

Early/late heterobimetallics: unusual tetranuclear Zr/Ni and octanuclear Zr/Pd complexes with bridging bifunctional sulfidoacetato ligands †

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Unexpectedly the zirconocene metalloligand [$\text{Cp}^\circ_2\text{Zr}(\text{OOCCH}_2\text{SH}-\kappa^1\text{O})(\text{OOCCH}_2\text{SH}-\kappa^2\text{O},\text{O}')$] (**1**; $\text{Cp}^\circ = \text{C}_5\text{-EtMe}_4$) reacts with $[\text{NiCl}_2(\text{PMe}_2\text{Ph})_2]$ or $[\text{PdCl}_2(\text{P}n\text{Bu}_3)_2]$ in the presence of NEt_3 (ratio 1 : 1 : 2) to give the tetranuclear $\text{Zr}^{\text{IV}}-\text{Ni}^{\text{II}}$ complex **2** and the octanuclear $\text{Zr}^{\text{IV}}-\text{Pd}^{\text{II}}$ complex **3**, respectively.

Early/late heterobimetallics (ELHBs) have received increasing attention in recent times as they can be employed as biomimetic compounds or in homogeneous catalysis.¹ In heterogeneous catalysis, a combination of two or more different metals often enhances the catalytic properties.^{2–6} We expect that in heterobimetallic complexes each metal should exhibit its specific reactivity, as well as being influenced by the second metal.

The ELHBs can be prepared from so-called metalloligands, in which a bifunctional ligand is coordinated to a transition metal. In a second step, a second transition metal is introduced. To date, various bifunctional ligands, for example, S/P,^{7–9} S/S,^{10,11} S/N,¹² O/P,^{13–15} and N/N,^{16,17} have been employed. Due to the different electronic properties of the two transition metals in ELHBs, the use of bifunctional ligands with two different donor atoms seems favorable (Pearson's HSAB concept).¹⁸ We chose the dianion of mercaptoacetic acid as an O,S ligand and Zr^{IV} as the early transition metal.

The zirconocene metalloligand [$\text{Cp}^\circ_2\text{Zr}(\text{OOCCH}_2\text{SH}-\kappa^1\text{O})(\text{OOCCH}_2\text{SH}-\kappa^2\text{O},\text{O}')$] (**1**; $\text{Cp}^\circ = \text{C}_5\text{EtMe}_4$) was obtained from [$\text{Cp}^\circ_2\text{ZrMe}_2$] and mercaptoacetic acid (1 : 2). † In the solid state, **1** contains one mono- and one bi-dentate mercaptoacetato ligand (Fig. 1), § and thus attains 18 valence electrons. This bonding mode was also observed in related zirconocene bis-carboxylato complexes.^{19–22} In solution, **1** is dynamic (equivalent CH_2 groups in the ^1H NMR spectrum) even at -90°C .

Complex **1** reacts with $[\text{NiCl}_2(\text{PMe}_2\text{Ph})_2]$ in the presence of NEt_3 (ratio 1 : 1 : 2) to give the tetranuclear $\text{Zr}^{\text{IV}}-\text{Ni}^{\text{II}}$ complex **2** in high yield (Scheme 1). † Complex **2** decomposes in the presence of PMe_2Ph with formation of $[\text{Ni}(\text{OOCCH}_2\text{S}-\kappa^2\text{O},\text{S})(\text{PMe}_2\text{Ph})_2]$,²³ which can be prevented by rapid workup. The molecular structure of **2** shows a centrosymmetric molecule (Fig. 2), § in which both Zr atoms are five-coordinate with one monodentate and one bidentate sulfidoacetato ligand. Each sulfido group of the sulfidoacetato ligands of one zirconocene fragment is coordinated to a Ni atom. Additionally, the second O atom of the monodentate ligand is also coordinated to Ni to give a planar tetracoordinate Ni atom with an energetically stable five-membered O–C–C–S–Ni chelate ring. The atoms of the central 18-membered ring in **2** and the P, S, C and O atoms (total of 26 atoms) are almost coplanar [max. deviation from best plane 0.310(2) Å].

A comparable tetranuclear complex, **2b**, is formed in the reaction of **1** with $[\text{NiCl}_2(\text{P}n\text{Bu}_3)_2]$, † that is, the substituents on P have no major influence on the observed course of reaction.

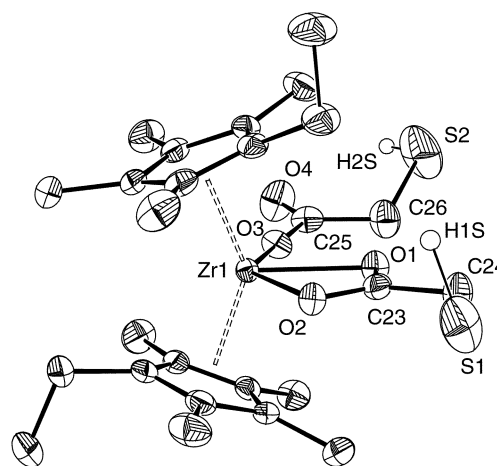
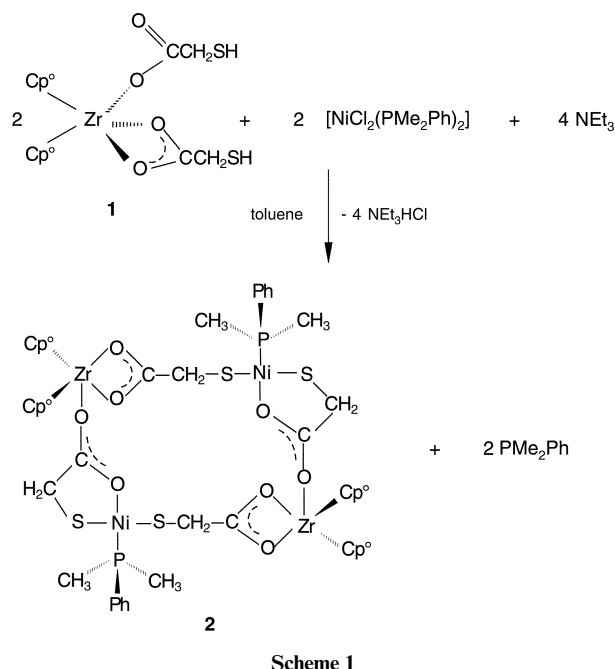


Fig. 1 Structure of **1** (hydrogen atoms other than S–H are omitted for clarity). Selected bond lengths (Å) and angles ($^\circ$) (Cen = centre of the Cp° ring): Zr1–O1 2.282(2), Zr1–O2 2.296(2), Zr1–O3 2.082(2), O1–C23 1.273(3), O2–C23 1.257(3), O3–C25 1.293(3), O4–C25 1.218(3), Zr1–Cen 2.260; O1–Zr1–O2 56.62(6), O1–Zr1–O3 79.47(7), O2–C23–O1 118.2(2), O4–C25–O3 123.9(3), Cen1–Zr1–Cen2 137.7.



However, when **1** was treated with $[\text{PdCl}_2(\text{P}n\text{Bu}_3)_2]$, the octanuclear $\text{Zr}^{\text{IV}}-\text{Pd}^{\text{II}}$ complex, **3**, was formed unexpectedly, albeit in low yield (Scheme 2). † In the centrosymmetric molecule of **3** (Fig. 3), § two Zr atoms are pentacoordinate, as in **1** and **2**, while

† Electronic supplementary information (ESI) available: experimental details. See <http://www.rsc.org/suppdata/dt/b1/b109041k/>

‡ Crystal structure determinations.

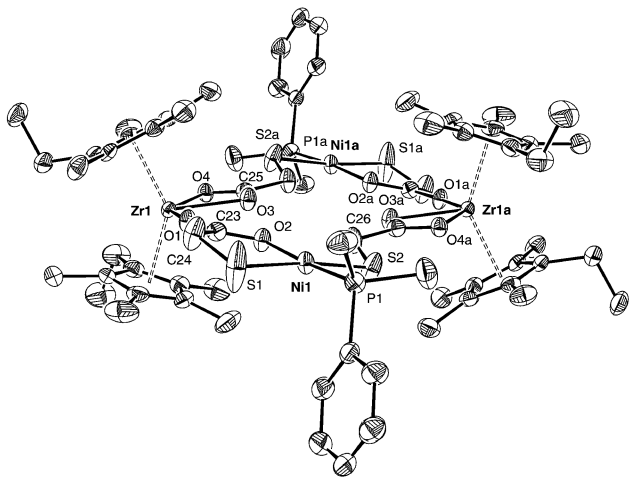


Fig. 2 Structure of **2** (hydrogen atoms are omitted for clarity). Selected bond lengths (Å) and angles (°): Zr1–O1 2.133(3), Zr1–O3 2.248(3), Zr1–O4 2.235(3), Ni1–S1 2.182(2), Ni1–S2 2.179(1), Ni1–O2 1.925(3), Ni1–P1 2.145(1), O1–C23 1.270(5), O2–C23 1.244(5), O3–C25 1.279(5), O4–C25 1.258(5), Zr1–Cen 2.263, 2.255; O3–Zr1–O4 57.9(1), S1–Ni1–O2 88.08(9), P1–Ni1–S2 89.49(5), P1–Ni1–S1 89.17(5), O2–C23–O1 123.5(4), O4–C25–O3 117.4(4), Cen1–Zr1–Cen2 137.3.

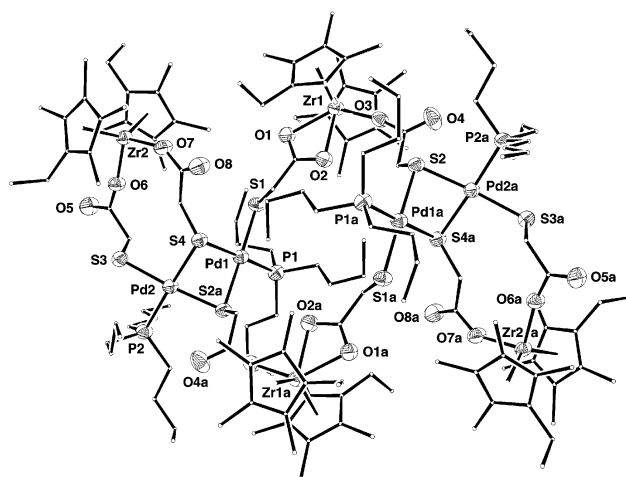
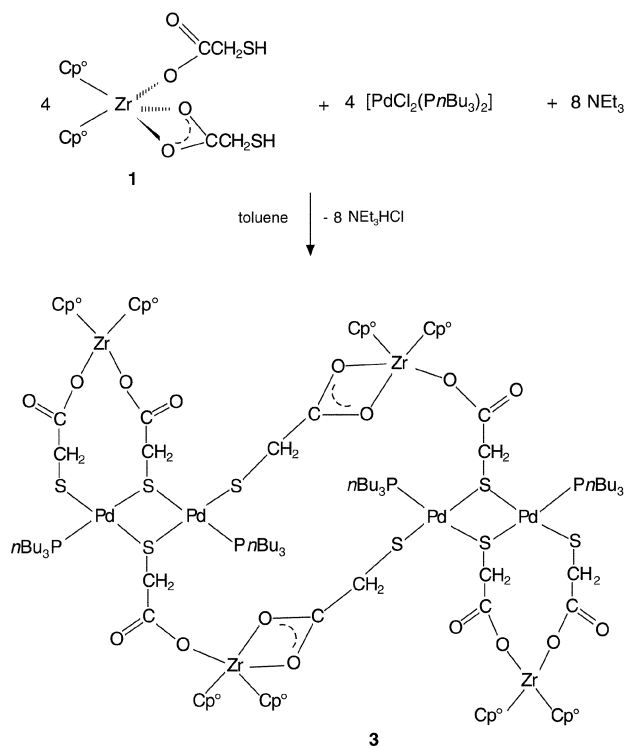


Fig. 3 Structure of **3** (hydrogen atoms are omitted for clarity). Selected bond lengths (Å) and angles (°): Zr1–O1 2.303(6), Zr1–O2 2.262(6), Zr1–O3 2.073(6), Zr2–O6 2.020(6), Zr2–O7 2.035(6), Pd1–S1 2.338(2), Pd1–S2a 2.353(2), Pd1–S4 2.374(2), Pd1–P1 2.268(2), Pd2–S2a 2.345(2), Pd2–S3 2.349(2), Pd2–S4 2.410(2), Pd2–P2 2.271(2), Zr1–Cen 2.268, 2.264, Zr2–Cen 2.241, 2.231; O1–Zr1–O2 57.0(2), O6–Zr2–O7 97.6(2), S1–Pd1–P1 84.96(9), S2a–Pd1–P1 97.15(8), S1–Pd1–S4 95.63(8), S2a–Pd2–P2 96.22(8), S3–Pd2–P2 85.92(9), S3–Pd2–S4 96.69(8), Cen1–Zr1–Cen2 136.8, Cen3–Zr2–Cen4 137.9.



Scheme 2

the other two have a coordination number of four, whereby both sulfidoacetato ligands are monodentate due to geometric requirements. This type of coordination is rare and was only observed in $[\text{Cp}^*\text{Zr}(\text{OOCCH}_2\text{S})_2]_2$.²⁴

Each Pd atom has a square-planar coordination environment with two bridging and one terminal sulfido group of the sulfidoacetato ligands and one phosphine ligand. As in **2**, substitution of one phosphine ligand is observed. There is no Pd–Pd interaction [Pd1...Pd2 3.141(1) Å]. The cavity of the central 20-membered ring (Zr1–Pd1–Zr1a–Pd1a) is filled by the *n*-butyl groups of the phosphine ligands. Additionally, two 10-membered rings are formed by Zr2, Pd2, and the monodentate sulfidoacetato ligands. Apparently, the flexibility of the sulfidoacetato ligands is restricted by coordination to Pd2, and this results in an unfavorable coordination number of four at Zr2.

The oligonuclear complexes **2** and **3** are the first hetero-bimetallic complexes with sulfidoacetato groups as bridging ligands. It is remarkable that the formation of these unprecedented large ring-like molecules is apparently preferred over the formation of simple heterodinuclear complexes.

Complexes **1** and **2** were tested as oxidation catalysts with the model system O_2/PPh_3 (the $\text{PPh}_3 : \text{PPh}_3\text{O}$ ratio was determined by ^{31}P NMR spectroscopy). Complex **1** catalyzes the oxidation of PPh_3 without apparent decomposition of the mononuclear complex over a period of 1.5 h at 50 °C (presumably, *via* coordination of PPh_3 at Zr). For **2**, only minor amounts of PPh_3O were observed, and decomposition of the tetranuclear complex occurred. We assume that the catalytic activity of **1** is due to the Lewis acidic Zr atom, which, in contrast to those of **2**, is coordinatively unsaturated in solution. Further investigations of the catalytic properties of these novel complexes are in progress.

Acknowledgements

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Notes and references

§ Crystal data. For **1**: $\text{ZrS}_2\text{O}_4\text{C}_{26}\text{H}_{40}$, MW = 571.92, monoclinic, space group $P2_1/n$, $a = 1245.62(1)$, $b = 1314.54(2)$, $c = 1680.12(3)$ pm, $\beta = 99.202(1)^\circ$; $V = 2.71565(7)$ nm³, $Z = 4$, $D_c = 1.399$ Mg m⁻³, $\lambda(\text{Mo-K}\alpha) = 71.073$ pm, $\mu = 0.587$ mm⁻¹, 14232 reflections, 5453 independent reflections ($R_{\text{int}} = 0.0828$), 458 parameters, residual electron density: 0.732/–1.462 e Å⁻³, $R = 0.0399$, $R_w = 0.0868$.

For **2**: $\text{Zr}_2\text{Ni}_2\text{S}_4\text{P}_2\text{O}_{10}\text{C}_{76}\text{H}_{114}$, MW = 1677.71, triclinic, space group $P\bar{1}$, $a = 1110.12(5)$, $b = 1324.91(6)$, $c = 1467.88(7)$ pm, $a = 66.313(1)$, $\beta = 83.020(1)$, $\gamma = 88.965(1)^\circ$; $V = 1.96131(16)$ nm³, $Z = 1$, $D_c = 1.420$ Mg m⁻³, $\lambda(\text{Mo-K}\alpha) = 71.073$ pm, $\mu = 0.933$ mm⁻¹, 11963 reflections, 8667 independent reflections ($R_{\text{int}} = 0.0168$), 629 parameters, residual electron density: 1.040/–1.000 e Å⁻³, $R = 0.0655$, $R_w = 0.1282$.

For **3**: $\text{Zr}_4\text{Pd}_4\text{S}_8\text{O}_{16}\text{P}_4\text{C}_{152}\text{H}_{260}$, MW = 3514.44, triclinic, space group $P\bar{1}$, $a = 1338.5(2)$, $b = 1895.4(2)$, $c = 2179.0(2)$ pm, $a = 108.654(2)$, $\beta = 104.881(2)$, $\gamma = 92.592(2)^\circ$; $V = 5.0129(10)$ nm³, $Z = 1$, $D_c = 1.164$ Mg m⁻³, $\lambda(\text{Mo-K}\alpha) = 71.073$ pm, $\mu = 0.711$ mm⁻¹, 30114 reflections, 20168 independent reflections ($R_{\text{int}} = 0.0525$), 872 parameters, residual electron density: 1.703/–1.555 e Å⁻³, $R = 0.0829$, $R_w = 0.2931$. Data collection used a Siemens SMART CCD diffractometer [$T = 223(2)$ K]. Absorption correction was performed using the SADABS program,²⁵ with structure solution by SHELXS-97²⁶ and refinement by SHELXL-97.²⁷ CCDC reference numbers 169655 (**1**), 169656 (**2**), and 169657 (**3**).

See <http://www.rsc.org/suppdata/dt/b1/b109041k/> for crystallographic data in CIF or other electronic format.

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