

Bifunctional dithiocarbamates: A bridge between coordination chemistry and nanoscale materials

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Received (in XXX, XXX) Xth XXXXXXXXXX 200X, Accepted Xth XXXXXXXXXX 200X

First published on the web Xth XXXXXXXXXX 200X

DOI: 10.1039/b000000x

A dithiocarbamate-based methodology is employed to prepare linked heterometallic complexes and then further exploited in the surface functionalisation of gold nanoparticles.

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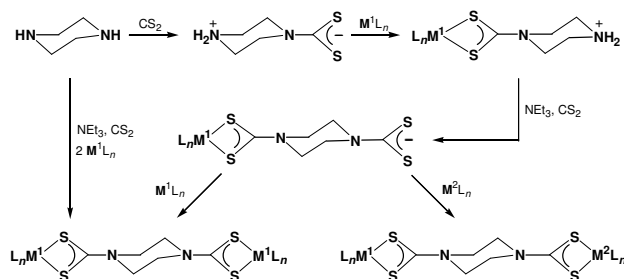
A vast range of transition metal dithiocarbamate complexes is known¹ with examples finding use in applications as diverse as materials science, medicine and agriculture. Their ability to stabilise a wide range of oxidation states and their associated metal-centred electrochemistry² have often

15 proved key factors in these applications.

While polyfunctional variants of many ligands have been used to create multimetallic systems, this approach to dithiocarbamates has rarely been exploited. Recent work to harness their versatility in the field of supramolecular design has illustrated their utility in this regard.³ Our recent

20 contributions in this area have centred on the use of a piperazine dithiocarbamate that exists as a zwitterion, S₂CNC₄H₈NH₂.⁴ This species can be used to coordinate a first metal centre, while retaining the potential to bond to a second at the other end of the molecule on deprotonation and functionalisation with CS₂. A general strategy for the synthesis of homo-

25 and hetero-bimetallic complexes using a piperazine dithiocarbamate ligand is shown in Scheme 1.



Scheme 1 General scheme for generation of bimetallic complexes.

30 The key aspect is the accessibility of heterobimetallic systems via this route. Until now, the metal units linked by such bis(dithiocarbamate) ligands¹ have all been identical, producing symmetrical compounds. Treatment of [Ru(S₂CNC₄H₈NH₂)(dppm)₂](BF₄)₂ (**1**)⁴ with carbon disulfide under basic conditions followed by addition of [PdCl₂(PPh₃)₂]

35 led to the formation of the complex [(dppm)₂Ru(S₂CNC₄H₈NCS₂)Pd(PPh₃)₂](BF₄)₂ (**2**) in 94% yield. The overall composition for this and the complexes discussed below was supported by multinuclear NMR and IR spectroscopy, FAB mass spectrometry and microanalysis. Single crystals suitable for X-ray

40 diffraction were obtained of complex **2** allowing the structure determination shown in Figure 1. The distorted octahedral environment of the ruthenium centre contrasts with the near perfect square planar geometry of the

palladium unit. The two metals are linked by a piperazine bis(dithiocarbamate) bridge in the chair conformation.⁵

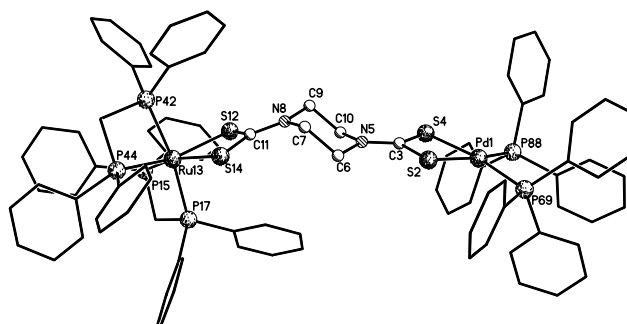


Fig. 1 Structure of [(dppm)₂Ru(S₂CNC₄H₈NCS₂)Pd(PPh₃)₂]²⁺ (**2**).

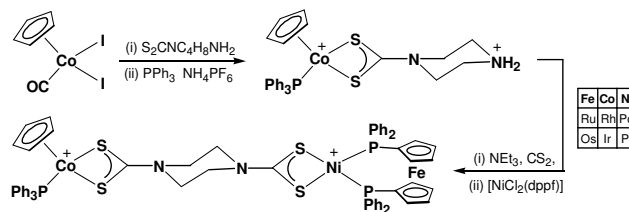
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This result illustrated the utility of the above approach to prepare heterobimetallic species but it was clear that further metals could be

50 introduced by judicious choice of ligands. Using 1,1'-bis(diphenyl)phosphinoferrocene as a convenient example, it was sought to combine all three first row transition metals of groups 8-10 within the same molecule. This was achieved as shown in Scheme 2 starting from [Co(η⁵-C₅H₅)₂(CO)].

55 Deprotonation and treatment of [Co(η⁵-C₅H₅)(S₂CNC₄H₈NH₂)(PPh₃)](PF₆)₂ (**3**) with CS₂ was followed by addition of [NiCl₂(dppf)] to yield the heterotrimetallic [(dppf)Ni(S₂CNC₄H₈NCS₂)Co(η⁵-C₅H₅)(PPh₃)](PF₆)₂ (**4**). A literature search revealed that this complex is only the second example of a non-cluster compound containing just the three metals, Fe, Co and Ni. The

60 first was the unusual trimetallic triple-decker metallacarborane compound [(η⁵-C₉H₇)Fe(Et₂C₂B₄H₄)Ni(Et₂MeC₃B₂Et₂)Co(η⁵-C₅H₅)].⁶



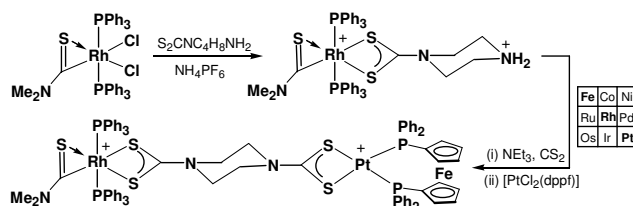
Scheme 2 Constructing the FeCoNi trimetallic **4**.

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Encouraged by this success, an attempt was made to prepare a heterotrimetallic complex of the same groups, but diagonally across the periodic table, incorporating the metals Fe, Rh and Pt. We recently reported a synthesis of the thiocarbamoyl compound [Rh(η²-SCNMe₂)Cl₂(PPh₃)₂].⁷

70 This complex reacts with the zwitterion S₂CNC₄H₈NH₂ to yield [Rh(η²-

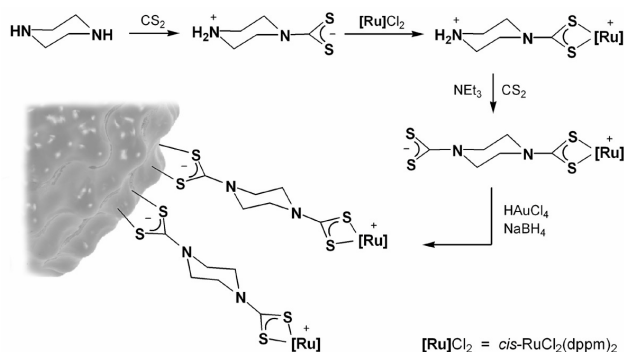
SCNMe₂(S₂CNC₄H₈NH₂)(PPh₃)₂⁺ (**5**) by displacement of the chloride ligands. The target complex [(dppf)Pt(S₂CNC₄H₈NCS₂)Rh(η²-SCNMe₂)(PPh₃)₂](PF₆)₂ (**6**) is obtained on treatment of **5** with NEt₃, CS₂ and [PtCl₂(dppf)] (Scheme 3). To the best of our knowledge, compound **6** appears to be the only molecular complex containing just the three metals, Fe, Rh and Pt.



Scheme 3 Constructing the FeRhPt trimetallic **6**.

The generation of a metalla-dithiocarbamate of the form [L_nM(S₂CNC₄H₈NCS₂)] underpins the synthetic routes described above. The application of such species to the emerging field of functionalised gold nanoparticles was then explored.⁸ These materials have received much attention but very few reports exist in which the surface is modified to incorporate transition metal units.⁹ Despite the widespread use of thiols to stabilise gold colloids, dithiocarbamates were only first used very recently in this manner.¹⁰ The first report of complexed metals being tethered to the surface through dithiocarbamates appeared shortly afterwards.¹¹

Using a modification of the Brust-Schiffrin method,¹² HAuCl₄ was reduced by sodium borohydride in the presence of a phase transfer agent (*n*-tetraoctylammonium bromide, TOAB) followed by addition of the zwitterionic complex [Ru(S₂CNC₄H₈NCS₂)(dppm)₂] generated in situ (Scheme 4).



Scheme 4 Preparation of ruthenium-functionalised nanoparticles (**NP1**) using the Brust-Schiffrin method.

The black nanoparticles formed (**NP1**) were characterised by NMR (³¹P, ¹H) spectroscopy in CDCl₃ and this revealed broadened resonances at chemical shift values only slightly deviating from those observed for the molecular precursor. Transmission Electron Microscopy (TEM) showed that the particles displayed an average diameter of 3.4 (± 0.3) nm (Fig. 2). Material containing nanoparticles of larger diameter were obtained by displacing the outer shell of citrate-stabilised gold colloids using [Ru(S₂CNC₄H₈NCS₂)(dppm)₂]. TEM measurements of this blue material (**NP2**) gave a diameter of 14.4 (± 2.5) nm (Fig. 2). Before analysis, the nanoparticles were washed copiously with water and warm ethanol to

remove salts (TOAB, citrate etc.) and excess compound **1**, respectively. Complex **1** is soluble in warm ethanol and washing was continued until no further free metalla-dithiocarbamate was present (NMR spectroscopy). Both types of nanoparticles gave rise to absorptions in the UV-Visible spectra with λ_{max} = 265, 333 nm, attributable to LMCT bands, which are also observed in [Ru(S₂CNC₄H₈NH₂)(dppm)₂](BF₄)₂.¹³ Broad, less intense bands were observed at 574 and 683 nm for **NP1** and **NP2**, respectively. These were attributed to a superimposition of ruthenium-based features and the Surface Plasmon Resonance band normally found at around 520 nm. The latter is sometimes observed to be shifted away from this value, particularly in chloroform solution.¹⁴ Other contributory factors may also include the surface charge on the nanoparticles and interparticle interactions (TEM of **NP2** in Fig. 2). Infrared absorptions attributable to the diphosphine ligands and a clearly identifiable ν_{C-S} band at 1000 cm⁻¹ was observed for **NP1** and **NP2**. The presence of the surface units was also supported by EDX data. In addition to gold, phosphorus, sulfur and ruthenium were clearly present. Based on the TEM measurements, the approximate number of gold atoms in **NP1** is around 1600 with 550 at the surface.¹⁵ This contrasts with the substantially greater surface area of **NP2** (11000 surface atoms with 145000 core gold atoms). The surface area covered by the tethered species will play an important role when examining catalytic or sensing properties. In preliminary work aimed at the latter application, we were pleased to discover that the nanoparticles displayed well-behaved, reversible electrochemistry with a Ru(II)/Ru(III) couple at 0.73 V (vs. Fc/Fc⁺). This is a similar potential to that found in the complex [Ru(S₂CNC₄H₈NH₂)(dppm)₂](BF₄)₂,¹³ and bodes well for future work addressing the electrochemical sensing of anions by ruthenium dithiocarbamate systems immobilised on gold nanoparticles.

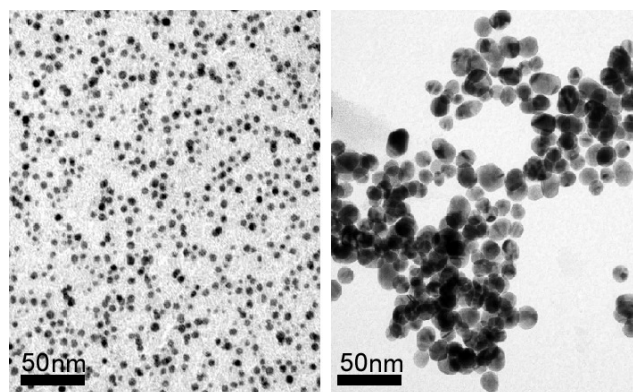


Fig. 2 TEM images of nanoparticles **NP1** (3.2 ± 0.3 nm, left) and **NP2** (14.4 ± 2.5 nm, right).

In conclusion, the versatility of the approach described here has been applied to the preparation of unsymmetrical bi- and trimetallic complexes, including triads of consecutive metals in the periodic table. Furthermore, its utility for the introduction of transition metals onto the surface of gold nanoparticles has also been illustrated, paving the way for facile functionalisation of these materials for applications in catalysis and sensing. The accessibility of S₂CNC₄H₈NH₂ from inexpensive piperazine in multigram quantities¹³ and the ready preparation of the dithiocarbamate complexes, make it possible to prepare nanoparticles with a wide range of transition metal surface units in a few hours without the need for specialised chelates with thiol tethers.

Notes and references

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† Electronic Supplementary Information (ESI) available: Experimental, spectral data and crystallographic details. See DOI: 10.1039/b000000x/

‡ The authors thank Prof. D. J. Watkin and Dr. A. L. Thompson for assistance with crystallography and Dr. K. B. Holt (UCL) for electrochemical measurements. Merton College, Oxford, is acknowledged for a Fitzjames Research Fellowship.

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- 5 Crystals of **2**(OEt₂)(CH₂Cl₂)₃ were grown by slow diffusion of diethylether into dichloromethane. Single crystal X-ray diffraction data were collected using an Enraf-Nonius KappaCCD diffractometer equipped with a Cryostream N₂ open-flow cooling device.¹⁶ Cell parameters and intensity data were processed using the DENZO-SMN package.¹⁷ The structure was solved by direct methods using SIR92¹⁸ and refined on F using the CRYSTALS suite.¹⁹ **Crystal data.** C₉₉H₉₈B₂Cl₆F₈N₂OPdRuS₄, *M* = 2239.78, triclinic, *a* = 13.9532(2) Å, *b* = 15.4074(2) Å, *c* = 25.2067(4) Å, α = 102.9433(6)°, β = 92.8485(6)°, γ = 106.8897(6)°, *V* = 5015.09(13) Å³, *T* = 150(2) K, space group *P*-1, *Z* = 2, μ (Mo-K α) = 0.732 mm⁻¹, *D*_{calcd} = 1.483 g/cm³, 75176 reflections collected, 22434 independent (*R*_{int} = 0.044), *R*₁ = 0.0647, *wR*₂ = 0.0650 [*I* > 2 σ (*I*)]. Crystallographic data for the structure have been deposited with the Cambridge Crystallographic Data Centre, CCDC 677009. Copies of the data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.
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