A Variation of Titanium-Induced Carbonyl Coupling – Synthesis and Conformations of Terfluorenyl

Sergey Pogodin,[a] **Shmuel Cohen,**[a] **and Israel Agranat***[a]

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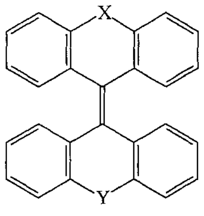
Reaction of fluorenone (**4**) with a low-valent titanium reagent generated from $TiCl_4$ and Zn in THF in the presence of pyridine gave terfluorenyl (**6**) in 71% yield, bifluorenylidene (**2**), the conventional McMurry reaction product, in 2% yield, and additional reduction products. The reductive "trimerization" was rationalized in terms of an attack of the intermediate fluorenone dianion on bifluorenylidene. The molecular structure of a single crystal of **6** indicated an approximately C_2 conformation, with a slightly twisted central ring, and two equally folded side moieties with dihedral angles of 58.1° and 58.0° between the central and side five-membered rings. The AM1 and PM3 calculations showed C_2 global minima, similar to the conformation in the crystal. The calculated C_s transition state conformations were found to be 21.3 (AM1) and 19.9 (PM3) kcal/mol higher in energy than the global C_2 minima. A 2D-NMR NOESY experiment on **6** supported the C_2 (+*sc*,+*sc*) or C_2 (–*sc*,–*sc*) conformation in solution.

Introduction

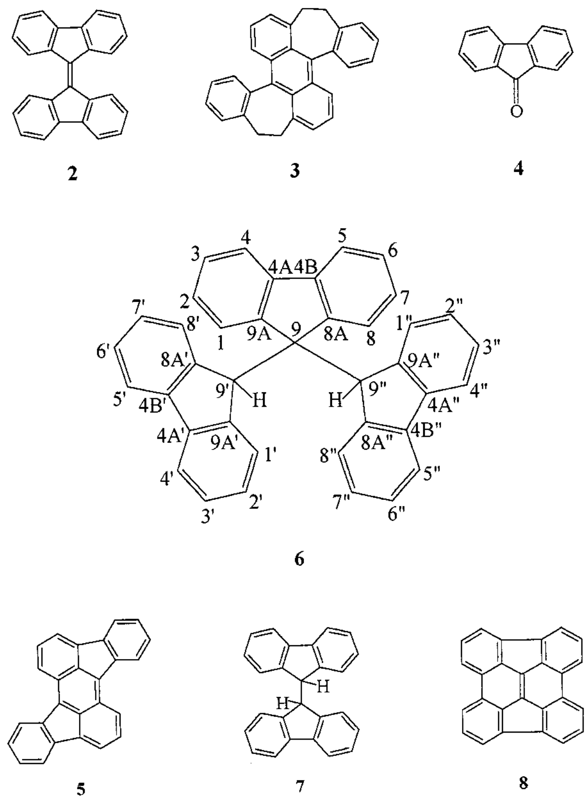
The bistricyclic enes **1** (Scheme 1) have fascinated chemists since the red hydrocarbon bifluorenylidene [9-(9*H*-fluoren-9-ylidene)-9*H*-fluorene (**2**)] (Scheme 2) was synthesized in 1875.[1] During the course of our studies of these overcrowded aromatic enes,[2][3] we have investigated the low-valent titanium-induced reductive carbonyl coupling of polycyclic aromatic ketones (PAKs) as a promising direct entry into the series of homomerous **1** (X = Y).



Homomerous: X=Y
Heteromerous: X≠Y

Scheme 1. Bistricyclic aromatic enes **1**

The low-valent titanium-induced reductive coupling of carbonyl compounds to produce alkenes is a prominent reaction in synthetic organic chemistry. The reaction was invented in 1973 by Mukaiyama et al.[4] and by Tyrlik et al.,[5] but is referred to in the literature as the McMurry reaction.[6] Recent advances in titanium-induced carbonyl coupling have been summarized in several reviews.[7] Among the by-products of the reaction are alcohols and hydrocarbons related to starting and “dimerized” carbonyl compounds. A notable variation is the titanium-induced coupling of 10,11-dihydro-5*H*-dibenzo[*a*,*d*]cyclohepten-5-one to give the chiral strained *syn*-8,9,17,18-tetrahydro-bis(benzo[4,5]cyclohept)[1,2,3-*de*;1′,2′,3′-*kl*]anthracene (**3**).[8] This unusual course of the McMurry reaction is reminiscent of the Clar reaction, a reductive *peri*-*peri* bimolecular coupling of 1-phenalenone-type PAKs ($Zn/ZnCl_2/NaCl$/ca. 300 °C) to give large polycyclic aromatic hydrocarbons (LPAHs).[9]



Scheme 2. Two-dimensional representation of compounds **2−8**

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[a] Department of Organic Chemistry, The Hebrew University of Jerusalem
Jerusalem 91904, Israel
Fax: (internat.) + 972-2/6511907
E-mail: isria@vms.huji.ac.il

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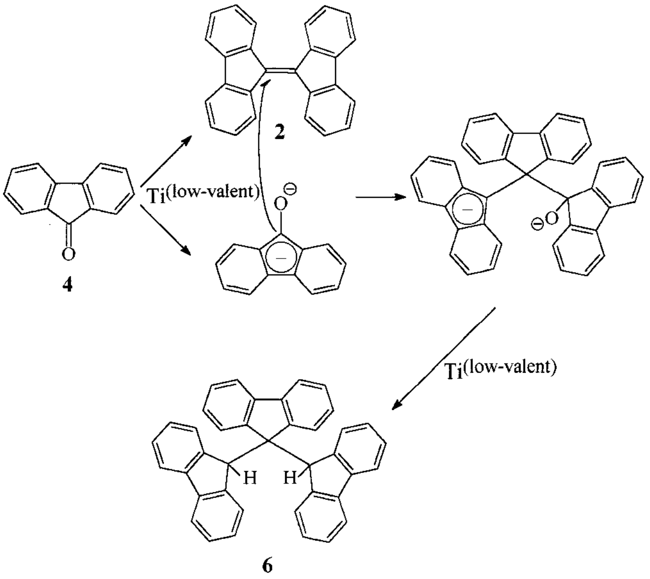
Fluorenone [9*H*-fluoren-9-one (**4**)], the simplest PAK, has been subjected to many successful attempts of titanium-induced reductive coupling, under a variety of experimental conditions.[10] In most cases, the formation of bifluorenylidene (**2**), the expected product of the McMurry reaction, has been reported. The yield of **2** varies and may reach 95%.

In view of the unusual course of the McMurry reaction of 10,11-dihydro-5*H*-dibenzo[*a*,*d*]cyclohepten-5-one with $TiCl_4$/Zn/pyridine/THF, it seemed worthwhile to search for the formation of rubicene (**5**), a possible *peri-peri* coupling product of fluorenone (**4**), under the above conditions (the Mukaiyama−Lenoir recipe[4,10c,10d]) of the McMurry reaction. We report here a novel course of the low-valent titanium-induced reductive coupling of **4**, leading to a reductive "trimerization" and the formation of terfluorenyl [9,9-bis(9*H*-fluorenyl)-9*H*-fluorene (**6**)] as the main product. Terfluorenyl (**6**) has previously been prepared by various methods, mostly from bifluorenylidene (**2**) (vide infra). The crystal and molecular structure of a single crystal of **6** as determined by X-ray crystallography and conformations of **6** as revealed by semi empirical calculations with AM1 and PM3 methods are also described.

Results and Discussion

Treatment of fluorenone (**4**) with low-valent titanium species generated from $TiCl_4$ and Zn in THF in the presence of pyridine afforded terfluorenyl (**6**) in 71% yield. Colorless crystals of **6** (m.p. 290−291°C) were obtained by recrystallization from toluene. Terfluorenyl[11][12] (**6**) was characterized by melting point, ^1H- and ^{13}C-NMR spectra (1D, COSY, NOESY, HSQC) and X-ray crystallography. In addition to **6**, the following compounds were identified in the product mixture: fluorene (2% yield), bifluorenylidene (**2**) (2%), bifluorenyl [9,9′-bi-9*H*-fluorene (**7**)] (7%), fluorenone (**4**) (3%), fluorenol (9*H*-fluoren-9-ol) (1%). The very low yield of **2**, the usual main product of the carbonyl coupling reaction, is noted. The formation of fluorene, fluorenol, and **7** as by-products of the McMurry reaction is not surprising. However, the formation of **6** was unexpected. Among the various reported syntheses of **6**, the following methods are worth mentioning: (a) a nucleophilic attack of fluorenyl anion on bifluorenylidene (**2**);[11b,11e,11h] (b) irradiation of diazofluorene to give **6** according to a carbene mechanism;[11d,11i] (c) reaction of fluorenone thioketal and $W(CO)_6$ to give **6** according to a radical mechanism.[12] The mechanism of formation of **6** in the titanium-induced reductive coupling reaction of **4** may be deduced from the mechanism of the McMurry reaction[7] and the chemical behavior of bifluorenylidene[11][13] (**2**). Scheme 3 shows a possible pathway for the formation of **6**. Bifluorenylidene (**2**), obtained in the earlier steps of the process, undergoes a nucleophilic attack by the fluorenone dianion yielding a "trimeric" product. Deoxygenation of the latter intermediate, promoted by low-valent titanium, leads to the final product **6**. It is interesting to note in this context that Bronstein and Scott have recently shown that the bowl-shaped $C_{26}H_{12}$ PAH diindeno[1,2,3,4-*defg*;1′,2′,3′,4′-*mnop*]chrysene (**8**) undergoes a successive nucleophilic and electrophilic attack (by MeLi and MeI, respectively) at the central quaternary carbon atoms, thus resembling the reactivity of buckminsterfullerene C_{60}.[14] The results suggested that the reactivity of fullerenes, which is driven largely by the strain associated with curving an aromatic network, can be extended to curved PAHs.[14] The mechanism of formation of terfluorenyl (**6**) (Scheme 3) suggests that such a reactivity is not limited to bowl-shaped fullerene fragments (e.g. **8**) and fullerenes, but is exhibited also by the twisted fullerene fragment bifluorenylidene (**2**). The driving force of the process is the strain arising in the fjord region of **2** due to overcrowding. The reactivity of **2** towards nucleophiles, including fluorenyl anion, is well documented.[11][13] The reductive trimerization of **4** to **6** requires eight electrons per three molecules of **4**.



Scheme 3. Proposed mechanism of formation of terfluorenyl (**6**) from fluorenone (**4**) under the conditions of the McMurry reaction.

Figure 1 gives the ORTEP drawing of the single molecule of terfluorenyl (**6**). The crystal structure of **6** is found to be distinctly different from the structure of the same compound reported by Luh et al.[12] An attempt to match our triclinic cell to the $P2_1/n$ cell of Luh was unsuccessful. Table 1 gives unit cell parameters and other information on the crystal structure of **6** obtained in the present study and, for comparison, the corresponding data reported by Luh et al.[12] The values of related bond lengths and angles of the two asymmetric units in both crystal structures are quite similar, but not identical; both structures describe essentially the same conformation of **6** (see below). A significant difference between these two structures is the higher symmetry ascribed by Luh et al. to the molecule.

The semi empirical calculations of terfluorenyl were performed with the AM1 and PM3 methods, as implemented in the program MOPAC6.[15] The structures of all the species were fully optimized with symmetry constraints as indicated. All the minima and transition states were verified

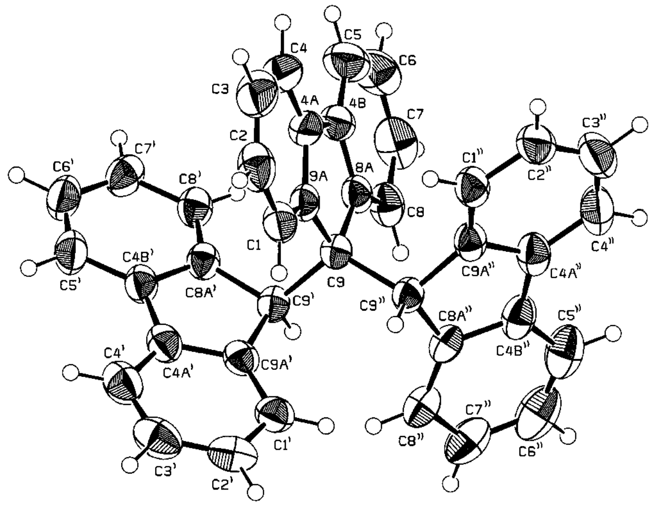


Figure 1. ORTEP drawing of terfluorenyl (**6**)

Table 1. Crystallographic data of terfluorenyl (**6**)

	Present study	T.-Y. Luh[12]
Space group	$P\bar{1}$	$P2_1/n$
Crystal system	Triclinic	Monoclinic
a [Å]	11.952(3)	11.948(5)
b [Å]	13.516(3)	16.8795(14)
c [Å]	9.504(2)	13.491(6)
α [°]	108.29(2)	90
β [°]	103.68(2)	105.03(3)
γ [°]	105.19(1)	90
V [Å^3]	1319.0(8)	2628(2)
Z	2	4
$\rho_{calcd.}$ [g·cm^{-1}]	1.25	1.25
No. unique refl. $I > 2\sigma_I$	3292	2142
R	0.0480	0.061
R_w	0.0615	0.051

by computing the vibrational frequencies. Table 2 describes optimized (AM1 and PM3) conformations of **6** and their heats of formation, relative heats of formation, symmetries, dihedral angles (ϕ) between the planes of the central five-membered ring and each of the side five-membered rings, and torsion angles (ω) around C9−C9′ and C9−C9′′ bonds (only minima and transition states are shown). Table 3 gives representative torsion angles of the crystal structures of **6** and of the calculated AM1 and PM3 structures of the most stable conformation of **6**. Table 4 gives a comparison of selected bond lengths of the crystal structure of **6** and of the AM1- and PM3-optimized global minimum conformations.

Table 3. Selected torsion angles [°] around the C9−C9′ and C9−C9′′ bonds and related dihedral angles of the crystal structures of terfluorenyl (**6**) and of the calculated (AM1 and PM3) most stable conformation of **6**

	Crystal structure[a]	Crystal structure[b]	AM1 calculations	PM3 calculations
C9A−C9−C9′−C8A′	−177.9	−174.3	176.9	173.0
C9A−C9−C9′−C9A′	−61.8	−59.3	64.8	61.2
C8A−C9−C9′−C8A′	−66.2	−61.9	58.4	54.4
C8A−C9−C9′−C9A′	50.0	53.1	−53.8	−57.4
C9A−C9−C9′′−C8A′′	54.0	50.9	−53.8	−57.4
C9A−C9−C9′′−C9A′′	−61.7	−64.7	58.4	54.4
C8A−C9−C9′′−C8A′′	−57.0	−61.0	64.8	61.2
C8A−C9−C9′′−C9A′′	−172.8	−176.6	176.9	173.0
ϕ[c]	58.1	56.4	62.9	65.8
	58.0	59.2	62.9	65.8

[a] Present study. – [b] Ref.[12] – [c] Dihedral angles between the planes of the five-membered rings of the central and a side moiety of **6**.

The calculated most stable conformation (global minimum) is a C_2 conformation with a slightly twisted central ring and two equally folded side moieties. This conformation resembles the conformation shown by the crystal structure of terfluorenyl (**6**), with dihedral angles of 62.9° (AM1) and 65.8° (PM3) between the central and side five-membered rings as compared with the corresponding dihedral angles of the crystal structures of **6** (present study: 58.1° and 58.0°; Luh et al.:[12] 56.4° and 59.2°). The bond lengths (Table 4) and bond angles of the AM1- and PM3-optimized global minima are also close to those of both crystal structures; the differences are in the range usually found when such a comparison is made. The conclusion can

Table 2. Optimized comformations of terfluorenyl (**6**)

		AM1 optimization					PM3 optimization			
Symmetry	[a]	$\Delta H_f°$ [kcal/mol]	$\Delta\Delta H_f°$ [kcal/mol]	ϕ[b] [°]	ω[d] [°]	[a]	ΔH_f [kcal/mol]	$\Delta\Delta H_f°$ [kcal/mol]	ϕ[b] [°]	ω[d] [°]
C_2	GM	202.0	0.0	62.9	64.8	GM	177.1	0.0	65.8	61.2
				62.9	64.8				65.8	61.2
C_1	LM	207.9	5.9	142.6	144.2	LM	183.4	6.3	143.6	149.5
				67.4	−45.0				68.3	−47.5
C_2	LM	215.7	13.7	141.9	−130.5	LM	189.2	12.1	144.6	−134.7
				141.9	−130.5				144.6	−134.7
C_1	[c]					LM	190.2	13.1	31.1	26.9
									70.4	−5.31
C_s	TS	222.6	20.6	172.5	−173.9	LM	198.0	20.9	166.0	−155.4
				172.5	173.9				166.0	155.4
C_s	TS	223.3	21.3	58.4	−30.5	TS	197.0	19.9	67.5	−17.0
				58.4	30.5				67.5	−17.0

[a] GM: global minimum; LM: local minimum; TS: transition state. – [b] Dihedral angles between the planes of the five-membered rings of the central and a side moiety of **6**: [c] Not found. – [d] Representative torsion angles around C9−C9′ (C9A−C9−C9′−C9A′) and C9−C9′′ (C8A−C9−C9′′−C8A′′).

Table 4. Selected bond lengths [Å] of the crystal structure and of the calculated (AM1 and PM3) most stable conformation of terfluorenyl (**6**)

Bond	Crystal structure	AM1	PM3
C4A−C4B	1.468(4)	1.460	1.460
C4A−C9A	1.391(3)	1.428	1.415
C4B−C8A	1.397(3)	1.428	1.415
C8A−C9	1.526(3)	1.525	1.526
C9−C9A	1.525(3)	1.525	1.526
C9−C9′	1.570(3)	1.540	1.553
C9−C9′′	1.580(3)	1.540	1.553
C4A′−C4B′	1.458(3)	1.458	1.458
C4A′−C9A′	1.404(3)	1.430	1.414
C4B′−C8A′	1.397(3)	1.415	1.415
C8A′−C9′	1.533(3)	1.518	1.520
C9′−C9A′	1.521(3)	1.519	1.518
C4A′′−C4B′′	1.461(4)	1.458	1.458
C4A′′−C9A′′	1.399(3)	1.426	1.415
C4B′′−C8A′′	1.402(3)	1.430	1.414
C8A′′−C9′′	1.524(3)	1.519	1.518
C9′′−C9A′′	1.520(3)	1.518	1.520

be made that all these structures describe the same conformation of terfluorenyl. A transition state C_s conformation was identified 21.3 and 19.9 kcal/mol above the global minimum with dihedral angles of 58.4° and 67.5° (at AM1 and PM3, respectively). The stereoview of the PM3 global-minimum conformation C_2 is presented in Figure 2, while the stereoview of the PM3 transition state C_s conformation is depicted in Figure 3. The latter conformation may serve as a transition state for the enantiomerization of **6**.

The question of rotational isomerism due to restricted rotations around the C9−C9′ and C9−C9′′ single bonds in **6** has been controversial.[16−18] According to Oki, there are six possible rotamers of terfluorenyl: one (*E*,*E*) rotamer (*ap*,*ap*), two (*Z*,*E*) rotamers [(+*sc*,*ap*) and (−*sc*,*ap*)], and three (*Z*,*Z*) rotamers [(+*sc*,+*sc*), (+*sc*,−*sc*), (−*sc*,+*sc*)].[16][19] Suzuki and Minabe reported the formation of two stable stereoisomers of **6**, m.p. 293 °C (dec.) and m.p. 257 °C (dec.), assigning the structures *s-cis*, *s-cis* and *s-cis*, *s-trans*, respectively, to these rotamers on the basis of spectral evidence.[11g,11h] However, Kajigaeshi et al. concluded on the basis of ^{1}H-NMR spectra that the conformation of the parent terfluorenyl **6**, m.p. 293 °C, is (+*sc*,+*sc*) or (−*sc*,−*sc*).[17][20] These authors revealed that the barrier of rotation in a series of substituted terfluorenyls is at most 20.9 kcal/mol at 120 °C. This barrier indicates fast interconversion of the rotamers of terfluorenyls at room temperature.[17][20] Our calculated AM1 and PM3 barriers for terfluorenyl (Table 2) are in good agreement with the experimental value. In the present study, a 2D-NMR NOESY experiment was carried out in order to determine the conformation of **6** in solution. The low-field chemical shifts of the overcrowded bucking 1′-H and 8′′-H (δ = 8.53) and the high-field chemical shifts of 8′-H and 1′′-H (δ = 5.36) and 1-H and 8-H (δ = 6.31) are noted. NOE interactions have been found between the 8′-H aromatic proton of a side fluorene ring and the 1-H, 2-H, 3-H, 4-H protons of the central fluorene (and likewise between 1′′-H and 5-H, 6-H, 7-H, 8-H), suggesting the placement of 8′-H, 1′′-H above the planes of the aromatic rings of the central fluorene moiety in their shielding zone, which causes high-field shifts of the 8′-H, 1′′-H signals. The 1-H and 8-H protons of the central fluorene ring are also significantly shielded as a consequence of their location above the aromatic rings of the terminal fluorene units. This is confirmed

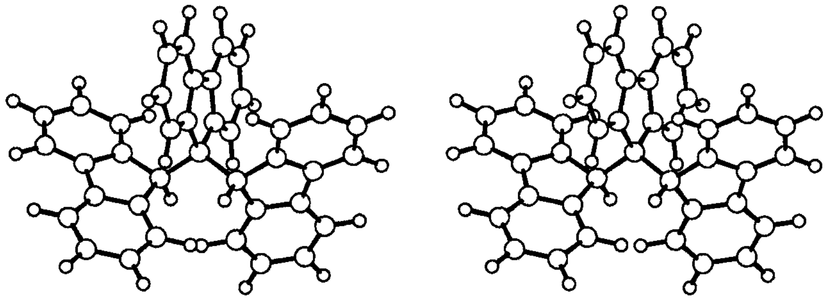


Figure 2. Stereoview of the PM3-calculated C_2 global minima conformation of **6**

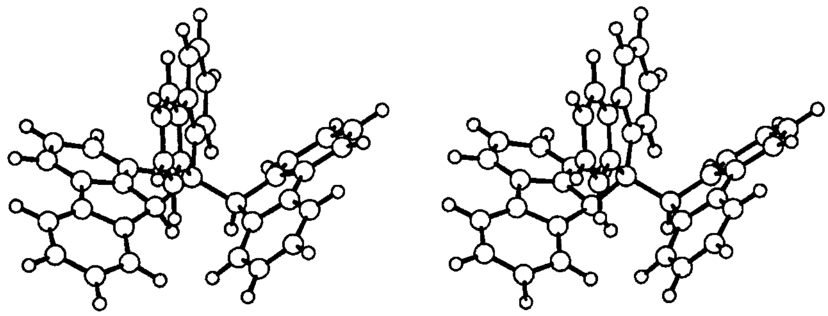


Figure 3. Stereoview of the PM3-calculated C_s transition state conformation of **6**

by the observation of NOE interactions between 1-H and 1′-H, 4′-H (and likewise between 8-H and 5′′-H, 8′′-H protons). Strong NOE signals arising from the interactions between 8′-H and 8′′-H, 7′-H and 7′′-H, and 6′-H and 6′′-H of the side fluorene rings have been observed, in accordance with the existence of a two-fold symmetry axis in the molecule. These results are in close agreement with the (+*sc*,+*sc*) or (−*sc*,−*sc*) conformation proposed above as well as with the conformations obtained from the X-ray studies and the semi-empirical calculations.

In conclusion, the formation of terfluorenyl (**6**) in the low-valent titanium induced reductive coupling of fluorenone (**4**) widens the scope of the McMurry reaction and opens new avenues for the synthesis of polycyclic aromatic hydrocarbons.

Experimental Section

General: Melting points are uncorrected. All NMR spectra were recorded with Bruker DRX 400 and AMX 300 spectrometers; ^{1}H-NMR spectra were recorded at 400.1 MHz and 300.1 MHz with $CDCl_3$ as solvent and as internal standard [$\delta(CHCl_3) = 7.26$]. ^{13}C-NMR spectra were recorded at 100.6 MHz with $CDCl_3$ as solvent and as internal standard [$\delta(CHCl_3) = 77.01$].

X-ray Crystallographic Study:[21] A single crystal of **6** was obtained by recrystallization from dichloromethane. Crystal data are given in Table 1. The X-ray intensity data of **6** were measured with a PW1100/20 Philips four-circle computer-controlled diffractometer. Mo-K_α ($\lambda = 0.71069$ Å) radiation with a graphite crystal monochromator in the incident beam was used. The lattice parameters were obtained by a least-squares fit of 24 centered reflections in the range $10° \leq \theta \leq 15°$. Intensity data were collected using the ω-2θ technique to a maximum 2θ of 50°. The scan width, Δω, for each reflection was $1.00 + 0.35 \cdot \tan\theta$ with a scan speed of 3.0 °/min. The intensities of three standard reflections were monitored during data collection, and no decay was observed. Intensities were corrected for Lorentz and polarization effects. The positions of the carbon atoms were obtained from the results of the SHELXS-86 direct method analysis.[22] After several cycles of refinements, the positions of the hydrogen atoms were found, and added to the refinement process. All carbon atoms were refined anisotropically, while the positions of hydrogen atoms were kept fixed, using a riding model. The refinement proceeded to convergence by minimizing the function $\Sigma w(|F_o| - |F_c|)^2$ ($w = \sigma_F^{-2}$).

The Low-Valent Titanium-Induced Reductive Coupling of Fluorenone (4): The reaction was carried out under dry argon in a 100-mL three-necked round-bottomed flask equipped with a reflux condenser (protected from moisture), a septum for adding the reagents and sampling the reaction mixture and an inlet for purging the flask with dried argon. The reaction flask was purged with argon for half an hour and dry THF (freshly distilled from sodium diphenyl ketyl, 10 mL) was added and cooled to −20 °C. Slow dropwise injection of $TiCl_4$ (0.48 mL, 4.50 mmol) by means of a glass syringe gave a yellow complex. The mixture was stirred for 20 min at −20 °C and treated with Zn dust (0.50 g, 7.68 mmol). The temperature was gradually raised to room temperature, and the mixture was stirred for another 45 min to give a bluish suspension, and then refluxed for 3.5 h to give a black suspension. THF (10 mL) was added during the reflux to maintain the volume. After cooling to 0 °C, the mixture was treated with pyridine (dried with KOH and freshly refluxed, 0.30 mL), followed by a dropwise addition by glass syringe over 20 min of a solution of fluorenone (0.54 g, 3.02 mmol) in dry THF (3 mL). The resulting mixture was refluxed for 6 h and was kept for about 12 h under argon. The mixture was further refluxed for 3 h; THF (5 mL) was added during refluxing. After cooling to room temperature, the mixture was treated with dichloromethane (20 mL), stirred for 15 min, and poured into 100 mL of aqueous HCl (0.1 N) to give two layers. The organic layer was separated, and the aqueous layer was extracted with dichloromethane. The combined organic layers were dried ($MgSO_4$) and the solvents were removed in vacuo. The crude products were dissolved in chloroform and chromatographed on a silica gel column (Silica gel 60, 0.063−0.200 mm), using light petroleum ether (b.p. 60−80 °C) − dichloromethane (up to 100% dichloromethane) as eluent. The following fractions were eluted:

(1) Fluorene: 11 mg, 2% yield; m.p. 113−115 °C (ref.[23a] m.p. 116 °C).

(2) Bifluorenylidene (**2**): 12 mg, 2% yield. − Recrystallization from ethanol afforded red crystals, m.p. 190−192 °C (ref.[23b] m.p. 191−192 °C). − ^{1}H NMR (300.1 MHz): $\delta = 8.40$ (d, $J = 7.9$ Hz, 4H), 7.72 (d, $J = 7.6$ Hz, 4H), 7.35 (t, $J = 7.5$ Hz, 4H), 7.23 (t, $J = 7.4$ Hz and $J = 7.9$ Hz, 4H). − ^{13}C NMR (100.6 MHz): $\delta =$ 141.29 ($4C_q$), 140.98 ($4C_q$), 138.25 ($4C_q$), 129.13 ($4C_t$), 126.84 ($4C_t$), 126.70 ($4C_t$), 119.87 ($4C_t$) (cf. ref.[24][25]).

(3) Bifluorenyl (**7**): 33 mg, 7% yield. − M.p. 244−247 °C (ref.[23c] m.p. 246 °C). − ^{1}H NMR (400.1 MHz): $\delta = 7.66$ (d, $J = 7.7$ Hz, 4H), 7.29 (t, $J = 7.5$ Hz, 4H), 7.10 (br. t, $J = 7.4$ Hz, 4H), 6.97 (br. d, $J = 7.0$ Hz, 4H), 4.85 (s, 2H). − ^{13}C NMR (100.6 MHz): $\delta = 144.64$ ($4C_q$), 141.50 ($4C_q$), 127.27 ($4C_t$), 126.69 ($4C_t$), 124.06 ($4C_t$), 119.63 ($4C_t$), 49.79 (2CH).

(4) Terfluorenyl (**6**): 335 mg, 71% yield. − Recrystallization from toluene gave colorless crystals, m.p. 290−291 °C (ref.[12] m.p. 293 °C). − ^{1}H NMR (400.1 MHz): $\delta = 8.53$ (d, $J = 7.4$ Hz, $H_{1'}$, $H_{8''}$), 7.83 (d, $J = 7.5$ Hz, $H_{4'}$, $H_{5''}$), 7.60 (t, $J = 7.3$ Hz, $H_{3'}$, $H_{6''}$), 7.55 (t, $J = 7.5$ Hz, $H_{2'}$, $H_{7''}$), 7.44 (d, $J = 7.4$ Hz, $H_{5'}$, $H_{4''}$), 7.31 (d, $J = 7.5$ Hz, H_4, H_5), 7.11 (t, $J = 7.5$ Hz, H_3, H_6), 6.97 (t, $J = 7.5$ Hz, $H_{6'}$, $H_{3''}$), 6.86 (t, $J = 7.5$ Hz, H_2, H_7), 6.51 (t, $J = 7.6$ Hz, $H_{7'}$, $H_{2''}$), 6.31 (d, $J = 7.7$ Hz, H_1, H_8), 5.42 (s, $H_{9'}$, $H_{9''}$), 5.36 (d, $J = 7.8$ Hz, $H_{8'}$, $H_{1''}$). − ^{13}C NMR (100.6 MHz): $\delta = 146.14$ (C_{8a}, C_{9a}), 144.20 ($C_{9a'}$, $C_{8a''}$), 143.74 ($C_{4a'}$, $C_{4b''}$), 143.58 ($C_{8a'}$, $C_{9a''}$), 141.60 (C_{4a}, C_{4b}), 140.90 ($C_{4b'}$, $C_{4a''}$), 127.98 ($C_{3'}$, $C_{6''}$), 127.48 (C_3, C_6), 127.28 ($C_{1'}$, $C_{8''}$), 126.75 ($C_{6'}$, $C_{3''}$), 126.68 ($C_{2'}$, $C_{7''}$), 126.14 (C_2, C_7), 125.83 ($C_{7'}$, $C_{2''}$), 124.48 ($C_{8'}$, $C_{1''}$), 123.41 (C_1, C_8), 120.27 ($C_{4'}$, $C_{5''}$), 119.15 (C_4, C_5), 118.66 ($C_{5'}$, $C_{4''}$), 58.94 (C_9), 52.78 ($C_{9'}$, $C_{9''}$). − MS (50 → 400°C); *m*/*z* (%): 329 (100) [$C_{26}H_{17}^+$], 165 (35) [$C_{13}H_9^+$]. − $C_{39}H_{26}$ (494.64): calcd. C 94.70, H 5.30; found C 95.13, H 5.12.

(5) Fluorenone (**4**): 16 mg, 3% yield. − M.p. 81−82 °C (ref.[23d] m.p. 83−83.5 °C).

(6) Fluorenol: 20 mg, 1% yield. − M.p. 152−154 °C, mixed m.p. 152−154°C (ref.[23d] m.p. 156 °C).

Oxidation products (eluted by methanol): 32 mg.

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