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SYNTHESIS AND CHEMICAL PROPERTIES OF DICYCLOPENTADIENYLZIRCONIUM BIS(DIPHENYLARSENIDE) AND BIS(DIPHENYLANTIMONIDE), $[(\eta\text{-}C_5H_5)_2Zr(EPh_2)_2]$ (E = As OR Sb)

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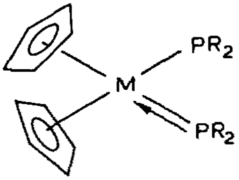
Summary

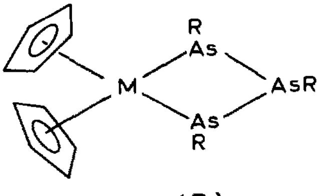
Treatment of Cp_2ZrCl_2 ($Cp = \eta\text{-}C_5H_5$) with $LiEPh_2$ (E = As or Sb) affords the corresponding pentelide complexes $Cp_2Zr(EPh_2)_2$. In the particular case of the $Cp_2TiCl_2/LiAsPh_2$ system there is evidence for reduction to $Cp_2TiAsPh_2$. The spectral and elemental characterisation and thermal degradation properties (from mass spectrometric studies) of these new compounds are discussed. The reactions of the metal(IV) pentelide complexes with protic reagents (including water) and halogen-containing compounds have been investigated, and compared with similar reactions for the phosphido-derivative $Cp_2Zr(PPh_2)_2$; the majority are metathetical reactions involving halide $/EPh_2$ exchange.

Introduction

The chemistry of Group IVA metal complexes containing an $M–ER_2$ bond (where M = Ti, Zr or Hf; E = N, P, As or Sb; R = alkyl or aryl) is only well-documented for the nitrogen derivatives [1]. We have previously reported various cyclopentadienylmetal complexes containing PR_2 groups e.g., $Cp_2M(PR_2)_2$ and $[Cp_2M(PR_2)]_2$ featuring the metal (M = Ti, Zr or Hf) in the 4+ and 3+ oxidation states respectively [2]. More recently a series of $Cp_2M(PR_2)_2$ compounds (where M = Zr or Hf; R = Et, Ph or cyclo-C_6H_{11}) based on a distorted tetrahedral geometry for metal(IV) and shown to contain both single and double metal–phosphorus bonds (see **A**) which interconvert rapidly on the NMR time scale, have been described [3].



(A)



(B)

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We now report an extension of this work to the arsenic and antimony derivatives, as part of a general comparative study of the chemistry of heterobimetallic species containing an early transition metal bonded to a Group VB element. There are no examples to date of compounds containing a Ti/Zr/Hf–Sb bond, and only two reports of covalent Ti–As bonds. The ion $[Cp_2Ti(AsPh_2)_2]^-$ has been postulated from ESR spectral evidence, but not isolated [4], while the cyclic system (**B**) has been obtained by the action of $(AsC_2H_5)_5$ on Cp_2TiCl_2 [5]. Other compounds where arsenic acts as a donor atom have been obtained as $CpTiCl_3 \cdot$ pdma [6], $[\eta\text{-}C_5H_4(SiMe_3)]TiCl_3 \cdot$ pdma [7] (pdma = *o*-phenylenebis(dimethylarsine)), and $(Cp_2TiCl_2) \cdot Ph_2P(CH_2)_2AsPh_2$ [8,9]. A related compound, which does not contain a Ti–As bond, has also been reported as $Cp_2Ti(CH_2)_3AsMe_2$ [10].

Results and discussion

Treatment of Cp_2ZrCl_2 with two mole equivalents of $LiEPh_2$ (E = As or Sb) in tetrahydrofuran (THF) at room temperature, resulted in mildly exothermic reactions, and the formation of brown (E = As), and dark red (E = Sb), solutions of the exchange products $Cp_2Zr(EPh_2)_2$.

$$Cp_2ZrCl_2 + 2\ LiEPh_2 \xrightarrow[25°C]{THF} Cp_2Zr(EPh_2)_2 + 2\ LiCl$$

The reagents $LiEPh_2$ (where E = As or Sb) can be prepared conveniently in THF solution by treating the corresponding EPh_3 with lithium metal; the yield of $LiEPh_2$ can be estimated by the quantity of lithium consumed in the reaction:

$$EPh_3 + 2\ Li \xrightarrow{THF} LiEPh_2 + LiPh$$

(E = As [11] or Sb)

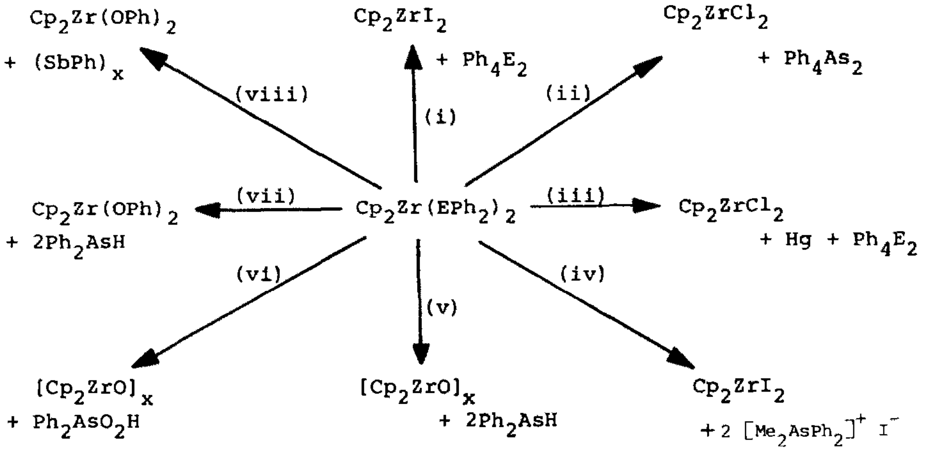
The unwanted LiPh side product is removed by reaction with a calculated amount of Bu^tCl [12]:

$$LiPh + Bu^tCl \rightarrow LiCl + PhH + Me_2C{=}CH_2$$

As in the case of the $Cp_2MCl_2/LiPPh_2$ (M = Zr or Hf) systems [3], no evidence was found for reduction to zirconium(III) species with either $LiAsPh_2$ or $LiSbPh_2$. However, some evidence for the reducing properties of $LiAsPh_2$ was found in the specific case of the $Cp_2TiCl_2/LiAsPh_2$ system, where the resulting dark brown solid approximates to $Cp_2TiAsPh_2$ (contaminated with As_2Ph_4). This product is similar in both its chemical behaviour and infrared (IR) spectrum to the phosphorus analogue based on titanium(III) viz., $[Cp_2TiPPh_2]_2$ [2]. The reduction potentials of Cp_2MCl_2 (M = Ti, Zr) certainly bear out the preference and tendency for $Ti^{IV} \rightarrow Ti^{III}$ [13].

Both $Cp_2Zr(AsPh_2)_2$ and $Cp_2Zr(SbPh_2)_2$ are sensitive to moist air, decomposing fairly rapidly over a few minutes to white solids. Both are soluble in hydrocarbons (benzene, toluene), ethers (THF, Et_2O) and acetonitrile, apparently without change, but are insoluble in n-pentane, and decompose in halogenated solvents. Reactions of $Cp_2Zr(EPh_2)_2$ with a number of protic species and halogen sources are summarised in Scheme 1.

Reactions were in general carried out in THF solutions using ca. 0.5 g of the zirconium pentelides and the products identified by ^1H NMR and IR spectral



(i)	1 equivalent of I_2 / THF	(E = As,Sb)	, 25°,	10 min
(ii)	1 equivalent of Ph_2AsCl / THF	(E = As)	, 25°,	10 min
(iii)	1 equivalent of $HgCl_2$ / THF	(E = As,Sb)	, 25°,	2 h
(iv)	excess MeI / MeI	(E = As)	, 25°,	2 h
(v)	1 equivalent of H_2O / C_6H_6	(E = As)	, 25°,	30 min
(vi)	Exposure to moist air	(E = As)	, 25°,	4 h
(vii)	2 equivalents of PhOH / THF	(E = As)	, 25°,	3 h
(viii)	2 equivalents of PhOH / THF	(E = Sb)	, 25°,	3 h

SCHEME 1. Some reactions of $Cp_2Zr(EPh_2)_2$.

comparisons with those of authentic samples. $Cp_2Zr(EPh_2)_2$ give smooth metathetical exchange with I_2 or Ph_2AsCl with the formation of Cp_2ZrI_2 and Cp_2ZrCl_2 respectively; the corresponding side products, e.g. colourless As_2Ph_4 and pale yellow Sb_2Ph_4, were subsequently isolated following extraction of the reaction residues with boiling n-hexane. Cp_2ZrCl_2 was the common product from the reactions of $Cp_2Zr(SbPh_2)_2$ with Ph_2AsCl, and $Cp_2Zr(EPh_2)_2$ (where E = As or Sb) with Ph_2PCl, but the mixed P/As/Sb side-product was not fully identified. In liquid methyl iodide, $Cp_2Zr(AsPh_2)_2$ reacts over several hours to give a yellow solution which slowly deposits crystals of $[Me_2AsPh_2]^+$ I^-. After removal of these crystals, slow addition of dry ether to the mother liquor resulted in Cp_2ZrI_2 depositing from solution. Although $Cp_2Zr(SbPh_2)_2$ also reacted with an excess of methyl iodide (over 6 h) to give a similar yellow solution of Cp_2ZrI_2, we were unable to isolate pure samples of $[Me_2SbPh_2]^+$ I^-. The rates of reaction of $Cp_2Zr(EPh_2)_2$ (where E = P, As or Sb) parallels the ease of formation of the corresponding onium salts, which is in the order P > As ≫ Sb [14].

No evidence was found in any of these halide/EPh_2 (E = As or Sb) exchange reactions for the existence of a mixed $Cp_2ZrX(EPh_2)$ product (X = halide), in contrast to the bis(diorganophosphide) derivatives where crystals of $Cp_2ZrCl(PPh_2)$ could be obtained [2].

Hydrolysis of $Cp_2Zr(AsPh_2)_2$ in benzene affords a white precipitate of $[Cp_2ZrO]_x$, (ν(Zr–O–Zr) 725 cm^{-1}) [15] and, after filtration and removal of the solvent, a colourless liquid identified as Ph_2AsH from its IR spectrum. The same solid $[Cp_2ZrO]_x$ was also formed on exposure of $Cp_2Zr(AsPh_2)_2$ to moist air, but in this case the accompanying arsenic derivative (which could be separated by washing with benzene) was Ph_2AsO_2H [16]. A similar reaction occurs with $Cp_2Zr(SbPh_2)_2$ yielding Ph_2SbO_2H [17], but in this case the polymeric nature of the latter prevents its removal from the $[Cp_2ZrO]_x$.

Phenol immediately decolourises solutions of $Cp_2Zr(AsPh_2)_2$; replacement of the THF solvent with n-hexane yields colourless crystals of $Cp_2Zr(OPh)_2$ on cooling, and concentration of the mother liquor affords Ph_2AsH. A similar reaction occurs with $Cp_2Zr(SbPh_2)_2$ in that $Cp_2Zr(OPh)_2$ is again produced, but instead of diphenylstibine, a dark brown solid precipitates slowly from the mother liquor. This solid is soluble in mineral acids, but insoluble in all common organic solvents. The analysis, properties, and IR spectrum which shows only absorptions attributable to phenyl groups, suggest an approximate formulation of SbPh. Such $(RSb)_x$ 'antimonobenzene' compounds are poorly characterised in the literature, and appear to be both polymeric and non-stoicheiometric [14,18].

The IR spectra of $Cp_2Zr(EPh_2)_2$ (E = As and Sb) in the 4000–200 cm^{-1} region are similar as expected, with bands at 1020, 805 cm^{-1} (E = As), and 1013, 808 cm^{-1} (E = Sb) consistent with the presence of Cp groups [19]. Other strong absorptions at 1573, 1430, 728, 691 and 452 cm^{-1} (E = As), and 1571, 1428, 725, 695 and 453 cm^{-1} (E = Sb), arise from the EPh_2 groups. The ^1H NMR spectra (in THF) show a single sharp resonance associated with the Cp protons (integral 10, δ 5.80 ppm (E = P) [2], δ 6.19 ppm (E = As), δ 6.31 ppm (E = Sb)) and bond multiplets for the phenyl protons (integral 20, δ 7.03–7.47 ppm (E = P) [2], δ 6.87–7.40 ppm (E = As), δ 7.0–7.62 ppm (E = Sb)). The downfield shift in the Cp resonance Sb > As > P is in the reverse order of that expected from simple electronegativity values and implies that $M(d_\pi)$–$E(p_\pi, d_\pi)$ bonding is more pronounced in the order Zr–Sb > Zr–As > Zr–P. Although we have no X-ray structural data available for the present pentelide complexes, a tetrahedral arrangement is favoured, as found in the recent structure determination of $Cp_2Hf(PEt_2)_2$ [3] (see A). Here the π-bonding involvement is quite conspicuous and involves discrete pyramidal and trigonal planar P centres thereby reinforcing earlier suggestions of such bonding being an incipient component of the Group IVA–E linkage [1]. A simple electron count (EAN) (2 × Cp (12), M^{IV} (0), σ-ER_2 (2), (σ-) (π-)ER_2 (4)] signifies $Cp_2M(ER_2)_2$ as 18-*e* complexes.

Mass spectrometric studies on $Cp_2Zr(AsPh_2)_2$, by electron impact at 20 eV, failed (surprisingly) to detect any zirconium containing fragments, but did reveal a series of ions derived from polyarsenic species e.g. $As_4Ph_7^+$ (m/z = 839), $As_3Ph_6^+$ (687), $As_2Ph_5^+$ (535), As_2Ph^+ (458), $AsPh_3^+$ (306), $AsPh_2^+$ (229), $As_2Ph_4^+$ (458), $AsPh_3^+$ (306), $AsPh_2^+$ (229), As_2Ph^+ (228), and $AsPh^+$ (152). These ions are presumably generated by thermal decomposition of $Cp_2Zr(AsPh_2)_2$ in the ion source at the temperatures (~ 200°C) used.

These results give a clear indication that arsenide and stibide derivatives of the Group IVA elements are stable, and in the light of recent results for the phosphide compounds [2,3,20], an equally varied chemistry should be expected. We are currently examining such possibilities further.

Experimental

All the reactions were carried out under argon using Schlenk apparatus. The solvents THF and benzene were distilled from Na-benzophenone and CaH_2 respectively, and degassed with Ar before use. IR spectra were recorded using a PE 580B spectrophotometer with samples as Nujol mulls between CsI plates. Hydrogen-1 NMR spectra were obtained using a PE R34 instrument (220 MHz) from THF solutions, with shifts being measured relative to $SiMe_4$ ($\delta = 0$ ppm) as standard. Microanalyses were obtained from BMAC Limited, Teddington.

Preparation of $Cp_2Zr(EPh_2)_2$ ($E = As$ or Sb)

Flattened Li wire (0.105 g, 15.1 mmol) was added to Ph_3As (4.0 g, 13.1 mmol) dissolved in THF (60 cm^3). An exothermic reaction ensued with the formation of deep red Ph_2AsLi. After the reaction was complete, the solution was filtered and unconsumed Li (0.041 g, 5.96 mmol) was recovered. *Care should be taken in handling the recovered Li as it is often spontaneously inflammable.* Bu^tCl (0.85 g, 9.14 mmol) was added to the deep red solution, and after stirring for 30 min Cp_2ZrCl_2 (1.34 g, 4.58 mmol) in THF (50 cm^3) was added dropwise to give a deep red/brown solution. The solvent was removed in vacuo, and the dark solid thus produced extracted with 2 × 100 cm^3 portions of benzene. Concentration of the solvent to 50 cm^3, and addition of 100 cm^3 of dry n-pentane precipitated dark red microcrystals of $Cp_2Zr(AsPh_2)_2$ (2.14 g, 92%). Analysis: Found: C, 59.9; H, 4.6. $C_{34}H_{30}As_2Zr$ calcd.: C, 60.1; H, 4.5%. The preparation of $Cp_2Zr(SbPh_2)_2$ (62.1% yield) was carried out similarly using $LiSbPh_2$. Analysis: Found: C, 44.0; H, 3.2. $C_{34}H_{30}As_2Zr$ calcd.: C, 42.7; H, 3.3%.

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