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# Fluorenyl derivatives of early transition elements: a synthetic and structural study

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## Abstract

The tetracarbonyls of niobium(I) and tantalum(I), M($\eta^5$-9-phenylfluorenyl)(CO)$_4$, have been prepared from the dinuclear tetracarbonyl anions [$M_2(\mu\text{-Cl})_3(CO)_8$]$^-$ and Li(9-phenylfluorenyl). A slightly distorted four-legged piano stool geometry, due to the presence of the sterically demanding phenyl substituent, has been found in the case of the niobium derivative. The crystal and molecular structures of Zr(fluorenyl)$_2$Me$_2$ and of the 9-phenyl-substituted derivative have been solved. The structure of Zr(fluorenyl)$_2$Me$_2$ is similar to that of the known dichloride, Zr(fluorenyl)$_2$Cl$_2$, where fluorenyl ligands of different hapticity are present. On the other hand, the use of the more sterically demanding phenyl-substituted fluorenyl ligand in Zr($\eta^5$-9-phenylfluorenyl)$_2$Me$_2$, induces the fluorenyl ligands to be symmetrically and pentahapto-coordinated to zirconium. © 2001 Elsevier Science B.V. All rights reserved.

*Keywords:* Zirconium; Niobium; Tantalum; Fluorenyl; Structures; Complexes

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## 1. Introduction

Cyclopentadienyl- and indenyl derivatives of transition d-metals have been extensively studied since the discovery of ferrocene in 1951 [1]; on the other hand, sandwich or half-sandwich compounds containing the fluorenyl ligand have been elusive compounds for some time. For example, attempts to prepare FeCp(fluorenyl) or Fe(fluorenyl)$_2$ failed, presumably due to the involvement of the $\pi$-electrons of the central five-membered ring with the aromaticity of the fused six-membered rings [2]. Although some earlier reports appeared concerning the use of fluorenyl derivatives of Group 4 elements as catalytic precursors for the polymerization of olefins, the first example of a fluorenyl derivative was Zr(fluorenyl)$_2$Cl$_2$ described by Samuel and Setton in 1965 [3] and characterized some years later by X-ray diffraction [4] as containing $\eta^5$- and the $\eta^3$-fluorenyl ligands. A new impetus in the field of Group 4 metal fluorenyl derivatives came from the discovery of the metallocene/MAO combination for the polymerization of olefins; studies aimed at increasing the activity of the catalytic systems allowed a number of new fluorenyl compounds of zirconium to be prepared and structurally characterized [2].

In this paper we report the synthesis and the structure of the half-sandwich derivatives of niobium(I) and tantalum(I), M($\eta^5$-9-phenylfluorenyl)(CO)$_4$, and a structural study of the known [5,6] dimethyl derivatives of zirconium(IV) containing the fluorenyl and the 9-phenyifluorenyl ligands.

## 2. Results and discussion

### 2.1. Niobium and tantalum

By reaction of the dinuclear tetracarbonyl anions of niobium(I) and tantalum(I), [$M_2(\mu\text{-Cl})_3(CO)_8$]$^-$ with

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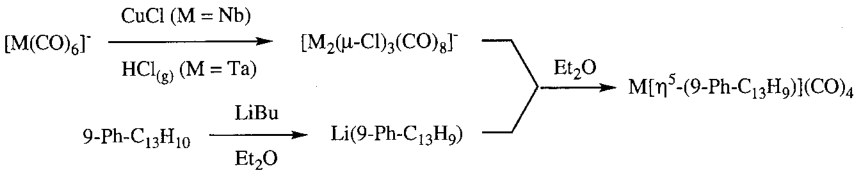

Scheme 1.

Table 1
Crystallographic data and details of the structure refinement for Nb($\eta^5$-9-phenylfluorenyl)(CO)$_4$, Zr(fluorenyl)$_2$Me$_2$, and Zr($\eta^5$-9-phenylfluorenyl)$_2$Me$_2$

| | Nb($\eta^5$-9-Ph-C$_{13}$H$_9$)(CO)$_4$ | Zr(C$_{13}$H$_9$)$_2$Me$_2$ | Zr($\eta^5$-9-Ph-C$_{13}$H$_9$)$_2$Me$_2$ |
|---|---|---|---|
| Empirical formula | $C_{23}H_{13}NbO_4$ | $C_{28}H_{24}Zr$ | $C_{40}H_{32}Zr$ |
| Formula weight | 446.24 | 451.69 | 603.88 |
| Temperature (K) | 293(2) | 293(2) | 293(2) |
| Crystal system | Monoclinic | Monoclinic | Monoclinic |
| Space group | $C2/c$ (no.15) | $P2_1/c$ (no.14) | $C2/c$ (no.15) |
| Unit cell dimensions | | | |
| $a$ (Å) | 16.190(2) | 13.657(3) | 21.035(4) |
| $b$ (Å) | 7.476(1) | 8.015(1) | 8.688(3) |
| $c$ (Å) | 31.771(3) | 20.248(3) | 17.296(4) |
| $\beta$ (°) | 90.26(1) | 109.59(1) | 114.26(1) |
| $Z$ | 8 | 4 | 4 |
| $\rho_{calc}$ (Mg m$^{-3}$) | 1.542 | 1.437 | 1.392 |
| Volume (Å$^3$) | 3845.4(8) | 2088.1(6) | 2882(1) |
| $\mu$ (mm$^{-1}$) | 0.652 | 0.538 | 0.409 |
| Data/restraints/parameters | 3395/0/266 | 2727/0/264 | 2519/0/186 |
| $R(F_o)$ [$I>2\sigma(I)$] | 0.0350 | 0.0425 | 0.0685 |
| $Rw(F_o)$ [$I>2(I)$] | 0.0686 | 0.0742 | 0.1693 |

$R(F_o)=\Sigma\,||F_o|-|F_c||/\Sigma\,|F_o|$; $Rw(F_o^2)=[\Sigma\,[w(F_o^2-F_c^2)^2]/\Sigma\,[w(F_o^2)^2]]$; $w=1/[\sigma^2(F_o^2)+(AQ)^2+BQ]$ where $Q=[\mathrm{MAX}(F_o^2,0)+2F_c^2]/3$.

lithium(9-phenylfluorenyl) in Et$_2$O, the tetracarbonyl derivatives M($\eta^5$-9-phenylfluorenyl)(CO)$_4$ have been obtained according to Scheme 1, a reaction sequence successfully applied to the synthesis of cyclopentadienyl-substituted tetracarbonyl derivatives of Group 5 metals [7].

The niobium and tantalum derivatives are red to orange solids, stable in air for short periods of time, soluble in hydrocarbons and in CH$_2$Cl$_2$. Although they dissolve in THF, a colourless solid forms quickly which was shown to be 9-phenylfluorene by $^1$H-NMR [8]. The well documented decomposition of transition metal fluorenyl derivatives in the presence of THF can explain the medium-to-low yields (51 and 24% in the case of the niobium and tantalum compounds, respectively) [9]. Although we used Et$_2$O as reaction medium, THF was present in the reaction mixture due to solvation of the cation in the starting materials Na(THF)$_{3.35}$[Nb$_2$($\mu$-Cl)$_3$(CO)$_8$] and H(THF)$_2$[Ta$_2$($\mu$-Cl)$_3$(CO)$_8$].

The tetracarbonyl Nb($\eta^5$-9-phenylfluorenyl)(CO)$_4$ was studied by X-ray diffraction. Crystallographic data are summarized in Table 1, selected bond distance and angles are reported in Table 2, while Fig. 1 shows the molecular structure of the compound. The niobium centre is bonded to the fluorenyl ligand in a pentahapto fashion and to the four carbonyl groups, the coordination around niobium being square-pyramidal. The niobium–centroid distance of 2.109 Å is larger than that observed in other tetracarbonyl cylopentadienyl derivatives which ranges from 2.069 Å in NbCp(CO)$_4$ [10] to

Table 2
Bond distances (Å) and angles (°) in Nb($\eta^5$-9-phenylfluorenyl)(CO)$_4$.

| | | | |
|---|---|---|---|
| *Bond distances* | | | |
| Nb–C(5) | 2.410(4) | Nb–C(1) | 2.070(4) |
| Nb–C(6) | 2.452(4) | Nb–C(2) | 2.077(4) |
| Nb–C(11) | 2.446(4) | Nb–C(3) | 2.077(5) |
| Nb–C(12) | 2.441(4) | Nb–C(4) | 2.086(4) |
| Nb–C(17) | 2.443(4) | Mean | 2.077 |
| Mean | 2.438 | | |
| Nb–Cp [a] | 2.109(4) | | |
| *Bond angles* | | | |
| C(1)–Nb–C(3) | 114.0(2) | C(2)–Nb–C(4) | 117.8(2) |
| C(1)–Nb–C(2) | 75.2(2) | C(1)–Nb–Cp | 122.5(1) |
| C(3)–Nb–C(2) | 74.7(2) | C(2)–Nb–Cp | 120.7(2) |
| C(1)–Nb–C(4) | 71.7(1) | C(3)–Nb–Cp | 123.4(2) |
| C(3)–Nb–C(4) | 73.1(2) | C(4)–Nb–Cp | 121.6(1) |

[a] Cp indicates the centroid of the 9-phenylfluorenyl five-membered ring.

Estimated standard deviations in parentheses refer to the least significant digit

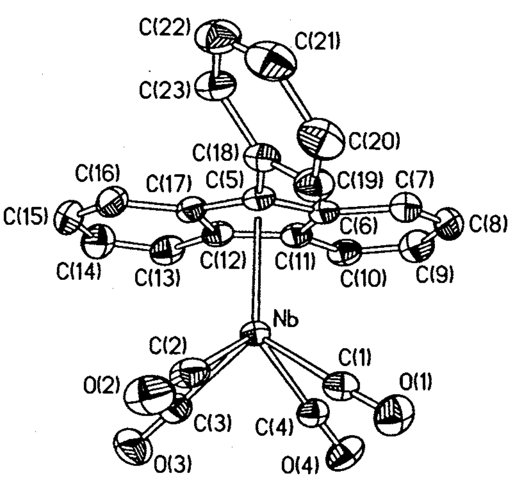

Fig. 1. View of the molecular structure of Nb($\eta^5$-9-phenylfluorenyl)(CO)$_4$. Thermal ellipsoids are at 30% probability.

Table 3
Bond distances (Å) and angles (°) in Zr(fluorenyl)$_2$Me$_2$

| | | | |
|---|---|---|---|
| *Bond distances* | | | |
| Zr–C(1) | 2.248(5) | Zr–C(2) | 2.239(5) |
| Zr–C(3) | 2.474(6) | Zr–C(16) | 2.439(5) |
| Zr–C(4) | 2.566(5) | Zr–C(17) | 2.589(5) |
| Zr–C(9) | 2.641(5) | Zr–C(22) | 2.726(5) |
| Zr–C(10) | 2.645(5) | Zr–C(23) | 2.728(5) |
| Zr–C(15) | 2.588(5) | Zr–C(28) | 2.585(5) |
| Mean | 2.583 | Mean | 2.613 |
| Zr–Cp1 [a] | 2.281(5) | Zr–Cp2 | 2.317(6) |
| *Bond angles* | | | |
| C(1)–Zr–Cp1 | 106.6(2) | C(2)–Zr–Cp1 | 106.6(2) |
| C(1)–Zr–Cp2 | 105.2(2) | C(2)–Zr–Cp2 | 104.6(2) |
| C(1)–Zr–C(2) | 94.9(2) | Cp1–Zr–Cp2 | 132.6(2) |

[a] Cp indicates the centroid of the fluorenyl five-membered ring. Estimated standard deviations in parentheses refer to the least significant digit

2.091(4) Å in Nb($\eta^5$-C$_5$H$_4$COOCH$_3$)(CO)$_4$ [7b]. The mean Nb–CO distance (2.077 Å) is shorter than that observed in analogous compounds and similar to that observed in noncyclopentadienyl carbonyl derivatives of niobium(I) [7a,11].

In spite of a slight distortion (the two condensed six-membered rings are slightly bent on the opposite side of the metal), the fluorenyl moiety is essentially planar; on the other hand, the C(5)–C(18) vector deviates by 8.4° from the five-membered ring plane. The dihedral angle between the fluorenyl mean plane and the plane containing the phenyl ring C(18)–C(23) is 50.3°, probably due to the repulsion between the hydrogens on C(7) and C(16) and those on C(19) and C(23), respectively. The five-membered ring plane is almost exactly perpendicular (89.2°) to the Nb–Cp vector. A very similar coordination geometry has been found in Mn($\eta^5$-9-phenylfluorenyl)(CO)$_3$ [12], which to the best of our knowledge represents the only example known until now of a structurally characterized metal-coordinated phenylfluorenyl ligand. The Nb–CO bond angles are between 120.3 and 122.5°, with a slightly asymmetric Nb(CO)$_4$ fragment. Such asymmetry is maintained in solution: the infrared spectrum in heptane shows a strong absorption at 2034s, and a very strong doublet at 1936–1927 cm$^{-1}$, the relative intensity being unchanged after recrystallization thus excluding a mixture of isomers. The doublet is not present in CH$_2$Cl$_2$. Due to coupling with the Nb nucleus ($I = 9/2$) [7b], no peak due to the carbonyl fragment was found in the $^{13}$C-NMR spectrum of Nb($\eta^5$-9-phenylfluorenyl)(CO)$_4$; on the other hand, a broad signal is present at 239.2 ppm in the $^{13}$C-NMR spectrum of the corresponding tantalum compound.

### 2.2. Zirconium

Some bis(fluorenyl) derivatives of zirconium have been reported in the literature [6]. The structure of Zr(fluorenyl)$_2$Cl$_2$ [4], which was proposed to contain one $\eta^5$- and one $\eta^3$-coordinated fluorenyl ligand, prompted us to investigate the crystal structure of Zr(fluorenyl)$_2$Me$_2$ and to compare it with the structure of the dichloride. It was reckoned that the presence of the two methyl groups would eliminate the proposed [4] Cl···Cl contacts of the dichloride. The dimethyl derivative was prepared in a 60% yield by a slight modification of the published literature (use of Et$_2$O and toluene instead of THF) and recrystallized from toluene–heptane. Crystallographic data are summarized in Table 1, selected bond distances and angles are reported in Table 3. Fig. 2 shows the molecular structure of the compound which is reminiscent of Zr($\eta^5$-fluorenyl)($\eta^3$-fluorenyl)Cl$_2$. The C(1)–Zr–C(2) angle [94.9(2)°] is close to the Cl(1)–Zr–Cl(2) angle of 93.6°. The fluorenyl ligands face the metal in a pseudo-staggered conformation and are both warped as reversed umbrellas far from the metal (maximum deviation from the plane 0.19 Å). Such bending does not involve the five-membered ring which is planar within 0.029 Å. The five-membered rings are not exactly perpendicular to the ZrCp vectors but they are tilted by 4.4 and 7.9°, respectively, so that significantly different Zr–C distances are observed. As a matter of fact, the Zr–C(fluorenyl-1) distances range between 2.47 and 2.64 Å, while the corresponding distances from zirconium to the carbon atoms of the other fluorenyl ligand range between 2.44 and 2.73 Å: the shortest distance involves the C(3) and C(16) atoms. Similar differences have been considered evidence of $\eta^3$-coordination of the fluorenyl ligand [4].

In order to test whether a more sterically demanding ligand could induce some structural changes, we studied the crystal and molecular structure of the derivative containing the 9-phenylfluorenyl ligand. The synthetic pathway to Zr($\eta^5$-9-phenylfluorenyl)$_2$Me$_2$ was that reported in the literature and the compound was isolated in 75% yield after recrystallization from toluene–heptane. Crystallographic data are summarized in Table 1, selected bond distances and angles being reported in Table 4. Fig. 3 shows the molecular structure of the compound.

The zirconium atom lies in a special position on the twofold axis parallel to *b* placed at 0*a* and (1/4)*c*. This operation relates the two halves of the molecule. The zirconium centre adopts the pseudo-tetrahedral coordination geometry generally observed in MCp$_2$X$_2$ compounds. The 9-phenylfluorenyl ligands face the metal at a distance greater than that observed in Zr(fluorenyl)$_2$X$_2$ (X = Cl, CH$_3$), which is probably due to the presence of the sterically demanding ligands. As observed in Nb($\eta^5$-9-phenylfluorenyl)(CO)$_4$, the 9-phenylfluorenyl group is substantially planar as far as the five-membered ring is concerned, the rest of the ligand being slightly bent far away from the metal.

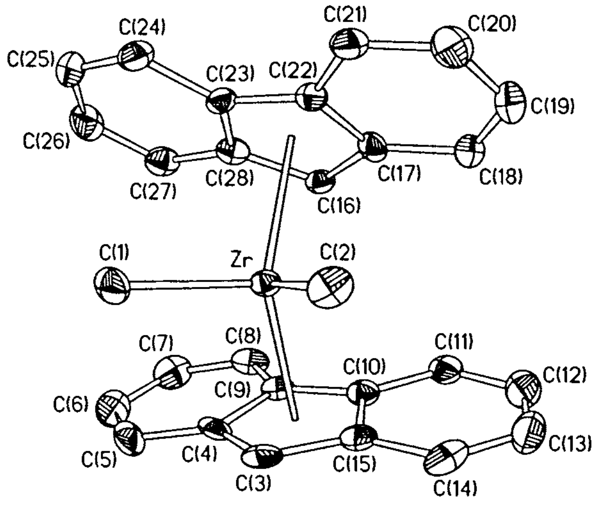

Fig. 2. View of the molecular structure of Zr(fluorenyl)$_2$Me$_2$. Thermal ellipsoids are at 30% probability.

Table 4
Bond distances (Å) and angles (°) in Zr($\eta^5$-9-phenylfluorenyl)$_2$Me$_2$

| | | | |
|---|---|---|---|
| *Bond distances* | | | |
| Zr–C(1) | 2.392(5) | Zr–C(10) | 2.532(6) |
| Zr–Cp [a] | 2.299(6) | Zr–C(11) | 2.631(5) |
| | | Zr–C(12) | 2.628(6) |
| | | Zr–C(13) | 2.616(6) |
| | | Zr–C(14) | 2.605(6) |
| | | Mean | 2.602 |
| *Bond angles* | | | |
| C(1)–Zr–C(1′) | 94.4(3) | Cp–Zr–Cp | 138.0(2) |
| C(1)–Zr–Cp | 102.5(2) | | |

Symmetry transformations used to generate equivalent atoms: ′ $-x$, $y$, $-z+1/2$.

[a] Cp indicates the centroid of the 9-phenylfluorenyl five-membered ring.

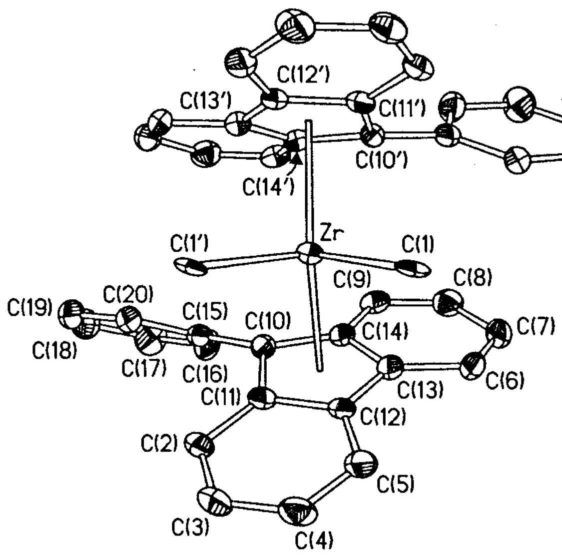

Fig. 3. View of the molecular structure of Zr($\eta^5$-9-phenylfluorenyl)$_2$Me$_2$. Thermal ellipsoids are at 30% probability.

The maximum deviation from the plane is 0.396 Å at C(3). The dihedral angle between the plane of the phenyl substituent and that of the fluorenyl is smaller (41.4°) than in the case of Nb($\eta^5$-9-phenylfluorenyl)(CO)$_4$ (50.3°). As in Zr(fluorenyl)$_2$Cl$_2$, the five-membered ring plane is almost perpendicular to the Zr–centroid vector, the tilting angle being 2.2° with the C(10) atom slightly closer to the metal than C(12) and C(13). The differences in Zr–C(fluorenyl) bond lengths are however smaller than that observed in Zr(fluorenyl)$_2$Me$_2$.

The mean C–C bond distance within the five-membered ring is 1.434(9) Å to be compared with the same bond distances in the free ligand [1.462(7) Å] [13].

## 3. Experimental

Unless otherwise stated, all of the operations were carried out under an atmosphere of prepurified argon. Solvents were dried by conventional methods prior to use.

IR spectra were measured with the FT-1725X instrument on solutions or on Nujol mulls prepared under rigorous exclusion of moisture and air. $^1$H- and $^{13}$C-NMR spectra were measured with a Varian Gemini 200BB instrument.

ZrCl$_4$ (Fluka) was treated with boiling SOCl$_2$; the solution was partially evaporated under reduced pressure, and heptane was added to precipitate the product. The suspension was filtered and the solid dried in vacuo at ca. 200 °C. Fluorene (Fluka) was used without further purification. 9-phenylfluorene was prepared according to the literature [8]. Na(THF)$_{3.35}$[Nb$_2$(μ-Cl)$_3$(CO)$_8$] and H(THF)$_2$[Ta$_2$(μ-Cl)$_3$(CO)$_8$] were obtained as previously reported [7a].

### *3.1. Preparation of M(η$^5$-9-phenylfluorenyl)(CO)$_4$, M = Nb, Ta*

Only the preparation of Nb(η$^5$-9-phenylfluorenyl)(CO)$_4$ is described in detail, the tantalum compound being obtained in a similar way. A solution of fluorene (0.44 g, 1.82 mmol) in Et$_2$O (30 ml) was treated with a 1.6 M solution of LiBu in hexane (1.15 ml, 1.84 mmol of LiBu). The colour of the solution turned red–orange. After 1 h stirring at room temperature (r.t.), the solution was treated at room temperature with Na(THF)$_{3.35}$[Nb$_2$(μ-Cl)$_3$(CO)$_8$] (0.71 g, 0.91 mmol). The red–brown suspension was stirred at r.t. overnight, the solvent was evaporated in vacuo at room temperature and the residue was partially dissolved in heptane (25 ml). The suspension was stirred for 1 h and the solid was recovered by filtration and washed with heptane (6 × 2 ml). The volume of the orange solution was reduced to ca. 20 ml and cooled at ca. − 30 °C, giving large red crystals (0.42 g, 51% yield) of Nb(η$^5$-9-phenylfluorenyl)(CO)$_4$. Anal. Found: C, 61.9; H, 3.2. Calc. for $C_{23}H_{13}NbO_4$: C, 61,9; H, 2,9%. IR (Nujol): $\tilde{\nu} = 3053$ m, 2023 s, 1923 s, 1903 s, 1658 w, 1596 w, 1262 m, 1096 m, 1074 m, 1028 m, 802 m, 744 m, 659 w, 437 m cm$^{-1}$. IR (heptane): 2034 s, 1936 vs, 1927 vs cm$^{-1}$. (CH$_2$C1$_2$): 2032 s, 1921 vs cm$^{-1}$. (THF, 5 min after mixing) 2030 m, 1922 vs cm$^{-1}$. $^1$H-NMR (C$_6$D$_6$, 25°C): $\delta = 6.70$–6.86 (m, 4H), 6.90–7.20 (m, 5H), 7.4–7.7 (m, 4H) ppm. $^{13}$C-NMR (C$_6$D$_6$, 25°C): $\delta = 106.2$, 120.1, 130.7, 134.3 (quaternary carbon atoms), 116.9, 122.3, 123.2, 124.2, 125.8, 126.2, 128.2, 129.0 (*C*H carbon atoms) ppm.

Ta(η$^5$-9-phenylfluorenyl)(CO)$_4$. The preparation of this compound was performed in a similar way starting from H(THF)$_2$[Ta$_2$(μ-Cl)$_3$(CO)$_8$]. Yellow orange, 24% yield [14]. Anal. Found: C, 51.5; H, 2.3. Calc. for $C_{23}H_{13}O_4Ta$: C, 51,7; H, 2.4%. IR (Nujol): $\tilde{\nu} = 3056$ m, 2021 s, 1920 s, 1898 s, 1658 w, 1594 w, 1266 m, 1091 m, 1078 m, 1024 m, 796 m, 740 m, 651 w, 432 m cm$^{-1}$. IR (heptane): 2031 s, 1932 vs, 1923 vs cm$^{-1}$. (CH$_2$Cl$_2$): 2028 s, 1918 vs cm$^{-1}$. (THF, 5 min after mixing) 2025 m, 1918 vs cm$^{-1}$. $^1$H-NMR (C$_6$D$_6$, 25°C): $\delta = 6.68$–6.87 (m, 4H), 6.93–7.18 (m, SH), 7.35–7.69 (m, 4H) ppm. $^{13}$C-NMR (C$_6$D$_6$, 25°C): $\delta = 106.8$, 120.4, 130.6, 134.7 (quaternary carbon atoms) 117.0, 122.1, 123.5, 124.5, 125.7, 126.1, 128.5, 129.6 (*C*H carbon atoms), 239.2 (broad, CO) ppm.

### *3.2. Preparation of Zr(fluorenyl)$_2$Me$_2$*

A solution of fluorene (1.5 g, 9.02 mmol) in Et$_2$O (30 ml) was treated with a 1.6 M solution of LiBu in hexane (5.6 ml, 8.96 mmol of LiBu). The colour of the solution turned orange. After 5 h stirring at r.t., the orange solution was treated at r.t. with ZrCl$_4$ (1.05 g, 4.5 mmol). The orange suspension was stirred at r.t. for 24 h, the solvent was evaporated in vacuo at r.t. and the residue was partially dissolved in toluene (70 ml). The suspension was cooled at ca. 0 °C and treated dropwise with a 1.6 M solution of LiMe in Et$_2$O (5.6 ml, 8.96 mmol of LiMe). At the end of the addition the orange–brown suspension was stirred for 3 h at r.t., filtered and the filtrate was cooled at ca. 4°C. The orange crystalline solid (0.360 g) which formed was isolated by filtration and dried in vacuo. By cooling the mother liquor at ca. − 30 °C, an additional crop (0.936 g) of orange crystals of Zr(fluorenyl)$_2$Me$_2$ [5] was isolated (63% total yield) and characterized by spectroscopic and analytical data.

### *3.3. Preparation of Zr(η$^5$-9-phenylfluorenyl)$_2$Me$_2$*

A solution of 9-phenylfluorene (0.51 g, 2.09 mmol) in Et$_2$O (25 ml) was treated with a 1.6 M solution of LiBu in hexane (1.3 ml, 2.1 mmol of LiBu). The colour of the solution turned red–orange. After 1 h stirring at r.t., the solution was treated at r.t. with ZrCl$_4$ (0.22 g, 0.9 mmol). The orange suspension was stirred at r.t. for 1 h, the solvent was evaporated in vacuo at r.t. and the residue was partially dissolved in toluene (25 ml). The suspension was cooled at ca. 0 °C and treated dropwise with a 1.6 M solution of LiMe in Et$_2$O (1.1 ml, 1.8 mmol of LiMe). At the end of the addition the orange brown suspension was stirred at r.t. for 2 h, filtered and the volume of the filtrate was reduced to ca. 5 ml. Heptane (20 ml) was layered on the brown–orange solution. Large orange crystals formed after 24 h which were recovered, and briefly dried in vacuo at r.t. (0.15 g). The volume of the solution was reduced to 5 ml and the residue was cooled at ca. − 30 °C, giving another crop (0.25 g, 75% total yield) of crystalline Zr(η$^5$-9-phenylfluorenyl)$_2$Me$_2$ [6] which was characterized by spectroscopic and analytical data.

### *3.4. Data collection and refinement of Nb(η$^5$-9-phenylfluorenyl)(CO)$_4$, Zr(fluorenyl)$_2$Me$_2$ and Zr(η$^5$-9-phenylfluorenyl)$_2$Me$_2$*

The X-ray diffraction measurements have been carried out at 293 K by means of a Siemens P4 diffractometer equipped with graphite-monochromated Mo–K$_\alpha$ radiation ($\lambda = 0.71073$ Å). The samples were sealed in glass capillaries under argon atmosphere. The intensity data collection was carried out with the $\omega/2\theta$

scan mode, collecting a redundant set of data. Three standard reflections were measured every 97 measurements to check sample decay and equipment stability. The intensities were corrected for Lorentz and polarization effects and for absorption by means of a $\theta$-scan method [15]. The structure solutions, obtained by means of the automatic direct methods, and the refinements, based on full-matrix least-squares on $F^2$, were carried out by using the SHELX97 program [16]. Data reduction of measured intensities was performed by the XSCANS package [17]. Some other utilities contained in the WINGX suite [18] were also used.

### 3.4.1. Nb($\eta^5$-9-phenylfluorenyl)(CO)$_4$

Red crystals suitable for the X-ray diffraction experiment were obtained as reported above. A crystal of dimensions 0.40 × 0.36 × 0.05 mm had the unit cell parameters listed in Table 1. A set of 4422 intensity data were collected between $2.5 \leq \theta \leq 25.0°$. By merging the equivalent ones, a set of 3395 independent intensities ($R_{\text{int}} = [\Sigma\,|F_o^2 - F_o^2(\text{mean})|/\Sigma\,(F_o^2)] = 0.0558$) was obtained, 2554 of them satisfying the condition $I > 2\sigma(I)$. The structure solution was obtained in the $C2/c$ space group. The final refinement cycle was done by using anisotropic thermal parameters for all heavy atoms. The hydrogen atoms were placed in calculated positions and allowed to ride on the connected atoms. The resulting reliability factors are listed in Table 1.

### 3.4.2. Zr(fluorenyl)$_2$Me$_2$

Yellow–orange crystals suitable for the X-ray diffraction experiment were obtained by slow diffusion of heptane into a diluted solution of the compound in toluene. A crystal of dimensions 0.28 × 0.18 × 0.08 mm showed the unit cell parameters listed in Table 1. 3660 intensity data were collected between $2.1 \leq \theta \leq 22.5°$. By merging the equivalent ones, a set of 2727 independent intensities ($R_{\text{int}} = 0.0352$) was obtained, 1706 of them satisfying the condition $I > 2\sigma(I)$. The structure solution was obtained in the space group $P2_1/c$. The final refinement cycle was done by using anisotropic thermal parameters for all heavy atoms. The hydrogen atoms were placed in calculated positions and allowed to ride on the connected atoms. The final reliability factors are in Table 1.

### 3.4.3. Zr($\eta^5$-9-phenylfluorenyl)$_2$Me$_2$

Yellow–orange crystals suitable for the X-ray diffraction experiment were obtained by slow diffusion of heptane into a diluted solution of the compound in toluene. A crystal of dimensions 0.36 × 0.21 × 0.10 mm had the cell parameters listed in Table 1. By merging the equivalent ones among 3131 collected intensities ($3.0 \leq \theta \leq 25.0°$), a set of 2519 independent data was obtained ($R_{\text{int}} = 0.0510$), 1837 of them satisfying the condition $I > 2\sigma(I)$. The structure solution was obtained by standard direct methods in the $C2/c$ space group. Hydrogen atoms were introduced in calculated positions and allowed to ride on the connected carbon atoms. In the final refinement cycle anisotropic thermal parameters were used for all heavy atoms, obtaining the reliability factors listed in Table 1.

## 4. Conclusions

This paper has described a synthetic pathway to 9-phenylfluorenyl derivatives of niobium and tantalum and shown that these compounds are unstable in the presence of Lewis base, in particular THF. As far as the zirconium derivatives are concerned, the solution of the structure of the bis fluorenyl derivative Zr(fluorenyl)$_2$Me$_2$ has shown that the coordination mode of the fluorenyl ligand and the metric of the molecule do not substantially differ from that of the dichloride, Zr(fluorenyl)$_2$Cl$_2$. The five-membered ring carbon atoms of the fluorenyl ligands in both these compounds bind to the metal at uneven distances in such a way that one fluorenyl ligand may be considered as $\eta^3$-coordinated.

In the structures examined in this paper, the fluorenyl ligands are bent away from the metal upon coordination, the amount of bending depending on the ML fragment. When a pseudo tetrahedral coordination is adopted and two fluorenyls are present, they prefer to coordinate with their major axes perpendicular to the line bisecting the angle formed by the other ligands. In the latter case, the plane of the phenyl ring reduces its tilting with respect to the fluorenyl plane.

Our data indicate that the 9-substituted fluorenyl ligand approaches closer to the metal than the unsubstituted one: the fact that the L–Zr–L angle becomes larger [132.6(2) versus 138.0(2)° on going from fluorenyl to the 9-substituted derivative] with similar Zr–C distances suggests that a regular $\eta^5$-coordination of the ligand is adopted.

## 5. Supplementary material

Crystallographic data for the structural analyses have been deposited with the Cambridge Crystallographic Data Centre, CCDC, no.159645 for Nb($\eta^5$-9-phenylfluorenyl)(CO)$_4$, 159646 for Zr(fluorenyl)$_2$Me$_2$, 159647 for Zr($\eta^5$-9-phenylfluorenyl)$_2$Me$_2$. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44-1223-336-033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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