Bis(trimethylsilyl)phosphinodithioformates, the Phosphorus Analogues of Dithiocarbamates; *X*-Ray Structures of [Zr(cp)$_2$(Cl)(η^2-S$_2$CPR$_2$)] and its Thermolysis Product [{Zr(cp)$_2$(μ-S)}$_2$] (cp = η-C$_5$H$_5$, R = SiMe$_3$)†

Evamarie Hey,[a] Michael F. Lappert,[a] Jerry L. Atwood,[b] and Simon G. Bott[b]

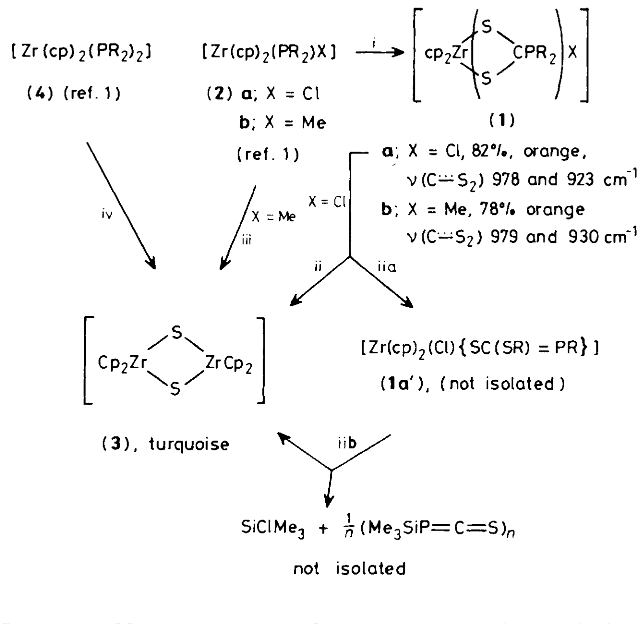
[a] *School of Chemistry and Molecular Sciences, University of Sussex, Brighton BN1 9QJ, U.K.*
[b] *Department of Chemistry, University of Alabama, Alabama 35486, U.S.A.*

Carbon disulphide inserts under ambient conditions into the Zr–P bond of [Zr(cp)$_2$(PR$_2$)X] [cp = η-C$_5$H$_5$, R = SiMe$_3$] to yield [Zr(cp)$_2$(η^2-S$_2$CPR$_2$)X] [X = Cl (**1a**) or Me (**1b**)] (having the novel phosphinodithioformato ligand, a phosphorus analogue of the dithiocarbamate), which upon heating affords [{Zr(cp)$_2$(μ-S)}$_2$] (**3**) {also obtained from S$_8$ and [Zr(cp)$_2$(PR$_2$)X] (X = Me or PR$_2$)}; the $\overline{\text{ZrSCS}}$ and $\overline{\text{ZrSZrS}}$ rings in (**1a**) and (**3**) are planar and the P environment in (**1a**) is pyramidal, with <Zr–S> 2.686(8) (**1a**) and 2.483(3) Å (**3**) and SZrS′ 63.4(2) (**1a**) and 89.5(2)° (**3**).

Whereas the co-ordination chemistry of the dithiocarbamato ligand $\bar{S}_2CNR^1R^2$ has been much explored, virtually nothing is known of the phosphorus analogue. We now report the synthesis of two such complexes of Zr^{IV}, of formula [Zr(cp)$_2${η^2-S$_2$CPR$_2$}X] [cp = η-C$_5$H$_5$, R = SiMe$_3$, and X = Cl (**1a**) or Me (**1b**)]. The *X*-ray structure of one of them, (**1a**), confirms the bidentate nature of the bonding (Figure 1), which is also inferred from i.r. data on compounds (**1**) (Scheme 1).

The orange complexes (**1**) were obtained by the facile insertion of carbon disulphide into the Zr–P bond of the appropriate recently discovered[1] bis(trimethylsilyl)phosphidozirconium complex [Zr(cp)$_2$(PR$_2$)X] [X = Cl (**2a**) or Me (**2b**); reaction i in Scheme 1]. They were isolated in high yield by crystallisation from n-C$_5$H$_{12}$–PhMe (**1a**) or (at −30 °C) n-C$_5$H$_{12}$ (**1b**). Attempts similarly to insert CO$_2$ or SO$_2$ into the ZrP bonds of complexes (**2**) yielded mixtures of products containing Zr–O bonds (i.r.), while CO did not react under ambient conditions with (**2a**).

Attempts to determine the m.p.s of complexes (**1**) showed that they turned orange–red at *ca.* 60 °C (**1a**) or 105 °C (**1b**) and thereafter appeared to decompose. N.m.r. spectra in [^{2}H$_8$] toluene were recorded, but there was evidence of decomposition. For complex (**1a**) the initial step (iia in Scheme 1) appeared to involve a 1,3-SiMe$_3$ migration[2] to afford the isomer (**1a′**) (proposed on the basis of i.r. and ^{1}H n.m.r. spectra), which subsequently on heating in PhMe eliminated SiClMe$_3$ to yield (iib in Scheme 1) the hot toluene-soluble dimeric zirconocene(IV) sulphide [{Zr(cp)$_2$-(μ-S)}$_2$] (**3**) and a yellow intractable solid believed to be a



Scheme 1. *Abbreviations:* cp = η-C$_5$H$_5$, R = SiMe$_3$, thf = tetrahydrofuran. *Reagents and conditions:* i, CS$_2$, n-C$_5$H$_{12}$, 25 °C, 1 h; ii, PhMe, 130 °C, 2 h, then 25 °C at 10^{-1} Torr; iii, excess S$_8$, thf, 25 °C, 1 day; iv, $\frac{1}{8}$S$_8$, n-C$_6$H$_{14}$, 25 °C [excess of (**4**) remained in solution]. N.m.r. chemical shift (δ) data (C$_7$D$_8$): (**1a**) ^{1}H (−50 °C): 5.71s (cp), 0.34d (SiMe$_3$) [$^4J(^{31}P^1H)$ 3.6 Hz], and ^{31}P (30 °C): −13.6s; (**1b**) ^{1}H (30 °C): 5.61s (cp), 0.46d (SiMe$_3$) [$^4J(^{31}P^1H)$ 5 Hz], 0.27s (Me), and ^{31}P (30 °C): −12.1s.

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† No reprints available.

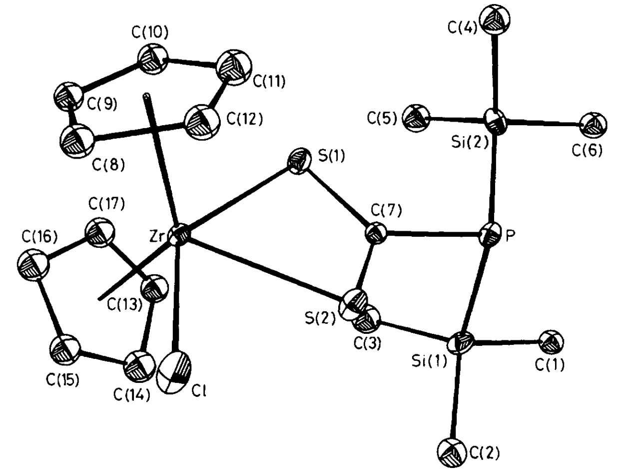

Figure 1. *X*-Ray structure and atom numbering scheme for $[\mathrm{Zr}(\eta\text{-}\mathrm{C_5H_5})_2(\mathrm{Cl})\{\eta^2\text{-}\mathrm{S_2CP(SiMe_3)_2}\}]$ (**1a**). Selected bond distances and angles are as follows: Zr–S(1) 2.733(7), Zr–S(2) 2.640(8), S(1)–C(7) 1.68(3), S(2)–C(7) 1.64(3), C(7)–P 1.87(2), <P–Si> 2.27(2) Å, S(1)–Zr–S(2) 63.4(2), Zr–S(1)–C(7) 87.7(8), Zr–S(2)–C(7) 91.9(9), C(7)–P–Si(1), 96.8(8), C(7)–P–Si(2) 107.6(9), and Si(1)–P–Si(2) 108.4(4)°.

polymeric phosphathioketene $(\mathrm{S{=}C{=}PR})_n$.

The zirconocene(IV) sulphide (**3**) was also accessible from $[\mathrm{Zr(cp)_2(PR_2)X}]$ [X = Cl (**2a**) or X = $\mathrm{PR_2}$ (**4**)],[1] by treatment with elemental sulphur at ambient temperatures, iii or iv in Scheme 1. *X*-Ray quality crystals were obtained from hot toluene.

The bis(trimethylsilyl)phosphinodithioformato ligand $\overline{\mathrm{S_2}}\mathrm{CP(SiMe_3)_2}$ in complex (**1a**) (Figure 1)‡ is bidentate. The most direct comparison with a dithiocarbamato analogue relates to $[\mathrm{Zr(cp)_2(Cl)}(\eta^2\text{-}\mathrm{S_2CNEt_2})]$ (**5**).[3] Both have a planar ZrSCSE framework (E = P or N) and similar endocyclic parameters [for (**5**): <Zr–S> 2.723(2), <C–S> 1.710(5) Å, and S–Zr–S′ 64.6(0)°]. However, whereas N is trigonal planar in (**5**), P in (**1a**) is pyramidal (the sum of bond angles at P 307°); the $\mathrm{PSi_2}$ plane is roughly orthogonal (78.7°) to the ZrSCSP plane in (**1a**), while the atoms $\mathrm{ZrSCSNC_2}$ in (**5**) are coplanar. The C=S double bond character is clearly greater in (**1a**) than (**5**), while the PC bond in (**1a**) is more nearly a single bond than the N$\overset{\cdots}{-}$C in (**5**).

Compound (**3**) (Figure 2)‡ was previously obtained either (i) in low yield from $[\mathrm{Zr(cp)_2Cl_2}]$ and $\mathrm{H_2S}$ + $\mathrm{NEt_3}$ (and assumed to be a dimer from its mass spectrum),[4] or (ii) from the dichloride, $\mathrm{Li[BHEt_3]}$, and $\mathrm{S_8}$ in thf;[5a] and an analogue was also made photochemically from $[\mathrm{Zr}(\eta\text{-}\mathrm{C_5H_4Bu^t})_2(\eta\text{-}\mathrm{C_4H_8})]$ and $\mathrm{S_8}$.[5b] However, the presence of the $\overline{\mathrm{ZrSZrS}}$ core for (**3**) is surprising in the light of the *X*-ray-authenticated trimer for the *O*-analogue $[\{\mathrm{Zr(cp)_2}(\mu\text{-O})\}_3]$.[6] Other Zr compounds containing Zr–S bonds include $[\mathrm{Zr}(\eta\text{-}\mathrm{C_5Me_5})_2\text{-}(\mathrm{S}_{3\ \mathrm{or}\ 5})]$,[4] but the only crystallographically characterised compounds containing $\mathrm{S^{2-}}$ are $[\mathrm{Zr_3}(\mu_3\text{-S})_2(\mu_2\text{-S})(\mu_2\text{-SBu^t})_2(\mathrm{BH_4})_4(\mathrm{thf})_2]$ (**6**),[7] $[\mathrm{Zr_6}(\mu_3\text{-S})_6(\mu_2\text{-SBu^t})_4(\mathrm{BH_4})_8(\mathrm{thf})_2]$, and $[\mathrm{Zr_3}(\mu_3\text{-S})(\mu_3\text{-SBu^t})(\mu_2\text{-SBu^t})_3(\mathrm{SBu^t})_6]$ (**7**);[8] the mean Zr–S distances are 2.594 in (**6**) and 2.601 Å in (**7**). The short Zr–S distances in (**3**), as well as its turquoise colour, may be indicative of delocalised π-electrons in the $\mathrm{(ZrS)_2}$ ring.

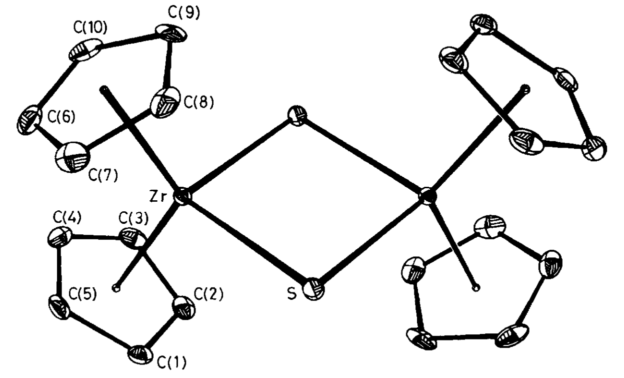

Figure 2. *X*-Ray structure and atom numbering scheme for $[\{\mathrm{Zr}(\eta\text{-}\mathrm{C_5H_5})_2(\mu\text{-S})\}_2]$ (**3**). Selected bond distances and angles are as follows: Zr–S 2.480(2) and 2.487(2) Å, S · · · S′ 3.50, Zr · · · Zr′ 3.53 Å, S–Zr–S′ 89.5(2)°.

Insertion of the heterocumulene $\mathrm{CS_2}$ into an $\mathrm{M{-}NR_2}$ bond is well known to yield a dithiocarbamate, but there appear to be only very few previous examples of related $\mathrm{M{-}PR_2/CS_2}$ reactions, with these restricted to main group elements, *e.g.*, M = $\mathrm{Sn^{IV}}$.[9] By contrast, insertion of $\mathrm{CS_2}$ into many transition metal M–X bonds often affords metallodithioformates $[\mathrm{M\{C(S)SX\}L}_n]$. The complex $[\mathrm{Hf}(\eta\text{-}\mathrm{C_5Me_5})\mathrm{Cl_2(PBu^t_2)}]$ reacted readily with CO under ambient conditions to yield $[\mathrm{Hf}(\eta\text{-}\mathrm{C_5Me_5})\{\eta^2\text{-}\mathrm{C(O)PBu^t_2}\}\mathrm{Cl_2}]$.[10]

Added in proof: Compound (**3**) has been independently prepared {from $[\mathrm{2r(cp)_2(CO)_2}]$ and $\mathrm{H_2S}$}, and its *X*-ray structure determined (with very similar results to those reported herein).[11]

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‡ *Crystal data.* (**1a**), $\mathrm{C_{17}H_{28}ClPS_2Si_2Zr}$, orthorhombic, space group $P2_1/c$, a = 7.159(9), b = 21.574(9), c = 15.925(6) Å, U = 2460 Å^3, Z = 4, D_c = 1.38 g cm^{-3}, μ = 8.23 cm^{-1}, 653 observed reflections, $2\theta_{\mathrm{max.}}$ = 44°, R = 0.047, R' = 0.051; (**3**), $\mathrm{C_{20}H_{20}S_2Zr_2}$, monoclinic, space group $P2_1/n$, a = 8.393(5), b = 8.245(2), c = 13.666(9) Å, β = 94.75(5)°, U = 942 Å^3, Z = 2, D_c = 1.79 g cm^{-3}, μ = 13.03 cm^{-1}, 1065 observed reflections, $2\theta_{\mathrm{max.}}$ = 44°, R = 0.030, R' = 0.038 [Mo-K_α radiation, λ = 0.71069 Å, T = 295 K]. Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.