matographed with hexane–toluene (70:30): R_f ~0.5; yield 1 g (42%) of a mixture 7a and 7b. 7a and 7b were obtained in the pure state by fractional crystallization from CH_2Cl_2–pentane. 1-Morpholino-3-methyl-1-butene was obtained by the same procedure as for 1-morpholinoisobutene.[9]

7a: ^{31}P NMR (C_6D_6) δ -33.4 ($^1J(^{183}W-^{31}P)$ = 232 Hz); IR (decalin) ν(CO) 2070 (m), 1985 (w), 1952 (sh), 1945 (vs) cm^{-1} (KBr) ν(PH) 2360 cm^{-1}, ν(CO aldehyde) 1710 cm^{-1}; ^{1}H NMR (C_6D_6) δ 0.72 (d, $^3J(H-H)$ 6.8 Hz, 3 H, CH_3), 0.74 (d, $^3J(H-H)$ = 6.8 Hz, 3 H, CH_3), 1.8–2.3 (m, 1 H, CHMe$_2$), 2.5–2.8 (m, 1 H, CHCHO), 5.70 (dd, $^1J(H-P)$ = 342.0 Hz, $^3J(H-H)$ = 7.8 Hz, 1 H, PH), 6.8–7.2 (m, 5 H, Ph), 9.17 (pseudo t, $^3J(H-P)$ ≃ $^3J(H-H)$ = 3.7 Hz, 1 H, CHO), mass spectrum (EI, 70 eV, ^{184}W), m/e (relative intensity) 518 (M, 10), 490 (M – CO, 75), 462 (M – 2CO, 12), 434 (M – 3CO, 29), 406 (M – 4CO, 33), 378 (M – 5CO, 100). Anal. Calcd for $C_{16}H_{15}O_6PW$: C, 37.09; H, 2.92; P, 5.98; W, 35.48. Found: C, 37.32; H, 3.03; P, 6.01; W, 36.16.

7b: ^{31}P NMR (C_6D_6) δ -33.8 ($^1J(^{183}W-^{31}P)$ = 232 Hz); IR (decalin) ν(CO) 2070 (m), 1984 (w), 1950 (sh), 1945 (vs) cm^{-1}; ^{1}H NMR (C_6D_6) δ 0.5–0.8 (m, 6 H, CH_3), 1.6–2.1 (m, 1 H, CHMe$_2$), 2.5–2.8 (m, 1 H, CHCHO), 5.66 (dd, $^1J(H-P)$ = 346.2 Hz, $^2J(H-H)$ = 6.1 Hz, 1 H, PH), 6.8–7.3 (m, 5 H, Ph), 9.41 (dd, $^3J(H-P)$ =

4.9 Hz, $^3J(H-H)$ = 2.9 Hz, 1 H, CHO).

[4-Morpholino-5-(phenylphosphino)-1,6-dimethyl-3-heptene]pentacarbonyltungsten (9). Complex 1 (4.5 g, 6.9 mmol) was heated at 115 °C for 5 h with 4-morpholino-1,6-dimethyl-3-heptene (3.5 g, 15.6 mmol) in anhydrous xylene (50 mL). After hydrolysis and evaporation of the solvent, the residue was chromatographed with toluene (R_f ~0.4); yield 1.8 g (41%). The product thus obtained was a mixture of at least two isomers according to ^{31}P NMR: δ -7.2 and -13.8 (hexane). The major complex (δ -7.2) could be further purified by recrystallization in hexane. 4-Morpholino-1,6-dimethyl-3-heptene was synthesized by the same procedure as for 1-morpholino-p-methylstyrene.[7] Anal. Calcd for $C_{24}H_{30}NO_6PW$: C, 44.81; H, 4.70; P, 4.81; W, 28.58. Found: C, 44.80; H, 4.20; P. 4.64; W, 29.17.

Registry No. 1, 82265-64-3; 2a, 91083-06-6; 2b, 91176-75-9; 3, 91083-07-7; 4a, 91083-08-8; 4b, 91176-76-0; 5, 91110-39-3; 6, 91083-09-9; 7a, 91083-10-2; 7b, 91176-77-1; 9, 91110-38-2; 1-morpholinocyclohexene, 670-80-4; 1-morpholino-p-methylstyrene, 55949-65-0; 1-morpholinocyclopentene, 936-52-7; 1-morpholino-isobutene, 2403-55-6; 1-morpholino-3-methyl-1-butene, 53828-74-3; 4-morpholino-1,6-dimethyl-3-heptene, 78593-92-7.

Trapping of (Aryne)metallocene Complexes by Elemental Selenium. Crystal Structure of (η⁵-*t*-BuC₅H₄)₂ZrSe₂C₆H₄-*o*

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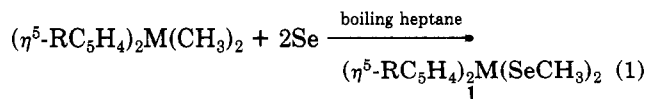
Elemental selenium reacts with diarylmetallocenes (η^5-RC$_5$H$_4$)$_2$M(C$_6$H$_4$R')$_2$ (M = Zr, R = t-Bu, R' = H and p-CH$_3$; M = Ti, R = R' = H) in boiling heptane, leading to the corresponding phenylenedi-selenometallocenes (η^5-RC$_5$H$_4$)$_2$MSe$_2$C$_6$H$_4$R'-o. It is suggested that upon heating (aryne)metallocenes are generated in which the insertion of two selenium atoms occurs. The molecular structure of (η^5-t-BuC$_5$H$_4$)$_2$ZrSe$_2$C$_6$H$_4$-o is reported. The deep red crystals are monoclinic of space group $P2_1/n$ (a = 13.679 (3) Å, b = 22.649 (3) Å, c = 7.749 (3) Å, β = 103.06 (3)°, V = 2338.8 Å^3, Z = 4, F_{000} = 1128, D = 1611 Kg·m^{-3}). The central ring consists of one Zr atom, two Se atoms, and two aromatic carbon atoms. The Zr atom is 1.67 Å from the phenyl group plane. The dihedral angles between the two cyclopentadienyl rings and between the phenyl–Se–Se and Se–Zr planes are 53.8 and 56.1°, respectively. The distances from zirconium to cyclopentadienyl carbons lie within the range of 2.45–2.61 Å and show that the metal is displaced far from the ring centroids and the substituted carbon atoms.

Introduction

Metallic complexes containing chalcogenides in their framework are the subject of great attention due to their apparent implication in catalysis and biology and their potential application in organic synthesis as well as their interest in theoretical chemistry.[1-4] In a preceding paper[5]

we reported the synthesis and the spectroscopic characterization of new selenium complexes of zirconium and hafnium, and we pointed out the insertion of elemental selenium into the M–CH$_3$ bond according to eq 1.

$$(\eta^5\text{-RC}_5\text{H}_4)_2\text{M(CH}_3)_2 + 2\text{Se} \xrightarrow{\text{boiling heptane}} (\eta^5\text{-RC}_5\text{H}_4)_2\text{M(SeCH}_3)_2 \quad (1)$$

$$\mathbf{1}$$

$$\text{M = Zr, Hf; R = H, } t\text{-Bu}$$

(1) Gates, B. C.; Katzer, J. R.; Schuit, G. C. A. "Chemistry of Catalytic Processes"; McGraw-Hill: New York, 1979.
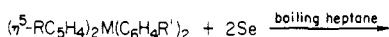
(2) McCleverty, J. A. *Prog. Inorg. Chem.* 1968, *10*, 49.

(3) Madon, R. J.; Shaw, H. *Catal. Rev. Sci. Eng.* 1977, *15*, 69.

(4) For a general view on selenium topics, see: Klayman, D. L.; Günther, W. H. H. "Organic Selenium Compounds: Their Chemistry and Biology"; Wiley: New York, 1973. For a full bibliography, consult: "Selenium and Tellurium Abstracts" prepared for Selenium-Tellurium Development Association, Inc., P.O. Box 3096, Darien, Conn. 06820.
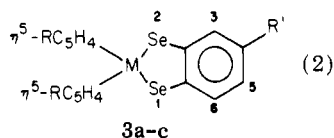
(5) Gautheron, B.; Tainturier, G.; Meunier, Ph. *J. Organomet. Chem.* 1981, *209*, C49 and references therein.

(6) Surprisingly, when Cp$_2$Zr(C$_6$H$_4$R)$_2$ is allowed to react with Se under the same experimental conditions, an apparently polymeric insoluble red material is obtained while Cp$_2$Ti(C$_6$H$_5$)$_2$ gives the expected product.

It is shown in eq 2 that elemental selenium reacts with diarylmetallocenes of the type **2** by a very different reaction, leading predominantly to phenylenediselenometallocenes of type **3**.

$$(\eta^5\text{-RC}_5\text{H}_4)_2\text{M}(\text{C}_6\text{H}_4\text{R}')_2 \;+\; 2\text{Se} \xrightarrow{\text{boiling heptane}}$$

2a–c

(2)

3a–c

a, M = Zr, R = *t*-Bu, R' = H; b, M = Zr, R = *t*-Bu, R' = *p*-CH$_3$; c, M = Ti, R = R' = H

We report in this paper the original synthesis and spectroscopic properties of complexes **3a–c**. The molecular structure of **3a** is also described.
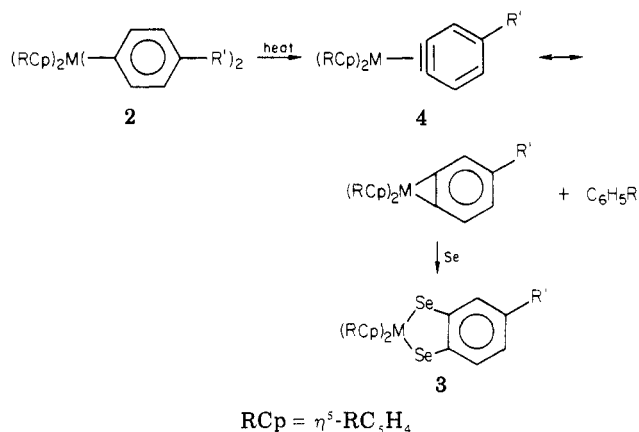
In a typical run, diarylmetallocene and gray selenium powder are warmed in boiling heptane under argon. After some hours of boiling (depending of the metallocene), no more selenium is present and the deep colored solution, upon cooling, leads to bright prismatic crystals of complexes **3** practically pure. The ^{1}H NMR, ^{77}Se NMR, and mass spectra of the complexes are in perfect agreement with those of the proposed structure.

Especially the ^{1}H NMR spectrum of **3a** exhibits two AA'BB' systems consistent with a complex containing monosubstituted cyclopentadienyl ligands in a symmetrical environment and two double doublets (A$_2$X$_2$ system) consistent with a 1,2-disubstituted phenyl group while that of **3b**, besides the AA'BB' system, shows a set of three spins characteristic of a 1,2,4-trisubstituted phenyl group. Moreover, the mass spectra of complexes **3** exhibit isotopic distribution patterns typical of ions containing one zirconium (or titanium) atom and two selenium atoms.

Results and Discussion

To our knowledge, very few metallacycles of bis(cyclopentadienyl)M$_T$ (M$_T$ = transition metal) with chalcogen–M$_T$ bonds are reported in the literature. Only four papers deal with the phenylenedithio ligand.[7–9] The corresponding complexes are obtained in the zirconium and titanium series from the metallocene dichloride and 1,2-dithiols in the presence of a base (or as the disodium dithiolates).[7–9] Otherwise, some 1,2-didehydrobenzene complexes of transition metals have been previously isolated[10] and proposed as reactive intermediates.[11] In addition, thermolysis of diphenyltitanocene and diarylzirconocene was reported to lead to the corresponding aryne complex (1,2-didehydrobenzene)metallocene[12,13] that could be

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Scheme I

$$\text{RCp} = \eta^5\text{-RC}_5\text{H}_4$$

trapped with carbon dioxide or acetylenes.

Upon thermolysis in aromatic hydrocarbon solvents, Erker mentioned[13] that diarylzirconocenes undergo successive replacement of their σ-bonded ligands by aryl groups from the solvent, via an (aryne)zirconocene intermediate. In order to avoid such replacement, we used no aromatic solvent in our work.

Then, the direct, and apparently exclusive, formation of complexes **3** suggests immediately that the reaction could evolve through a zirconocene–aryne intermediate.

In our experimental conditions, 2 equiv of selenium was used and we never could characterize any monoselenide derivative. However, if stoichiometric amounts of the starting zirconium complex and selenium are allowed to react, the reaction mixture contains **3a**, some starting material, a small amount of (*t*-BuCp)$_2$Zr(SeC$_6$H$_5$)$_2$,[5] and a new product that could be considered monoselenide.

We propose the mechanism summarized in Scheme I that accounts for the observed reaction.

Under thermal conditions, the aryne complex **4** is directly formed via the abstraction of an ortho proton from one of the σ-bonded aryl ligands by the other σ ligand.[13] Among the different proposals reported in the literature,[10–13] that one seems to us the most likely for two main reasons: first, the retention of the metallocene moiety precludes the abstraction of a proton from a cyclopentadienyl ligand and, furthermore, the fact that no detectable amount of radical coupling products was found precludes the homolytic cleavage of the σ-phenyl substituent.

The aryne intermediate subsequently inserts selenium as previously observed in the case of dialkylzirconocene.[5]

Although there is no doubt concerning the structure of the phenylenediselenometallocenes, the molecular structure of (η^5-*t*-BuC$_5$H$_4$)$_2$ZrSe$_2$C$_6$H$_4$-*o* has been definitively established by RX diffraction and compared to that of similar complexes reported in the literature.

Crystal Structure of Phenylenediseleno-*tert*-butylzirconocene (3a). Determination of the Structure. The crystal with a platelet shape had a maximum size of 0.2 mm. It has been studied by X-ray diffraction at 291 K using Cu Kα radiation (λ = 1.540 51 Å). Crystals of **3a** (M_r = 567.2) were monoclinic of space group P2$_1$/n (a = 13.679 (3) Å, b = 22.649 (3) Å, c = 7.749 (3) Å, β = 103.06 (3)°, V = 2338.8 Å^3, Z = 4, F$_{000}$ = 1128, calculated density D = 1611 Kg·m^{-3}).

Intensities were measured with a CAD4 diffractometer. A total of 25 reflections with 7° < θ < 46° were used to

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Table I. Atomic Coordinates for Heavy Atoms

	x	y	z	B_{eq}, Å^2
Zr	0.12809 (5)	0.21941 (3)	1.13028 (9)	3.38 (2)
Se(1)	0.2747 (1)	0.23289 (4)	0.9573 (1)	4.72 (4)
Se(2)	0.2688 (1)	0.15647 (4)	1.3401 (1)	4.33 (4)
C(31)	0.3061 (6)	0.1493 (4)	0.985 (1)	4.3 (4)
C(32)	0.3028 (6)	0.1182 (4)	1.139 (1)	3.9 (4)
C(33)	0.3287 (7)	0.0592 (4)	1.152 (1)	5.3 (5)
C(34)	0.3535 (9)	0.0303 (5)	1.009 (2)	7.1 (6)
C(35)	0.3522 (9)	0.0607 (5)	0.854 (2)	7.8 (7)
C(36)	0.3285 (8)	0.1183 (5)	0.842 (1)	6.6 (6)
C(11)	0.5064 (6)	0.3707 (4)	0.599 (1)	4.1 (4)
C(12)	0.4513 (6)	0.3191 (5)	0.550 (1)	5.2 (4)
C(13)	0.4752 (7)	0.2947 (5)	0.397 (1)	5.5 (5)
C(14)	0.5449 (7)	0.3327 (5)	0.350 (1)	5.3 (5)
C(15)	0.5665 (7)	0.3791 (4)	0.474 (1)	4.7 (4)
C(16)	0.4904 (8)	0.4140 (4)	0.741 (1)	5.8 (5)
C(17)	0.5663 (9)	0.4646 (5)	0.766 (2)	7.6 (7)
C(18)	0.4968 (8)	0.3846 (5)	0.917 (1)	6.4 (5)
C(19)	0.3852 (9)	0.4413 (5)	0.675 (2)	7.5 (7)
C(21)	0.1221 (6)	0.3332 (3)	0.145 (1)	3.9 (3)
C(22)	0.0330 (6)	0.3081 (4)	0.185 (1)	4.2 (4)
C(23)	0.0576 (7)	0.2771 (4)	0.343 (1)	5.0 (4)
C(24)	0.1602 (7)	0.2792 (4)	0.409 (1)	5.0 (4)
C(25)	0.1988 (6)	0.3134 (4)	0.286 (1)	4.7 (4)
C(26)	0.1270 (7)	0.3781 (4)	0.003 (1)	5.5 (5)
C(27)	0.0828 (9)	0.3545 (5)	-0.184 (1)	6.5 (6)
C(28)	0.2327 (9)	0.3986 (5)	0.018 (2)	8.4 (7)
C(29)	0.0618 (9)	0.4309 (4)	0.032 (2)	7.0 (6)

Figure 1. ORTEP view of (t-BuC$_5$H$_4$)$_2$ZrSe$_2$C$_6$H$_4$(o.)

Figure 2. Molecular structure of the title compound with arbitrary spheres.

Figure 3. Crystal packing of the title compound. The outlined area corresponds to a projection along (001).

refine the lattice parameters. A total of 5006 intensities were collected for 0.01 < (sin θ)/λ < 0.62, 0 $\leq$ h $\leq$ 16, 0 $\leq$ k $\leq$ 27, and -9 < l $\leq$ +9. Internal consistency before absorption correction was R_{int} = 0.1149 for 4668 unique reflections. Heavy atoms (Zr, Se) were located by direct methods using program SHELX[17] and instruction EEES. Carbon atoms were located by "Fourier difference" calculations. Refinements of F magnitudes were performed by using f' and f'' from ref 18. Most H atoms were visible on a Fourier difference map. Nevertheless H positions were introduced in the calculations by using facilities offered by SHELX for rigid methyl groups, phenyl hydrogens, etc. with C–H bond lengths equal to 1.08 Å. Refinements with isotropic temperature factors yielded a conventional R factor of 19%.

Absorption was corrected by using program DIFABS;[19] minimum absorption correction was 0.656 and maximum absorption 2.121; internal consistency dropped to R_{int} = 0.0368. The R factor dropped to 0.108, and after introduction of anisotropic temperature factors it dropped to 0.063. For reflections having F > $\sigma(F)$, R = 0.052, the maximal shift/error ratio in the final cycle was 0.21. Maximum and minimum peaks in the final Fourier difference map were 0.61 and -0.64 e Å^{-3}, respectively.

Description of the Structure. Atomic coordinates for heavy atoms are listed in Table I. Anisotropic temperature factors, U_{ij}, are listed in Table II and coordinates for hydrogen atoms in Table III. In that later case no esd's were provided since these atoms are riding on carbon atoms. Interatomic distances and relevant angles and distances to the plane are listed in Tables IV and V. Figure 1 was drawn with the ORTEP program.[20]

The coordination polyhedron around the zirconium atom defined by the cyclopentadienyl ring centroids and
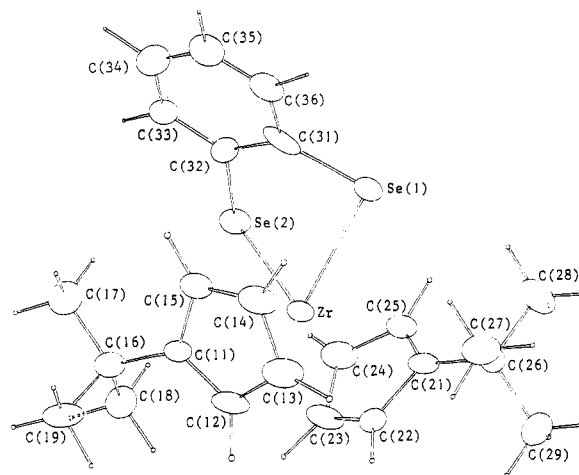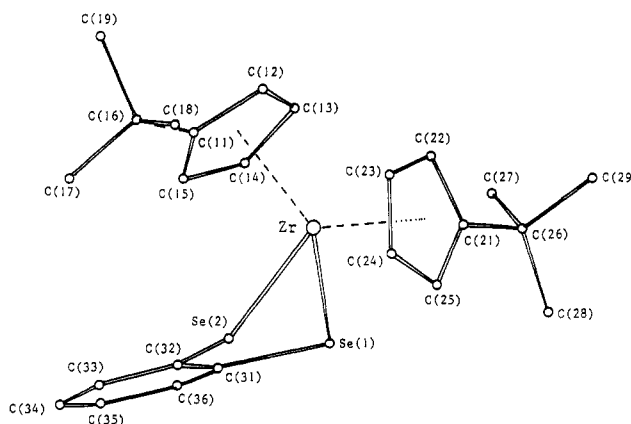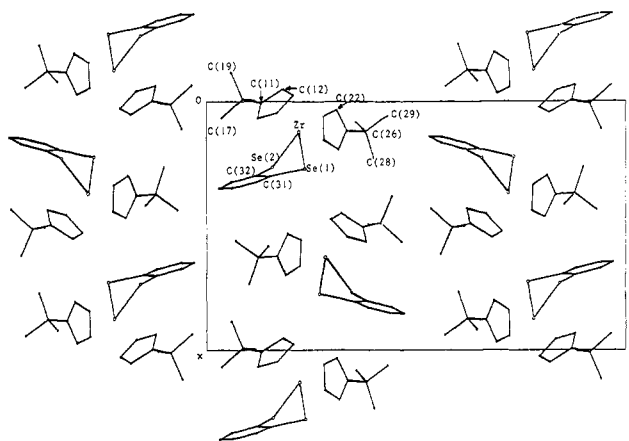
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(20) Johnson, C. K. ORTEP, Report ORNL-3794; Oak Ridge National Laboratory: Oak Ridge, Tenn., 1965.

the selenium atoms is a distorted tetrahedron of nearly C_{2v} symmetry. The molecule presents nearly a mirror plane bisecting only the benzodiselenazirconacycle because the bulky *tert*-butyl groups repel from each other in the sterically least hindered conformation.

Each of the cyclopentadienyl and phenyl rings are planar within 0.02 Å (Table V) and the former one shows a staggered arrangement from each other. The zirconium–carbon distances systematically vary within the range of 2.45–2.61 Å (Table IV) around each of the rings and thereby indicate that the normal from the planar rings to the zirconium atom is slightly displaced from the ring centroids G and G' (Zr–G = 2.23 Å for C(11)–C(15) cycle

Table IV. Interatomic Distances (Å) and Bond Angles (deg)

Bond Distances

Zr-Se(1)	2.670 (1)	Zr-C(11)	2.610 (8)	Zr-C(21)	2.581 (7)
Zr-Se(2)	2.639 (1)	-C(12)	2.513 (8)	-C(22)	2.482 (8)
Se(1)-C(31)	1.943 (9)	-C(13)	2.458 (8)	-C(23)	2.465 (8)
Se(2)-C(32)	1.929 (8)	-C(14)	2.511 (8)	-C(24)	2.502 (8)
C(31)-C(32)	1.394 (11)	-C(15)	2.587 (8)	-C(25)	2.527 (8)

C(31)-C(32)	1.394 (11)	C(13)-C(14)	1.394 (14)	C(22)-C(23)	1.383 (12)
C(32)-C(33)	1.382 (12)	C(14)-C(15)	1.413 (13)	C(23)-C(24)	1.381 (12)
C(33)-C(34)	1.391 (14)	C(11)-C(15)	1.419 (11)	C(24)-C(25)	1.421 (13)
C(34)-C(35)	1.380 (15)	C(11)-C(16)	1.522 (12)	C(21)-C(25)	1.402 (12)
C(35)-C(36)	1.342 (14)	C(16)-C(17)	1.528 (14)	C(21)-C(26)	1.511 (12)
C(36)-C(31)	1.402 (12)	C(16)-C(18)	1.504 (13)	C(26)-C(27)	1.533 (14)
C(11)-C(12)	1.397 (13)	C(16)-C(19)	1.543 (13)	C(26)-C(28)	1.499 (13)
C(12)-C(13)	1.415 (13)	C(21)-C(22)	1.442 (11)	C(26)-C(29)	1.536 (12)

Bond Angles

Se(1)-Zr-Se(2)	81.1 (1)	C(15)-C(11)-C(12)	106.7 (8)	C(25)-C(21)-C(22)	103.2 (7)
Zr-Se(2)-C(32)	91.2 (2)	C(11)-C(12)-C(13)	110.0 (9)	C(21)-C(22)-C(23)	109.9 (8)
Se(2)-C(32)-C(31)	122.5 (4)	C(12)-C(13)-C(14)	106.4 (9)	C(22)-C(23)-C(24)	109.4 (9)
C(32)-C(31)-Se(1)	121.6 (4)	C(13)-C(14)-C(15)	109.2 (9)	C(23)-C(24)-C(25)	105.8 (9)
C(31)-Se(1)-Zr	90.3 (2)	C(14)-C(15)-C(11)	107.7 (9)	C(24)-C(25)-C(21)	111.6 (8)
C(36)-C(31)-C(32)	118.6 (8)	C(11)-C(16)-C(17)	111.8 (8)	C(21)-C(26)-C(27)	112.4 (8)
C(31)-C(32)-C(33)	119.5 (8)	C(11)-C(16)-C(18)	112.2 (8)	C(21)-C(26)-C(29)	110.7 (9)
C(32)-C(33)-C(34)	120.2 (1.0)	C(11)-C(16)-C(19)	107.3 (9)	C(21)-C(26)-C(29)	107.3 (8)
C(33)-C(34)-C(35)	120.0 (1.0)	C(17)-C(16)-C(18)	108.5 (1.0)	C(27)-C(26)-C(28)	110.3 (1.0)
C(34)-C(35)-C(36)	120.0 (1.0)	C(17)-C(16)-C(19)	107.4 (9)	C(27)-C(26)-C(29)	106.8 (9)
C(35)-C(36)-C(31)	121.6 (1.0)	C(18)-C(16)-C(19)	109.5 (8)	C(28)-C(26)-C(29)	109.1 (9)

Interatomic Distances and Angles

G-Zr-G'[a]	129.9	Zr-N	2.230 (5)	G-N	0.14
N-Zr-N'	126.2	Zr-N'	2.207 (5)	G'-N'	0.10

[a] G and G', centroids of the Cp rings. N and N', normal foot from Zr atom to Cp rings.

Table VI. Structural Main Values of Some Benzodichalcogenametallacyles
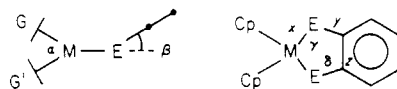
M-E	α, deg	β, deg	γ, deg	δ,[a] deg	x,[a] Å	y,[a] Å	z, Å	ref
Ti-S	130	46	82.2	96.5	2.42 (2.40)[c]	1.74 (1.70)	1.41	22
Mo-S	138	9	81.9	108	2.43 (2.45)	1.78 (1.70)	1.35	23
Zr-Se	129.9	56	81.1	91.5	2.65 (2.70)	1.94 (1.85)	1.39	this work
Zr-CH$_2$		53[b]			2.99 (2.22)	1.48	1.42	24

[a] Mean values. [b] E-C-C-E plane and the phenyl ring are not coplanar. [c] Calculated. G and G' are the centroids of the Cp rings.

and Zr-G' = 2.21 Å for C(21)-C(25) cycle).

The metal atom is the most distant from the substituted carbon atom. The central atom of the *tert*-butyl groups is not exactly in the cyclopentadienyl plane. C(16) is 0.21 Å away from the C(11)-C(15) plane while C(26) is 0.23 Å away from the C(21)-C(25) plane. Such geometry is the result of an appreciable strain within the π-bonded ligand as it has been already reported.[21]

The dihedral angle between the plane of the cyclopentadienyl rings is 53.8°, and we may therefore define the angle between the normals to Cp rings as α' = 126.2° and that of G-Zr-G' as α = 129.9°. That last value is of the same order of magnitude as those mentioned elsewhere (Table VI). The angle α', smaller than α, indicates that the cyclopentadienyl rings tip slightly about the Zr-G and

Zr-G' lines[28] toward the zirconium center (dihedral angle between G-Zr-G' and the C(11)-C(15) plane = 3.75° and between G-Zr-G' and the C(21)-C(25) plane = 2.61°).

The carbon-carbon distances typically range from 1.28 to 1.44 Å for the π ligands and from 1.38 to 1.40 Å for the phenyl ring.[26,27] The Zr-Se bond is only 0.05 Å shorter than the sum of the atomic radii of the two atoms,[25] but the Se-C distances are about 0.1 Å longer than those calculated.

The Cp ligands and the phenyl group are not regular polyhedrons; the C-C-C angles vary from 103.2 to 111.6° (to be compared to 108° for a regular pentagon) and from 118.6 to 121.6° for the phenyl group. The angles at the substituted carbon atoms are the smallest.

The central ring consists of one Zr atom, two selenium atoms, and two carbon atoms from the phenyl group; it is far from being flat, since the sum of the five central angles is 506.7° compared to 540° for a flat pentagon.

The Se(1)-Se(2)-C(31) and Se(1)-Se(2)-C(32) angles are coplanar with the phenyl group,[24] while zirconium is 1.67 Å from the plane. So the dihedral angle between that plane and the Se(1)-Zr-Se(2) plane is 56.1°. That value

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is substantially greater than those observed for the analogue sulfur complexes of the Ti and Mo series (Table VI).

Further studies in the field of metallocene chalcogens as well as the synthetic application of the reported reaction are under investigation in our laboratory.

Experimental Section

All reagents and chemicals obtained from commercial sources were of analytical or reagent grade purity and were used without further purification. Solvents were distilled from a sodium-benzophenone ketyl complex prior to use. All reactions were carried out in Schlenk type glassware under argon. NMR spectra were recorded on a JEOL FX-100 spectrometer (δ, reference Me$_4$Si; appearance and intensity in parentheses (s, singlet; d, doublet; t, triplet; m, multiplet; pt, pseudotriplet; dd, double doublet); except for ^{77}Se NMR, reference (CH$_3$)$_2$Se).

Mass spectra were performed with a FINNIGAN device, Model 3002 (electronic ionization = 70 eV); only the most characteristic fragments are reported (abundance in parentheses).

Elemental analysis were done by the "Service Central de Microanalyses du C.N.R.S.", Villeurbanne, France.

Diphenyltitanocene was obtained from titanocene dichloride and phenyllithium according to the procedure described by Summer.[15]

Diaryl-*tert*-butylzirconocenes were prepared by adaptation of Rausch's procedure used for diphenylzirconocene.[14] The *tert*-butylzirconocene dichloride in ether was added slowly with stirring to 2 equiv of aryllithium (from aryl bromide and lithium wires in ether) at 0 °C. Then the mixture was allowed to warm to room temperature, and the stirring was maintained for 4 h more. The supernatant solution was evaporated, and the organometallics were extracted with warm hexane. The crude complexes were recrystallized in hexane as slightly pale yellow crystals.

2a: mp 131 °C; yield 72%; ^{1}H NMR (CDCl$_3$) δ 1.00 (s, 18), 6.00 (t, 4), 6.30 (t, 4), 7.00 (m, 6), 7.28 (m, 4); ^{77}Se NMR (CDCl$_3$) δ 696.8;[16] mass fragments, m/e 486 (M$^+$, 4), 409 ((M – C$_6$H$_5$)$^+$, 6), 332 ((M – 2C$_6$H$_5$)$^+$, 30), 154 ((C$_5$H$_4$Zr)$^+$ 100), 106 ((C$_5$H$_4$C$_3$H$_6$)$^+$, 50), 91 ((C$_5$H$_4$C$_2$H$_3$)$^+$, 56). Anal. Calcd for C$_{30}$H$_{36}$Zr: C, 73.89; H, 7.39; Zr, 18.72. Found: C, 73.57; H, 7.30; Zr, 18.11.

2b: mp 152 °C; yield 75%; ^{1}H NMR (CDCl$_3$) δ 1.01 (s, 18), 2.23 (s, 6), 6.02 (t, 4), 6.35 (t, 4), 6.80 (d, 2), 7.20 (d, 2); ^{77}Se NMR (CDCl$_3$) δ 682.2;[16] mass fragments, m/e 554 (M$^+$, 3.5), 423 ((M – C$_6$H$_4$CH$_3$)$^+$, 4), 332 ((M – 2C$_6$H$_4$CH$_3$)$^+$, 35), 106 ((C$_5$H$_4$C$_3$H$_6$)$^+$, 40), 91 ((C$_6$H$_4$CH$_3$ and C$_5$H$_4$C$_2$H$_3$)$^+$, 100). Anal. Calcd for C$_{32}$H$_{40}$Zr: C, 74.53; H, 7.76; Zr, 17.70. Found: C, 73.93; H, 7.98; Zr, 17.21.

Phenylenediseleno-*tert*-butylzirconocenes (3, M = Zr). General Procedure. Gray selenium powder (2 mmol) and 1 mmol of diaryl-*tert*-butylzirconocene were warmed in boiling heptane (about 100 mL) under argon. Within a few minutes, the black suspension progressively turned to a red solution and after 8 h of boiling no more selenium was present. The deep red solution was cooled to room temperature overnight, and the red needles that formed were filtered off under argon. Crystals thus obtained were pure and did not need any further recrystallization.

3a: red crystals: mp 205 °C; yield 75%; mass fragments, m/e 568 (M$^+$, 45), 447 ((M – C$_5$H$_4$C$_4$H$_9$)$^+$, 53), 236 ((C$_6$H$_4$Se$_2$)$^+$, 72), 156 ((C$_6$H$_4$Se)$^+$, 77), 121 ((C$_5$H$_4$C$_4$H$_9$)$^+$, 11), 106 ((C$_5$H$_4$C$_3$H$_6$)$^+$, 30), 91 ((C$_5$H$_4$C$_2$H$_3$)$^+$, 100); ^{1}H NMR (C$_6$D$_6$) δ 1.11 (s, 18), 5.71 (pt, 4), 5.83 (pt, 4), 6.95 (dd, 2, H$_4$H$_5$), 7.94 (dd, 2, H$_3$H$_6$); ^{77}Se NMR (CDCl$_3$) δ 562.9. Anal. Calcd for C$_{24}$H$_{30}$ZrSe$_2$: C, 50.79; H, 5.33; Zr, 16.07; Se, 27.82. Found: C, 50.64; H, 5.58; Zr, 15.83; Se, 28.05.

3b: red crystals; mp 188 °C; yield 70%; mass fragments, m/e 582 (M$^+$, 30), 461 ((M – C$_5$H$_4$C$_4$H$_9$)$^+$, 81), 250 ((H$_3$CC$_6$H$_3$Se$_2$)$^+$, 43), 170 ((H$_3$CC$_6$H$_3$Se)$^+$, 15), 106 ((C$_5$H$_4$C$_3$H$_6$)$^+$, 25), 91 ((C$_5$H$_4$C$_2$H$_3$)$^+$, 100); ^{1}H NMR (C$_6$D$_6$) δ 1.13 (s, 18), 5.74 (pt, 4), 5.84 (pt, 4), 6.78 (m), 6.86 (m, 1, H$_5$), 7.86 (d, 1, H$_6$), 7.84 (m, 1, H$_3$); ^{77}Se NMR (CDCl$_3$) 568.8 (Se(1)), 574.5 (Se(2)) (eq 1). Anal. Calcd for C$_{25}$H$_{32}$ZrSe$_2$: C, 51.63; H, 5.50; Zr, 15.66; Se, 27.19. Found: C, 51.86; H, 5.60; Zr, 15.11; Se, 26.01.

Phenylenediselenotitanocene (3c, M = Ti, R = R' = H). The procedure described above was used, but the reaction was complete after only 5 days in boiling heptane. Then the solution was deep green.

3c: deep green crystals; mp > 260 °C; yield 60%; mass fragments, m/e 414 (M$^+$, 10), 349 ((M – C$_5$H$_5$)$^+$, 9), 268 ((C$_5$H$_5$TiSeC$_6$H$_3$)$^+$, 9.5), 178 ((C$_{10}$H$_{10}$Ti)$^+$, 100), 113 ((C$_5$H$_5$Ti)$^+$, 24); ^{1}H NMR (C$_6$D$_6$) δ 5.60 s (10), 6.95 (dd, 2), 7.98 (dd, 2). Anal. Calcd for C$_{16}$H$_{14}$TiSe$_2$: C, 46.63; H, 3.42; Ti, 11.62; Se, 38.32. Found: C, 47.06; H, 3.88; Ti, 11.08; Se, 36.6.