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THE FORMATION AND PHOTOLYSIS OF BIS(FLUORENYL)-DIMETHYLZIRCONIUM

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Summary

Bis(fluorenyl)dimethylzirconium has been prepared from fluorene, methyllithium and zirconium tetrachloride by a new and convenient route. The compound was characterized by elemental analysis, proton NMR and mass spectrometry. Photolysis of bis(fluorenyl)dimethylzirconium in solution leads to cleavage of the methyl groups, with formation of methane and a bis(fluorenyl)zirconium-type compound of possible polynuclear nature. Infrared studies using specifically deuterated analogs have shown that this process occurs, at least in part, by intramolecular proton abstraction from the π-coordinated fluorenyl rings.

Introduction

Cyclopentadienyl derivatives of the transition metals have been extensively synthesized and studied since the discovery of ferrocene in 1951, and a limited number of indenyl—transition metal compounds have also been described. In striking contrast, however, early attempts to form fluorenyl derivatives of transition metals such as iron and cobalt met with failure [1] and at the present time, only two such compounds are known. Samuel and Setton [2] first prepared bis(fluorenyl)zirconium dichloride (I) from a reaction between fluorenylsodium and zirconium tetrachloride in dimethoxyethane, and a very recent X-ray structural determination of this product has been interpreted as indicating both *pentahapto* and *trihapto* (π-allylic) coordination of the two fluorenyl ligands, respectively, to the metal [3]. King and Efraty [4] have recently reported that a reaction between fluorenylsodium and $Mn(CO)_5Br$ in tetrahydrofuran solution produces the compound fluorenyltricarbonylmanganese, in which the fluorenyl ligand is undoubtedly π-bonded to manganese in a *pentahapto* manner.

Results and discussion

By a method similar to the formation of cyclopentadienyl and indenyl derivatives of titanium, zirconium and hafnium containing σ-bonded organic substituents [5], a reaction between I and two equivalents of methyllithium has produced bis(fluorenyl)dimethylzirconium (II) in 71% yield. In contrast to our earlier studies [5], it was found convenient to form I directly from fluorene, zirconium tetrachloride and methyllithium, and to react it in situ. This procedure avoids the isolation of any intermediates.

$$C_{13}H_{10} + CH_3Li \xrightarrow{THF} C_{13}H_9Li + CH_4$$

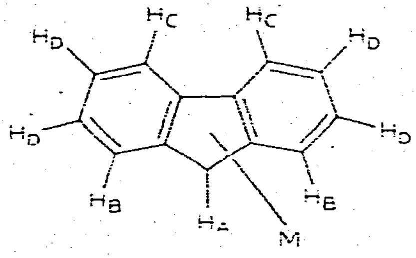
$$2\,C_{13}H_9Li + ZrCl_4 \xrightarrow{THF} \underset{(I)}{(C_{13}H_9)_2ZrCl_2} + 2\,LiCl$$

$$(C_{13}H_9)_2ZrCl_2 + 2\,CH_3Li \xrightarrow{THF} \underset{(II)}{(C_{13}H_9)_2Zr(CH_3)_2} + 2\,LiCl$$

$(C_{13}H_9)_2Zr(CH_3)_2$ (II) is a light yellow solid and is stable in air for a short period of time. It is extremely sensitive to moisture, both in solution and in the solid state. Although it can be sublimed at ca. 200°C with decomposition, it is best purified by crystallization from pentane at low temperatures. Even under argon at −30°C, however, II slowly changes color and forms white decomposition products, mainly fluorene and bifluorenyl, as evidenced by proton NMR and mass spectrometry.

The mass spectrum of II is presented in Table 1, and is consistent with the proposed structure.

The proton NMR spectrum of II in CCl_4 solution at 35°C exhibits resonances for the fluorenyl ligand which are very similar to the resonances for fluorene itself, and is illustrated in Fig. 1.



(II)

In II, the protons H_A, H_B, H_C and H_D of the fluorenyl ring are all shifted to lower field compared to the corresponding protons in fluorene when measured in the same solvent. This result is indicative of a lower electron density in the

TABLE 1

THE MASS SPECTRUM OF $(C_{13}H_9)_2Zr(CH_3)_2$

m/e	Ion	Rel. Intensity
451	$(C_{13}H_9)_2Zr(CH_3)_2^+$	2
436	$(C_{13}H_9)_2ZrCH_3^+$	32
421	$(C_{13}H_9)_2Zr^+$	24
256	$(C_{13}H_9)Zr^+$	8
166	$C_{13}H_{10}^+$	100
165	$C_{13}H_9^+$	100
164	$C_{13}H_8^+$	31
163	$C_{13}H_7^+$	47

complexed fluorenyl rings as a result of coordination to the metal. The one-proton signal at τ 4.39 is assignable to H_A (C_9-position) and represents a shift of $\Delta\tau$ 3.11 ppm to lower field. The low field multiplet of relative intensity two at τ 2.05 can be assigned to either protons H_B or H_C, while the higher field multiplet of relative intensity six at τ 2.70 represents two of these protons as well as the four H_D protons. These two multiplet resonances are shifted by $\Delta\tau$ 1.0 ppm and 0.65 ppm, respectively, compared to the corresponding resonances in fluorene. The coordinated methyl substituents exhibit a resonance of relative intensity three at τ 12.06, indicating that they are very strongly shielded. The occurence of this resonance at such high field can be compared with corresponding methyl proton resonances in bis(cyclopentadienyl)dimethylzirconium (τ 10.39) [5] and bis(indenyl)dimethylzirconium (τ 11.13) [5], and is indicative of the increased shielding imposed by the condensed aromatic rings in the indenyl and fluorenyl systems, respectively.

A more precise description of the structure of II will be possible only via an X-ray crystallographic investigation, since *mono-* [6], *tri-* [3], and *pentahapto-* [3,4] bonding modes of the five-membered ring of the fluorenyl ligands are all possible. It is interesting to note, however, that a recently completed X-ray crystallographic investigation of bis(indenyl)dimethylzirconium has indicated that both indenyl substituents are essentially π-bonded in a *pentahapto* manner to the zirconium atom [7].

As in the case of bis(cyclopentadienyl)- and bis(indenyl)dimethylzirconium [8], photolysis of II in solution results in cleavage of both methyl ligands. The

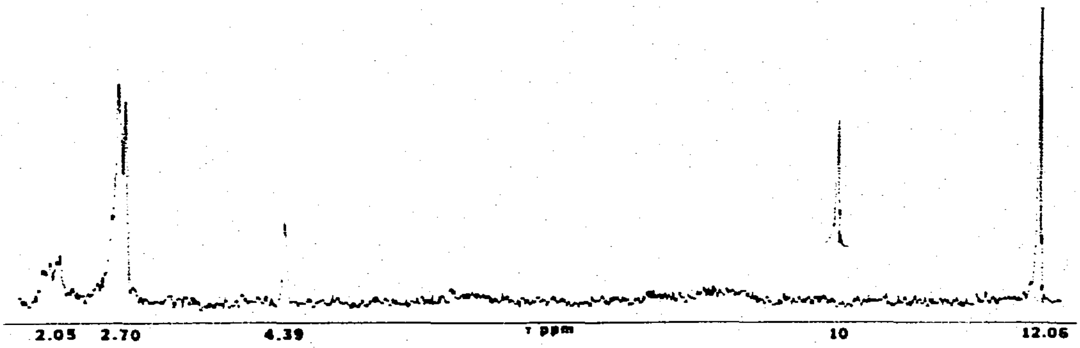


Fig. 1. The proton NMR spectrum of $(C_{13}H_9)_2Zr(CH_3)_2$ (II) in CCl_4 solution.

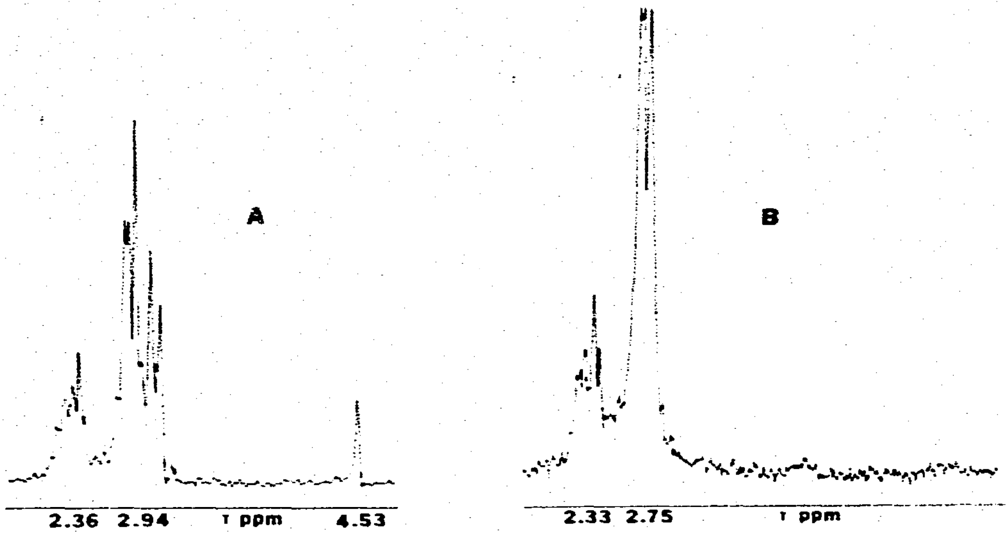


Fig. 2. The proton NMR spectra of (A) $(C_{13}H_9)_2Zr(CH_3)_2$ (II) and (B) the photolysis product III derived from II in C_6D_6 solution.

resulting diamagnetic dark-olive product III analyzes essentially for $(C_{13}H_9)_2Zr$ and is pyrophoric. The gas that is released from this photolysis reaction consists mainly of methane (ca. 95%), with smaller amounts of ethylene and ethane. The proton NMR spectrum of this demethylated product in C_6D_6 solution exhibits only aromatic proton resonances at τ 2.33 and τ 2.75, and is illustrated in Fig. 2. It is noteworthy that not only the methyl proton resonance but also the resonance for the unique fluorenyl ring proton H_A is not apparent in the spectrum of the photolysis product. Furthermore, the higher field multiplet at τ 2.75 is shifted to slightly lower field compared with the corresponding resonance for II in the same solvent (τ 2.94), and is noticeably less broad (Fig. 2).

The absence of a resonance representing H_A in the spectrum of the demethylated product III could be due to the fact that this resonance is hidden under one of the two multiplets, or that the five-membered ring forms a carbon—zirconium σ-bond of the type that has been observed recently in $[(C_5H_5)(C_5H_4)NbH]_2$ [9,10], and $[(C_5H_5)_2(C_5H_4)Th]_2$ [11]. The loss of hydrogen from the five-membered ring of the fluorenyl ligand could be due to abstraction by photochemically generated methyl radicals to form methane. The abstraction of hydrogen atoms from π-cyclopentadienyl rings has already been demonstrated by deuteration studies in the case of the photolysis of $(\pi\text{-}C_5H_5)_2Ti(CH_3)_2$ in solution [12], the thermolysis of solid $(\pi\text{-}C_5H_5)_2Ti(CH_3)_2$ [13], and the thermolysis of $(\pi\text{-}C_5H_5)_2Ti(C_6H_5)_2$ both in solution and in the solid state [14].

The demethylated product III could not be sublimed in vacuo without extensive decomposition, and a mass spectrum exhibiting monomeric $(C_{13}H_9)_2Zr$ could not be obtained. At 240°C, the product gave only fragments that were due to $C_{13}H_{10}^+$, $(C_{13}H_9)_2^+$, and $(C_{13}H_9)_3^+$. The above data indicates that III is probably a polynuclear bis(fluorenyl)zirconium-type derivative. Although the nature of the metal—ring bonding in III is not yet clear, infrared studies detailed below lend support to the argument that photolysis is accompanied by abstraction of the C_5-ring proton H_A.

Infrared spectra

Compounds I and II provide a rare example of polyhapto transition metal derivatives containing one proton (H_A, C_9-position) in the aromatic ring bonded to the metal. The location of the vibrational modes of the C—H_A fragment should allow a straightforward determination by infrared of the presence or absence of this proton in the photolysis product. For this purpose, bis(9-deuteriofluorenyl)zirconium dichloride (IV) was prepared, together with its dimethyl derivative V and the product VI resulting from photolysis of V in benzene solution. The infrared spectra of the dichlorides I and IV were compared with those of III and VI in order to determine the modifications brought about on the fluorenyl ring by photolysis.

The infrared spectrum of I in the frequency region 3200 to 600 cm^{-1} contains bands belonging exclusively to the internal vibrations of the aromatic ligand. This is usually assumed in the analysis of the vibrational spectra of metallocenes [15,16]. Furthermore, interaction between the two fluorenyl ligands in the molecule is neglected. The fluorenyl ligand is taken to be of C_{2v} symmetry, in which case the infrared active modes are of the A_1, B_1, and B_2 species. The absorptions belonging to the C—H_A vibrations are expected to fall in the region of 3100 cm^{-1} for the A_1 mode and 800 to 600 cm^{-1} for the B_1 and the B_2 modes.

3100 cm^{-1} region: The $\nu(C—H_A)A_1$ band expected to occur in this region cannot be distinguished from the bands due to the other aromatic protons. Deuterium exchange of the H_A proton (i.e., compound IV) gives rise to a sharp band of weak intensity at 2340 cm^{-1}. If this band corresponds to the absorption at ca. 3100 cm^{-1} as expected, this would give a ratio of $\nu(C—H_A)/\nu(C—D_A)$ of approximately 1.3, which is the same order of magnitude of $\nu(C—H)/\nu(C—D)$ ratio in ferrocene (1.31 to 1.34) [17].

900 to 400 cm^{-1} region: Detailed vibrational studies on ferrocene and other cyclopentadienyl compounds have shown that the intense band usually observed at ca. 800 cm^{-1} (811 cm^{-1} in ferrocene, 806 cm^{-1} in ruthenocene and 773 cm^{-1} in nickelocene) can be assigned to C—H bending ($\perp$) vibrations [17,18]. In the fluorenyl compound I, two C—H_A bands are expected to occur in this region corresponding to the γ and δ modes of B_1 and B_2 symmetry, along with bands belonging to the same modes for the other aromatic protons. These two C—H_A bands are expected to be isotope-sensitive and should shift to lower frequencies upon deuteration; this provides a convenient method for their assignment. Indeed, examination of the spectra of I and its deuterated analog IV clearly show the expected distinctive features (Fig. 3).

In the spectrum of I, among the set of eight bands of medium to strong intensity lying between 800 and 700 cm^{-1} (806, 786, 767, 751, 739, 735, 730 and 718 cm^{-1}), two of them lying at 806 * and 767 cm^{-1} * almost completely disappear upon deuteration (the weak residual peaks are due to non-deuterated product) whereas the others remain unchanged. Moreover, two new bands appear

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* Denoted with an asterisk in Fig. 3A.

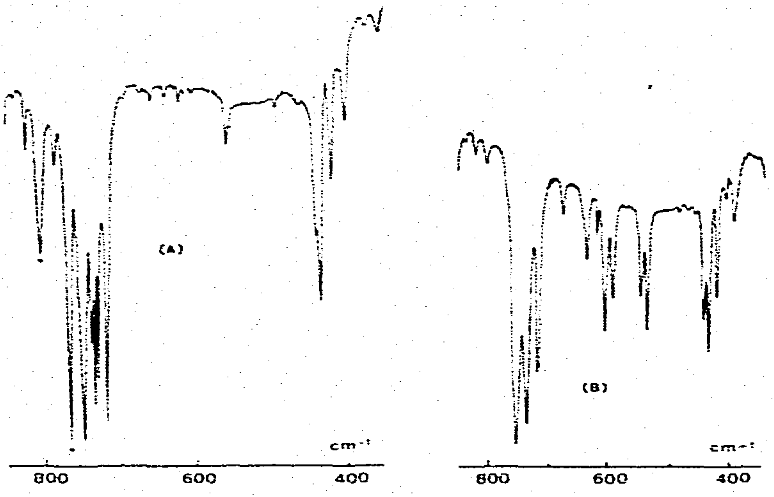

Fig. 3. The infrared spectra of (A) $(C_{13}H_9)_2ZrCl_2$ (I) and (B) $(C_{13}H_8D)_2ZrCl_2$ (IV) in nujol.

in the spectrum of IV at 607—589 and 544—533 cm^{-1} (split into doublets probably due to solid state-effects). If these originate from the bands at 806 and 767 cm^{-1}, the isotope ratios (C—H$_A$)/(C—D$_A$) are 1.34 and 1.41, respectively, for the γ and δ modes. This result is comparable to similar shifts in benzene (C_6H_6/C_6D_6 = 1.20 to 1.28) and in ferrocene [$(C_5H_5)_2Fe/(C_5D_5)_2Fe$ = 1.22 to 1.30] [17]. The bands at 806 and 767 cm^{-1} in I can therefore be reasonably assigned to the γ(C—H$_A$) and δ(C—H$_A$) vibrational modes.

Infrared spectrum of the photolysis products: The infrared spectra of the products obtained from photolysis of the dimethyl compounds II and V are identical (Fig. 4), and both show the absence of bands due to γ and δ(C—H$_A$) or (C—D$_A$). They show, however, the presence of a wide intense band at about 750 cm^{-1} due to aromatic C—H vibrations. Moreover, the ν(C—D$_A$) band at 2340 cm^{-1} (not shown in Fig. 4) is also absent. These observations corroborate the results discussed above concerning the absence of the H$_A$ proton NMR signal, and lend support to the argument that photolysis of the dimethyl compound II takes place with abstraction of the H$_A$ proton from the C$_5$-ring π-bonded to the metal.

It may well be a general phenomenon that photolysis of dialkyl metallocenes of the titanium group in the absence of a suitable substrate is associated with intramolecular rearrangement with proton abstraction from the cyclopentadienyl ring. In the presence of a substrate such as diphenylacetylene, however, the corresponding metallocycle is obtained in which the cyclopentadienyl rings remain intact [8]. This observation has also been made in the case of molybdenum compounds [19] where photolysis of $Cp_2Mo(CO)$ in the presence of RC≡CR leads to alkyne complexes, whereas in the absence of a substrate, an insoluble material containing possibly some polymeric $(Cp_2Mo)_n$ is obtained.

In an analogous manner, a reaction between two equivalents of fluorenyllithium and hafnium tetrachloride followed by treatment with methyllithium produced bis(fluorenyl)dimethylhafnium in moderate yield as a very labile, cream-colored solid. Bis(fluorenyl)dimethylhafnium is appreciably less stable

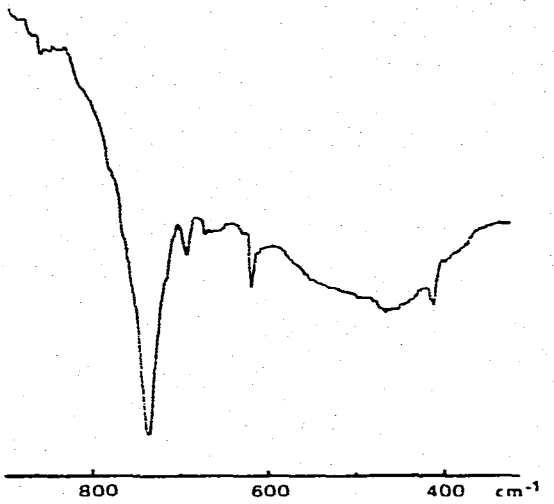

Fig. 4. The infrared spectrum of compound VI obtained from the photolysis of $(C_{13}H_8D)_2Zr(CH_3)_2$ (V) in benzene.

thermally than the zirconium analog II, both in the solid state and in solution, and attempts to obtain proton NMR and mass spectra were unsuccessful. The product was therefore characterized by treatment in pentane solution with anhydrous hydrogen chloride to form methane and bis(fluorenyl)hafnium dichloride.

Experimental

All operations were conducted under a dry, oxygen-free argon atmosphere. All solvents were dried and distilled over $LiAlH_4$, and were kept under argon until use. Anhydrous zirconium tetrachloride (99.9%, hafnium-free) and hafnium tetrachloride (99.9%, ultra-pure) were obtained from Research Organic/Inorganic Chemical Corp. Photolyses were carried out using a Hanovia 450 watt mercury lamp. No filters were used, and all reactions were conducted in standard Pyrex Schlenk tubes. Proton NMR spectra were recorded on a Perkin—Elmer R-12A NMR spectrometer, and were referenced to TMS as an external standard. Mass spectra were recorded on a Perkin—Elmer—Hitachi RMU-6L spectrometer at 70 electron volts. Elemental analyses were performed by the Microanalytical Laboratory, Office of Research Services, University of Massachusetts, Amherst, Mass. Infrared spectra were recorded on Perkin—Elmer 457 and 225 spectrometers.

Preparation of bis(fluorenyl)dimethylzirconium (II)

Fluorene (1.00 g, 6.0 mmol) was dissolved in 20 ml of tetrahydrofuran and 6 mmol of methyllithium in ether solution was added at room temperature. Within seconds a clear dark orange-red solution was obtained and methane was released. The solution was cooled to —78°C and zirconium tetrachloride (0.70 g, 3.0 mmol) was added. The reaction mixture was then allowed to warm to room temperature and at this point a completely clear dark red solution of $(C_{13}H_9)_2$-$ZrCl_2$ was obtained.

This solution was again cooled to —78°C and 6 mmol of methyllithium in ether solution was added dropwise. After the addition, the solution was allowed to warm slowly to 0°C, and at this point, the solvent was removed via a water aspirator and finally under high vacuum. The dark yellow-red oil was extracted five times with hot pentane and the combined extracts were filtered over a frit. Crystallization of the filtrate at —78°C gave 955 mg (71%) of yellow $(C_{13}H_9)_2$-$Zr(CH_3)_2$, which was subsequently dried in vacuo. (Found: C, 74.35; H, 5.35; Zr, 20.0. $C_{28}H_{24}Zr$ calcd.: C, 74.45; H, 5.35; Zr, 20.19%.)

C_6-Deuterated bis(fluorenyl)zirconium dichloride (IV), $(C_{13}H_8D)_2ZrCl_2$, and its dimethyl derivative V, $(C_{13}H_8D)_2Zr(CH_3)_2$, were prepared in an analogous manner, starting with 9,9-dideuterio-fluorene [20].

Bis(fluorenyl)dimethylhafnium was also prepared analogously, starting with fluorene, methyllithium and hafnium tetrachloride. The product proved to be exceedingly difficult to isolate and characterize, since pentane extracts of this compound were very sensitive thermally, even at low temperatures.

Photolysis of bis(fluorenyl)dimethylzirconium (II)

$(C_{13}H_9)_2Zr(CH_3)_2$ (0.20 g, 0.44 mmol) was dissolved in 250 ml of pentane and the solution was irradiated at room temperature. After 30 min, the yellow color was discharged and the formation of a dark brown-black precipitate III was observed. The irradiation was continued for 3 h, and the resulting precipitate was collected on a frit, washed two times with pentane, and dried in vacuo to produce a dark olive residue (160 mg, 81%). (Found: C, 73.50; H, 4.41; Zr, 20.72. $C_{26}H_{18}Zr$ calcd.: C, 74.06; H, 4.30; Zr, 21.63. $C_{26}H_{16}Zr$ calcd.: C, 74.41; H, 3.84; Zr, 21.73%.) The photolysis product is pyrophoric and turned scarlet-red when exposed slowly to air. It reacts violently with CCl_4 but is reasonably soluble and stable in benzene.

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