Early Metal Macrocycles as Metalloligands: The Synthesis and Structure of $Cp_2Zr(\mu\text{-}SCH_2CH_2CH_2S)_2ZrCp_2$ and Its Silver Complex $[\{Cp_2Zr(\mu\text{-}SCH_2CH_2CH_2S)_2ZrCp_2\}Ag]BPh_4$ ($Cp = C_5H_5$)

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Reaction of Cp_2ZrMe_2 with propane-1,3-dithiol affords the early metal macrocycle $Cp_2Zr(\mu\text{-}SCH_2CH_2CH_2S)_2ZrCp_2$ **1**; X-ray structural data confirm that this species acts as a macrocyclic metalloligand for Ag^I yielding $[\{Cp_2Zr(\mu\text{-}SCH_2CH_2CH_2S)_2ZrCp_2\}Ag]BPh_4$ **2** in which Ag^I is pseudo-tetrahedrally coordinated by the sulphur atoms of **1**.

Unique reactivity patterns result from heterogeneous catalyst systems in which late metals are dispersed on early metal, Lewis acidic supports.[1] These observations have prompted interest in the synthesis of complexes where early, oxophilic and late electron-rich metal centres are placed in close proximity.[2] One approach to the synthesis of such species is the use of early metal complexes as 'metalloligands.' Titanium and vanadium thiolate derivatives can be employed to synthesize thiolato-bridged heterobimetallic systems in which close proximity of disparate metal centres[3–5] is achieved;

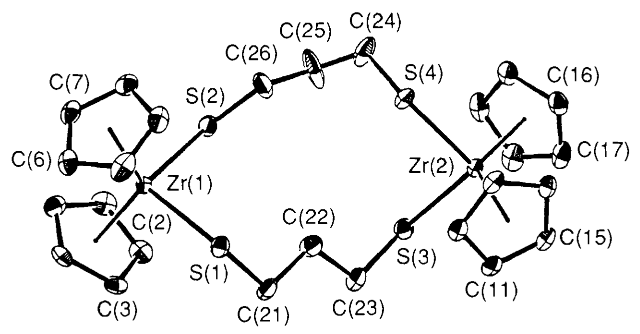

Fig. 1 ORTEP drawing of molecule **1**, 20% thermal ellipsoids are shown. Hydrogen atoms are omitted for clarity. Zr(1)–S(1) 2.515(2), Zr(1)–S(2) 2.480(2), Zr(2)–S(3) 2.518(2), Zr(2)–S(4) 2.499(2) Å; S(1)–Zr(1)–S(2) 99.87(6), S(3)–Zr(2)–S(4) 100.83(6)°, Zr(1) · · · Zr(2) 7.570(1) Å.

however, such systems have proved to be generally unstable and difficult to handle. In contrast, macrocyclic ligands containing chalcogenide donors have been shown to stabilize a variety of metal complexes. For example, a wide variety of crown ether complexes has been studied over the years.[6] More recently, the groups of Cooper,[7] Schröder,[8] Weighardt[9] and others[10] have described interesting systems dervied from macrocyclic crown thioether ligands, while Pinto *et al.*[11] have initiated the study of related selenium-based macrocycles. The demonstrated stability and ability of macrocycles to bind transition metals in various oxidation states and our continuing interest in early/late heterobimetallics have prompted our investigations of synthetic routes to early metal-based macrocyclic metalloligands. Previous reports have described mononuclear, early metal, metallocene derivatives of chelating dithiolates.[12] We report herein the synthesis and structure of the first bimetallic, macrocyclic, zirconocenedithiolate, $Cp_2Zr(\mu\text{-}SCH_2CH_2CH_2S)_2ZrCp_2$. Further, we describe its use as a macrocyclic metalloligand in the formation of a silver complex.

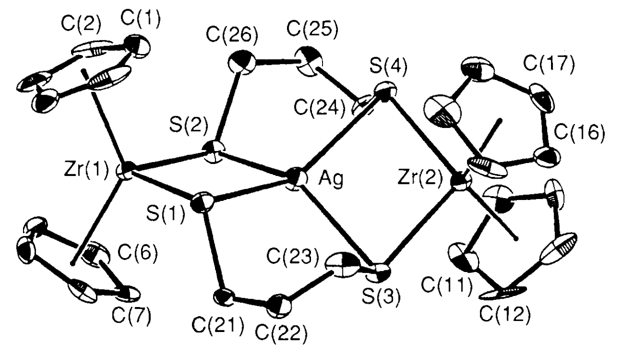

Fig. 2 ORTEP drawing of the cation of molecule **2**, 20% thermal ellipsoids are shown. Hydrogen atoms are omitted for clarity. Ag–S(1) 2.590(5), Ag–S(2) 2.657(5), Ag–S(3) 2.658(5), Ag–S(4) 2.599(5), Zr(1)–S(1) 2.550(5), Zr(1)–S(2) 2.550(5), Zr(2)–S(3) 2.551(5), Zr(2)–S(4) 2.559(5) Å; S(1)–Ag–S(2) 97.8(2), S(1)–Ag–S(3) 92.3(2), S(1)–Ag–S(4) 145.9(2), S(2)–Ag–S(3) 144.3(2), S(2)–Ag–S(4) 91.1(2), S(3)–Ag–S(4) 99.5(2), S(1)–Zr(1)–S(2) 101.7(2), S(3)–Zr(2)–S(4) 103.4(2)°, Ag···Zr(1) 3.333(3), Ag···Zr(2) 3.280(3) Å.

The reaction of Cp_2ZrMe_2 with equimolar amounts of a variety of dithiols including $HS(CH_2)_nSH$, n = 2,3,4, and *o*- and *m*-$(HSCH_2)_2C_6H_4$ in tetrahydrofuran (THF) proceed with the evolution of methane. The solutions gradually become yellow on standing and following addition of hexane, crystalline products are obtained. In all cases, the compounds prove to be insoluble in any solvents in which they are stable. Combustion analyses data were consistent with the empirical formulae, Cp_2Zr(dithiolate). The lack of solubility is uncharacteristic of simple mononuclear metallocenedithiolates,[5] suggesting formulation as dimeric or higher order oligomers. In the case of the product derived from propane-1,3-dithiol, an X-ray structural study† showed that the product is the dimetallated, macrocyclic species $Cp_2Zr(\mu\text{-}SCH_2CH_2CH_2S)_2ZrCp_2$ **1** (Fig. 1). The pseudo-tetrahedral coordination spheres of the Zr atoms are well separated, the Zr(1) · · · Zr(2) distance being 7.570(1) Å. The alkyl substituents on the sulphur atoms adopt an *endo-transoid* conformation while the angle between the ZrS_2 planes is 92.9°. These structural features suggest that this early metal macrocycle is pre-organized for the encapsulation of a late metal which can assume a pseudo-tetrahedral environment.

The reaction of **1** with an equivalent of $AgBPh_4$ proceeds in dichloromethane with the gradual dissolution of the crystals of **1** and the generation of a yellow solution. Addition of THF and hexane yields, on standing, yellow crystals of **2**. The ^1H NMR data are consistent with the formulation of **2** as a 1 : 1 salt-complex of **1** with $AgBPh_4$.

An X-ray structural study confirms that **2** is the complex $[Cp_2Zr(\mu\text{-}SCH_2CH_2CH_2S)_2ZrCp_2Ag]BPh_4$ in which **1** acts as a macrocyclic metalloligand to bind silver (Fig. 2). The geometry about the silver is that of tetrahedron flattened towards square planar. The angles about Ag fall into three groups. The four-membered rings give rise to angles at silver of 97.8(2) and 99.5(2)° while the six-membered chelates give bite angles at silver of 91.1(2) and 92.3(2)°. The 'flattening' of the tetrahedral coordination sphere about silver is evidenced by the *'trans'* S–Ag–S angles of 145.9(2) and 144.3(2)°. The Ag–S distances are typical, ranging from 2.590(5) to 2.658(5) Å. The geometry of the macrocyclic metalloligand has been altered upon complexation; however, the perturbation of the geometry is not dramatic. Reorientation of the methylene chains and a closer approach of the Zr centres [Zr(1) · · · Zr(2) 6.613(1) Å] result in a slight twisting of the Zr coordination spheres with respect to each other. This twist, which minimizes the steric interactions between the cyclopentadienyl rings and the bridging alkyl chains, results in increase in the angle between the ZrS_2 planes to 133.0° in **2**. The Zr · · · Ag distances of 3.333(3) and 3.280(3) Å do not suggest $d^{10} \rightarrow d^0$ dative bonding as has been implied in other early/late heterobimetallic systems.[3–5,13] The S · · · S distances within the six-membered rings [S(1) · · · S(3) 3.784(7) Å; S(2) · · · S(4) 3.752(7) Å] are similar to those between sulphur atoms on each zirconium centre [S(1) · · · S(2) 3.954(7) Å, S(3) · · · S(4) 4.012(7) Å]. This suggests the $Cp_2Zr(SR)_2$ moiety is similar in bite to a three-carbon chain. This leads to the likening of **1** to a metallated version of [16]aneS_4.

In conclusion, the present results establish synthetic methodology for the incorporation of early metal centres into

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† *Crystal data:* **1**, $C_{26}H_{32}S_4Zr_2$, M = 655.22 orthorhombic, space group, *Pbca* (No. 61), a = 25.772(2), b = 15.607(2), c = 13.008(1) Å, V = 3229(1) Å^3, Z = 8, D_c = 1.66 g cm^{-3}, Mo-Kα radiation, λ = 0.71069 Å, μ(Mo-Kα) = 11.05 cm^{-1}. *Crystal data* **2**: $C_{50}H_{52}BAgS_4Zr_2$, M = 1082.31, triclinic space group, $P\bar{1}$ (No. 2), a = 11.242(4), b = 12.790(7), c = 18.270(10) Å, α = 112.33(4), β = 111.23(4), γ = 81.81(4)°, V = 2265(2) Å^3, Z = 2, D_c = 1.59 g cm^{-3} Mo-Kα radiation, λ = 0.71069 Å, μ(Mo-Kα) = 10.79 cm^{-1}. Crystals were sealed in 0.5 mm capillaries under N_2 for crystallographic study. A Nicolet P2$_1$ four-circle diffractometer was employed to collect reflections (4.5 < 2θ < 45.0°). Three standards were recorded every 200 reflections and in each case showed no decay. The structures were solved employing direct methods (MITHRIL) and refined employing the TEXSAN software package from MSC running on a VAX workstation 3520. *Refinement*: **1**, 2674 data with $I > 3\sigma(I)$, 290 variables, R = 0.0410, R_w = 0.0554; **2**, 2933 data with $I > 3\sigma(I)$, 398 variables, R = 0.692, R_w = 0.0790. In each case the final difference map showed residual electron density of no chemical significance.

Atomic coordinates, bond distances and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

the backbones of macrocycles. Further, these early metal macrocycles are capable of acting as metalloligands for late metals.

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