Synthesis and structural characterisation of the first hexaphosphastrontocene [Sr(η5-P3C2But2)2] and its pyrazine adduct

Matthew D. Francis, Peter B. Hitchcock and John F. Nixon*

School of Chemistry, Physics and Environmental Sciences, University of Sussex, Falmer, Brighton, UK BN1 9QJ. E-mail: j.nixon@sussex.ac.uk

Treatment of SrI_2 with 2 equivalents of $K[P_3C_2Bu^t_2]$ affords the hexaphosphastrontocene $[\{Sr(\eta^5\text{-}P_3C_2Bu^t_2)_2\}_\infty]$ which is polymeric in the solid state; treatment of this complex with an excess of pyrazine leads to the corresponding Lewis base adduct $[\{Sr(\eta^5\text{-}P_3C_2Bu^t_2)_2(\mu\text{-}C_4H_4N_2)\}_\infty]$ which is also polymeric in the solid state.

There has been increasing interest in the structure and bonding in metallocene complexes of the heavier alkaline earth elements (Ca, Sr, Ba) in recent years and several reviews have appeared.[1–3] With the exception of $[Ca(\eta^5\text{-}C_5H_5)_2]$ which is a three-dimensional polymer, these compounds are generally monomeric in the solid state or weakly associated, the degree of association depending on both the steric bulk of the cyclopentadienyl ligand and size of the central metal. Moreover, where the cyclopentadienyl ligands are not excessively bulky (typified by encapsulated metallocenes), additional coordination of Lewis bases may occur.

In contrast, however, sandwich compounds of the alkaline earth metals with heteroatom substituted cyclopentadienyl ligands are extremely rare. To the best of our knowledge only two structurally characterised examples, incorporating the 2,5-di-*tert*-butylpyrrolyl ligand and coordinated THF have been reported[4] namely $[M(\eta^5\text{-}NC_4H_2Bu^t_2)_2(THF)]$ **1** (M = Ca, Sr). Westerhausen and co-workers[5,6] showed that the 2,5-diphenyl-3,4-bis(trimethylsilyl)phospholyl ligand coordinates in an η^1-fashion to the metal dications $[M(THF)_4]^{2+}$ (M = Ca, Sr), however unpublished calculations by the same authors on the solvent free systems favour an η^5-ligating mode. Motivated by our recent observation[7] that the complex $[In(\eta^5\text{-}P_3C_2Bu^t_2)]$, containing the aromatic 3,5-di-*tert*-butyl-1,2,4-triphospholyl anion **2**, is a source of pure InP by chemical vapour deposition, we decided to react **2** with alkaline earth metal halides. We now report the first synthesis and structural characterisation of the hexaphosphastrontocene, $[\{Sr(\eta^5\text{-}P_3C_2Bu^t_2)_2\}_\infty]$ **3** and its pyrazine adduct $[\{Sr(\eta^5\text{-}P_3C_2Bu^t_2)_2(N_2C_4H_4)\}_\infty]$ **4**.

Thus, treatment of a THF solution of SrI_2 with two equivalents of **2** (Scheme 1) leads to the formation of air and moisture sensitive, but thermally stable, $[\{Sr(\eta^5\text{-}P_3C_2Bu^t_2)_2\}_\infty]$ **3** (*ca.* 50% yield). Complex **3**, which is a pale yellow solid, can be extracted from the initial reaction residue with toluene but sublimation or prolonged evacuation of the extracted residue renders it insoluble in all but donor solvents. We believe the initially formed complex is a THF solvated monomeric species $[Sr(\eta^5\text{-}P_3C_2Bu^t_2)_2(THF)_n]$ which readily loses THF to afford polymeric strands of **3** (*vide infra*). This behaviour also occurs
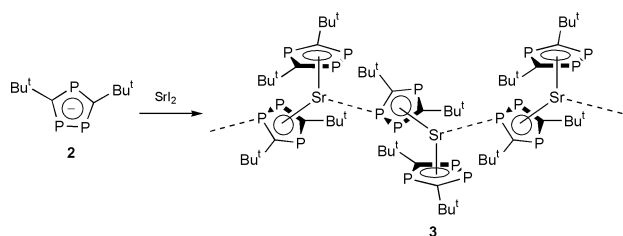
in the case of strontocenes such as $[Sr(\eta^5\text{-}C_5H_4Bu^t)(THF)_2]$ and $[Sr\{\eta^5\text{-}C_5H_3(SiMe_3)_2\}_2(THF)]$ which both readily desolvate on sublimation, although they remain monomeric.[8,9]

The $^{31}P\{^1H\}$ NMR spectrum of **3**† is consistent with η^5 ligated triphospholyl rings and the chemical shifts are similar to those of $[K(\eta^5\text{-}P_3C_2Bu^t_2)]$ (δ 252.8 and 244.8). This is in contrast to the generally observed *upfield* shift in the ^{31}P resonances of **2** upon coordination to transition metals {*e.g.* AB_2 pattern at δ 65 in $[Ru(\eta^5\text{-}P_3C_2Bu^t_2)_2]$}[10] and this may indicate a significant degree of ionic character in the metal–ligand bonding in **3** in solution. The EI mass spectrum of **3** exhibits a strong molecular ion (*m/z* 550, 58%) but no higher peaks, suggesting that in the gas phase **3** exists primarily as a monomeric species.

A single crystal X-ray diffraction study‡ reveals that in the solid state, **3** consists of bent sandwich units linked in chains along the crystallographic *c*-glide plane (Fig. 1). Each unit bears one solely η^5 bound triphospholyl ligand and a second η^5 ligand which also acts as a bridge linking the molecules into extended chains *via* a further η^1 interaction involving one of the two adjacent phosphorus ring atoms. This strontium–phosphorus bond distance [3.2200(7) Å] is only marginally longer than the average strontium–phosphorus distances within the sandwich unit (3.1837 Å) and all lie within the sum of the van der Waals radii for the two elements. The centroid–metal–centroid angle of 141.50(7)° in **3** is larger than that observed in analogous strontocenes bearing substituted cyclopentadienyl ligands of comparable steric bulk {*e.g.* 122 and 124° in **1**[4] and 134° in $[Sr\{\eta^5\text{-}C_5H_3(SiMe_3)_2\text{-}1,3\}_2]$ **5**).[8] Similarly, the metal–centroid distances of 2.692(3) and 2.788(3) Å in **3** are somewhat larger than those in **1** (2.525 Å) and **5** (2.551 Å), which probably results from replacement of three ring carbon atoms with the
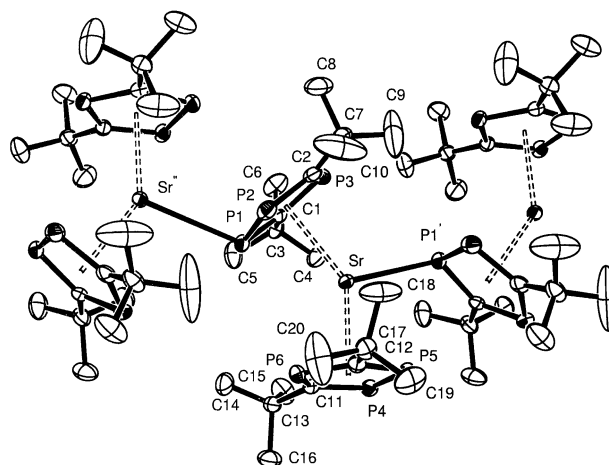

Fig. 1 Solid state structure of **3**. Selected bond distances (Å) and angles (°): M(1)–Sr–M(2) 141.50(7); Sr–M(1) 2.788(3), Sr–M(2) 2.692(3), P(1)–P(2) 2.1150(11), P(2)–C(2) 1.749(3), C(2)–P(3) 1.745(3), P(3)–C(1) 1.749(3), C(1)–P(1) 1.753(3), P(4)–P(5) 2.1069(11), P(5)–C(12) 1.756(3), C(12)–P(6) 1.755(3), P(6)–C(11) 1.751(3), C(11)–P(4) 1.759(3). M(1) and M(2) are the centroids of the rings defined by C(1), C(2), P(1), P(2), P(3) and C(11), C(12), P(4), P(5), P(6), respectively.
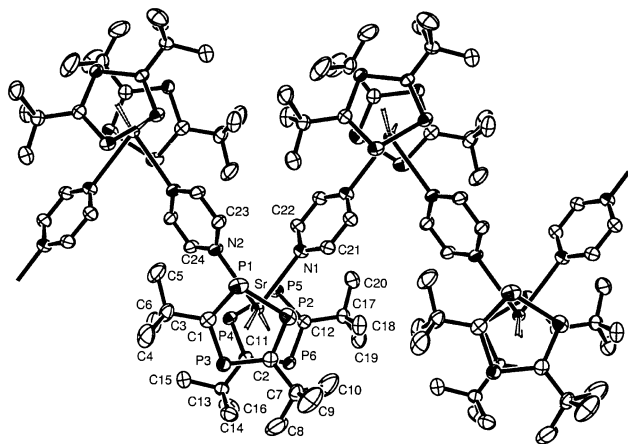

Scheme 1

Fig. 2 Solid state structure of **4**. Selected bond distances (Å) and angles (°): M(1)–Sr–M(2) 146.73(6); Sr–M(1) 2.794(2), Sr–M(2) 2.791(2), P(1)–P(2) 2.1073(10), P(2)–C(2) 1.751(3), C(2)–P(3) 1.748(5), P(3)–C(1) 1.754(2), C(1)–P(1) 1.746(3), P(4)–P(5) 2.1101(9), P(5)–C(12) 1.748(2), C(12)–P(6) 1.755(2), P(6)–C(11) 1.750(2), C(11)–P(4) 1.749(2). M(1) and M(2) are the centroids of the rings defined by C(1), C(2), P(1), P(2), P(3) and C(11), C(12), P(4), P(5), respectively.

larger phosphorus atoms. The bridging strontium–phosphorus interaction in **3**, not possible in the related strontocenes, obviates the need for any additional ligation to THF or other donor solvent molecules.

However, treatment of **3** with an excess of pyrazine in refluxing toluene leads *quantitatively* to [{Sr(η^5-P$_3$C$_2$Bu$^t_2$)$_2$(μ-C$_4$H$_4$N$_2$)}$_\infty$] **4** in which the strontium–phosphorus bridges of **3** have been broken and replaced with pyrazine units. Complex **4**, which is an orange solid, is insoluble in all but donor solvents but could be recrystallised from a hot saturated toluene solution. The room temperature mass spectrum of **4**† indicates a ready loss of pyrazine and at higher temperature the spectrum is essentially that of the parent complex **3**. Furthermore, the NMR spectroscopic data for **3** and **4** are essentially identical, suggesting that **4** undergoes complete dissociation into **3** and free pyrazine in solution.†

The solid state, polymeric structure of **4** determined by a single crystal X-ray diffraction study‡ is shown in Fig. 2. The pyrazine units act as bridges linking the hexaphospha-strontocene molecules into zigzag chains, each sandwich unit being related to the next by a crystallographic inversion centre lying at the middle of the pyrazine ring. The *intra*ring parameters of **4** do not differ significantly from those in **3**: the average phosphorus–carbon (1.750 Å) and phosphorus–phosphorus (2.1087 Å) distances within the strontium hexaphospha-metallocene unit in **4** are very similar to those observed in **3** (1.752 and 2.1109 Å, respectively). Moreover, the centroid–metal–centroid angle in **4** is 146.73(6)° compared with 141.50(7)° in **3** and the two individual metal–centroid distances of 2.791(2) and 2.794(2) Å are similar to those in **3** [2.692(3) and 2.788(3) Å].

Notes and references

1 P. Jutzi and N. Burford, *J. Chem. Soc., Dalton Trans.*, 2000, 2237; P. Jutzi and N. Burford, *Chem. Rev.*, 1999, **99**, 969.
2 T. P. Hanusa, *Chem. Rev.*, 1993, **93**, 1023.
3 T. P. Hanusa, *Polyhedron*, 1990, **9**, 1345.
4 H. Schumann, J. Gottfriedsen and J. Demtschuk, *Chem. Commun.*, 1999, 2091.
5 M. Westerhausen, M. H. Digeser, H. Noth, W. Ponikwar, T. Seifert and K. Polborn, *Inorg. Chem.*, 1999, **38**, 3207.
6 M. Westerhausen, M. H. Digeser, C. Guckel, H. Noth, J. Knizek and W. Ponikwar, *Organometallics*, 1999, **18**, 2491.
7 M. D. Francis J. F. Nixon and W. S. Rees Jr., manuscript in preparation.
8 M. G. Gardiner, C. L. Raston and C. H. L. Kennard, *Organometallics*, 1991, **10**, 3680.
9 L. M. Engelhardt, P. C. Junk, C. L. Raston and A. L. White, *J. Chem. Soc., Chem. Commun.*, 1988, 1500.
10 P. B. Hitchcock, R. M. Matos and J. F. Nixon, *J. Organomet. Chem.*, 1995, **490**, 155.
11 G. M. Sheldrick, SHELX-97, University of Göttingen, Göttingen, Germany, 1997.