Organometallics 1993, *12*, 2472–2477

Ferrocenyl- and Ethynyl-Substituted Fluorenes via Addition–Elimination Reactions and Two-Electron Reductions from Fluorenone. Syntheses of Heterodinuclear Acetylene and Fluorenyl Complexes

Michael Buchmeiser and Herwig Schottenberger*

Institut für Anorganische und Analytische Chemie, Leopold Franzens Universität Innsbruck, Innrain 52a, A-6020 Innsbruck, Austria

Received February 1, 1993

Addition of lithioferrocene, ferrocenylacetylide, and unsubstituted acetylides to fluorenone leads to the corresponding 9-fluorenols. Subsequent protonation–dehydration with etheral tetrafluoroboric acid to 9-carbocations, followed by various two-electron reductions, was examined. Also the influence and reaction behavior of hexacarbonyldicobalt-protected acetylene substituents was investigated. The terminal complexes show reeliminations different from those of the bridging analogs. The isolated new compounds **1**–**14**, 9-ferrocenylfluoren-9-ol (**1**), 9-ferrocenylfluorenium tetrafluoroborate (**2**), 9-ferrocenylfluorene (**3**), (η^5-9-ferrocenylfluorenyl)(η^5-pentamethylcyclopentadienyl)ruthenium(II) (**4**), 9-(ferrocenylethynyl)fluoren-9-ol (**5**), 9-(ferrocenylethynyl)fluoren-9-ol–hexacarbonyldicobalt complex (**6**), 9-(ferrocenylethynyl)fluorenium tetrafluoroborate–hexacarbonyldicobalt complex (**7**), 9-(ferrocenylethynyl)fluorene (**8a**), 1-ferrocenyl-2-(9-fluorenylidene)ethene (**8b**), 9-(ferrocenylethynyl)fluorenium tetrafluoroborate (**9**), dimer of 9-(ferrocenylethynyl)fluorene (**10**), 9-hydroxy-9-ethynylfluorene–hexacarbonyldicobalt complex (**11**), bis(9-fluoreniumyl)ethyne ditetrafluoroborate (**12**), bis(9-hydroxyfluoren-9-yl)ethyne–hexacarbonyldicobalt complex (**13**), and bis(9-fluoreniumyl)ethyne ditetrafluoroborate–hexacarbonyldicobalt complex (**14**), were characterized by MS, IR, NMR, and elemental analysis.

Introduction

Preparative approaches to linked cyclopentadienyl ligand chemistry, especially for the access of new strongly interacting oligonuclear π-complexes, represent a field of actual demand.[1] The distinct proximity and binding situation of adjacent moieties with different modes of resulting interactions[2] are a prerequisite for systematic studies on cooperative systems.[3] The primary intention of the present work was to contribute to the synthesis of substituted and homologous fulvalene structures, since they can serve as variable elements for the construction of combined molecular working devices.

Results and Discussion

A widely established route to functionalized cyclopentadienes is the general concept of nucleophilic attack on cyclopentenones to form alcoholates, followed by protic quenching with elimination of water to form monomeric cyclopentadienes like substituted indenes[4] or, depending of their stability, the respective dimerization products.

Stable precursors with the formal substructure of pentasubstituted cyclopentadienols, e.g. 9-fluorenol derivatives, also belong to the starting materials of choice, but consequently they require alternative dehydroxylation sequences, which can be realized with convenience as discribed in the following.

Water removal from the protonated carbinol function of ferrocenylfluorenol (**1**) yields an additionally stabilized α-cation,[5] which requires straightforward 2e reduction to form the fluorenide, respectively fluorene (**3**), by any type of acidification.

Obviously, **3** has a high synthetic potential for the preparation of new bi- or termetallocenes, as exemplified by the mixed-metal dibenzofulvalene complex **4**.

For the case of (ferrocenylethynyl)fluorenol (**5**) or underived ethynylfluorenols no similar concepts are applicable, since different cations may stem from competing protonation sites and give rise to unexpected side reactions or decomposition. Indeed, an attempt to isolate analytically consistent 9-ethynylfluorenium tetrafluoroborate from 9-ethynylfluorenol under conditions identical to those for bis(9-fluoreniumyl)ethyne ditetrafluoroborate (**12**), Scheme II, failed.

Furthermore, quenching of the bis(9-fluorenyl)ethyne dianion leads to different products, strongly depending of the temperature and the protonating agent.[6] By addition of methanol, bis(9-fluorenylidene)-1,3-butadiene,[7] a formal bifulvene, is obtained by a very slow reaction; when acetic acid was used, in addition to the bifulvene the tautomeric difluorenylethyne[8] was also a main product. By our experience, a similar product composition is obtained by quenching with wet 2-propanol. For (ferrocenylethynyl)fluorene (**8a**), interconversion to the higher conjugated form occurs during chromatographical workup. The

---

(1) Abriel, W.; Baum, G.; Burdorf, H.; Heck, J. *Z. Naturforsch.* **1991**, *46B*, 841 and references therein.

(2) Delville-Desbois, M.-H.; Vollhardt, K. P. C.; Astruc, D. *New J. Chem.* **1992**, *16*, 899.

(3) Wielstra, Y.; Duchateau, R.; Gambarotta, S. *J. Organomet. Chem.* **1991**, *418*, 183.

(4) (a) Plenio, H. *Organometallics* **1992**, *11*, 1856 and references therein. (b) Bunuel, E. E.; Valle, L.; Jones, N. L.; Carroll, P. J.; Gonzalez, M.; Munoz, N.; Manriquez, J. N. *Organometallics* **1988**, *7*, 789.

(5) Allenmark, S. *Tetrahedron Lett.* **1974**, *4*, 371.

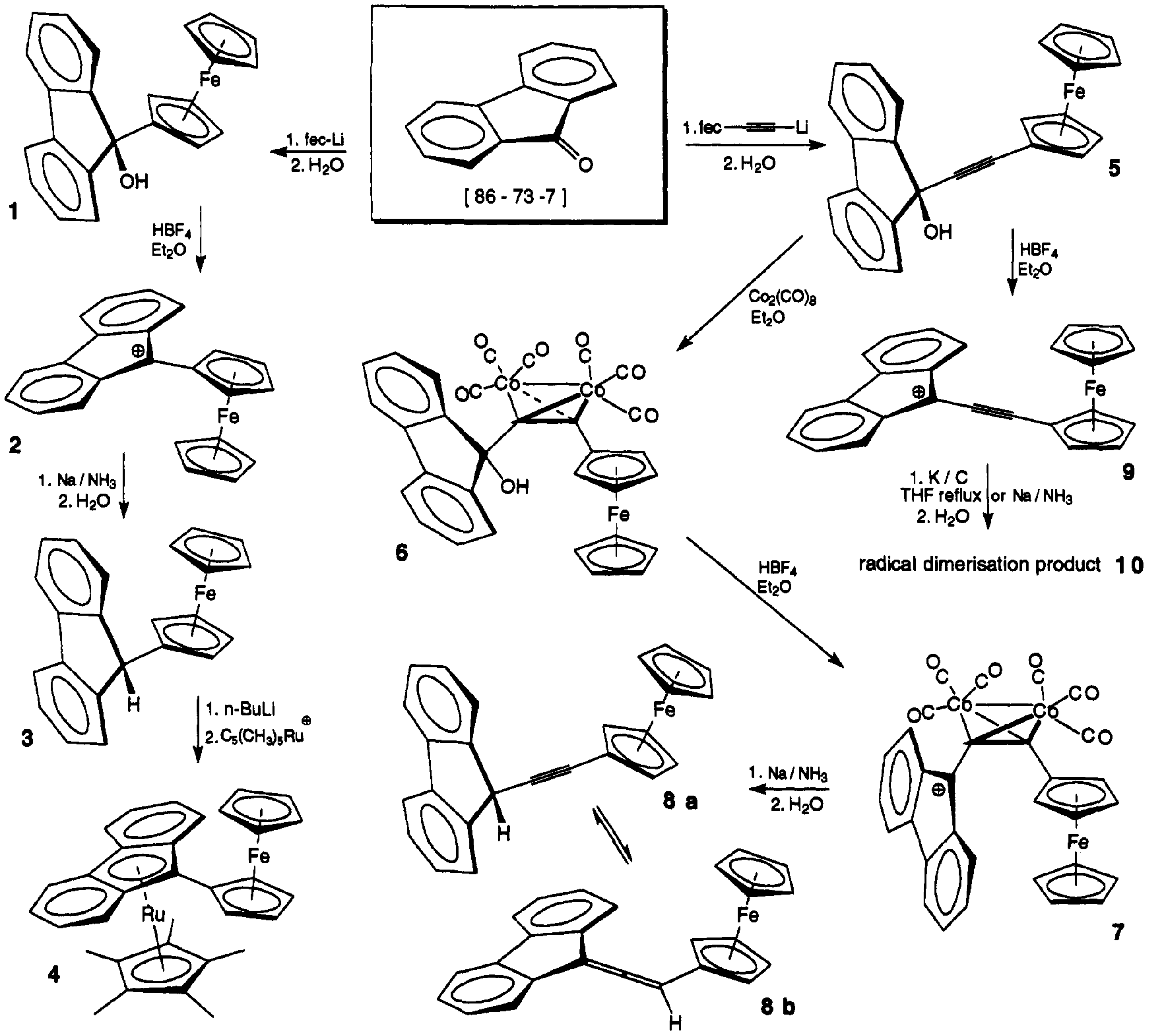
(6) Edinger, J. M.; Day, A. R. *J. Org. Chem.* **1971**, *36*, 240.

(7) Curtin, D. J.; Richardson, W. H. *J. Am. Chem. Soc.* **1959**, *81*, 4719.

(8) Kuhn, R.; Fischer, H. *Chem. Ber.* **1961**, *94*, 3060.

0276-7333/93/2312-2472$04.00/0

Scheme I. Preparation and Reactions of Compounds 1–10



resulting tautomer (**8b**) is not stable due to further dimerization.

Taking this into consideration, we were interested in evaluating the stabilizing effects, any site-specific protonation preferences, and the protecting–deprotecting chemistry of the respective dicobalt hexacarbonyl adducts. The eliminative reduction of ethynedicobalt hexacarbonyls was investigated by electrochemical techniques[9] and cleavage of tetracarbonylcobaltate from the generated anionic species was confirmed as the first step, followed by complete ethyne liberation after further reduction.

This is also the result for chemical reductions with C/K or solvated electrons, despite the fact one might expect some influence of adsorptivity phenomena on the graphite or the generated metallic cobalt surface, e.g. distinct charge localization to the 9-fluorenyl position. The reduction of **12** and cleaved **14** should result in anionic species identical with those for 9,9′-(1,2-ethenediylidene)bis(9*H*-fluorene) (bis(fluorenylidene)ethene), of which hydrogenation with sodium amalgam in wet tetrahydrofuran was reported to give exclusively the acetylene tautomer.[8] This result was attributed to the primary reaction of nascent hydrogen with radical monoanions of the conjugated bis(fluorene) system. (In order to retain the bridge in **14** unaffected for possible formation of bent ansametallocene structures, we tried a milder reduction variant with samarium diiodide in tetrahydrofuran, but immediate effervescence gave evidence for the fragmentation of the dicobalt hexacarbonyl group.) Due to their different solubilities, the separation of the quenched tautomeric forms is best achievable by means of extraction steps.[6]

A double Nicholas cation was reported recently,[10] which exhibits instability similar to that of **14**. Warming above −20 °C gives bis(fluorenylidene)ethene in quantitative conversion. In contrast to **14**, treatment of a solution of the protected alcohol **11** with tetrafluoroboric acid at ambient temperature does not lead to spontaneous elimination to the corresponding allene system. However, 9-ethenylidenefluorene[11] is easily prepared by the direct reduction of 9-hydroxy-9-ethynylfluorene with stannous chloride in glacial acetic acid, a method formerly applied only to the acetylene glycols and their homologs.[7]

---

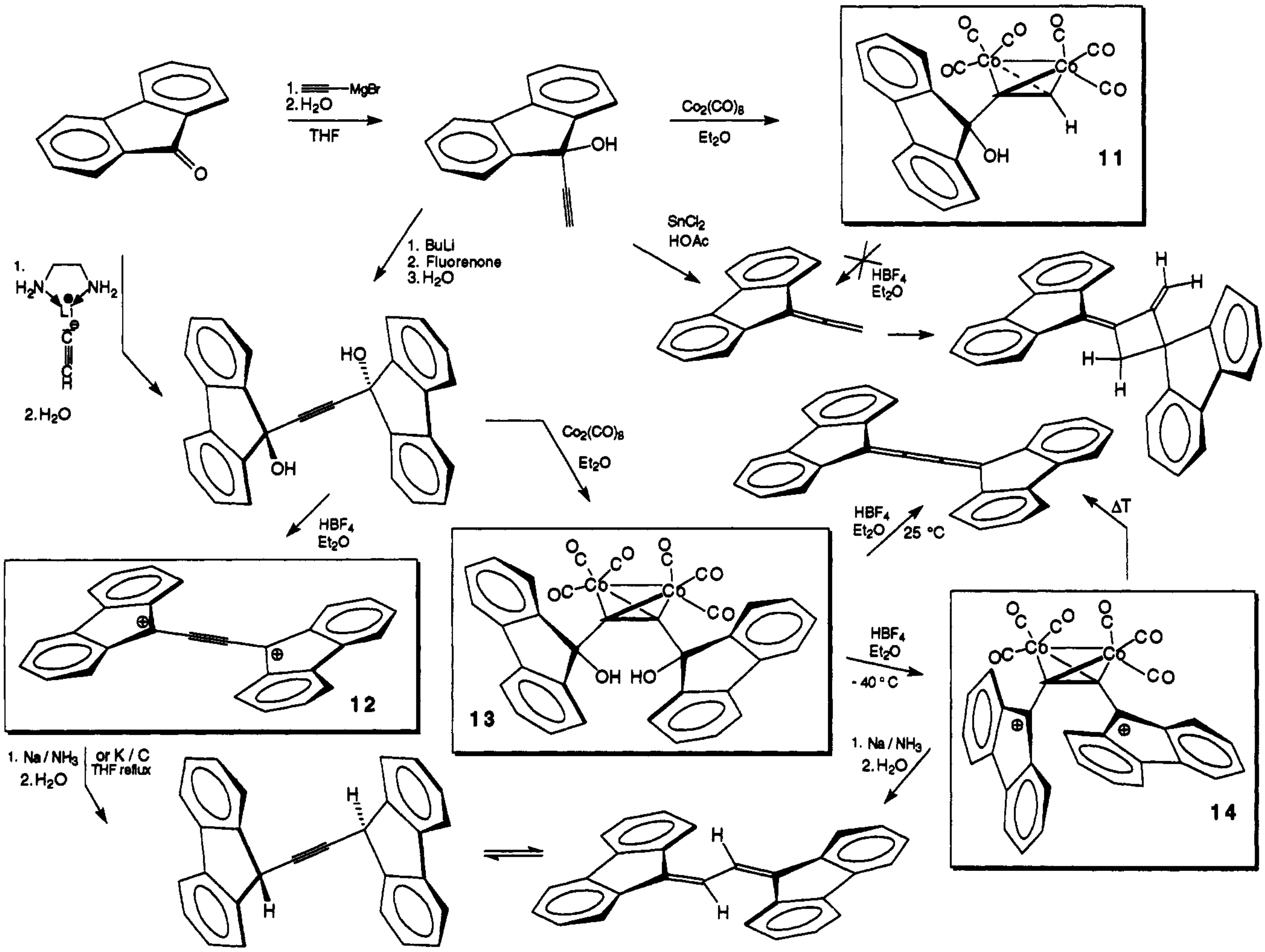
[9] Osella, D.; Fiedler, J. *Organometallics* **1992**, *11*, 3875 and references therein.

[10] Takano, S.; Sugihara, T.; Ogasawara, K. *Synlett.* **1992**, *1*, 70.

[11] Ranganathan, S.; Ranganathan, P. V.; Ramachandran, M. K.; Mahanty, M. K.; Bamezai, S. *Tetrahedron* **1981**, *37*, 4171.

[12] Schottenberger, H.; Ingram G.; Obendorf, D. *J. Organomet. Chem.* **1992**, *426*, 109.

Scheme II. Preparation and Reactions of Compounds 11–14



With the novel preparative route presented here, the allene is stable enough to allow rapid isolation, but it dimerizes also slowly in solution, as monitored by infrared spectroscopy.

Experimental Section

All experiments with air or moisture sensitive compounds were carried out under dry argon using standard Schlenk techniques. Commercially available starting materials were used as received. Basic experimental procedures, supplementary instrumentation, and laboratory equipment have already been described.[5] NMR spectra were recorded at 300 K on Bruker AM 300 and VarianEM 360L spectrometers. KBr moldings were analyzed on a Nicolet 510M FT-IR spectrometer. EI mass spectrometry was done on a CH-7 MAT, and FD mass spectrometry, on a Finnigan MAT 90 instrument. Elemental analyses were performed at Mikroanalytisches Laboratorium, Institut für Physikalische Chemie der Universität Wien. In addition, the purity of the described compounds was confirmed by TLC. Procedures for starting materials are additionally described if higher yields or purer products were obtainable by our modifications: 9-hydroxy-9-ethynylfluorene,[13] 9-ethenylidene-9*H*-fluorene,[11] bis(9-hydroxyfluoren-9-yl)ethyne,[14] 9-ethenylidenefluorene,[11] di-9-fluorenylacetylene and bis(9-fluorenylidene)-1,3-butadiene.[7]

9-Ferrocenylfluoren-9-ol (1). Monolithioferrocene[15] (0.893 g, 4.65 mmol), precipitated from diethyl ether, is dissolved in 30 mL of THF and cooled to −60 °C; fluoren-9-one (0.850 g, 4.72 mmol) is added, the reaction mixture is brought to room temperature and then quenched with a few drops of water, and the solvent is evaporated. The residue is dissolved in diethyl ether and purified by means of flash chromatography (silica G 60, 220–440 mesh, Fluka; petroleum ether:diethyl ether = 85:15). Analytically pure product can be obtained from the second band. Yield: 1.34 g (78.8%), orange solid. IR (KBr): 3540 (b, s), 3060 (w), 1480 (w), 1450 (vs), 1110 (s), 1055 (m), 1045 (m), 1020 (vs), 1000 (s), 845 (m), 840 (m), 820 (s), 780 (vs), 730 (vs), 505 (vs), 495 (vs). ^{1}H-NMR ($CDCl_3$, TMS): δ 2.86 (s, 1 H), 4.17 ("t", 2 H, J = 1.5 Hz), 4.20 (s, 5 H), 4.20 ("t", 2 H, J = 1.5 Hz), 7.20–7.80 (m, 8 H). ^{13}C-NMR ($CDCl_3$, TMS): δ 66.9, 68.1, 68.9, 119.9, 124.2, 127.5, 128.8. MS (EI, 70 eV): m/z 366 ($M^{\bullet+}$, 100%) Anal. Calcd for $C_{23}H_{18}FeO$ (M_r = 366.25): C, 75.43; H, 4.95; O, 4.37. Found: C, 74.81; H, 4.69; O, 4.67. Mp: 168–170 °C.

9-Ferrocenylfluorenium Tetrafluoroborate (2). 9-Ferrocenylfluoren-9-ol (1) (1.054 g, 2.88 mmol) is dissolved in 30 mL of diethyl ether, and tetrafluoroboric acid–diethyl ether (1.0 mL, 54% in diethyl ether, 7.3 mmol) is added dropwise under vigorous stirring. After 10 min the solution is filtered, and the residue is washed twice with 100 mL diethyl ether and dried under vacuum. Yield: 1.17 g (95%), green solid. IR (KBr): 3450 (b, s), 3090 (w), 1480 (w), 1450 (vs), 1070 (b, vs), 850 (w), 825 (w), 750 (b, s). MS (EI, 70 eV): m/z 349 ($M^{\bullet+}$, 70%).

9-Ferrocenylfluorene (3). Potassium (0.5 g, 12.5 mmol) is added to graphite (1.30 g, 108 mmol), and the mixture[16] is heated to 150 °C. The color turns to bronze, and after 20 min, the reaction mixture is cooled to room temperature;[7] 30 mL of THF and 9-ferrocenylfluorenium tetrafluoroborate (2) (2.50 g, 5.87 mmol)

---

(13) Lavie, D.; Bergmann, E. D. *J. Org. Chem.* **1953**, *58*, 367.

(14) (a) Beumel, F. O.; Harris, R. F. *J. Org. Chem.* **1964**, *29*, 1872. (b) Bergmann, E.; Hoffmann, H.; Winter, D. *Chem. Ber.* **1933**, *66*, 46.

(15) Rebiere, F.; Samuel, O.; Kagan, H. B. *Tetrahedron Lett.* **1990**, *31*, 3121.

(16) Fürstner, A.; Weidmann, H. *Synthesis* **1987**, 1071.

are added. The solution is refluxed for 1 h and then cooled to 0 °C and quenched with ethanol/water (80:20). The solvent is evaporated and the black residue extracted with diethyl ether, filtered, and purified by means of flash chromatography (silica G 60, 220–440 mesh, Fluka; *n*-hexane:diethyl ether = 50:50). Yield: 1.85 g (90%), orange solid. IR (KBr): 3090 (w), 3080 (w), 1480 (w), 1450 (s), 1265 (m), 1110 (s), 1050 (w), 1030 (m), 1000 (m), 820 (b, s), 745 (vs), 695 (w), 480 (b, s). ^1H-NMR ($CDCl_3$, TMS): ∂ 4.10 (s, 5 H), 4.16 ("t", 2 H, *J* = 1.5 Hz), 4.19 ("t", 2 H, *J* = 1.5 Hz), 4.87 (s, 1 H), 7.36–7.77 (m, 8 H). ^{13}C-NMR ($CDCl_3$, TMS): ∂ 47.2, 66.9, 67.3, 68.7, 88.8, 119.8, 125.3, 126.7, 127.2, 140.5, 146.5 MS (EI, 70 eV): *m/z* = 350 ($M^{\bullet+}$, 100%), 280 ($M^{\bullet+}$ – 70, 20%), 229 ($M^{\bullet+}$ – 121, 60%, 9-cyclopentadienylfluorene). Anal. Calcd for $C_{23}H_{18}Fe$ (M_r = 350.25): C, 78.87; H, 5.18. Found: C, 77.72; H, 5.08. Mp: 157–160 °C.

(η^5-9-Ferrocenylfluorenyl)(η^5-pentamethylcyclopentadienyl)ruthenium(II) (4). 9-Ferrocenylfluorene (3) (120 mg, 0.35 mmol) is dissolved in 20 mL of THF, cooled to –70 °C and *tert*-butyllithium (0.22 mL, 1.6 M in hexane, 0.35 mmol) is added. After 2 min (pentamethylcyclopentadienyl)ruthenium trifluoromethanesulfonate[17] (133 mg, 0.35 mmol) is added. The reaction mixture is brought to room temperature and stirred for 20 h; finally, the solvent is evaporated, and the residue is dissolved in *n*-hexane and filtered. The product may be separated by cooling the solution to 0 °C. Due to the instability of the product, the yield is very low: 50 mg (25%), yellow-orange solid. IR (KBr): 2964 (w), 1636 (w), 1447 (w), 1387 (w), 1378 (w), 1358 (w), 1262 (vs), 1208 (w), 1096 (b, vs), 1028 (b, vs), 866 (w), 851 (w), 805 (vs), 745 (w), 502 (w), 488 (w), 442 (w). ^1H-NMR ($CDCl_3$, TMS): ∂ 0.95 (s, 15 H), 3.90 (s, 5 H), 4.19 ("t", 2 H, *J* = 1.8 Hz), 4.62 ("t", 2 H, *J* = 1.8 Hz), 6.84–7.60 (m, 8 H). ^{13}C-NMR ($CDCl_3$, TMS): ∂ 8.54, 66.8, 67.8, 68.4, 68.8, 118.5, 121.7, 123.7, 124.2, 125.0, 127.0, 128.8. MS (EI, 70 eV): *m/z* = 586.3 ($M^{\bullet+}$, 100%).

9-(Ferrocenylethynyl)fluoren-9-ol (5). Ethynylferrocene[18] (2.035 g, 9.98 mmol) is dissolved in 20 mL of THF, and the resulting solution is cooled to –70 °C. *tert*-Butyllithium (3.5 mL, 3.0 M in hexane, 10.5 mmol) is added, and the reaction mixture is stirred for 5 min. After fluoren-9-one (1.80 g, 10.0 mmol) is added, the solution is brought to room temperature, and under stirring, 1 mL of water is added. The solvent is evaporated and the crude product purified by means of flash chromatography (silica G 60, 220–440 mesh, Fluka; hexane:diethyl ether = 50:50). The product is obtained in analytically pure form from the second orange band. Yield: 3.10 g (82%), orange solid, only stable for longer periods under inert storage conditions. IR (KBr): 3550 (b, m), 3100 (w), 1610 (m), 1460 (s), 1415 (s), 1330 (b, s), 1200 (s), 1110 (s), 1080 (b, s), 1035 (b, s), 1000 (b, s), 945 (s), 890 (s), 845 (s), 835 (s), 815 (s), 770 (vs), 760 (vs), 745 (vs), 650 (vs), 600 (s), 540 (vs), 510 (vs), 500 (vs), 490 (vs). ^1H-NMR ($CDCl_3$, TMS): ∂ 2.70 (s, 1 H), 4.16 (s, 5 H), 4.17 ("t", 2 H, *J* = 1.5 Hz), 4.42, ("t", 2 H, *J* = 1.5 Hz), 7.34–7.92 (m, 8 H). ^{13}C-NMR ($CDCl_3$, TMS): ∂ 68.6, 69.8, 71.5, 120.1, 124.2, 128.5, 129.5. MS (EI, 70 eV): *m/z* = 390 ($M^{\bullet+}$, 80%). Anal. Calcd for $C_{25}H_{18}FeO$ (M_r = 390.3): C, 76.94; H, 4.65; O, 4.10. Found: C, 76.70; H, 4.59; O. 4.53.

9-(Ferrocenylethynyl)fluoren-9-ol–Hexacarbonyldicobalt Complex (6). 9-(Ferrocenylethynyl)fluoren-9-ol (5) (2.40 g, 615 mmol) is dissolved in 50 mL of diethyl ether, and a solution of octacarbonyldicobalt (2.10 g, 6.14 mmol) in 30 mL of diethyl ether is added dropwise at room temperature. After 3 h of stirring the solvent is evaporated and the green, oily residue is purified by means of flash chromatography (silica G 60, 220–440 mesh, Fluka; *n*-hexane:diethyl ether = 80:20). Yield: 3.30 g (79%), green solid. IR (KBr): 3712 (m), 2960 (w), 2933 (w), 2088 (w), 2051 (vs), 2026 (vs), 1715 (s), 1613 (s), 1602 (s), 1455 (s), 1302 (m), 1100 (m), 1005 (m), 918 (s). ^1H-NMR ($CDCl_3$, TMS): ∂ 2.51 (s, 1 H), 3.77 (s, 5 H). 3.78 ("t", 2 H, *J* = 1.5 Hz), 4.12 ("t", 2 H, *J* = 1.5 Hz), 7.18–7.65 (m, 8 H). ^{13}C-NMR ($CDCl_3$, TMS): ∂ 68.9, 69.6, 69.8, 120.3, 124.3, 124.7, 127.7, 129.0, 129.7, 134.6, 139.2, 149.8, 179.6, 199.3, 199.4, 222.0, 225.8 MS (FD): *m/z* 676.1 ($M^{\bullet+}$, 100%).

9-(Ferrocenylethynyl)fluorenium Tetrafluoroborate–Hexacarbonyldicobalt Complex (7). Hexacarbonyldicobalt-protected 9-(ferrocenylethynyl)fluoren-9-ol (7) (3.30 g, 4.4. mmol) is dissolved in 50 mL of diethyl ether, the solution is cooled down to –50 °C, and tetrafluoroboric acid–diethyl ether (1.50 mL, 54% in diethyl ether, 10.9 mmol) and propionic anhydride (2.0 mL, 15.4 mmol) are added. The solution is allowed to warm to –20 °C. After 10 min the suspension is filtered, and the residue is washed twice with 100 mL of diethyl ether and dried under vacuum. Yield: 2.13 g (58.6%), brown solid. IR (KBr): 3440 (b, w), 2122 (vs), 2101 (vs), 2083 (vs), 2047 (vs), 1627 (s), 1596 (s), 1486 (s), 1474 (m), 1449 (s), 1299 (s), 1207 (s), 1107 (vs), 1071 (vs), 1030 (vs), 1007 (vs), 962 (s), 907 (m), 893 (m), 824 (m), 789 (s), 735 (s), 517 (b, s). MS (FAB): *m/z* 659 ($M^{\bullet+}$, 4.2%).

9-(Ferrocenylethynyl)fluorene (8a) and 1-Ferrocenyl-2-(9-fluorenylidene)ethene (8b). Sodium (0.30 g, 13 mmol) is dissolved in 50 mL of liquid ammonia. The solution is combined with one of hexacarbonyldicobalt-protected (ferrocenylethynyl)-fluorenium tetrafluoroborate (8) (1.93 g, 2.6 mmol) in 50 mL of THF, cooled to –50 °C. The reaction mixture is allowed to warm to room temperature and, afterwards, carefully quenched with 2-propanol. Ammonium acetate (300 mg) is added, and the mixture is poured on water. The extraction is carried out with three 100-mL portions of diethyl ether, the combined organic layers are dried over anhydrous sodium sulfate, and finally, all the solvent is evaporated. The crude product is purified by means of flash chromatography (silica G 60, 220–440 mesh, Fluka, *n*-hexane:diethyl ether = 66.33 (first fraction), 50:50 (second fraction), 33:66 (third fraction). The orange oily product can be obtained from the first fraction and may be further purified by reprecipitation from *n*-hexane. Due to the instability of the product, which may be attributed to further conversion of the allene tautomer, no exact interpretation of the NMR spectra is possible. Therefore only the most dominant signals are given. IR (KBr): 3064 (m), 2956 (m), 2925 (m), 2857 (m), 2361 (s), 2342 (s), 1607 (s), 1476 (s), 1447 (vs), 1412 (s), 1154 (s), 1105 (s), 818 (s), 741 (vs), 484 (s). ^1H-NMR ($CDCl_3$, TMS): ∂ 3.70 (s), 3.82 (s), 408 (s), 4.11 ("t", *J* = 1.5 Hz), 4.16 ("t", *J* = 1.5 Hz), 7.1–7.6 (m). ^{13}C-NMR ($CDCl_3$, TMS): ∂ 67.7, 68.4, 68.6, 119.7, 123.8, 125.0, 126.8, 127.3. MS (EI, 70 eV): *m/z* 374 ($M^{\bullet+}$, 100%), 309 ($M^{\bullet+}$ – 65 (Cp), 40%), 253 ($M^{\bullet+}$ – 121 (CpFe), 72%).

9-(Ferrocenylethynyl)fluorenium Tetrafluoroborate (9). 9-(Ferrocenylethynyl)fluoren-9-ol (5) (0.812 g, 2.10 mmol) is dissolved in 150 mL of diethyl ether, and the solution is cooled to –50 °C. Under vigorous stirring, tetrafluoroboric acid–diethyl etherate (2.50 mL, 54% in diethyl ether, 18.3 mmol) is added dropwise and the reaction mixture is stirred for 30 min. Afterward, the suspension is filtered, and the residue is washed twice with 50 mL of diethyl ether and dried under vacuum. Yield: 1.0 g (100%), brown solid. IR (KBr): 3415 (b, s), 3104 (w), 2234 (vw), 1928 (vw), 1636 (m), 1447 (s), 1418 (m), 1106 (vs), 1063 (vs), 1036 (vs), 853 (m), 820 (m), 774 (s), 765 (s), 749 (s), 733 (s), 535 (m), 521 (m). MS (FAB): *m/z* 373.0 ($M^{\bullet+}$, 60%). MS (EI, 70 eV): *m/z* 373 ($M^{\bullet+}$, 80%).

Dimer of 9-(Ferrocenylethynyl)fluorene (10). Sodium (0.50 g, 21.7 mmol) is added to 100 mL of liquid ammonia. A deep, blue solution is formed and 9-(ferrocenylethynyl)fluorenium tetrafluoroborate (2) (0.83 g, 1.8 mmol) is added. The resulting red solution is stirred until all of the ammonia has evaporated. The residue is subsequently quenched with 10 mL of boiling acetic acid. Water (100 mL) and 30 mL of diethyl ether are added, the organic layer is concentrated under vacuum, and the mixture is purified by means of flash chromatography (silica G 60, 220–440 mesh, Fluka; *n*-hexane). Yield: 150 mg (22.2%), red oily material. IR (KBr): 3437 (b, m), 3093 (w), 2963 (m), 2856 (w), 2182 (w), 1609 (w), 1445 (m), 1270 (vs), 1097 (b, vs), 1027 (b, vs), 864 (w), 803 (vs), 731 (s), 480 (b, s). MS (EI, 70 eV): *m/z* 748 ($M^{\bullet+}$, 100%), 374 (20%). The same product is obtained when

---

[17] Fagan, P. J.; Ward, M. D.; Calabrese, C. *J. Am. Chem. Soc.* **1989**, *111*, 1698.

[18] (a) Doisneau, G.; Balavoine, G.; Fillebeen-Khan, T. *J. Organomet. Chem.* **1992**, *425*, 113. (b) Abrahm, T. S.; Watts, W. E. *Synth. React. Inorg. Met.-Org. Chem.* **1976**, *6*, 31.

the reduction is carried out with potassium/graphite in refluxing THF followed by analogous workup.

9-Hydroxy-9-ethynylfluorene. Fluorenone (6.64 g, 36.9 mmol) is dissolved in 50 mL of THF, the solution is cooled to −20 °C, and a solution of ethynylmagnesium bromide (5.2 g, 40 mmol) in 80 mL of THF is added dropwise. The reaction mixture is warmed to room temperature and then stirred for 2.5 h. Afterward the solution is poured onto 200 mL of a saturated ammonium chloride solution and extracted with three 50-mL portions of diethyl ether, and the combined organic extracts are dried over sodium sulfate. After the solvent is removed under vacuum, the residue is purified by means of flash chromatography (silica G 60, 220–440 mesh, Fluka, diethyl ether:petroleum ether = 20:80). The white compound can be obtained from the third fraction. Yield: 4.16 g (56.2%), white crystals. IR (KBr): 3400 (b, m), 3044 (w), 2110 (m), 1605 (m), 1585 (m), 1485 (m), 1476 (m), 1451 (s), 1383 (s), 1286 (s), 1261 (s), 1223 (m), 1196 (s), 1156 (m) 1055 (vs), 998 (vs), 901 (vs), 770 (vs), 758 (vs), 669 (b, vs), 637 (s), 548 (s), 448 (s), 423 (s). ^{1}H-NMR (CDCl$_3$, TMS): ∂ 2.32 (s, 1 H), 3.00 (s, 1 H), 7.12–7.58 (m, 8 H). ^{13}C-NMR (CDCl$_3$, TMS): ∂ 71.0, 119.9, 124.1, 128.3, 129.5. MS (EI, 70 eV): *m/z* 206 (M$^{\bullet+}$, 100%), 189 (M$^{\bullet+}$ − 17, 90%), 180 (M$^{\bullet+}$ − 26, 80%). Mp: 111–112 °C. (Lit.:[13] yellow oily product, respectively orange solid).

Bis(9-hydroxyfluoren-9-yl)ethyne (Variant A). Fluoren-9-one (1.41 g, 7.83 mmol) is dissolved in 30 mL of DME, and lithium acetylide–diaminoethane (0.70 g, 7.86 mmol) is added. The solution is refluxed for 1 h, subsequently 5 mL of TMEDA (40 mmol) and lithium acetylide–diaminoethane (0.70 g, 7.86 mmol) as well as further fluoren-9-one (1.40 g, 7.78 mmol) are added, and the reaction mixture is again refluxed for 1 h. After cooling to room temperature, the solution is poured onto water and extracted with three 80-mL poritions of diethyl ether. The combined organic extracts are dried over sodium sulfate and filtered, and the solvent is evaporated. The resulting crude product is washed with petroleum ether until the washings are colorless and can be purified either by washing with small portions of diethyl ether or by recrystallization from acetone/petroleum ether. Yield: 0.62 g (43%), white crystals.

Bis(9-hydroxyfluoren-9-yl)ethyne (Variant B). 9-Hydroxy-9-ethynylfluorene (1.005 g, 4.88 mmol) is dissolved in 30 mL of THF, and the solution is cooled to −60 °C. *tert*-Butyllithium (6.0 mL, 1.7 M in pentane, 10.2 mmol) and, after 2 min, 1.00 g of fluoren-9-one (5.56 mmol) as well as 5.0 mL of TMEDA (40 mmol) are added, and the reaction mixture is brought to room temperature. Refluxing the solution for 1 h completes the reaction. Quenching is carried out with 3 mL of water, and the solvent is evaporated. The residue is washed with hot petroleum ether and recrystallized from acetone/petroleum ether. Yield: 1.10 g (58.6%), white crystals. IR (KBr): 3550 (b, s), 3300 (vb, s), 3060 (w), 3040 (w), 1950 (w), 1920 (w), 1810 (w), 1680 (s), 1610 (s), 1590 (m), 1460 (b, s), 1290 (s), 1240 (s), 1220 (s), 1200 (s), 1145 (s) 1110 (s), 1050 (s), 1020 (s), 985 (s), 940 (s), 910 (s), 835 (s), 770 (s), 755 (s), 735 (s), 600 (m), 510 (m). ^{1}H-NMR (CD$_3$–CO–CD$_3$, TMS): ∂ 3.15 (s, 2 H), 7.17–7.56 (m, 16 H). ^{13}C-NMR (CD$_3$–CO–CD$_3$, TMS): ∂ 120.0, 124.5, 128.2, 129.2, 139.0, 148.2. MS (EI, 70 eV): *m/z* 386 (M$^{\bullet+}$, 100%). Mp: 228 °C dec (lit.:[14b] 238 °C).

Bis(9-fluoreniumyl)ethyne Ditetrafluoroborate (12). Bis-(9-hydroxyfluoren-9-yl)ethyne (0.508 g, 1.32 mmol) is dissolved in propionic anhydride (10 mL, 77 mmol) and tetrafluoroboric acid–diethyl etherate (1.0 mL, 54% in diethyl ether, 7.3 mmol) is added. After 20 min the dication is precipitated with 100 mL of diethyl ether, filtered out, washed twice with 50 mL of diethyl ether, and dried under vacuum. Yield: 0.473 g (63%), orange solid. IR (KBr): 3415 (b, s), 3062 (w), 2971 (w), 1930 (m), 1605 (b, m), 1449 (s), 1339 (m), 1297 (b), 1263 (s), 1198 (vs), 1156 (vs), 1105 (vs), 1084 (vs), 1047 (vs), 937 (w), 903 (w), 822 (s), 772 (vs), 639 (m). MS (FD): *m/z* 175.2 (z = 2, 100%).

Bis(9-hydroxyfluoren-9-yl)ethyne–Hexacarbonyldicobalt Complex (13). Bis(9-hydroxyfluoren-9-yl)ethyne (0.60 g, 1.55 mmol) is suspended in 50 mL of diethyl ether, and a solution of 0.83 g of octacarbonyl dicobalt (2.43 mmol) in 50 mL of diethyl ether is added dropwise. After 3 h the solvent is removed and the residue is purified by means of flash chromatography (silica G 60, 220–440 mesh, Fluka; *n*-hexane:diethyl ether = 67:33). Yield: 0.958 g (92.0%), brownish red solid. IR (KBr): 3530 (b, s), 3070 (w), 2090 (vs), 2060 (vs), 2020 (vs), 2000 (vs), 1610 (w), 1570 (m), 1480 (w), 1450 (s), 1200 (m), 1110 (m), 1040 (s), 920 (m); 910 (m), 815 (s), 770 (s), 750 (vs), 745 (vs), 730 (vs), 690 (vs), 665 (s), 655 (vs), 620 (s), 590 (s), 550 (s), 515 (b, s) 460 (m). MS (FAB): *m/z* 570 (M$^{\bullet+}$ − 101 (3CO + OH), 2.04%), 543 (M$^{\bullet+}$ − 129 (4CO + OH), 7.0%). Mp: 160 °C dec.

Bis(9-fluoreniumyl)ethyne Ditetrafluoroborate–Hexacarbonyldicobalt Complex (14). Hexacarbonyl dicobalt-protected bis(9-hydroxyflouren-9-yl)ethyne (13) (0.80 g, 1.19 mmol) is dissolved in a mixture of propionic anhydride (6 mL, 115 mmol) and 30 mL of diethyl ether, cooled to −35 to −40 °C; tetrafluoroboric acid–diethyl etherate (1.0 mL, 54% in diethyl ether, 7.2 mmol) is added dropwise. After 1 h of intensive stirring, the dicationic species is collected by decantation or filtration with a cooled sintered frit. The residue, which is extremely sensitive toward traces of acid or higher temperatures is washed twice with 50 mL of diethyl ether and dried under vacuum. Yield: 0.22 g (29%), brown solid. IR (KBr): 3351 (vb, m), 3056 (w), 2089 (s), 2072 (vs), 2024 (vs), 1939 (w), 1903 (w), 1870 (w), 1629 (b, m), 1445 (s), 1438 (s), 1353 (s), 1082 (b, s), 936 (m), 909 (m), 772 (s), 724 (s), 616 (m), 571 (m).

Bis(9-fluorenyl)ethyne (Variant A). Hexacarbonyl dicobalt-protected bis(9-fluoreniumyl)ethyne ditetrafluoroborate (14) (200 mg, 0.25 mmol) is dissolved in 20 mL of THF, the solution is cooled down to −60 °C, and a solution of sodium (0.15 g, 6.5 mmol) in 20 mL of liquid ammonia is added. The reaction mixture is warmed to room temperature, quenched with 2-propanol, and poured onto water. After extraction with diethyl ether the combined organic layers are dried over sodium sulfate, and the solvent is evaporated. The crude product is purified by washing with petroleum ether and recrystallization from THF/petroleum ether. Yield: 75 mg (85%), yellow solid. For analytical data, see below.

Bis(9-fluorenyl)ethyne (Variant B). Bis(9-hydroxyfluoreniumyl)ethyne ditetrafluoroborate (14) (0.65 g, 1.24 mmol) is dissolved in 30 mL of THF, the solution is cooled to −50 °C, and a solution of 0.40 g of sodium (17.4 mmol) in 20 mL of liquid ammonia, diluted with 20 mL of diethyl ether, is added. The solution is allowed to warm to room temperature and is then quenched with 2-propanol. Afterward, the solution is poured onto water and extracted with diethyl ether. (The product may precipitate. In this case it is best collected by filtration). After evaporation of the solvent, the residue is washed with petroleum ether and is recrystallized from THF/petroleum ether. Yield: 0.36 g (82%), yellow solid. IR (KBr): 3018 (m), 2923 (s), 2856 (m), 2360 (m), 1717 (m), 1607 (m), 1466 (m), 1450 (s), 1101 (m), 1067 (b, s), 808 (m), 739 (vs), 667 (m), 621 (m), 426 (m). MS (EI, 70 eV): *m/z* 354 (M$^{\bullet+}$, 100%). The reduction can also be performed with potassium–graphite in refluxing THF, followed by analogous workup. The yield differs between 40 and 60%.

9-Ethenylidene-9*H*-fluorene. 9-Hydroxy-9-ethynylfluorene (0.60 g, 2.90 mmol) is dissolved in 15 mL of ethanol and a solution of 5.0 g of stannous chloride–dihydrate (22.2 mmol), dissolved in 15 mL of acetic acid (15%), is added. The solution is refluxed for 4 h, then poured onto water, and extracted with diethyl ether. The solvent is removed, and the residue is washed with petroleum ether. As the product rapidly dimerizes to the dispiro compound,[11] it can only be characterized by IR and MS spectroscopy. Monomer compound (yellowish orange solid): IR (KBr) 3060 (m), 2954 (w), 1918 (vs), 1605 (m), 1551 (b, m), 1476 (w), 1447 (vs), 1343 (w), 1075 (w), 1030 (w), 770 (s), 710 (vs), 644 (w), 619 (w), 548 (w); MS (EI, 70 eV) *m/z* 380 (2M$^{\bullet+}$, 80%), 190 (M$^{\bullet+}$, 100%), 177 (M$^{\bullet+}$ − 13, 50%), 165 (M$^{\bullet+}$ 25, 65%). Dimer compound (yellow solid): IR (KBr) 3050 (w), 2950 (w), 2925 (w), 1720 (w), 1600 (b, m), 1490 (m), 1449 (s), 1262 (w), 1098 (w), 795 (s), 735 (b, vs), 619 (w); MS (EI, 70 eV): *m/z* 380 (M$^{\bullet+}$, 80%), 365 (M$^{\bullet+}$ − 15 (CH$_3$), 100%).

1,4-Bis(Fluoren-9-ylidene)butatriene by Deprotection of Bis(9-hydroxyfluoren-9-yl)ethyne–Hexacarbonyldicobalt Complex. Hexacarbonyl dicobalt-protected bis(9-hydroxyfluoren-9-yl)ethyne (1.00 g, 1.49 mmol) is dissolved in 20 mL of diethyl ether, and 1 mL of tetrafluoric acid–diethyl etherate (54% in diethyl ether, 7.3 mmol) is added at ambient temperature. After 30 min, the red precipitate is filtered off, washed with petroleum ether, and dried under vacuum. Yield: 520 mg (99%), deep red solid. IR (KBr): 3050 (vw), 1530 (s), 1460 (m), 1300 (w), 950 (m), 895 (m), 870 (w), 790 (vs), 765 (w), 720 (vs), 640 (m), 580 (w). ^{1}H-NMR (THF-d_8, TMS): ∂ 7.32–7.42 (m, 8 H), 7.70–7.90 (m, 4 H), 7.95–8.05 (m, 2 H), 8.20–8.30 (m, 2 H). ^{13}C-NMR (THF-d_8, TMS): ∂ 120.3, 120.7, 121.6, 122.7, 126.8, 127.8, 127.9, 129.3, 129.4. MS (EI, 70 eV): *m/z* 352 ($M^{\bullet+}$, 100%).

9-Hydroxy-9-ethynylfluorene–Hexacarbonyldicobalt Complex (11). 9-Hydroxy-9-ethynylfluorene (0.56 g, 2.72 mmol) is dissolved in 50 mL of diethyl ether, and a solution of 1.30 g of octacarbonyldicobalt (3.54 mmol) in 50 mL of diethyl ether is added. The reaction mixture is stirred for 4 h. Afterward the solvent is removed and the crude product purified by means of flash chromatography (silica G 60, 220–440 mesh, Fluka, *n*-hexane). Yield: 1.20 g (89.6%), brownish red solid. IR (KBr): 3550 (b, s), 2030 (vs), 2000 (vs), 1975 (vs), 1654 (s), 1607 (s), 1586 (s), 1519 (s), 1484 (s), 1328 (m), 1194 (s), 1036 (s), 940 (s), 917 (s), 874 (s), 795 (s), 766 (s), 733 (s), 670 (s), 650 (s), 610 (s). MS (EI, 70 eV): *m/z* 464 ($M^{\bullet+}$ – 28 (CO), 5.5%), 436 ($M^{\bullet+}$ – 56 (2CO), 4.3%), 408 ($M^{\bullet+}$ – 84 (3CO), 24.1%), 380 ($M^{\bullet+}$ – 112 (4CO), 13.4%), 352 ($M^{\bullet+}$ – 140 (5CO), 21.2%), 324 ($M^{\bullet+}$ – 168 (6CO), 72.0%). Mp: 130 °C dec. Treatment of a solution of the protected alcohol with tetrafluoroboric acid at room temperature showed no analogous reaction to the allene species such as that for the corresponding hexacarbonyl dicobalt-protected bis(9-hydroxy-9-fluorenyl)ethyne.

Acknowledgment. We wish to thank Prof. F. Kreissl and R. Dumitrescu, Anorganisch-Chemisches Institut der Technischen Universität München, for the measurement of the FD and FAB mass spectra.

OM9300540