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Isolation, dynamic NMR study and X-ray characterisation of a bis sulfonium zirconocene-ate dimer†

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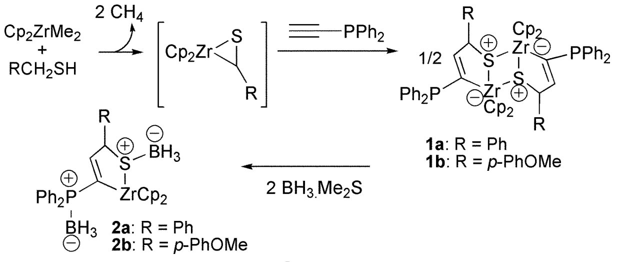
The novel dimer $[Cp_2\overline{Zr^{\ominus}S^{\oplus}CH(Ph)CH{=}C}PPh_2]_2$, the first example of a structurally characterised sulfur-bridged binuclear zirconathiolane complex, was prepared, characterised by NMR spectroscopy and X-ray crystallography, and some aspects of its solution behaviour were studied.

The very high reactivity of thio-, seleno- and tellurocarbonyl derivatives, formal analogs of carbonyl compounds, considerably restricts their use in organic chemistry.[1] Although some synthetical strategies of stabilisation (electronic or steric) have been proposed. The best way to circumvent these problems was certainly to use transition metal complexes. As in our group a primary objective concerns the development and the extension of zirconocene-based methodology for the elaboration of main group heterocycles, we developed for some years different coupling reactions of unsaturated heteroatom-containing molecules in the coordination sphere of zirconium.[2,3] More recently we have focused our efforts on zirconocene complexes of thioaldehydes and thioketones and related selenium and tellurium chemistry in order to prepare new chalcogenated heterocycles which have been regarded hard to prepare by classical methods. The present report deals with the synthesis and the full characterisation of a zirconacyclic precursor of unprecedented α-phosphino-substituted thiaheterocycles, potentially useful ligands in coordination chemistry.

A toluene solution of diphenylphosphinoacetylene and a zirconocene thioaldehyde equivalent $Cp_2Zr(Me)SCH_2Ph$, prepared from dimethylzirconocene and phenyl-methanethiol,[4] led to the precipitation of **1a** after 10 h of stirring at 90 °C (Scheme 1). This beige complex was isolated with variable yields (45% to 61%) depending on the contamination of the reaction mixture with some dithiolate $Cp_2Zr(SCH_2Ph)_2$.[5] Spectroscopic data were consistent with a dimeric formulation for **1a**.[6] The presence of a 1:1 ratio of two diastereomers was readily discernable in ^{31}P (two close singlets) and ^1H (for instance two sets of two Cp resonances: the four C_5H_5 ligands are equivalent by pairs in each diastereomer) NMR spectra.‡ Suitable crystals for X-ray diffraction study‡ were prepared by slow liquid-phase diffusion of pentane into a dichloromethane solution of **1a**. Fig. 1 shows the ORTEP view of the *meso* form of **1a** and important bond lengths and angles are summarized. The solid state structure corroborates that the five-membered zirconacycle arising from the reductive coupling reaction of $Ph_2PC{\equiv}CH$ with the transient $Cp_2Zr(\eta^2\text{-}S{=}CHPh)$ is an α-PPh_2-substituted zirconathiolane which is additionally stabilised by the formation of a coordination dimer. To our knowledge this is the first structural characterisation of an insertion complex starting from a thioaldehydezirconocene. In addition, X-ray data clearly confirmed the pentacoordinated character of **1a**: the two zirconium–sulfur distances Zr(1)–S(1) and Zr(1)–S(1a) and the large angle value C(1)–Zr(1)–S(1a) are typical for five-coordinated Cp_2–Zr(IV) complexes.[7,8] The Zr(1)–S(1a) distance (2.752(1) Å) is slightly shorter than the Zr–S bond length found in the complex $Cp_2\overline{Zr^{\ominus}C(Ph_2P^{\oplus}S)}{=}CPh(o\text{-}\underline{C_6}H_4)$ (2.797(1)Å).[2] Moreover the anionic character of zirconium atom for **1a** is consistent with the very large coupling constant J_{CP} (92.2 Hz) found in ^{13}C NMR spectrum for the *sp²* carbon PC= directly linked to the metal. This value compares well with the one found in the phosphonium zirconocene-ate complex $Cp_2\overline{Zr^{\ominus}C(Ph_2P^{\oplus}CH{=}C}PPh_2){=}CH(o\text{-}\underline{C_6}H_4)$ (97.6 Hz).[9] The long bridging Zr–S bonds can let us suppose of a weak interaction between each monomer. Therefore the variable-temperature NMR study of **1a** was anticipated. In the dynamic ^1H NMR spectra, broadening of the cyclopentadienyl resonances occurred on warming around 340 K (Fig. 2). Increasing the temperature also caused broadening of the resonances of –CHPh and =CH protons at lower temperatures. The same phenomenon was observable in variable-temperature ^{31}P NMR spectroscopy. The solution behaviour exhibited by **1a** was attributed to the rapid monomer–dimer equilibrium outlined in Scheme 2. From the temperature-dependent ^1H NMR spectra an activation energy of ΔG^* (343 K) = 69.9 ± 2 kJ.mol^{-1} at the coalescence temperature of the C_5H_5 resonances was estimated for the intermolecular equilibration of the **1a** dimers. This is in accord with the data found in catecholato-zirconocene dimers where the activation energy was above 90 kJ.mol^{-1} for a stronger zirconium–oxygen association.[10]

Under the same experimental conditions, dimeric complexes **1b** were formed after treatment of Cp_2ZrMe_2 with (4-methox-



Scheme 1

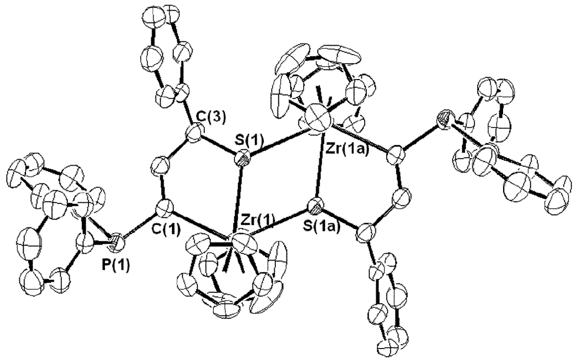


Fig. 1 Molecular structure of **1a**. Selected bond lengths (Å) and angles(°): Zr(1)–C(1) 2.399(3), Zr(1)–S(1) 2.574(1), Zr(1)–S(1a) 2.752(1); C(1)–Zr(1)–S(1a) 131.49(6), S(1)–Zr(1)–S(1a) 60.51(6), Zr(1)–S(1)–Zr(1a) 119.49(6), Zr(1)–S(1)–C(3) 110.64(6), Zr(1a)–S(1)–C(3) 127.24(6).

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† Electronic supplementary information (ESI) available: typical experimental procedure, physical and spectroscopic data of all new compounds and VT NMR studies of **1a–c**. See http://www.rsc.org/suppdata/cc/b3/b312954c/

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yphenyl)methanethiol and diphenylphosphinoacetylene (Scheme 1). ^{31}P, ^{1}H and ^{13}C NMR data of **1a** exhibited the same characteristic features as for the sulfur-bridged binuclear 2-phosphinozirconathiolane complex **1a** (δ ^{31}P (PPh$_2$) −0.4, −0.3 ppm; δ ^{1}H (Cp) 5.70, 5.79, 6.00, 6.16 (OMe) 3.28, 3.34 ppm; δ ^{13}C (Cp) 110.2, 110.5, 110.9, 111.3 (OMe) 55.6, 55.7 ppm).† Despite a lower solubility, the diastereoisomeric dimers **1a** showed very similar dynamic NMR spectra and the activation barrier for the fluxional process was found to be the same as for **1a** at the coalescence temperature of the C_5H_5 resonances.

In order to afford more information about the equilibrium mentioned in Scheme 2, and to verify our hypothesis of a monomeric intermediate, we heated at 90 °C a mixture of **1a** and **1b** for one hour.[11] Same experiment was also conducted at room temperature for a more long time (the mixed dimers became observable in the ^{1}H NMR spectrum after half a day). The new complexes **1a** were obtained along with the two known complexes **1a,b** (Scheme 3). Same result was obtained after heating Cp_2ZrMe_2, $Ph_2PC{\equiv}CH$ and a half-equivalent of the two thiols $PhCH_2SH$ and p-$MeOPhCH_2SH$. Spectroscopic NMR data were found to be quite simple. The ^{31}P NMR spectrum displayed beside the four singlets for **1a,b** four singlets for **1c**. The ^{1}H NMR spectrum exhibited as expected the four sets of two Cp resonances for **1a,b** and two sets of four Cp resonances for **1c** (the four cyclopentadienyl ligands are non equivalent in each diastereomer). The same type of fluxional process was indicated by the appearance of the ^{1}H NMR spectra at increasing monitoring temperature.§

Moreover, the cleavage of binuclear thiazirconacycles **1a,b** resulting from borane addition corroborated the weak association through bridging sulfur atoms. The BH_3 protected complexes **2a,b** were prepared quantitatively by addition of borane methylsulfide complex to the corresponding suspension in THF of dimers **1a,b** (Scheme 1). The NMR spectroscopic data for the obtained monomeric thiazirconacyclic complexes **2a,b** were typical of the phosphinozirconathiolane framework.† Their structural features would be interesting to compare with those of corresponding dimeric products, in particular for the geometry of the sulfur atom; but obtaining suitable crystals for X-ray structure analysis has failed to date.

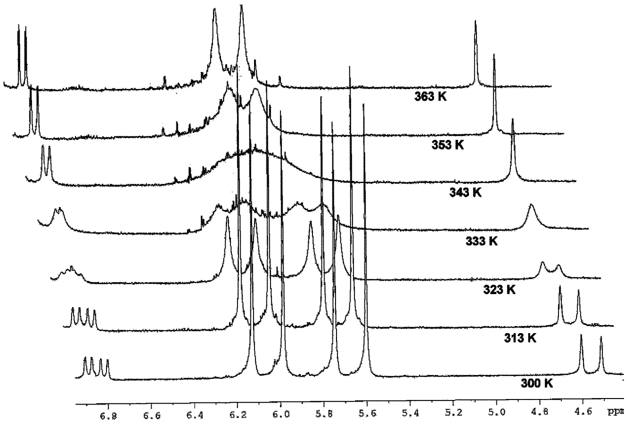
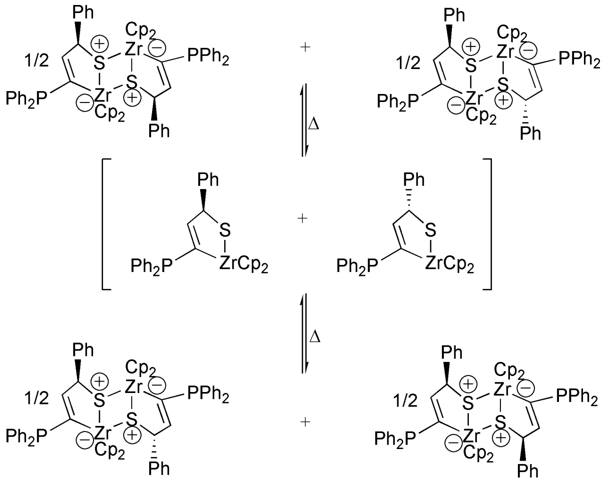
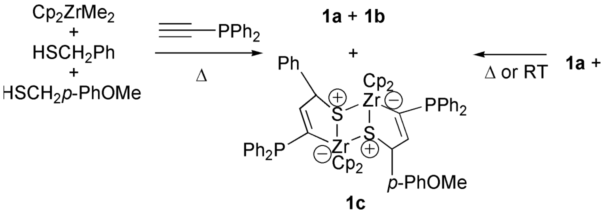


Fig. 2 Temperature-dependent ^{1}H NMR spectra of **1a** in toluene-d$_8$.



Scheme 2



Scheme 3

In conclusion, we have shown that a new organometallic precursor of α-phosphino-substituted thiaheterocycles can be easily prepared from a zirconocene complex of thiobenzaldehyde and diphenylphosphinoacetylene. The promising reactivity of these new dimeric complexes is currently under active investigation as is the unknown related chemistry with heavier congeners.

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Notes and references

‡ Most characteristic NMR data for **1a** (both diastereomers) and **2a** (300 K, Bruker DRX500). **1a**: ^{31}P{^{1}H} (toluene-d_8) δ −1.4, −1.1 (s); ^{1}H (toluene-d_8) δ 4.47, 4.56 (broad s, 2H, C*H*Ph), 5.56, 5.71, 5.94, 6.08 (s, 10H, H_{Cp}), 6.78, 6.85 (dd, J_{HP} = 15.6 Hz, J_{HH} = 2.3 Hz, 2H, =C*H*) ; ^{13}C{^{1}H} (CD_2Cl_2) δ 66.2, 67.8 (d, J_{CP} = 11.0 Hz, *C*HPh), 110.2, 110.5, 110.9, 111.3 (d, J_{CP} = 3.6 Hz, CH_{Cp}), 154.2, 155.1 (d, J_{CP} = 9.2 Hz, =*C*H), 180.8, 181.8 (d, J_{CP} = 92.2 Hz, Ph$_2$P*C*=). **2a**: ^{31}P{^{1}H} (C_6D_6) δ 27.0 (broad m); ^{1}H (C_6D_6) δ 0.10 (broad s, BH_3), 2.10 (broad d, J_{HP} = 105.7 Hz, BH_3), 4.12 (dd, J_{HP} = 5.5 Hz, J_{HH} = 1.9 Hz, 1H, C*H*Ph), 5.45, 6.00 (s, 5H, H_{Cp}), 6.78 (dd, J_{HP} = 27.0 Hz, J_{HH} = 1.9 Hz, 1H, =C*H*); ^{13}C{^{1}H} (C_6D_6) δ 64.3 (d, J_{CP} = 27.6 Hz, *C*HPh), 108.5, 110.8 (s, CH_{Cp}), 159.4 (d, J_{CP} = 6.3 Hz, =*C*H), 172.4 (d, J_{CP} = 21.8 Hz, Ph$_2$P*C*=).

§ *Crystal data* for **1a**: $C_{62}H_{54}P_2S_2Zr_2$, M = 1105.66, monoclinic, a = 15.724(5), b = 10.205(5), c = 15.825(5) Å, β = 98.201(5)°, V = 2538.0(17) Å^3, T = 293(2) K, space group $P\,21/c$, Z = 4, μ(MoKα) = 0.597 mm^{-1}, 19651 reflections measured, 4985 unique (R_{int} = 0.0484) which were used in all calculations. The final $wR(F^2)$ was 0.0875 (all data). CCDC reference number 215636. See http://www.rsc.org/suppdata/cc/b3/b312954c/ for crystallographic data in .cif or other electronic format.

1 H. Fischer, R. Stumpf and G. Roth, *Adv. Organomet. Chem.*, 1998, **43**, 125.
2 Y. Miquel, A. Igau, B. Donnadieu, J.-P. Majoral, L. Dupuis, N. Pirio and P. Meunier, *Chem. Commun.*, 1997, 279.
3 N. Pirio, S. Bredeau, L. Dupuis, P. Schütz, P. Meunier, B. Donnadieu, A. Igau and J.-P. Majoral, *Tetrahedron*, 2004, **60**, 1317.
4 S. L. Buchwald, R. B. Nielsen and J. C. Dewan, *J. Am. Chem. Soc.*, 1987, **109**, 1590.
5 S. Courtenay, S. Smith, E. Hollink, U. Blaschke, G. Kehr, R. Froehlich, G. Erker and D. W. Stephan, *Z. Naturforsch.*, 2002, **57b**, 1184.
6 Similar insertion products of formaldehyde or benzaldehyde into the zirconocene complex of bis(trimethylsilyl)acetylene were structurally characterised as dimeric and monomeric complexes respectivelly. N. Peulecke, A. Ohff, A. Tillack, W. Baumann, R. Kempe, V. V. Burlakov and U. Rosenthal, *Organometallics*, 1996, **15**, 1340.
7 V. Cadierno, M. Zablocka, B. Donnadieu, A. Igau and J.-P. Majoral, *Organometallics*, 1999, **18**, 1882.
8 The Zr–S distances found in the dimeric zirconocene dithiolate $Cp_2Zr(\mu\text{-}S(CH_2)_2S)_2ZrCp_2$ range from 2.56(1) to 2.80(2) Å. D. W. Stephan, *Organometallics*, 1991, **10**, 2037.
9 Y. Miquel, V. Cadierno, B. Donnadieu, A. Igau and J.-P. Majoral, *Organometallics*, 2000, **19**, 54.
10 G. Erker and R. Noe, *J. Chem. Soc., Dalton Trans.*, 1991, 685.
11 G. Erker, M. Mena, U. Hoffmann, B. Menjon and J. L. Petersen, *Organometallics*, 1991, **10**, 291.