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Exploring reactivity of a bis-sulfonium zirconocene-ate dimer: Synthesis of various zwitterionic phosphonium anionic zirconocene complexes

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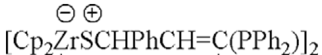
Dedicated to Professor Doctor Gerhard Erker on the occasion of his 60th birthday
in recognition of his important contributions in organometallic chemistry.

Abstract

Formal [3+2] cycloaddition reactions between the bis-sulfonium zirconocene-ate dimer  $[Cp_2\overset{\ominus}{Zr}\overset{\oplus}{S}CHPhCH{=}C(PPh_2)]_2$ **1a** and methylpropiolate, benzaldehyde and carbon disulfide afforded stable zwitterionic phosphonium zirconocene-ate complexes **2**–**4**, respectively, with two orthocondensed five-membered heterocycles. X-ray crystal structure of **4** has been determined. Elemental chalcogens (S, Se, Te) gave rise also to a new variety of five-coordinate zirconium(IV) complexes (**5**–**7**) by a formal [3+1] cycloaddition reaction. In these bicyclic zirconates, sulfur is included in a five-membered ring while the second chalcogen is in a four-membered one.
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Keywords: Zwitterionic complexes; Zirconocene-ate; Anionic zirconocene; Phosphonium; Sulfonium; Chalcogens

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1. Introduction

Among the tremendous development of the chemistry of transition metal complexes, zirconocene complexes play a particular role. Since the discovery of the catalytic properties of zirconium metallocenes, the usefulness of such complexes for the development of modern synthetic methodology has been demonstrated [1,2]. In these applications, bis(cyclopentadienyl) complexes have been extensively studied and presented very often a synthetical interest. Beside the classical 16-electron zirconium complexes, cationic 14-electron *ansa* metallocenes are the most active catalytic species in the homogeneous polymerization processes of olefins while transient 14-electron zirconocene equivalents such as alkene, alkyne or aryne complexes and related one are the key intermediate species in various stoichiometric transformations. In parallel, pentavalent 18-electron complexes are often postulated as key intermediates in a number of both stoichiometric and catalytic reactions. Only some of these zirconocene-ate complexes have been isolated and characterized by X-ray diffraction [3]. Furthermore few reactions are described starting from stable zwitterionic zirconocene complexes in marked contrast with the reactivity of unstable anionic ones. Recently we reported a novel class of reactive zirconates: the bis-sulfonium zirconocene-ate dimers **1** prepared from a toluene solution of diphenylphosphinoacetylene and a zirconocene thioaldehyde species generated *in situ* from dimethylzirconocene and RCH_2SH. These 18-electron zirconium complexes have been cleaved with borane to afford the corresponding monomeric BH_3 protected phosphinozirconathiolanes, thus pointing out a weak association through bridging sulfur atom in dimers **1** [4,5]. Pursuing our exploration of the reactivity of these promising dimers, here we describe the easy access to a novel class of stable zwitterionic phosphonium thiozirconocene-ate complexes containing up to three different Zr–X (X = S, C, O or Se or Te) σ-bonds using both

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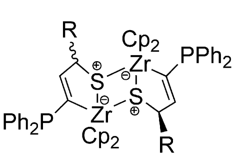
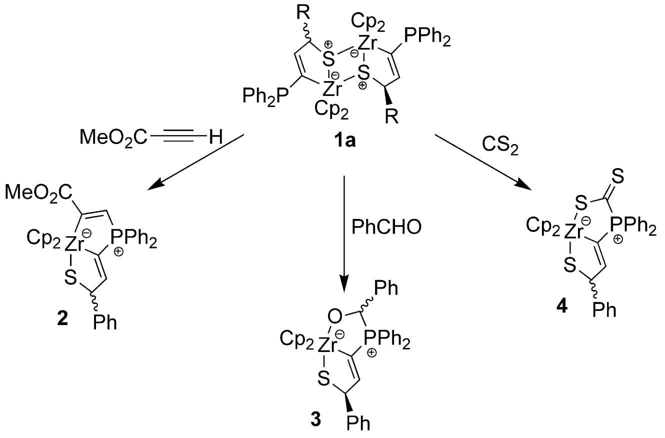
nucleophilic properties of tertiary phosphines and the Lewis acid character of zirconium(IV) complexes.



1a: R = Ph
1b: R = *p*-PhOMe
1c: R = Me

2. Results and discussion

Formal [3+2] cycloaddition reactions [6] involving the bis-sulfonium zirconocene-ate dimer **1a** and methylpropiolate, benzaldehyde or carbon disulfide led to zwitterionic phosphonium anionic zirconocene complexes (**2**–**4**) containing at least one group 16 atom (S, O) directly bonded to the metal (Scheme 1).



Scheme 1. Synthesis of zwitterionic (phosphonium anionic zirconocene-ate) complexes **2**–**4** by [3+2] cycloaddition.

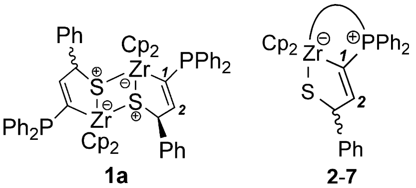
Thus, addition of $HC{\equiv}CCO_2Me$, PhCHO and CS_2 (2 equiv.) to a suspension of $[Cp_2\overset{\ominus}{Zr}S\overset{\oplus}{C}HPhCH{=}C(PPh_2)]_2$ **1a** (mixture of diastereoisomers in a 1:1 ratio) in toluene at room temperature gave in 72–84% isolated yield the complexes **2**–**4**. From their elemental analysis, compounds **2**–**4** appeared to have a correct composition for a 1:0.5 adduct of the two starting reagents [alkyne, aldehyde or heterocumulene: **1a**]. The ^{31}P NMR spectra showed the clean formation of a unique phosphorus product (singlet, $32.6 < \delta < 38.4$ ppm) in the region expected for a zwitterionic (phosphonium anionic zirconium) derivative [7–9]. As found for the analogous organo-zirconocene-ate complexes reported by Majoral's group (prepared from the phosphinozirconaindene $Cp_2ZrC(PPh_2)CH(o\text{-}C_6H_4)$ and various terminal alkynes), complex **2** was obtained as one regioisomer [7]. Surprisingly, only one racemate was detected for zirconate **3** suggesting a diastereoselective cycloaddition of benzaldehyde with the dimer **1a**. In addition to the two singlets corresponding to the unequivalent η^5-cyclopentadienyl ligands, the ^1H NMR spectra revealed the presence of the ethylenic and the methylenic protons from the thiolane skeleton (Table 1). Typical ^{13}C NMR data were detected for these pentavalent zirconocene-ate complexes (Table 1) [7–9]. The signal of the sp^2-carbon atom (C1) linked to zirconium and phosphorus was significantly shifted to high field with a low carbon–phosphorus coupling constant (δ from 158.7 to 164.7 ppm with $0 \leqslant {}^1J_{PC} < 8.3$ Hz, to be compared with $\delta = 181.3$, 180.8 ppm, ${}^1J_{PC} = 92.2$ Hz for **1a** and $\delta = 191.5$ ppm, ${}^1J_{PC} = 49$ Hz for $Cp_2ZrC(PPh_2)CH(o\text{-}C_6H_4)$ [10]). In marked contrast, the deshielded chemical shift at 172–

Table 1
Selected NMR spectroscopic data[a] for the anionic five-coordinate zirconocene complexes **2**–**7**[b]

Compound	$\delta^{31}P$	δ^1H (J_{HP})[a]		$\delta^{13}C$ (J_{CP})[a]	
		Cp	=CH	C1	C2
1a[c]	−1.1, −1.4	5.56, 5.71, 5.94, 6.08	6.78, 6.85 (15.6)	180.8, 181.8 (92.2)	154.2, 155.1 (9.2)
2	35.6	5.88, 6.03	7.91 (18.8)	159.5 (8.3)	174.4 (3.5)
3	32.6	5.99, 6.15	7.32	164.7	172.2
4	38.4	5.83, 6.10	7.31 (11.8)	158.7	176.8 (2.8)
5	33.0	5.92 (1), 6.06 (1)	7.45	152.3	164.8
6	19.6[d]	5.91, 6.07	7.56 (9.4)	152.4 (10.3)	165.3 (4.6)
7	−36.4[d]	5.88, 6.13	7.92	154.0 (20.7)	165.9

[a] Chemical shifts in ppm and couplings (between parentheses) in Hz.

[b] The numbering system is as follows:



[c] Both diastereoisomers.

[d] $J_{PSe} = 490$ Hz, $J_{PTe} = 1171$ Hz.

177 ppm was indicative of the ethylenic carbon atom (C2) of the initial dimer ($\delta = 154.2$, 155.1 ppm, $^2J_{PC} = 9.2$ Hz for **1a** and $\delta = 142.7$ ppm, $^2J_{PC} = 13.0$ Hz for $Cp_2\underline{ZrC(PPh_2)CH(o\text{-}C}_6H_4)$). Only significant change was observed for the carbon–phosphorus coupling constant of the asymmetric carbon (δ from 61.2 to 62.8 ppm with $31.3 \leqslant {}^3J_{PC} < 35.4$ Hz, to be compared with $\delta = 66.2$, 67.8 ppm, $^3J_{PC} = 11.0$ Hz for **1a**). It must be emphasized that these pentavalent zirconocene-ate complexes were very stable in comparison with the classical 16-electron organozirconocene complexes. No change has been observed after exposure to air owing to the electronically saturated zirconium centre. The structure of complex **4** was solved by an X-ray crystallography study which confirmed the overall geometry of the proposed zirconates **2**–**4**. Two independent molecules with very similar conformation were found in the asymmetric unit. Only one of the two molecular structures of complex **4** with relevant bond lengths and angles is illustrated in Fig. 1. For clarity, discussion of the geometry of **4** will be held for the structural parameters of this one. The zirconium atom is coordinated to two η^5-cyclopentadienyl rings with one sp^2-carbon atom and two different sulfur atoms. The Cp_2Zr fragment demonstrates typical features for bent metallocenes (Cp–Zr = 2.246(4), 2.223(4) Å and Cp(1)–Zr–Cp(2) = 127.1°). The molecular structure of **4** shows the structural characteristics of anionic five-coordinate $Cp_2Zr(IV)$ complexes previously reported [6–10]: (i) the large S(1)–Zr–S(2) angle value of 144.4(1)° due to the necessity of achieving a good orbital overlap for bonding the fifth ligand as well as the resolving of the steric requirements of the ligands [4–10] and consequently (ii) the three long Zr–X (X = C, S) bond lengths in the equatorial plane that bisects the Cp groups (Zr–C(13) 2.392(4), Zr–S(1) 2.6336(12), Zr–S(2) 2.7670(13) Å). The two S–C(14) bond lengths coming from the CS_2 reagent (S(2)–C(14) 1.687(5) and S(3)–C(14) 1.659(5) Å) are intermediate between single-bond and double-bond distances revealing a delocalized π-bonding scheme for this fragment (Chart 1) [9]. In addition the geometry around the phosphorus is fully consistent with a tetravalent cyclic phosphonium salt [6,9,11].

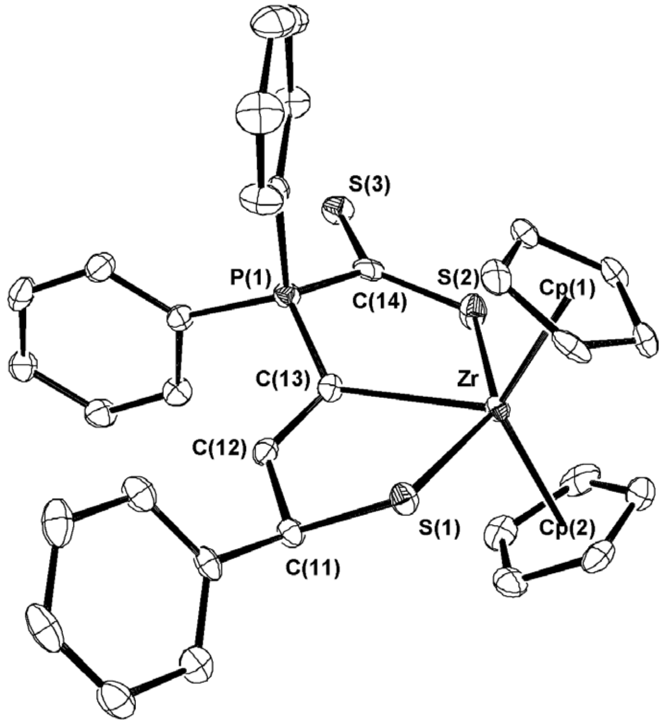


Fig. 1. ORTEP drawing of **4** and atom labeling scheme. For clarity only one of the two independent molecules found in the unit is represented. Selected bond lengths (Å) and angles (°): Zr–S(2) 2.7670(13), S(2)–C(14) 1.687(5), S(3)–C(14) 1.659(5), P(1)–C(14) 1.822(5), P(1)–C(13) 1.757(4), Zr–C(13) 2.392(4), C(13)–C(12) 1.355(6), C(12)–C(11) 1.499(6), C(11)–S(1) 1.838(4), Zr–S(1) 2.6336(12), S(2)–Zr–S(1) 144.4(1), S(2)–Zr–C(13) 73.5(1), C(13)–Zr–S(1) 70.9(1), Zr–S(2)–C(14) 113.96(17), Zr–C(13)–P(1)122.1(2), Zr–S(1)–C(11) 101.21(14), S(3)–C(14)–S(2) 126.7(3), C(13)–P(1)–C(14) 108.7(2).

In order to introduce other group 16 heteroelements in the framework of zwitterionic phosphonium zirconocene-ate complexes, cycloaddition reactions were performed with elemental chalcogens (Scheme 2).

Treatment at room temperature of **1a** with a large excess (3 equiv.) of sublimated S_8 afforded after 3 h the stable yellow complex **5** in 85% yield after workup. Elemental analysis and mass spectrum were in accord with a 1:0.5 [one sulfur atom: **1a**] adduct. In particular, ^{31}P and ^{13}C NMR spectra revealed the same representative features as for the above-described zwitterionic (phosphonium anionic zirconocene) complexes **2**–**4** (Table 1). Thus the four-coordinate phosphorus appeared in the expected region at 33.0 ppm. The central sp_2 carbon atom (C1) linked to zirconium

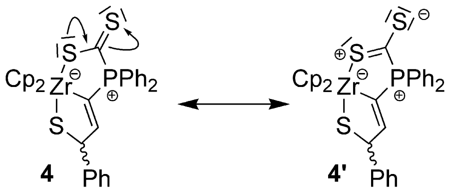
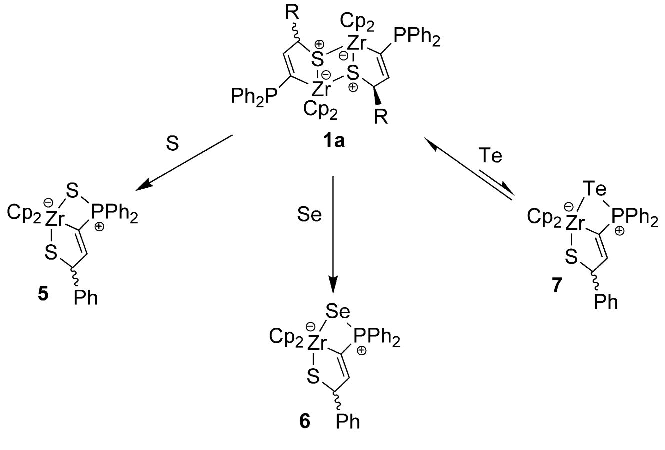


Chart 1.



Scheme 2. Synthesis of zwitterionic complexes **5**–**7** *via* sulfurization, selenization or tellurization of the bis-sulfonium zirconocene-ate dimer **1a**.

and phosphorus exhibited a typical shielded chemical shift (singlet at 152.3 ppm, to be compared with the similar resonance $\delta = 154.8$ ppm for the X-ray characterized cycloadduct of $(t\text{-Bu}\underbrace{Cp)_2ZrC(PPh_2)CPh(o\text{-}C}{}_6H_4)$ with S_8 [10]) while the second ethylenic carbon atom (C2) displayed a higher field chemical shift (164.8 ppm). Such formal [3+1] cycloaddition involving sulfur and the α-zirconated phosphane moiety in dimer **1a** have been extended to heavier chalcogens (Se, Te). Indeed reaction of **1a** with gray selenium was carried out at room temperature in toluene for 3 h leading to the green complex **6** with 85% yield after workup. Unexpectedly similar reaction conducted with elemental tellurium did not proceed. It was necessary to heat the reaction mixture during 2 days at 80 °C to form the compound **7** as a green solid with 80% yield. From their elemental analysis (and mass spectrum for **6**), these derivatives appeared to have a correct composition for a formally 1: 0.5 adduct of the starting reagents [Se or Te: **1a**]. Similar spectroscopic data were found to be closed to those of the above-described zirconate **5** (Table 1). In particular, in the ^{13}C NMR spectra, the resonance of the central sp^2 carbon bonded to zirconium and phosphorus (152.4 and 154.0 ppm, respectively) were closed to the one found in the zirconate **5**. The shielded ^{31}P chemical shifts (19.6 and −36.4 ppm, respectively) depending of the electronegativity of chalcogen atoms were in agreement with the phosphonium salt structure. In addition, the observed coupling constants between phosphorus and ^{77}Se or ^{128}Te (490 and 1171 Hz, respectively) indicated the presence of a selenium or a tellurium linked by a single-bond to the phosphorus centre (for instance J_{PSe} $(Ph_3PSe) = 738$ Hz and J_{PSe} $([Ph_3PSeCl]Cl) = 544$ Hz; J_{PTe} $(n\text{-}Bu_3PTe) = 1732$ Hz) [12–14]. Zirconates **6**–**7** demonstrating an unprecedented Zr–X (X = Se, Te) σ-bonds among the stable pentavalent anionic zirconocenes would have been of special interest to study for their molecular structure. Unfortunately, no suitable crystals for X-ray structural determination were obtained for these two compounds. Furthermore during our attempts to crystallize them, complex **7** was found to be instable in solution undergoing a slow detellurization as indicated by the appearance with time of a black precipitate in the flask. Indeed this reversible reaction was evidenced by the growth of the starting dimer **1a** in the ^{1}H and ^{31}P NMR spectra (four large Cp signals and two ^{31}P singlets for the mixture of diastereoisomeric dimers **1a** [4]). This particular behavior of the pentavalent complex **7** suggested a strained fused four-membered zirconacycle as a consequence of the large covalent radii of the tellurium atom.

3. Conclusions

We have shown that the bis-sulfonium zirconocene-ate dimer **1a**, owing to its weak bridging Zr–S bonds, behaves as a monomer in an analogous way to the phosphinozirco- naindene reported by Majoral's group offering the possibility to prepare an original class of zwitterionic phosphonium anionic thiozirconocene complexes, and especially the first examples of zirconates bearing a zirconium-heavier chalcogen (selenium or tellurium) σ-bond. We are currently studying the reactivity of this dimer in order to prepare unprecedented chalcogen-containing heterocycles.

4. Experimental

All reactions were carried out under argon using Schlenk-type glassware. Solvents, including deuterated solvents for the spectroscopic characterization, were dried and freshly distilled under argon from solutions of $NaK_{2.8}$/benzophenone (ether, pentane, THF), $NaK_{2.8}$ (toluene, benzene-d_6, THF-d_8), or CaH_2 (CH_2Cl_2, dichloromethane-d_2) prior to use. Reagents were purchased from commercial suppliers and used without further purification, except for CS_2 which was distilled and stored under argon. Nuclear magnetic resonance (NMR) spectra were recorded on Bruker Advance DRX 500 spectrometer at 300 K (^{1}H 500.13 MHz, ^{13}C 125.77 MHz and ^{31}P 202.46 MHz). Chemical shifts are reported in ppm relative to $SiMe_4$ (^{1}H; ^{13}C) or H_3PO_4 (^{31}P). ^{1}H and ^{13}C NMR assignments were confirmed by inverse gradient δ^1H–^{13}C HMQC and δ^1H–^{13}C HMBC NMR experiments. Electronic ionization (70 eV) Mass spectra (KRATOS Concept 32S/.) and elemental analysis (EAGER 200) were performed by the CSM (Centre de Spectrométrie Moléculaire) of the Université de Bourgogne.

4.1. Reaction of $[Cp_2\underbrace{\overset{\ominus}{Zr}\overset{\oplus}{S}CHPhCH{=}C}(PPh_2)]_2$ ***1a*** *with* $HC{\equiv}CCO_2Me$

To a suspension of **1a** (0.19 g; 0.17 mmol) in toluene (20 mL) was added 0.03 mL of methylpropiolate (0.34 mmol). The mixture was stirred for 45 min at room temperature and then evaporated to dryness. The resulting solid residue was extracted with 3 × 10 mL of ether and then washed with 10 mL of pentane yielding 0.15 g of zirconate **2** (0.24 mmol, 72%) as a red orange powder.

Anal. Calc. ($C_{35}H_{31}O_2PSZr$): C, 65.90; H, 4.90; S, 5.03. Found: C, 65.83; H, 4.93; S, 4.97%.

^{1}H NMR (dichloromethane-d_2): δ 3.52 (s, 3H, O*Me*), 5.14 (d, 1H, $J_{PH} = 15.8$ Hz, C*H*Ph), 5.88 (s, 5H, Cp), 6.03 (s, 5H, Cp), 6.49 (d, 1H, $J_{PH} = 38.8$ Hz, PC*H*═),7.01–7.32 (broad signal, Ph), 7.47 (m, Ph), 7.91 (d, 1H, $J_{PH} = 18.8$ Hz, ═C*H*) ppm.

^{13}C{^{1}H} NMR (dichloromethane-d_2): δ 51.5 (s, OMe), 61.2 (d, $J_{PC} = 31.3$ Hz, *C*HPh), 109.2 (s, Cp), 109.4 (s, Cp), 121.0 (d, $J_{PC} = 112.8$ Hz, P*C*H═), 126.6–129.7 (broad signal, Ph), 132.5 (d, $J_{PC} = 7.7$ Hz, Ph), 133.0 (d, $J_{PC} = 7.7$ Hz, Ph), 147.0 (s, *i*Ph), 159.5 (d, $J_{PC} = 8.3$ Hz, P*C*═), 174.4 (d, $J_{PC} = 3.5$ Hz, ═*C*H), 178.4 (d, $J_{PC} = 40.1$ Hz, *C*═O), 219.4 (d, $J_{PC} = 49.1$ Hz, ZrC═) ppm.

^{31}P{^{1}H} NMR (dichloromethane-d_2): δ 35.6 (s) ppm.

4.2. Reaction of $[Cp_2\underline{\overset{\ominus}{Zr}\overset{\oplus}{S}CHPhCH{=}C}(PPh_2)]_2$ **1a** with PhCHO

To a suspension of **1a** (0.44 g; 0.40 mmol) in toluene (15 mL) was added 0.65 mL of benzaldehyde in toluene solution (0.80 mmol; $C = 1.25$ mol/L). The mixture was stirred for 2 h at room temperature and then evaporated to dryness. THF (2 mL) was added, followed by pentane (25 mL). The resulting solid residue was washed twice with 10 mL of pentane yielding 0.40 g of zirconate **3** (0.61 mmol, 79%) as a white powder.

Anal. Calc. ($C_{38}H_{33}OPSZr$): C, 69.16; H, 5.04; S, 4.86. Found: C, 69.09; H, 4.99; S, 4.95%.

^{1}H NMR (dichloromethane-d_2): δ 4.92 (dd, 1H, $J_{PH} = 6.6$ Hz, $J_{HH} = 1.8$ Hz, SC*H*Ph), 5.99 (s, 5H, Cp), 6.15 (s, 5H, Cp), 6.19 (s, 1H, OC*H*Ph), 7.00–7.40 (broad signal, Ph), 7.32 (=C*H*, chemical shift detected by ^{1}H/^{13}C ghmbc experiment) ppm.

^{13}C{^{1}H} NMR (dichloromethane-d_2): δ 62.8 (d, $J_{PC} = 35.4$ Hz, S*C*HPh), 85.6 (d, $J_{PC} = 59.8$ Hz, O*C*HPh), 109.9 (s, Cp), 112.6 (s, Cp), 120.8 (d, $J_{PC} = 78.8$ Hz, *i*PPh$_2$), 126.6–130.0 (broad signal, Ph), 133.4–133.6 (broad signal, Ph), 135.7 (d, $J_{PC} = 8.0$ Hz, Ph), 141.2 (s, *i*PhCHO), 148.8 (s, *i*PhCHS), 164.7 (s, P*C*=), 172.2 (s, =*C*H) ppm.

^{31}P{^{1}H} NMR (dichloromethane-d_2): δ 33.8 (s) ppm.

4.3. Reaction of $[Cp_2\underline{\overset{\ominus}{Zr}\overset{\oplus}{S}CHPhCH{=}C}(PPh_2)]_2$ **1a** with CS$_2$

4.3.1. Preparation of zirconate **4**

To a suspension of **1a** (0.26 g; 0.23 mmol) in toluene (20 mL) was added 0.25 mL of carbon disulfide in toluene solution (0.47 mmol; $C = 1.85$ mol/L). The mixture was stirred for 2 h at room temperature and then evaporated to dryness. THF (2 mL) was added, followed by pentane (25 mL). The resulting solid residue was washed with 3 × 10 mL of pentane yielding 0.25 g of zirconate **4** (0.40 mmol, 84%) as an orange powder.

Anal. Calc. ($C_{32}H_{27}PS_3Zr$): C, 61.01; H, 4.32; S, 15.27. Found: C, 61.03; H, 4.19; S, 15.33%.

^{1}H NMR (dichloromethane-d_2): δ 4.99 (dd, 1H, $J_{PH} = 6.2$ Hz, $J_{HH} = 1.7$ Hz, C*H*Ph), 5.83 (s, 5H, Cp), 6.10 (s, 5H, Cp), 7.14 (m, Ph), 7.23–7.29 (broad signal, Ph), 7.31 (dd, 1H, $J_{PH} = 11.8$ Hz, $J_{HH} = 1.7$ Hz, =C*H*), 7.43 (m, Ph), 7.55 (m, Ph), 7.66 (m, ph), 7.74 (m, Ph), 8.00–8.05 (broad signal, Ph), ppm.

^{13}C{^{1}H} NMR (dichloromethane-d_2): δ 62.5 (d, $J_{PC} = 34.7$ Hz, *C*HPh), 111.0 (s, Cp), 111.5 (s, Cp), 124.0 (d, $J_{PC} = 79.8$ Hz, *i*PhP), 127.0 (s, Ph), 127.7 (d, $J_{PC} = 79.8$ Hz, *i*PhP), 128.3 (s, Ph), 128.9 (s, Ph), 129.4 (d, $J_{PC} = 11.5$ Hz, *o*PhP), 129.8 (d, $J_{PC} = 11.5$ Hz, *o*PhP), 133,2 (d, $J_{PC} = 2.9$ Hz, *p*PhP), 133.7 (d, $J_{PC} = 8.8$ Hz, *m*PhP), 134.0 (d, $J_{PC} = 2.9$ Hz, *p*PhP), 134.1 (d, $J_{PC} = 8.8$ Hz, *m*PhP), 147.0 (s, *i*Ph), 158.7 (s, P*C*=), 176.8 (d, $J_{PC} = 2.8$ Hz, =*C*H), 234.3 (d, $J_{PC} = 64.0$ Hz, *C*=S) ppm.

^{31}P{^{1}H} NMR (dichloromethane-d_2): δ 40.0 (s) ppm.

4.3.2. X-ray crystal structure analysis of **4**

Suitable single crystals of zirconate **4** were grown from dichloromethane solution, layered with pentane by slow diffusion at ambient temperature. Data were collected with a Nonius KappaCCD diffractometer at 110(2) K. The structure was solved *via* a Patterson search program and refined with full-matrix least squares methods based on F^2 (SHELX-97) [15] with the aid of the WINGX [16] program. All non-hydrogen atoms were refined with anisotropic thermal parameters. All H atoms were placed in idealized positions and refined using a riding model [Uiso(H) = 1.2U_{eq}(C)].

Formula $C_{32}H_{27}PS_3Zr$, $M = 629.91$, monoclinic, space group = $P2_1/c$ (No. 14), $a = 26.7008(6)$, $b = 13.9106(3)$, $c = 14.6635(2)$ Å, $\beta = 96.087(1)°$, $V = 5415.7(2)$ Å^3, $Z = 8$, $F(000) = 2576$, $D_{calc} = 1.545$ g/cm^3, mixture of ϕ rotations and ω scans, $\lambda = 0.71073$ Å, $\mu = 0.718$ mm^{-1}, $\sin(\theta)/\lambda_{max} = 0.65$ Å^{-1}, orange crystal 0.35 × 0.30 × 0.20 mm, index ranges = h: −33; 33, k: −17; 17, l: −17; 18, absorption correction *via* SCALEPACK, reflections collected (RC) = 32133, independent RC (IRC) = 11053 (R(int) = 0.0892), IRCGT = IRC ($I > 2\sigma(I)$) = 7308, refinement method with full-matrix LS on F^2, data/restraints/parameters = 11053/0/667, R for IRCGT: R_1[1] = 0.0532 wR_2[2] = 0.1023, R for IRC: R_1[1] = 0.1014 wR_2[2] = 0.1189, Goodness-of-fit[3] = 1.013, largest difference in peak and hole: $e = 0.572$ and −1.067 Å^{-3}.

4.4. Reaction of $[Cp_2\underline{\overset{\ominus}{Zr}\overset{\oplus}{S}CHPhCH{=}C}(PPh_2)]_2$ **1a** with S

To a suspension of **1a** (0.25 g; 0.23 mmol) in toluene (20 mL) was added a large excess of sulfur (0.04 g; 1.25 mmol; ≈3 equiv.). The mixture was stirred for 3 h at room temperature, and then was filtered. The volatiles were removed under vacuum and the resulting solid was washed with pentane (15 mL) yielding 0.23 g of zirconate **5** (0.39 mmol, 85%) as a yellow powder.

Anal. Calc. ($C_{31}H_{27}PS_2Zr$): C, 63.55; H, 4.65; S, 10.95. Found: C, 63.47; H, 4.61; S, 10.89%.

^{1}H NMR (benzene-d_6): δ 5.00 (d, 1H, $J_{HH} = 5.0$ Hz, C*H*Ph), 5.92 (d, 5H, $J_{PH} = 1.0$ Hz, Cp), 6.06 (d, 5H, $J_{PH} = 1.0$ Hz, Cp), 7.45 (m, 1H, =C*H*), 7.52–7.56 (broad signal, Ph), 7.83 (m, Ph) ppm.

^{13}C{^{1}H} NMR (THF-d_8): δ 61.1 (d, $J_{PC} = 40.0$ Hz, *C*HPh), 111.6 (s, Cp), 111.8 (s, Cp), 128.7–129.4 (broad signal, Ph), 131.1 (m, Ph), 131.8 (m, Ph), 132.5 (d, $J_{PC} = 62.3$ Hz, *i*Ph$_2$P), 134.5 (m, Ph), 147.5 (s, *i*Ph), 152.3 (s, P*C*=), 164.8 (s, =*C*H).

^{31}P{^{1}H} NMR (benzene-d_6): δ 33.0 (s) ppm.

EI MS (*m/z*): 584, M^{+}.

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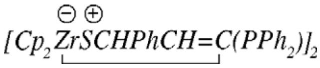
[1] $R_1 = \sum(||F_o| - |F_c||)/\sum|F_o|$.

[2] $wR_2 = [\sum w(F_o^2 - F_c^2)^2/\sum[w(F_o^2)^2]]^{1/2}$ where $w = 1/[\sigma^2(F_o^2) + 10.68P + (0.038P)^2]$ where $P = (\text{Max}(F_o^2,0) + 2 * F_c^2)/3$.

[3] Goodness of fit $= [\sum w(F_o^2 - F_c^2)^2/(N_o - N_v)]^{1/2}$.



4.5. Reaction of $[Cp_2\overset{\ominus}{Zr}\overset{\oplus}{S}CHPhCH{=}C(PPh_2)]_2$ **1a** with Se

To a suspension of **1a** (0.25 g; 0.23 mmol) in toluene (20 mL) was added a large excess of selenium (0.11 g; 1.39 mmol; ≈3 equiv.). The mixture was stirred for 3 h at room temperature, and then was filtered. The volatiles were removed under vacuum and the resulting solid was washed with pentane (15 mL) yielding 0.24 g of zirconate **6** (0.38 mmol, 85%) as a yellow green powder.

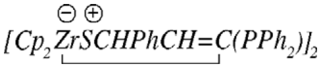
Anal. Calc. ($C_{31}H_{27}PSSeZr$): C, 58.84; H, 4.30; S, 5.07. Found: C, 58.89; H, 4.26; S, 5.14%.

^1H NMR (benzene-d_6): δ 5.03 (dd, 1H, $J_{HH} = 5.0$ Hz, $J_{PH} = 2.0$ Hz, C*H*Ph), 5.91 (s, 5H, Cp), 6.07 (s, 5H, Cp), 6.99–7.14 (broad signal, Ph), 7.23 (m, Ph), 7.52 (m, Ph), 7.56 (dd, 1H, $J_{PH} = 9.4$ Hz, $J_{HH} = 2.0$ Hz, =C*H*), 7.87 (m, Ph) ppm.

$^{13}C\{^1H\}$ (benzene-d_6): δ 60.3 (d, $J_{PC} = 40.1$ Hz, *C*HPh), 111.5 (s, Cp), 111.6 (s, Cp), 126.0 (s, Ph), 126.9 (s, Ph), 128.9 (s, Ph), 131.7 (d, $J_{PC} = 2.6$ Hz, *p*PhP), 131.8 (d, $J_{PC} = 10.3$ Hz, *o*Ph), 132.0 (d, $J_{PC} = 2.6$ Hz, *p*PhP), 132.2 (d, $J_{PC} = 10.3$ Hz, *o*PhP), 132.7 (d, $J_{PC} = 67.7$ Hz, *i*PhP), 133.1 (d, $J_{PC} = 67.7$ Hz, *i*PhP), 147.8 (s, *i*Ph), 152.4 (d, $J_{PC} = 10.3$ Hz, P*C*=), 165.3 (d, $J_{PC} = 4.6$ Hz, =*C*H) ppm.

$^{31}P\{^1H\}$ NMR (benzene-d_6): δ 19.6 (s/100%, d/7%, $J_{PSe} = 490$ Hz) ppm.

EI MS (*m*/*z*): 632, M^+.



4.6. Reaction of $[Cp_2\overset{\ominus}{Zr}\overset{\oplus}{S}CHPhCH{=}C(PPh_2)]_2$ **1a** with Te

To a suspension of **1a** (0.25 g; 0.23 mmol) in toluene (20 mL) was added a large excess of tellurium (0.17 g; 1.33 mmol; ≈3 equiv.). The mixture was heated at 80 °C during 48 h, and then was filtered. The volatiles were removed under vacuum and the resulting solid was washed with pentane (15 mL) yielding 0.25 g of zirconate **7** (0.37 mmol, 80%) as a green powder.

Anal. Calc. ($C_{31}H_{27}PSTeZr$): C, 54.64; H, 3.99; S, 4.71. Found: C, 54.71; H, 4.00; S, 4.62%.

^1H NMR (dichloromethane-d_2): δ 5.25 (dd, 1H, $J_{PH} = 5.0$ Hz, $J_{HH} = 1.9$ Hz, C*H*Ph), 5.88 (s, 5H, Cp), 6.13 (s, 5H, Cp), 7.05–7.37 (broad signal, Ph), 7.42 (m, Ph), 7.56 (m, Ph), 7.92 (dd, 1H, $J_{PH} = 12.8$ Hz, $J_{HH} = 1.9$ Hz, =C*H*) ppm.

$^{13}C\{^1H\}$ NMR (dichloromethane-d_2): δ 57.2 (d, $J_{PC} = 39.1$ Hz, *C*HPh), 111.2 (s, Cp), 112.3 (s, Cp), 128.9–130.0 (broad signal, Ph), 132.0–132.4 (broad signal, Ph), 132.7 (d, $J_{PC} = 11.5$ Hz, PhP), 133.3 (d, $J_{PC} = 11.5$ Hz, PhP), 140.3 (s, *i*Ph), 154.0 (d, $J_{PC} = 20.7$ Hz, P*C*=), 165.9 (s, =*C*H) ppm.

$^{31}P\{^1H\}$ NMR (dichloromethane-d_2): δ −36.4 (s/100%, d/7%, $J_{PTe} = 1171$ Hz) ppm.

5. Supplementary material

CCDC 640948 contains the supplementary crystallographic data for **4**. The data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.

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