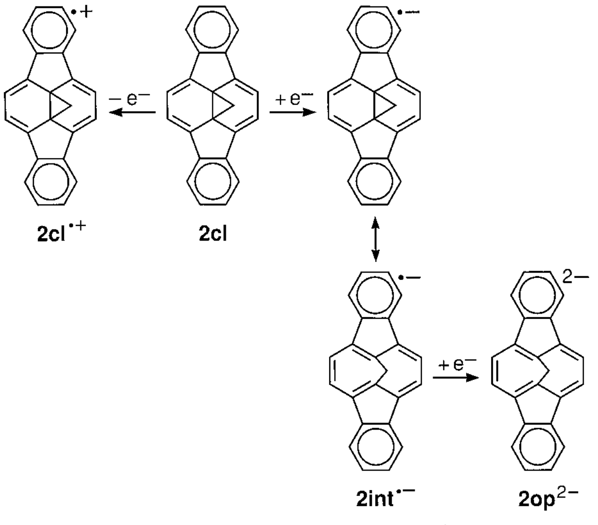
6op



6cl

Conclusion

In the redox sequence $\mathbf{2cl}^{\bullet +}$, **2cl**, $\mathbf{2int}^{\bullet -}$, and $\mathbf{2op}^{2-}$, transition from the "closed" (**cl**) to the "open" (**op**) form thus appears to occur at the radical anion stage (Scheme 2). If one accepts that **2cl** is a model compound for the "6-6-closed" methanofullerene $C_{61}H_2$, an analogous statement may hold for the radical ions and the dianion of this homo derivative of [60]fullerene. Thus, the radical cation $C_{61}H_2^{\bullet +}$, like the neutral methanofullerene $C_{61}H_2$, should have the "closed" form which is expected to "open" on reduction to the dianion $C_{61}H_2^{2-}$, and the structure of the radical anion $C_{61}H_2^{\bullet -}$ is "intermediate" (**int**) between the "closed" and the "open" forms (Scheme 2).



Scheme 2. Redox sequence $\mathbf{2cl}^{\bullet +}$, **2cl**, $\mathbf{2int}^{\bullet -}$, and $\mathbf{2op}^{2-}$.

Experimental Section

The ESR spectra were measured by using Varian-E9 and a Bruker-ESP-300 instruments. ENDOR and TRIPLE-resonance studies were also carried out with a Bruker-ESP-300. NMR spectra were recorded with a Bruker-DR-500 spectrometer.

Dibenzohomopyracylene (2): A deoxygenated solution of **4** (264 mg, 0.5 mmol), [18]crown-6 (528 mg, 2 mmol), potassium fluoride (1.45 g, 25 mmol), and water (0.45 mL, 25 mmol) in 1,2-dimethoxymethane (50 mL) was stirred for 1 h under an argon atmosphere at 0 °C. Dichloromethane (50 mL) was added to the reaction mixture, and the organic phase was washed with water (3×50 mL) and dried over magnesium sulfate. After the solution was concentrated to about 20 mL in vacuo and ethanol (50 mL) added, the remaining dichloromethane was removed. The resulting solution of **5** was treated with a stream of acetylene gas for 15 min at room temperature and atmospheric pressure. After a further 45 min, tris(triphenylphosphane)rhodium(I) chloride (37 mg, 0.04 mol) was added in portions at 50 °C and the supply of acetylene continued. The reaction mixture was stirred for 15 min and the solvent was removed in vacuo. The red solid residue was chromatographed on an Alox column (activity II–III; 50×1 cm) using hexane/ diethyl ether (9:1) as eluant. After removal of the solvent from the main fraction, the solids were recrystallized from hexane to give dark red rectangular crystals (m.p. 223–224 °C (decomp); 41 mg yield 28 %, based on **4**). UV/VIS (CH_2Cl_2): $\lambda_{\max}$ (ε [dm^3 mol^{-1} cm^{-1}]) = 272 (21500), 328 (54300), 343 (76000), 384 (1800), 406 (2000), 430 nm (1400); IR (KBr): $\tilde{\nu} = 3044, 3023, 2996, 1499, 1434, 1022, 833, 781, 742, 430$ cm^{-1}; for ^{1}H and ^{13}C NMR, see Table 2; MS (70 eV): *m*/*z* (%): 290 (55) [M^+], 289 (100) [$M - H$]$^+$, 276 (38) [$M - CH_2$]$^+$, 144 (19) [$M^{2+} - H$]; $C_{23}H_{14}$: calcd C 95.14, H 4.86; found C 95.28, H 4.77.

X-ray crystallography of 2: $C_{23}H_{14}$, $M_r = 290.34$, system orthorhombic, space group $P2_12_12_1$, $a = 794.9(1)$, $b = 1348.7(1)$, $c = 1401.8(1)$ pm, $V = 1.5028(2)$ nm^3, $Z = 4$, $\rho_{\mathrm{calcd}} = 1.283$ g cm^{-3}, $T = 293$ K; Nonius-Kappa-CCD diffractometer, $Mo_{K\alpha}$ radiation ($\lambda = 71.073$ pm), absorption coefficient 0.073 mm^{-1}, $F(000) = 608$, crystal size $0.35 \times 0.30 \times 0.25$ mm, θ range for data collection 2.95–27.10°, index ranges $-10 < h < 10$, $-17 < k < 17$, $-17 < l < 17$, reflections collected 3317, independent reflections 3297, refinement method full-matrix least-squares on F^2, data/restraints/parameters 3258/0/266, goodness-of-fit on F^2 1.028, $w_{\mathrm{calc}} = 1/[\sigma^2 F_o^2 + (0.0378P)^2 + 0.05P]$, where $P = (F_o^2 + 2F_c^2)/3$, final R [$I > 2\sigma(I)$]: $R_1 = 0.0419$, $wR_2 = 0.0780$, reflections observed [$I > 2\sigma(I)$]: 2161, R (all data): $R_1 = 0.0809$, $wR_2 = 0.0893$, extinction coefficient 0.030(3), largest diff. peak and hole 96 and -95 e nm^{-3}. Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-106899. 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).

Radical ions $\mathbf{2}^{\bullet +}$and $\mathbf{2}^{\bullet -}$: Oxidation of **2** with aluminum trichloride in dichloromethane to the cation $\mathbf{2}^{\bullet +}$ and reduction of **2** with potassium metal in 1,2-dimethoxyethane to the anion $\mathbf{2}^{\bullet -}$ were carried out according to the standard vacuum technique.[14]

Dianion $\mathbf{2}^{2-}$: Compound **2** (1 mg) was placed at the bottom of an evacuated 5 mm NMR tube connected to a lithium press. Dry perdeuteriotetrahydrofuran was distilled into the tube under vacuum and degassed by repeated freeze-pump cycles. Lithium wires were pressed into the tube and kept in the upper part by a constriction in the glass.[15] The tube was sealed and the solution was brought into contact with the Li metal for 74 h at −20 °C. The resulting dianion $\mathbf{2}^{2-}$ was characterized by its ^{1}H and ^{13}C NMR spectra (see above).

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Received: December 21, 1998 [F1502]