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Formation of aryneziraconocenes from substituted diaryl bis(t-butylcyclopentadienyl)zirconium: application to the synthesis of new functionalized *ortho*-dichalcogenobenzene compounds

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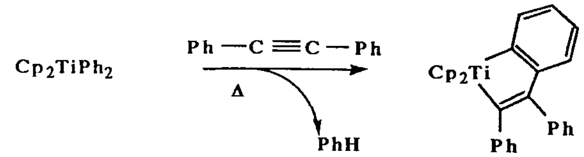
The *para*-substituted diphenylzirconocenes [(t-BuCp)$_2$Zr(*p*-C$_6$H$_4$R)$_2$; R = Br, NMe$_2$] (A) were easily obtained from the reaction of the appropriate organolithium reagent with bis(t-butylcyclopentadienyl)zirconium dichloride. Elimination of bromobenzene or *N,N*-dimethylaminobenzene from A by slight heating led to aryneziraconocenes into which were inserted two equivalents of elementary chalcogens. As a result dichalcogenated zirconacycles [(t-BuCp)$_2$ZrY$_2$C$_6$H$_3$R; Y = S, Se] (B) were obtained. Complexes B constitute useful potential synthons in organic synthesis and a large family of new functionalized dichalcogenated benzenic compounds was prepared by reacting electrophiles.

The structure of complexes B as well as related benzenic derivatives has been confirmed by microanalysis, ^{1}H NMR and mass spectrometry.

Keywords: Zirconocene, benzyne, chalcogen (S, Se), zirconacycle, ^{1}H NMR, mass spectrometry

INTRODUCTION

Many years ago chemists pointed out the particular utility of Group 4 diarylmetallocenes.[1] For example, moderate heating of diphenyltitanocene in the presence of diphenylacetylene causes the eliminaton of benzene and the formation of a metallacycle (Scheme 1).

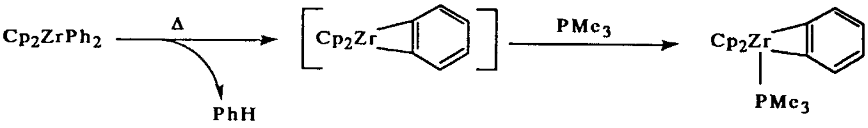


Scheme 1

At the same time, the results published by Vol'pin and co-workers[2] and Erker[3] gave some ideas about the mechanism of the reaction and the existence of a transient benzyne complex was firstly postulated and then proved. Immediately afterwards, many well-documented papers appeared in relation to the chemical reactivity of the transient benzyne.[4–12]

More recently, the fascinating works of Buchwald and colleagues[13] afforded spectacular advances in this field, among them:

(1) the isolation and X-ray structure determination of the trimethylphosphine-stabilized benzyne zirconocene[14] (Scheme 2);
(2) the formation of aryne zirconocenes via methane elimination allowing the synthesis of sterically crowded molecules;[15]
(3) the extension of the method to the synthesis of cycloalkynezirconocenes,[16,17] alkyne



Scheme 2

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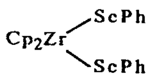
zirconocenes,[18,19] cycloalkene zirconocenes[20] and other complexes derived from imines[21] and benzdiynes.[22,23]

Usually the reactions were conducted by heating the precursor Cp_2ZrPh_2 or $Cp_2Zr(Me)R$ in the presence of the appropriate hydrocarbon reagent[13] (Scheme 1).

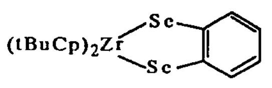
As we have shown previously,[24–26] the transformation is more complicated if some concurrent reactions can be effected. Thus, heating a stoichiometric mixture of diphenylzirconocene and grey selenium powder, only resulted in selenium insertion into the metal–carbon bonds leading to compound **c**.



c

It can be assumed that the insertion reaction is probably much faster than benzynezirconocene formation, which remains undetected. A similar transformation was observed for $Cp_2Zr(Me)Ph$ and a selenium insertion occurred into zirconium-methyl or -phenyl bonds.[27]

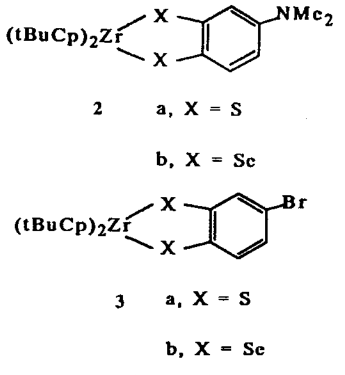
However, starting from bis(t-butylcyclopentadienyl)diphenylzirconium, only the diselenium metallacycle **1** was isolated in a good yield.[24,25]



1

This reaction was still observed when the benzene ring was substituted by a methyl[24] or a methoxy[29] group.

Continuing our researches in this field, we report here the synthesis and some synthetic potentialities of complexes **2** and **3** functionalized on the benzene ring (Scheme 3).



Scheme 3

EXPERIMENTAL

Materials and methods

All the zirconium complexes were synthesized and handled under an argon atmosphere. Solvents were dried and deoxygenated by sodium benzophenone ketyl complex and distilled just before use. Melting points were measured with a Kofler beam without any correction. Microanalyses were performed by the Service Central d'Analyses du CNRS. The mass spectra were recorded by the Service de Spectroscopie du CNRS from the electronic ionization (70 eV) of the sample. ^1H NMR spectra were obtained on a JEOL FX100 apparatus from deuterochloroform or deuterobenzene solutions containing tetramethylsilane as reference (abbreviations: s, singlet; d, doublet; t, triplet; pt, pseudo-triplet). Infrared spectra were recorded with a Perkin–Elmer 580B spectrometer from potassium bromide dispersion for solid samples or tetrahydrofuran solutions for liquids. Gas chromatography was performed with a Packard 427 chromatograph (capillary column, carbowax 20M, 25 m length).

Bis(t-butylcyclopentadienyl)zirconium dichloride was obtained from the reaction of t-butylcyclopentadienyl-lithium on zirconium tetrachloride.[30,31]

Flash chromatography was realised according to Still[32] with Merck 9385 silica gel (0.040–0.063 mm) as adsorbent. Neutral Merck 1077 alumina (activity I) was used for other liquid chromatography.

Commercial halides, used as received, were the initiators of the electrophilic cleavages.

Syntheses

Bis(t-butylcyclopentadienyl)-di(*p*-dimethylaminophenyl)zirconium (4)

A solution (0.225 mol dm^{-3}, acidic titration) of *p*-dimethylaminophenyl-lithium[33] was prepared from lithium chips (0.7 g; 0.1 mol) and *p*-dimethylaminobromobenzene (10 g; 0.05 mol) in diethyl ether (175 cm^3).

An aliquot (25 cm^3; 5.60 mmol) was slowly added at 0 °C to bis(t-butylcyclopentadienyl)-zirconium dichloride (1 g; 2.50 mmol) in diethyl ether (20 cm^3). After complete addition, the mixture was stirred for 1 h at 0 °C and 2 h at room temperature. The solvent was evaporated under reduced pressure and the yellow residue was

Table 1 Analytical data for diarylzirconocenes **4** and **5** and dichalcogenophenylenezirconocenes **2** and **3**

Compound	Molecular formula	Analysis (%) C Calcd	Analysis (%) C Found	Analysis (%) H Calcd	Analysis (%) H Found	Yield (%)	M.p. (°C)
4	$C_{34}H_{46}N_2Zr$	71.15	71.3	8.08	8.1	68	152–153
5	$C_{30}H_{34}Br_2Zr$	55.81	55.9	5.31	5.3	58	176–177
2a	$C_{26}H_{35}NS_2Zr$	60.41	60.1	6.82	6.9	64	158–159
2b	$C_{26}H_{35}NSe_2Zr$	51.14	50.9	5.78	5.6	76	130–131
3a	$C_{24}H_{29}BrS_2Zr$	52.15	51.9	5.29	5.4	67	173–174
3b	$C_{24}H_{29}BrSe_2Zr$	44.59	44.2	4.52	4.7	74	132–133

extracted with toluene (40 cm^3) to separate lithium chloride by filtration. The crude product obtained by removing the toluene was recrystallized from toluene/heptane (1:1), leading to yellow crystals, m.p. 152–153 °C (0.98 g, yield 68%).

^{1}H NMR (C_6D_6): δ 7.46 (d, 4H; Ph), 6.56 (d, 4H; Ph), 6.44 (pt, 4H; Cp), 6.02 (pt, 4H; Cp), 2.60 (s, 12H; CH_3), 1.03 (s, 18H; t-Bu).

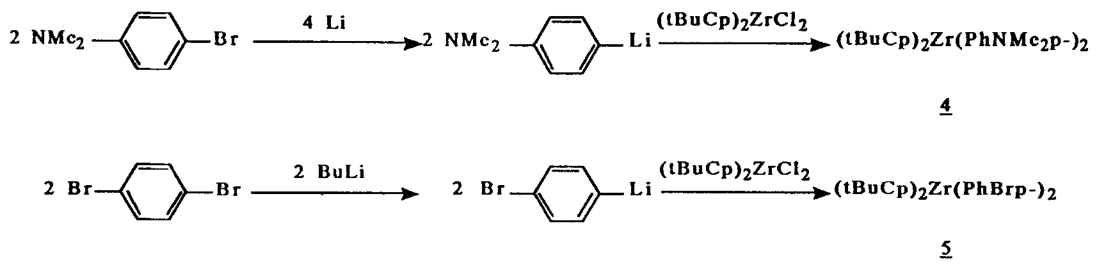
Bis(t-butylcyclopentadienyl)-di(*p*-bromophenyl)zirconium (5)

At room temperature, n-butyl-lithium solution in hexane (15 cm^3, 1.45 mol dm^{-3}) was added dropwise to *p*-dibromobenzene (5 g, 21 mmol) in 80 cm^3 of diethyl ether. The solution was stirred for 1 h and filtered off. Yield 90% (0.2 mol dm^{-3}, acidic titration). An aliquot (75 cm^3) was slowly added at 0 °C to 3 g (7.4 mmol) of

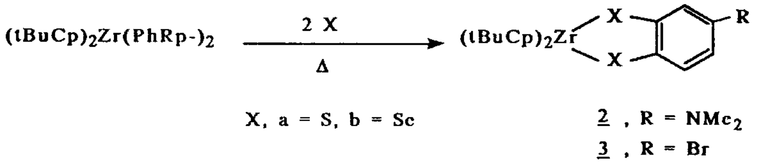
Table 2 Experimental conditions and analytical data for compounds **6** to **8**

Compound	Reaction time (h)	Temperature (°C)[a]	Chromatography[b] Adsorbent	Chromatography[b] Solvent	Recrystallization solvent[c]	Yield (%)	Melting point (°C)	Molecular formula	Analysis (%) C Calcd	Analysis (%) C Found	Analysis (%) H Calcd	Analysis (%) H Found
6a	48	r.THF	A	E	[d]	44	108	$C_{12}H_{13}N_3S_2$	54.72	54.5	4.97	4.7
6b	48	r.THF	A	E	[d]	63	112	$C_{12}H_{13}N_3Se_2$	40.35	40.9	3.66	3.2
6c	72	r.t.	A	E	F	44	80	$C_{10}H_7N_2S_2Br$	40.14	40.3	2.35	2.0
6d	16	r.t.	A	C	F	43	88	$C_{10}H_7N_2Se_2Br$	30.56	30.8	1.79	1.8
7a	12	r.t.	B	C	—	65	Oil	$C_{22}H_{19}O_2NS_2$	67.15	66.8	4.87	5.0
7b	18	r.t.	B	C	—	69	Oil	$C_{22}H_{19}O_2NSe_2$	54.22	54.0	3.93	3.8
7c	48	r.THF	A	C	—	67	Oil	$C_{20}H_{13}O_2S_2Br$	55.95	56.4	3.05	3.0
7d	12	r.t.	A	C	—	72	Oil	$C_{20}H_{13}O_2Se_2Br$	45.92	45.6	2.50	2.2
8a	17	r.THF	A	C	[d]	65	124	$C_{11}H_{13}ONS_2$	55.19	54.8	5.47	5.1
8b	12	r.t.	A	C	[d]	74	125	$C_{11}H_{13}ONSe_2$	39.65	40.0	3.93	3.7
8c	48	r.THF	A	E	F	43	172	$C_9H_7OS_2Br$	39.29	39.6	2.56	2.4
8d	3	r.t.	A	E	F	45	174	$C_9H_7OSe_2Br$	29.29	29.5	1.91	2.0

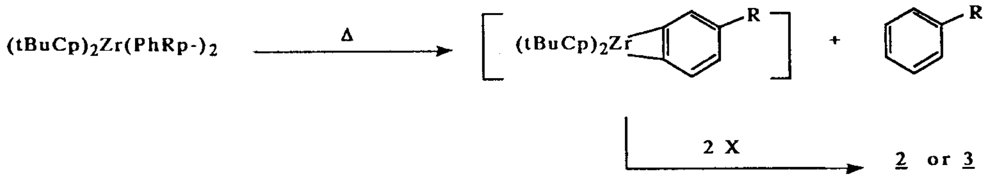
[a] r.THF, reflux THF; r.t. room temperature. [b] A, neutral alumina; B, silica gel; C, pentane/ether, 6:4; D, toluene/acetone, 9:1; E, (1) C/(2) D. [c] F, toluene/heptane, 1:1. [d] Pure compounds after chromatography.



Scheme 4

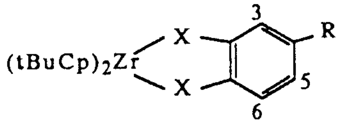


Scheme 5

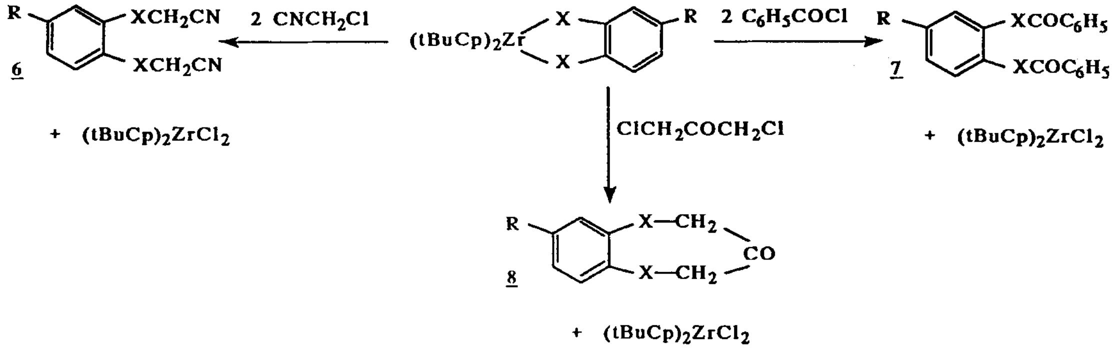


Scheme 6

Table 3 Spectroscopic data for zirconocene complexes **2** and **3**



Compound	^{1}H NMR (100 MHz, C_6D_6) δ (ppm/TMS); *J* (Hz)	Mass spectrometry main fragments, *m/z* (%)
2a X = S R = NMe$_2$	7.61 (d, 1, H^6, J = 8.79); 6.85 (d, 1, H$_3$, J = 2.68) 6.56 (dd, 1, H^5, J = 8.79 and 2.68); 5.82 (pt, 4, Cp); 5.63 (pt, 4, Cp); 2.48 (s, 6, CH$_3$); 1.22 (s, 18, t-Bu)	515 (M$^{\cdot+}$, 100); 394 (M − t-BuCp, 60); 378 (M − t-BuCp − CH$_4$, 100)
2b X = Se R = NMe$_2$	7.84 (d, 1, H^6, J = 8.66); 7.44 (d, 1, H^3, J = 2.93) 6.50 (dd, 1, H^5, J = 8.66 and 2.93); 5.89 (pt, 4, Cp); 5.72 (pt, 4, Cp); 2.47 (s, 6, CH$_3$); 1.17 (s, 18, t-Bu)	611 (M$^{\cdot+}$, 48); 554 (M − t-Bu, 2); 490 (M − t-BuCp, 44); 474 (M − t-BuCp − CH$_4$, 33)
3a X = S R = Br	7.96 (d, 1, H^3, J = 2.2); 7.33 (d, 1, H^6, J = 8.42) 7.07 (dd, 1, H^5, J = 8.42 and 2.20); 5.69 (pt, 4, Cp); 5.61 (pt, 4, Cp); 1.09 (s, 18, t-Bu)	552 (M$^{\cdot+}$, 61); 431 (M − t-BuCp, 65); 415 (M − t-BuCp − CH$_4$, 57)
3b X = Se R = Br	8.21 (d, 1, H^3, J = 2.2); 7.57 (d, 1, H^6, J = 8.18) 7.05 (dd, 1, H^5, J = 8.18 and 2.20); 5.73 (pt, 4, Cp); 5.70 (pt, 4, Cp); 1.06 (s, 18, t-Bu)	646 (M$^{\cdot+}$, 43); 525 (M − t-BuCp, 34); 509 (M − t-BuCp − CH$_4$, 29)



Scheme 7

$(t\text{-}BuC_5H_4)_2ZrCl_2$ in diethyl ether (90 cm^3). Stirring was maintained for 1 h at 0 °C and 2 h at room temperature.

Removing the solvent gave a residue which was extracted with toluene. Evaporation of the solvent and recrystallization from toluene/heptane (1:1) led to white crystals, m.p. 176–177 °C (2.7 g, yield 58%).

^{1}H NMR (C_6D_6): δ 7.26 (d, 4H; Ph), 6.98 (d, 4H; Ph), 5.99 (pt, 4H; Cp), 5.78 (pt, 4H; Cp), 0.82 (s, 18H; t-Bu).

Reaction of chalcogens on benzynezirconocenes generated *in situ*: general procedure

A mixture of diphenylzirconocene **4** or **5** (0.92 mmol) and elemental chalcogen (S or Se, 1.9 mmol) in heptane (50 cm^3) was refluxed for 18 h. The hot suspension was filtered off to eliminate the excess of chalcogen and the solvent was removed.

For the dimethylamino derivative, the residue was washed three times with pentane to exclude $PhNMe_2$.

In all cases red or orange crystals of dichalcogenophenylenezirconocenes **2** and **3** were obtained by recrystallization from heptane (analytical data in Table 1).

Electrophilic cleavages of dichalcogenophenylenezirconocenes 2 and 3: general procedure

The electrophile (1.8 mmol) in the THF (5 cm^3) was added dropwise at room temperature or at the solvent reflux to a red solution of **2** or **3** (0.9 mmol) in 20 cm^3 of tetrahydrofuran (THF). Some hours later the red colour became lighter, indicating the end of the reaction. The solvent was removed and the oily residue was extracted with diethyl ether (compounds **7**) to remove the insoluble $(t\text{-}BuCp)_2ZrCl_2$. The crude products were purified by flash chromatography. The compounds **6** and **8**, poorly soluble in diethyl ether, were directly chromatographed after elimination of the reaction solvent. Details and analytical data are reported in Table 2.

RESULTS AND DISCUSSION

Diphenyldialkylzirconocenes for which the benzene rings are substituted by a bromine atom or a dimethylamino group have been easily prepared by reacting dialkylzirconocene dichloride with the appropriate aryl-lithium according to Scheme 4.

When the complexes **4** and **5** were refluxed in heptane in the presence of two equivalents of chalcogen (S or Se), they led in good yields (60–80%) to dichalcogenometallacycles **2** and **3** respectively, as shown in Scheme 5.

A mechanism of the benzyne type could be reasonably involved to explain the formation of **2** and **3** (Scheme 6).

This mechanism is well supported by the fact that dimethylaniline was identified by ^{1}H NMR in the reaction mixture and pentane washings from compound **4**. From complex **5**, bromobenzene was characterized by analytical gas chromatography. These results point to the generation of

Table 4 Spectroscopic data for dichalcogenobenzene derivatives **6**, **7** and **8**

Compound	X	R	^1H NMR (100 MHz, $CDCl_3$) δ (ppm/TMS); *J* (Hz)	Mass spectrometry: main fragments, *m/z* (%)	Infrared spectroscopy, ν (cm^{-1})
6a	S	NMe_2	7.55 (d, 1, H^6, $J=8.66$); 6.78 (d, l, H^3, $J=2.80$); 6.60 (dd, 1, H^5, $J=8.66$ and 2.80); 3.70 (s, 2, CH_2); 3.48 (s, 2, CH_2); 3.04 (s, 6, Me)	263 ($M^{\cdot+}$, 54); 223 ($M-CH_2CN$, 60); 196 ($M-CH_2CN-HCN$, 61); 183 ($M-2CH_2CN$, 100); 139 ($C_6H_3S_2^+$, 7); 107 ($C_6H_3S^+$, 14)	$\nu_{CN}=2241$
6b	Se	NMe_2	7.58 (d, 1, H^6, $J=8.66$); 6.76 (d, 1, H^3, $J=2.68$); 6.56 (dd, 1, H^5, $J=8.66$ and 2.68); 3.47 (s, 2, CH_2); 3.33 (s, 2, CH_2); 3.03 (s, 6, Me)	359 ($M^{\cdot+}$, 29); 319 ($M-CH_2CN$, 13); 279 ($M-2CH_2CN$, 100)	$\nu_{CN}=2220$
6c	S	^{79}Br	7.63 (m, 1, Ph); 7.51 (m, 2, Ph); 3.69 (s, 2, CH_2); 3.63 (s, 2, CH_2)	298 ($M^{\cdot+}$, 62); 258 ($M-CH_2CN$, 38); 231 ($M-CH_2CN-HCN$, 87); 218 ($M-2CH_2CN$, 100); 179 ($C_6H_3S_2CH_2CN$, 41); 139 ($C_6H_3S_2$, 78)	$\nu_{CN}=2220$
6d	Se	^{79}Br	7.65 (m, 1, Ph); 7.49 (m, 2, Ph); 3.49 (s, 2, CH_2); 3.45 (s, 2, CH_2)	394 ($M^{\cdot+}$, 25); 354 ($M-CH_2CN$, 41); 314 ($M-2CH_2CN$, 100); 235 ($C_6H_3Se_2$, 21); 155 (C_6H_3Se, 15)	$\nu_{CN}=2236$
7a	S	NMe_2	7.95 (dd, 4, Ph); 7.50 (d, 1, H^6, $J=9.03$); 7.46 (m, 6, Ph); 7.03 (d, 1, H^3, $J=2.81$); 6.79 (dd, 1, H^5, $J=9.03$ and 2.81); 2.99 (s, 6, CH_3)	393 ($M^{\cdot+}$, 29); 272 ($M-NMe_2-C_6H_5$, 44); 105 ($C_6H_5CO^+$, 100); 77 ($C_6H_5^+$, 29)	$\nu_{C=O}=1681$
7b	Se	NMe_2	7.90 (dd, 4, Ph); 7.59 (d, 1, H^6, $J=8.70$); 7,47 (m, 6, Ph); 7.19 (d, 1, H^3, $J=2.93$); 6.75 (dd, 1, H^5, $J=8.70$ and 2.93); 3.02 (s, 6, CH_3)	489 ($M^{\cdot+}$, 6); 398 ($M-91$, 35); 357 ($M-132$, 13); 318 ($M-171$, 100); 279 ($Me_2NC_6H_3Se_2$, 67); 199 ($Me_2NC_6H_3Se$, 33); 105 ($C_6H_5CO^+$, 93); 77 ($C_6H_5^+$, 37)	$\nu_{C=O}=1689$
7c	S	Br	7.96 (m, 5) 7.54 (m, 8)	428 ($M^{\cdot+}$, 1); 307 ($M-121$, 9) 105 ($C_6H_5CO^+$, 100); 77 ($C_6H_5^+$, 100)	$\nu_{C=O}=1686$
7d	Se	Br	7.89 (m, 5) 7.50 (m, 8)	524 ($M^{\cdot+}$, 2); 312 ($M-212$, 3) 105 ($C_6H_5CO^+$, 100); 77 ($C_6H_5^+$, 74)	$\nu_{C=O}=1693$
8a	S	NMe_2	7.60 (d, 1, H^6, $J=8.66$); 7.11 (d, 1, H^3, $J=2.93$); 6.59 (dd, 1, H^5, $J=8.66$ and 2.93); 3.43 (s, 2, CH_2); 3.34 (s, 2, CH_2); 2.99 (s, 6, CH_3)	239 ($M^{\cdot+}$, 100); 196 ($M-43$, 50)	$\nu_{C=O}=1690$
8b	Se	NMe_2	7.83 (d, 1, H^6, $J=8.54$); 7.39 (d, 1, H^3, $J=2.93$); 6.59 (dd, 1, H^5, $J=8.54$ and 2.93); 3.38 (s, 2, CH_2); 3.33 (s, 2, CH_2); 2.99 (s, 6, CH_3)	335 ($M^{\cdot+}$, 100); 292 ($M-43$, 28); 276 ($M-59$, 33); 255 ($M-80$, 34)	$\nu_{C=O}=1693$
8c	S	Br	7.81 (d, 1, H^3, $J=2.07$); 7.51 (d, 1, H^6, $J=8.18$); 7.37 (dd, 1, H^5, $J=8.18$ and 2.07); 3.62 (s, 2, CH_2); 3.60 (s, 2, CH_2)	274 ($M^{\cdot+}$, 53); 231 ($M-43$, 100)	$\nu_{C=O}=1700$
8d	Se	Br	8.17 (d, 1, H^3, $J=2.20$); 7.87 (d, 1, H^6, $J=8.18$); 7.42 (dd, 1, H^5, $J=8.18$ and 2.20); 3.45 (s, 4, CH_2)	370 ($M^{\cdot+}$, 100); 327 ($M-43$, 97)	$\nu_{C=O}=1685$

substituted benzynezirconocenes via the concerted elimination of a molecule of dimethylamino- or bromo-benzene from complexes **4** and **5** respectively.

To the best of our knowledge the formation of arynezirconocenes by the elimination of functionalized molecules has not been reported in the literature.

The zirconium complexes have been characterized by microanalyses, ^1H NMR and mass spectrometry. The values are reported in Table 3.

The ^1H NMR spectra exhibit three sets of signals for aromatic protons. Two coupling constants are observed: one lying at 2.2–3.0 Hz is related to the *meta*-coupling; the other constant in the 8.2–8.8 Hz field is due to protons in the *ortho* position.

It must be noted that the proton H^6 is the most deshielded for $R = Me$,[24] OMe[29] and NMe_2. On the contrary H^3 is the most deshielded for $R = Br$. In addition, the signals for a selenium-containing complex always appear at a lower field than those for the sulphur-containing analogue, as we have already reported.[29]

Two pseudo-triplets characteristic for a AA'BB' system of spins are attached to the cyclopentadienyl protons.

Electrophilic cleavages of complexes 2 and 3

As we have mentioned in our previous papers[35,36] the dichalcogen complexes react with various electrophiles affording zirconocene dichloride and *ortho*-dichalcogenated benzenic compounds. Complexes **2** and **3** have been opposed to mono- and bi-functional electrophiles (Scheme 7).

Most of the complexes **6** to **8** were prepared in good yield (60–70%). However, more or less decomposition during the chromatography (greater on silica gel than on alumina) causes the yield to be reduced.

The structures of the compounds obtained are directly related to their synthesis and are perfectly confirmed by ^1H NMR and mass spectrometry (Table 4).

The ^1H NMR spectra of the dimethylamino complexes are generally well resolved in the phenyl area and account for a 1,2,4-trisubstituted phenyl group (J_{ortho} 8–9 Hz, J_{meta} 2–3 Hz). The spectra are much more confused for bromine complexes **6** and particularly **7**, for which two phenyl groups are due to the electrophile.

Well resolved spectra are obtained for **8c** and **8d**. It is of interest to note a similar inversion for the chemical shift of H_3, H_6 to that above mentioned for zirconium complexes **2** and **3**.

The molecular peak is always observed in the mass spectra. The typical fragmentation pattern for the compound **6** is consistent with the loss of a CH_2CN group followed by the elimination of HCN or/and the second CH_2CN substituent; a more extensive fragmentation is subsequently observed.

However, rearrangements are noticed for compounds **7** and **8**, making the interpretation of the spectra difficult.

The infrared frequencies noted for ν_{CO} (1680–1700 cm^{-1}) and for ν_{CN} (2220–2241 cm^{-1}) are typical for the structures proposed.

CONCLUSION

We have shown that benzynezirconocenes are easily prepared by heating bis(t-butylcyclopentadienyl)-substituted diarylzirconium. The metalloarynes insert 2 mol of chalcogen (S, Se) affording new dichalcogen metallacycles which represent convenient synthons to prepare a large family of *ortho*-dichalcogenated benzenic compounds functionalized on the benzene ring. Extension of the method is currently being investigated.

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